ROMANIAN ACADEMY
INSTITUTE OF PHYSICAL CHEMISTRY
"I.G. MURGULESCU"

UNIVERSITY OF BUCHAREST
PHYSICAL CHEMISTRY DEPARTMENT

ROMANIAN CHEMICAL SOCIETY
SECTION OF PHYSICAL CHEMISTRY

THE 8th CONFERENCE ON PHYSICAL CHEMISTRY

September 25-27, 1996
Bucharest, ROMANIA

- Abstracts -

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
26 February 1997

3. REPORT TYPE AND DATES COVERED
Conference Proceedings

4. TITLE AND SUBTITLE
Quantum Chemistry, Molecular Structure and Chemical Bond, Chemical Kinetics and Photochemistry, Biological Physical Chemistry and Environment

5. FUNDING NUMBERS
F6170896W0126

6. AUTHOR(S)
Conference Committee

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Academia Romania
Spl. Independentei Nr. 202
Bucharest Sector 6
Romania

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

EOARD
PSC 802 BOX 14
FPO 09499-0200

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
CSP 96-1033

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE
A

13. ABSTRACT (Maximum 200 words)

The Final Proceedings for The VIIIth Conference on Physical Chemistry, 25 September 1996 - 27 September 1996

The Topics covered include: Quantum Chemistry, Molecular Structure and Chemical Bond, Chemical Kinetics and Photochemistry, Biological Physical Chemistry and Environment.

DTIC QUALITY INSPECTED 3

14. SUBJECT TERMS
Physics, Discrete Mathematics

15. NUMBER OF PAGES
292

16. PRICE CODE
N/A

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19, SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

CONFERENCE SECTIONS

1. Quantum Chemistry; Molecular Structure; Chemical Bond.
2. Chemical Kinetics; Photochemistry; Radiochemistry.
3. Chemical Thermodinamics.
4. Adsorption and heterogeneous catalysis.
5. Electrochemistry; Ionic Liquids.
6. Corrosion and Anti-corrosion protection.
7. Physical Chemistry of colloids and macromolecules.
8. Physical Chemistry of Materials; Chemical Engineering.
9. Biophysical Chemistry.
10. Physical Chemistry of the Environment; Physicochemical Analysis.

1.1 ASYMPTOTICAL BEHAVIOUR OF CHEMICAL EVOLUTIONS

by Al. Ivanov, C.I. Hertia, G. Geadau
Institute of Physical Chemistry, 202 Splaiul Independentei, 77208-
Bucharest Romania

The time-evolution of chemical systems is studied. A chemical system is, by definition, a set $\{N_1,\ldots\ldots,N_n\}$ of observables, were N_k, $k\in[1,\ldots,n]$ coresponds to a chemical species S_k, the spectrum of N_k being the set of natural numbers (including 0). From the physical point of view this means that , when N_k is measured in a given state we get as result the number of particles of the species S_k in that state.

In our approach the observables $N_1,\ldots\ldots,N_n$ are selfadjoint operators in a separable Hilbert spaces H. We assume also that $N_1,\ldots\ldots,N_n$ are mutually compatible observables. The states of chemical systems are described by density operators.

The time-evolution of chemical systems are families $\{V_t\}$ (t running the set of real numbers) of unitary operators satisfying the following condition :

(i) If $\varphi \in H$ is a vector such that $N_k\varphi=0$ for all k, $k\in[1,\ldots,n]$, then $N_k (V_k \varphi)=0$ for all k and t ;

(ii) If $\varphi\in H$ is an eingenvector of all N_k $(k\in 1,n)$, then $\lim\limits_{t\to\infty} V_t \varphi$ exists.

For density operators whose eingenvectors are orthogonal on the subspace $\{\varphi\in H, N_k \varphi=0, k\in 1, n\}$, the following two assertions are proved :

T1: If $V_t N = N V_t$ $\left(N=\sum_{k=1}^{n} N_k\right)$ for all t , then $\lim\limits_{t\to\infty} TR\,(V_t \rho V^{*} N_i)$ exists for all k , $k\in[1,\ldots,n]$.

T2: If $\rho^{1/2}$ is a trace - class operator , then $\lim\limits_{t\to\infty} (V_t \rho V_t^{*} N_i)$ exists for all k , $k\in[1,\ldots,n]$.

1.2 THE IMPLICATION OF THE DYNAMICS ON THE SYMMETRY OF CHEMICAL REACTION

C. Ghirvu, I. Humelnicu, M. Constantinescu
The "Al.I. Cuza" University, Faculty of Chemistry, Department of Physical Chemistry , 71
D. Mangeron, 6600 Iasi, PO-BOX 10-2022, Romania

Some aspect concerning the conservation of the symmetry in chemical reactions are discussed on the basis of the fundamental equation of quantum dynamics. This equation permits to establish the physical observable which are constants of the motion, that is they are conserved during the time evolution of the system. However, this analysis is quit difficult when the evolution of the system follows more than one potential energy surface. In this case it is necessary to investigate the effect of the dynamics by doing laborious calculations. The discussions are illustrated for the reaction

$$C(^3P) + H_2\left(^1\Sigma_g^+\right) \rightarrow CH_2(^3B_1)$$

1.3 Regular and chaotic motion in nuclei and metallic cluster

Titus Sandu Institute of Physical Chemistry, 202 Splaiul Independentei,
77208-Bucharest Romania

Ovidiu Dumitrescu Department of Theoretical Physics, Institute of Atomic
Physics, Magurele-Bucharest, R-76900, Romania

Many phenomena observed in many body systems like nuclei and metallic cluster can be explained by mean field approach. The quantisation of a system of fermions moving in a common potential leads to a bunching of levels in a single particle spectrum. On the other hand the quantum mechanical analogue of classically chaotic is one of an intriguing problem. The high symmetry of the Hamilton function is reflected in first integrals of classical system. These give rise to quantum numbers. Classical systems that are nonintegrable have a chaotic behaviour. Chaotic motion in classical system shows in corresponding quantum system in that lesser or no quantum numbers exist. The paper reports the classical and quantum mechanical results for a single particle motion in harmonic oscillator potential with quadrupole deformation and combined with octupole and hexadecapole term.

THEORETICAL INVESTIGATION OF THE REACTION BETWEEN H AND HX (X = HALOGENS)

I. Humelnicu, M. Constantinescu, C. Ghirvu
The "Al.I. Cuza" University, Faculty of Chemistry, Department of Physical Chemistry , 71
D. Mangeron, 6600 Iasi, PO-BOX 10-2022, Romania

The potential energy surface and some aspects concerning the evolution of a chemical system along the minimum energy path are presented for the reaction H and HX (X = halogens). The calculations have performed by using the UHF-MNDO semiempirical method.

1.4 THE ADDITIVITY AND TRANSFERABILITY OF THE ANGULAR OVERLAP MODEL ENERGY PARAMETERS IN MONO- AND BICENTER COMPLEXES.

C.I.LEPADATU*, N.STANICA* and H.-H.SCHMIDTKE**
* Institute of Chemical Physics of the Romanian Academy, Sp.Independentei 202,Bucharest 77208 Romania,
**University of Düsseldorf, Institute of Theoretical Chemistry, Universitätsstrasse 1, 40225 Düsseldorf, Germany.

The additivity and transferability properties of the AOM energy parameters are analyzed using simple EHT models of interacting orbitals. The mono- and bi-center cluster-type complexes are simulated using simple models of interacting orbitals. The exact mathematical analysis of the energy shifts in these systems shows that the antibonding energy shifts located on the central orbital can under certain conditions be expressed in terms of antibonding energy shifts of each separate pair of interacting orbitals. Such analysis justifies the additivity and the transferability of the AOM parameters associated to each metal-ligand bond, so widely used to explain the spectral and stereochemical properties of the transition metal ions. For cluster-type models $\varphi_m - \{\varphi_1, \varphi_2, ..., \varphi_n\}$ of interacting orbitals, the exact formula connecting the energy shifts in this system is $(1 - \sum_{i=1}^{n} S_{im}^2)(\sum_{i=1}^{n} \delta_i + \delta_m) = \sum_{i=1}^{n}(1 - S_{im}^2)(\delta_i^m + \delta_m^i)$, where δ_i^m and δ_m^i are the shift energies in the $\varphi_m - \varphi_i, i = 1 - n$ systems of interacting orbitals(The EHT Coulomb integrals $\alpha_i < \alpha_m$). The obtained formula does not depend on the choice of EHT integrals. Considerations concerning the antibonding and bonding partition of the energy shifts in these systems are also made, in order to understand the additivity and transferability properties of AOM parameters.

1.5 THE INTRINSIC TREATMENT OF PSEUDO-JAHN-TELLER EFFECTS WITHIN ITERATIVE EXTENDED HUCKEL METHOD

L. F. Chibotaru [a], I.B. Bersuker [b] and Fanica Cimpoesu [c]

a) Institute of Chemistry, Academiei str. 3, 277028 Kishinev, Moldova
b) The University of Texas at Austin, Austin, Texas 78712-1074, USA
c) Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest 77208

This work is devoted to the application inside of Extended-Huckel method of our previous results concerning the improvement of the MO theory to be adequate for vibronic analysis. We have examined a Hartree-Fock frame when floating atomic orbitals are used. The flotation of each atomic basis together its own nucleus, during to a molecular distortion (along nuclear coordinate Q) allowed us to eliminate large artifactual, chemically irrelevant, contributions due to the electrostatic effects from cores.

The well known Extended-Huckel methods are oftenly used for inorganic and coordination compounds, i.e. for the systems where the stereochemical consequences of vibronic effects are most visible. The implementation of vibronic analysis within EH semiempiric method is a rather special problem because the separate components of effective Hamiltonian are not analytically available. By contrary, the implementation of vibronic treatment in the methods of ZDO type is only a routine problem, given our previous results that are valid at *ab-initio* level.

An interesting result is that the vibronic constants that describes the coupling of occupied i MO's with the unoccupied ones, n, can be expressed as function of elements from effective EH-type Hamiltonian, but computed in an enforced system of AO-populations, $\overline{\overline{p}}_{\alpha}$,

$$V_{in}(Q)=\sum_{\alpha}^{AO}\sum_{\beta}^{AO}a_{\alpha i}(0)\,a_{\beta n}(0)[H_{\alpha\beta}(\{\overline{\overline{p}}_{\alpha,\beta}(Q)\})-\varepsilon_i(0)\,S_{\alpha\beta}(Q)]$$ where $a_{\alpha i}$ denote LCAO set, which is generally a function of distortion Q.

The enforced populations are obtained from a formal Mulliken analysis:

$$\overline{\overline{p}}_{\alpha}(Q)=\sum_{j}^{occ}\sum_{\beta}n_j b_{\alpha j}(Q)\,b_{\beta j}(Q)\,S_{\alpha\beta}(Q) \text{ with } b_{\beta i}(Q)=\sum_{k}^{occ}\sum_{\gamma}a_{\beta k}(0)\left(a^{-1}(0)\right)_{k\gamma}a_{\gamma i}(Q).$$

1.6 SQUEEZING PHENOMENON IN THE E - e JAHN-TELLER SYSTEM

I.YA.Ogurtsov, S.G.Popa

Institute of Chemistry, Department of Quantum Chemistry,
Academy of Sciences of Moldova, Academiei Str. 3,
Chisinau 2028, Republic of Moldova

The systems in the states with reduced fluctuations of one of their selfadjoint characteristics and simultaneously increased other (the squeezed states (SS)) present continuous interest. Until now mainly the SS of the light were considered. However the electro-magnetic fields are not unique systems which permit creation of the SS.

In this study it is shown that the nonlinearity needed for generation of the SS is inherent to vibronic systems. The general relations between mean-square values of vibronic active coordinates and conjugated momenta are obtained. This relations being specified for the E-e system reveal vibronic dependent squeezing in vibrational subsystem - the reduction of momentum ($\langle p^2 \rangle$) and increasing of the coordinate ($\langle q^2 \rangle$) fluctuations in ground vibronic states. The reduction of the $\langle p^2 \rangle$ is expressed through well known factors of vibronic reduction of electronic operators. In the adiabatic approximation in the revers the expressions for the uncertainity of momentum and coordinates are given in analytical form.

It is established that in the vibronic systems the squeezing phenomenon takes place at the non-zero temperature also. However with temperature increazing the squeezing is less pronounced because in some excited states the coordinate fluctutions are reduced with simultaneous increasing of the $\langle p^2 \rangle$.

1.7 LOW LYING SPIN STATES OF THE NI^{2+}-O^{2-} -Ni^{2+} CLUSTER IN VALENCE-BOND APPROXIMATION

I.Ya.Ogurtsov - Institute of Chemistry,
Academy of Sciences of Moldova,
Academiei str. 3, Chisinau 2028 Md,
Republic of Moldova

G.Munteanu - Institute of Physical Chemistry,
Romanian Academy of Sciences,
Splaiul Independentei 203, Bucuresti,
Romania

After the famous articles of Kramers and Anderson the magnetic properties of the bridge-linked polynuclear compounds are described mainly using the Heisenberg Hamiltonian $-J\Sigma_{ij} S_i S_j$ for super exchange interaction between magnetic ions. The validity of this spin-hamiltonian in superexchange is demonstrate rigorously only for magnetic ions with the values of the spin S =1/2 (one unpaired electron (or hole) per ion). When S is larger than 1/2 the third order terms of perturbation theory (PT) will give the terms in spin-Hamiltonian proportional to $(S_i, S_j)^2$, which can essentialy influence the energy spectrum of cluster.

In this study the low-lying states of magnetic cluster Ni^{2+} -O^{2-} Ni^{2+} in the crystal MgO are investigated in the valence bond approximation. In the PT to third order consideration the 210 configurations of six electrons obtained using localized atomic orbitals d_{z2} and d_{x2-y2} of Ni^{2+} and one 2p-orbital of bridge oxygen are evaluated. The energy eigenvalues of the lowest singlet, triplet and quintet states (degenerated in zeroth order of the PT) are expressed as the functions of the values of the intraatomic exchange, electron two centre (Ni^{2+} - O^{2-}) integrals and the oxygen - nickel charge transfer energy. The results of the valence-band approach and those of Heisenberg Hamiltonian approximation are compared.

1.8 SPIN EXCHANGE SPECTRA OF Ni^{2+} IONS FROM THE $Ni_xMg_{1-x}O$ SYSTEM

F. Niţă and G. Munteanu

Institute of Physical Chemistry "I.G. Murgulescu" of the Romanian Academy
202 Splaiul Independenţei, 77208 - Bucharest, ROMANIA

It is known that when a Ni^{2+} ion is octahedrally coordinated and isolated from other Ni^{2+} ions, its ground state is $^3T_{1g}(^3F)$. In $Ni_xMg_{1-x}O$ system the Ni^{2+} ions are isolated only if $x<0.03$. If the nickel concentration is higher then this limit "NiO" clusters appear in the system and, due to spin exchange interaction, the ground state of a Ni^{2+} ion that belongs to a "NiO cluster" may be a singlet one.

Taking into account only the cationic lattice of the $Ni_xMg_{1-x}O$ system one may observe that in the second coordination sphere of any cation there a six cations located in octahedral positions. The central cation is bonded ***in line***, through an oxygen, with the other 6 cations. The central ion may interact by exchange with one of its neighbours only if the later is a Ni^{2+} ion.

In $Ni_xMg_{1-x}O$ system there are various "NiO clusters". Every Ni^{2+} ion, from such a cluster, is surrounded, in the first coordination sphere, by $\boldsymbol{n}$ Ni^{2+} ions. The probability as such a Ni^{2+} ion to be in a singlet state depends on the value of $\boldsymbol{n}$: this probability increases when $\boldsymbol{n}$ increases.

In a NiO-MgO solid solution there are various NiO clusters each Ni^{2+} that belongs to one of these clusters being characterized by a value of $\boldsymbol{n}$. Naturally $\boldsymbol{n}$ is an integer from 1 to 6, but one may define an average value, $\tilde{n}$, which is a real number. One may say that the probability as any Ni^{2+} ion to be in a singlet state depends on $\tilde{n}$ and, consequently, it is necessary to compute $\tilde{n}(x)$.

It is obvious that the average value, $\tilde{n}(x)$, depends on nickel concentration, increasing continuously from 1 to 6 when $\boldsymbol{x}$ increases from 0 to 1. This function may be computed simulating the $Ni_xMg_{1-x}O$ structure and analyzing, for every value of $\boldsymbol{x}$, the system composition in respect of NiO clusters.

Knowing the $\tilde{n}(x)$ function we computed the probabilities as a Ni^{2+} to be excited in a triplet state or in a singlet one. Having the values of these probabilities we finally computed the "d-d" spectra of $Ni_xMg_{1-x}O$. One observed a good agreement between the computed and measured spectra.

1.9 THE MAGNETIC PROPERTIES OF MIXED-VALENCE TETRAMERIC CLUSTERS

Coropceanu V.P., Paladii F.G., Boldyrev S.I., Gamurar V.J.
State University of Moldova, Department of Theoretical Physics,
Mateevici str.60, Kishinev 2009, Moldova

Mixed-valence clusters containing coupled metal ions in different oxidation degrees are the structural species of many polynuclear coordination compounds [1]. States of the mixed-valence clusters with localized electrons are not the stationary ones. Electron migration redetermines essentially the energy spectrum leading to the resonance splitting of exchange levels and the creation of delocalized states.

The energy spectrum and the magnetic properties of all possible tetrahedral and plane square tetrameric d^n-d^n-d^{n+1}-d^{n+1}-clusters ($n=1\div4$) with bielectron transfer are considered. A new method to determine the energy of tunnel exchange multiplets basing on secondary quantization technique is developed. The group theoretical classification of resonance states of all d^n-d^n-d^{n+1}-d^{n+1} -clusters is obtained. The ground state spin of the above mentioned systems as well as their magnetic properties are found as functions of all the Heisenberg-type, double exchange and transfer parameters. In the case of ferromagnetic Heisenberg-type exchange for the positive values of double exchange parameters the ground state of d^n-d^n-d^{n+1}-d^{n+1} -clusters is ferromagnetic. When double exchange is negative the ground state spin can take on only two values: S_{max} and S_{max}-1, where S_{max} is the maximum value of the full cluster spin. It is shown that the total suppression of ferromagnetism is possible only for the d^0-d^0-d^1-d^1 -cluster, for other clusters the partial suppression of ferromagnetism takes place. In the case of antiferromagnetic Heisenberg-type exchange the ground state of d^n-d^n-d^{n+1}-d^{n+1} -clusters remains antiferromagnetic for arbitrary values of the transfer parameter. In the model of symmetric exchange $J(d^n\text{-}d^n)=J(d^{n+1}\text{-}d^{n+1})=J(d^n\text{-}d^{n+1})$ the multiple "random" degeneration of energy levels takes place. The multiplicity of degeneration is increased essentially in a model with strong double exchange ($J=0$) [2].

The results obtained show the principal difference of tetrameric systems with bielectron transfer from the trimeric and tetrameric systems with one "excess" electron (hole). The latters have the strong double exchange ($P<0$ for clusters with migrating electron and $P>0$ for clusters with migrating hole) leading to the ferromagnetic ground state.

References

[1] G. Blondin, J.-J. Girerd: Chem. Reviews, 90 (1990) 1359-1376.

[2] V.Ia. Gamurar, S.N. Ghifeisman, V.P. Coropceanu, F.G. Paladii: Jurn. Struct. Himii, 36 (1995) 748-753.

1.1o THE MOLECULAR ORBITAL STUDY OF THE TRINUCLEAR $\{Mn_2^{III}Mn^{II}O\}$ CARBOXYLATE COMPLEXES

C.Turta,T.Spataru,L.Casian

Institute of Chemistry of the Moldavian Academy of
Sciences, Academiei str. 3, 2028, Chishinau, Moldova

The structure of the trinuclear carboxylate complexes is similar to that of polynuclear ferritine and can serve as a simple models of this compound. The iterative extended Huckel method (with a forced population of electrons on MO, including d- orbitals of metal in the self consisting process) was used to calculate the electronic structure of the molecular model $[Mn_2^{III}Mn^{II}O(CH_3COO)_6(NH_3)_6]$. The Ammeters expression for the nondiagonal elements was used.

The values of the overlap integrals, calculated using Slater orbitals, between d-atomic orbitals of manganese and p-orbitals of the oxygen atoms are smaller than the same magnitude between the others $\{S_{ij} < 0.07\}$. The energetical splitting of the d- orbitals of metal ions is the least and as a result they form the highest occupied and the lowest unoccupied molecular orbitals of the studied system.

The Jahn-Teller pseudo - effect takes place in the trinuclear carboxylate compound with the pseudo degenerate one electron energetical levels. The HOMO - LUMO interaction between MO, containing dz^2 and dx^2-y^2 atomic orbitals of the metal leads to the activation of the oscillations of M-O bonds. The result agrees with the X-ray data.

1.11 QUANTUM-CHEMISTRY STUDY OF INTERSYSTEM CROSSING IN ALUMOPORPHYRINS Al-P-L (L=methyl,ethyl,izobuthyl,octhyl)

I.Ya.Ogurtsov, N.N.Gorinchoi, A.O.Solonenko -
Institute of Chemistry, Academy of Sciences of Moldova,
Academy str. 3, Kishinev MD2028, Republic of MOLDOVA

R.-M.Ion - ZECASIN S.A., Photochemistry Department,
Splaiul Independentei 202, Bucharest, ROMANIA

The intersystem crossing (ISC) in photosensitisizer is one of the most important step in the process of photochemical generation of the singlet oxygen. The theoretical description of the ISC being complicated for simple chemical photosensitisizers presents extremely difficult problem in the case of big systems such as the alumoporphyrins first of all due to their complicated electronic structure.

In this study the semiempirical method of the quantum chemistry investigation of the ISC is developed. The electronic structure is calculated within the CNDO approximation. The eigenvalues and electronic wave functions of singlet $|S_i\rangle$ and triplet states $|T_j\rangle$ are calculated in the Tamm-Dancoff approximation within the basis set of the single-excited electron determinant functions. The matrix elements $\beta_{ij}=\langle S_i|\hat{h}_{so}|T_j\rangle$ of the spin-orbital interaction are calculated using semiempirical approximation

$$\hat{h} \approx \sum_{i\alpha} \zeta_\alpha g(r_\alpha) \vec{l}_\alpha \vec{s}_i$$

where s_i is the spin operator of the i-th electron, $g(r_\alpha)$ - empirical spin-orbital interaction constant on atom α, $\mathbf{l}_\alpha$ - operator of orbital momentum. In present study the lowest 20 singlets and 20 triplets are taken into consideration.

The ISC probabilities for the states which become populated after the irradiation were estimated. Although the contribution of ligand orbitals to these states is relatively small it was found that the values of β_{ij} strongly depend on the ligand. The results of this study are applicable to the explanation of the mechanism of catalytic activity of the investigated compounds.

1.12 QUANTUM CHEMICAL STUDIES OD DNA MINOR GROOVE BINDERS BISQUATERNARY AMMONIUM COMPOUNDS

Mihaela Hillebrand [1] , Peter Slichers [2] , Jurgen Suhnel [2],
[1] Dep.of Physical Chemistry, Faculty of Chemistry, Univ.of Bucharest,
Bd. Republicii 13 ,70034 Bucharest Romania.
[2] Institut fur Molekulare Biotechnologie, D-07708, Jena ,Germany

Quantitative footprinting studies on bisquaternary ammonium compounds (BQA) yield new data on the dependence of sequence -specific binding of these drugs to DNA AT streches fir different ligands and for different sequence lengths and compositions of the AT sequence regions

Quantum-chemical AM1 calculations were performed on ten compounds belonging to the bisquaternary ammonium heterocycle drugs (BQA), which posess to a differeny extent sequence specificity towards the AT region of the DNA minor groove, in order to obtain information on the lowest energy conformations and the barriers of energy for the conformational transitions; it was found that some conformations are more suitable for the binding processes; even if there are not those of lower energy, the difference is within the range of acceptable barriers. For the terephthalamide derivatives a different model for binding was suggested depending on the meta or para substitution of the benzene ring near the central terephthalic moiety. Some geometric parameters (radius of curvature, the angle between the centroids of aromatic rings..) were discussed in terms of sequence specific binding of the ligands.

The charge distribution pattern reflects a high delocalisation of the positive charges on the heterocycles, slightly influenced by the proximity of the amide or amine groups. Positive values for the electrostatic potentials account for the interaction with the AT negative region of the DNA minor groove.

1.13 MOLECULAR MODELING OF Mg(II AND Mn(II))ATP COMPLEXES AND THE INTERACTIONS IN PHOSPHORYL AND NUCLEOTIDYL ENZYMIC TRANSFER

Alexandrina Donescu*, Josette Weinberg* and
V. Em. Sahini**

* Roumanian Academy, Institute of Physical
Chemistry, Spl. Independentei 202, Bucharest,
Roumania

** University of Bucharest, Faculty of Chemistry,
Bd. Carol I 13, Bucharest, Roumania

The molecular modeling of ATP and its complexes with Mg(II) and Mn(II) was performed by MMX2 Allinger programme. The conformational analysis leads to the minimum energy conformer having ribose ring in the envelope conformation with C_2' atom endo and the triphosphate chain folded toward the base, in accordance with the X-ray data for the type A ATP molecule. The hexacoordinated complexes of ATP with Mg(II) and Mn(II) are performed taking account of the possible chelation centers: α, β, γ phosphate groups, N_7 and NH_2. There are discussed the diverse complexation models and the ligand conformational changes induced by chelation. The interaction of complexed ATP with enzyme in the nucleotidyl and phosphoryl transfer reactions was modeled. The formation of substrate bridge complexes (E-S-M) take place with no change in the ligand field about the metal, but with a large increase in the rigidity of the coordinated water. For the phosphoryl transpher , the atom wich accepts the phosphoryl group does not enter the coordination sphere of the metal, but the phosphoryl group wich is transfered das enter the coordination sphere. The role of the metal in phosphoryl and nucleotidyl transfer in E-S-M complex may be to activate the phosphorous atom wich is to be attacked and to form a rigid complex of the proper conformation in the quaternary complex.

1.14 THE QUANTUM CHEMICAL INVESTIGATION OF THE ORIGIN CHEMICAL BOND IN ACTIVE CENTRE OF THE PROCESSES OF THE POLIMERIZATION ALLENS WITH TRANSITION METALS

Budnikov S.S.
Institute of Chemistry, Departament of Quantum Chemistry, .
Academy of Sciences,
Repablic of Moldova, Academiei 3, Kisihinev 2028MD.

Lately the theoretical aspects of the homogeneous catalysis become very important, because they are developed of scientific bases for catalyst preparation. Bifunctional catalysts on the base of transition metals are one of this interesting type of the catalysts.

The electronic structure of the active centres bifunctional catalysies polimerization allens were investigated by the quantum chemical methods (CNDO and MNDO) . The origin of the chemical bond for two pairs of metals was analysed. The variation of the metals Al -Ti and Mg - Ti in the same conditions gives the biggest destribution of the charges in the active centres. This modification of the catalyst changes the equilibrium geometry of the active centre and increases the charges of the metals in the row Al - Ti<Mg - Ti. The distanses of the $R_{Me\text{-}Callen}$ inlarges in this case too. The oders of the chemical bonds in the whole system AC - R have been changed. The correlation between electronic parameters of the system AC - R and catalytic activity was shown. The catalytic activity of the system with Mg - Ti is more 10 times than Al - Ti one. The both methods give the same results in investigation case.

1.15 NOTE ABOUT CHEMICAL REACTIVITY

M. Mracec[a], Maria Mracec[b]

[a] Western University of Timisoara, Faculty of Chemistry, Department of Chemistry, Str. Pestalozzi 16, R-1900 Timisoara
[b] Romanian Academy, Timisoara Branch, Inorganic Chemistry Laboratory, Bv. Mihai Viteazu 24, R-1900 Timisoara

Some problems concerning the significance and the measures of chemical reactivity are discussed. Adopting the philosophical concept of global character of all interactions and responses [1,2] it follows that chemical reactivity must have the same significance in all fields of theoretical and experimental chemistry: thermodynamics, kinetics and structural chemistry.

From thermodynamics point of view the chemical reactivity can be the most appropriately expressed by the chemical potential, i.e., by the variation of the free energy with the concentration.

In structural chemistry there is a similar notion, i.e., the electronic chemical potential. For an atom, or a molecule with a certain internal structure, the variation of the free energy must be similar to the thermodynamical variation:

$$dF = dE - TdS - \mu dN \tag{1}$$

In relation (1), F, E and S are free energy, internal energy and electronic entropy, respectively. N is the number of electrons and μ is the electronic chemical potential. If the variation of internal energy depends only on the variation of the number of electrons, and if the free energy and entropy are constants, then:

$$\mu = -(\partial E/\partial N) \approx \chi_M = 1/2(I+A) \tag{2}$$

Thus, the electronic chemical potential is approximately the Mulliken electronegativity [3]. Relation (2) was demonstrated by Pearson [4] from the thermodynamic expression of the free enthalpy, but he supposed that the temperature and pressure must be equal to zero. Our demonstration does not imply this requirement.

References

[1] D. Bohm, **Wholeness and the implicate order**, Routledge, London, 1980

[2] N. Georgescu-Roegen, **The entropy low and the economic process**, Harvard Univ. Press, Cambridge, 1971

[3] R. P. Iczkowski şi J. L. Margrave, *J. Amer. Chem. Soc.*, **83**, 3547 (1961).

[4] R. G. Pearson, *CHEMTRACTS-Inorg.Chem.*, **3**, 317 (1991)

1.16 THE QUANTUM-CHEMICAL INTERPRETATION OF THE STAGES OF CATALYTIC INITIATION OF REDOX PROCESSES

Sichiov A.Ia., Ogurtsov I.IA., Sapunova N.V.
Department of Physical Chemistry
Moldova State University, Mateevici str.60,
Chisinau 2009 Md, Republic of Moldova

There are a lot of reactionable particles (intermediates, ferril complexes, free radicals) in the initiation stages of redox processes (substrate - H_2O_2) catalyzed by iron ions and coordination compounds. Even in those rare cases when it is turned out well to determine them it is vague why they are generated in the redox process.

With the aim of theoretical consideration of the initiation possibility of ferril particles in Fenton's system, the quantum chemical calculations $[Fe(H_2O)_6]^{2+}$ electronic strcucture and a number of hypothetical complex compounds which have been supposed as intermediates in literature and the calculations of all peroxy-particles (H_2O_2 , HO_2^-, $H^\circ O_2$, OH) have been carried out using the Mulliken-Wolfsberg-Helmholz method of SCF MO LCAO calculations. As a result, the values of selfconsistent charges and orbital populations and the values of electronic levels of MO energy have been obtained. The estimation of electronic transfer from MO of iron complex to MO of peroxy-particle has been carried out and the values of such charge transfer have been determined.

It has been shown by means of quantum-chemical calculations that the formation of ferril particles isn't possible in weak medium. The formation of $[Fe^{II}(H_2O)_5(HO_2^-)]^+$ peroxycomplex and ferril ion $[Fe^{IY}O(H_2O)]^{2+}$ is possible under increasing pH. The addition of α,α'-bypyridil (ligand) into Fe^{2+} -H_2O_2 system gives the possibility of the formation of $[Fe^{II}(\alpha,\alpha'\text{-bypyridil})_2(HO_2^-)]^{2+}$ peroxycomplex which may initiate ferril complex. The interaction of latter one with water molecule leads to the formation of $O^\circ H$ radical.

1.17 THE USE OF MN(II) COMPLEXES FOR THE ACTIVATION OF MOLECULAR DIOXYGEN

T.Spataru, S.Levitski*

Institute of Chemistry of the Moldavian Academy of
Sciences, Academiei str. 3, 2028, Chishinau, Moldova
* Moldova State University, Chishinau

An iterative extended Huckel method with a forced population of electrons on MO, including d-orbitals of metal, in the self-consisting process was used to calculate the electronic structure of complexes $[Mn(phen)_2H_2O]^{+2}$ (I) and $[Mn(HCO_3)_2(H_2O)_3]$ (II), where phen - 1,10- phenantroline.

In the second order approximation of the perturbation theory (Klopman's formula), it has been shown that the interaction of (I) with molecular dioxygen gives the perceptible change of the total energy of reagents. However, in the case of (II) the total energy of reagents is equal to zero in the used approximation.

Using the vibronic theory of the activation of small molecules the activation energy of O_2 by (I) during the elementary act has been calculated. The values obtained are equal to -4.59 eV for monocoordinated and -4.69 eV for bicoordinated dioxygen.

The following mechanism of the oxidation process of leuco-compound has been suggested:

1. $Mn^{+2} + 2\ phen = [Mn(phen)_2]^{+2}$

2. $[Mn(phen)_2]^{+2} + O_2 = [Mn(phen)_2O_2^{\delta-}]^{+2}$

3. $[Mn(phen)_2O_2^{\delta-}]^{+2}$ + leuco-compound = the oxidation products

The results agree with the experimental data of the activation of molecular dioxygen by Mn(II) complexes.

1.18 THEORETICAL STUDIES ON DEHYDROEPIANDROSTERONE SULFATE(DHEAS). THE MATHEMATICAL MODELING OF THE MACROCOMPLEX BETWEEN DHEAS AND AMP (ADENOSINE MONOPHOSPHATE) TAKING INTO ACCOUNT WATER MOLECULES.

Josette Weinberg[a] and Constantin Balaceanu-Stolnici[b]

[a] Institute of Physical Chemistry, Spl.Independentei 202 ,
Bucharest, Roumania.
[b] Ecological University of Bucharest, Roumania.

Dehydroepiandrosterone(DHEA) is one of the important hormon secreted by the adrenal cortex. Till now is yet little known about its biological function.

DHEAS(that means the sulfurylation of DHEA) is now a very promising hormon in the struggle against the aging process.

It is very important to elucidate the role of sulfurylation in steroid hormon formation.

The literature data postulate the stacking of adenine from AMP with the ring A from DHEAS for the enzyme-bound transition state. This structure explains some of the remarkable properties of DHEAS.

The present study is a theoretical one effected by molecular mechanics of Allinger in MM2 force field.

By this method were modeled DHEA, DHEAS, the macrocomplex DHEAS-AMP and this one taking into account a number of water molecules and also in the presence of Ca, Na, K and Cl atoms.

The interesting results, obtained sometimes using the docking, yield some hypothesis for elucidating the biological role of DHEAS.

1.19 STRUCTURE -NEUROTOXIC ACTIVITY OF ß-LACTAM ANTIBIOTICS. III . THE MATHEMATICAL MODELING OF THE CEPHALOSPORINE - SEROTONIN COMPLEX.

Josette Weinberg[a] , Constantin Balaceanu-Stolnici[b] , Dolphi Drimer[b] and Dan Lerner[c]

a- Institute of Physical Chemistry , Splaiul Independentei 202, Bucharest, Roumania
b- Ecological University of Bucharest, Roumania
c- ENSCM, France

In a previous paper, the autors have reported that in view of their great ressemblance (the nucleous structure of cephalosporines with the indolic rings from serotonine) , the last one should form with them a CT complex ; in this way, the serotonine may be the antibiotic carirer to the neuronal receptor situs .

The aim of the present paper is a theoretical study by molecular mechanics of the complexes of cefazoline , ceftezole and benzylpenicilline with serotonine and a reprezentative group for serotonine receptors.

The results , the total energy and the dipole moment , obtained in MM2 force field (using the docking) , emphasize the facillity of cefazoline-serotonine -R complex to form . From this series , cefazoline has the most neurotoxic activity.

1.20 CHEMICAL REACTIVITY OF SOME CATIONIC DYES IN AQUEOUS AND MICELLAR SOLUTIONS

L. Lupan

Institute of Physical Chemistry "I.G. Murgulescu" of the Romanian Academy
202 Splaiul Independenţei, 77208 - Bucharest, ROMANIA

The extreme sensitivity of the absorption spectrum to small changes in the medium polarity made acridine and thiazine dyes useful molecular probes in the study of micelle-solution interface.

In a previous paper we studied the association of acridine yellow, proflavine and methylene blue with sodium dodecylsulphate and its effect on the pK_a of the equilibrium between the monocationic and neutral forms of the dyes.

In this paper we present preliminary results regarding some reactivity indexes of acridine yellow, proflavine and methylene blue and their monocations, evaluated by semiempirical quantum chemical calculations in MO approximation. Taking into account these data we explained some properties of acridine yellow, proflavine and methylene blue like the basicity constants (pK_a), the reduction potentials and the order of stabilization of monocation form in micellar medium.

1.21 THE REACTIVITY STUDY OF 4-METHYL TRIAZOLINEDIONE

Ana-Maria ALSTANEI*, Micheline CARLES**, Jean-Pierre AYCARD**
*University of Bucharest,Faculty of Chemistry,Departement of Physical-Chemistry
**Universite de Provence, Aix-Marseille I, France

4-methyl-1,2,4-triazoline-3,5 dione (4-MTAD) is a molecule of special interest and versatility. For example, it reacts rapidly with conjugated dienes in a Diels-Alder fashion, with various olefins in an ene fashion and also with ethers.

We have studied the photochemical reactivity of 4-MTAD with 1,4-dioxan, 12-crown-4 and 18-crown-6. The obtained compounds have been studied by IR-TF spectroscopy, UV-VIS spectroscopy and 400 MHz ^{1}H and ^{13}C-NMR spectroscopy.

1,4-dioxan gives only equatorial monosubstituted compound, usually for cyclohexanic series with bulky substituent.

With macrocyclic ethers both mono- and disubstituted compounds are identified and characterized. The remarkable ability of macrocyclic ethers to selectively complex metal cations is well known.Thus we try to obtain the complexes with alkali cations and follow the modification of this property after the substitution.

1.22 SUPRAMOLECULAR COMPLEXES OF L-ALANINE-4-NITROANILIDE CATION WITH CROWN ETHERS INVOLVING TETRAPHENYLBORATE AS ANION PAIR

C. Luca[a], Irina Cristina Covaci[b], M.T. Caproiu[c], M. Maganu[c], P. Ionita[b] and T. Constantinescu[b]

a. "Polytechmica" University, Faculty of Chemistry, Str. Polizu, 1, Bucharest
b. Romanian Academy, Institute of Physical Chemistry, "I.G.Murgulescu", Spl. Independentei 202,
c. Romanian Academy, Institute of Organic Chemistry, "C.D. Nenitescu", Spl. Independentei, 202B, Bucharest

The supramolecular complexes **3a, b, c,** (**$[EC...H_3N\text{-}R]^+Ph_4B^-$**, where: **$H_3N^+\text{-}R$** = cation of L-alanine-4-nitroanilide, **Ph_4B^-** = tetraphenilborate anion, **EC** = crown ether like, **a** = 18C6, **b** = Dicyclohexyl-18C6, **c** = Benzo-18C6) were obtained in high yields (87-100%) in solid state (**eq.1, eq. 2** where: **1** = L-alanine-4-nitroanilide hydrochloride, **2** = L-alanine-4-nitroanilide tetraphenilborate).

$$\underline{\underline{1}} + Na^+Ph_4B^- \longrightarrow \underline{\underline{2}} + NaCl \qquad \text{(eq.1)}$$

$$\underline{\underline{2}} + CE\ (\underline{\underline{a}}, \underline{\underline{b}}, \underline{\underline{c}},) \longrightarrow \underline{\underline{3}}\ \underline{\underline{a}}, \underline{\underline{b}}, \underline{\underline{c}}, \qquad \text{(eq.2)}$$

The supramolecular complexex **3a, b, c,** where optically active and hydrophobic. The experimental results regardes the complexes characteristics (UV, NMR, and α_D) and also their stability in water/methylene chloride biphase syste, are presented.

1.23 THE SYNTHESIS AND PROPERTIES OF 4N,13N - BIS - (3' HYDROXY - 6' METHYL - 4' OXO - 4' PYRANYL - 2' METHYLENE) - 4,13 DIAZA - 1,7,10 16 -TETRAOXACYCLOOCTADECANE

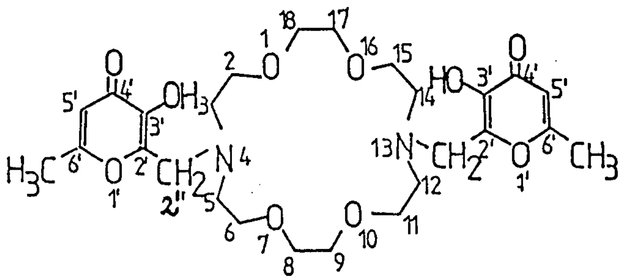
F. Badea[a], A. Stoica[b], M. T. Caproiu[c] and T. Constantinescu[b]

a.Polytechnic University, Department of Organic Chemistry, Str. Polizu 1, Bucharest, Romania

b.Institute of Physical Chemistry, Spl. Independentei 202, Bucharest, Romania.

c."C.D.Nenitescu", Institute of Organic Chemistry, NMR Department, Spl. Independentei 202 B, Bucharest, Romania.

The title compound (4N, 13N, - bis (3' hydroxy - 6' - methyl - 4' oxo - 4' pyranyl - 2 methylene)- 4,13 diaza - 1,7,10,16 -tetraoxa cyclooctadecane) , 5, was obtained by a Mannich condensation starting from 3-hydroxy -6 - methyl - 4H-pyran - 4 - one, 3, Kryptofix 22, 4, and formaldehide. The structure of the product was proved by spectral investigations (UV - Vis, IR, NMR). In agreement with the admitted structure, compound 5 shows hydrophobicity and chelating properties . The protonation constants of both 3' - hydroxyl groups and of the two nitrogen atoms were determined together with the isoelectric pH value.



5

1.24 HIGH-THERMALLY STABLE NiO PHASE OBTAINED FROM HYDROTALCITE-LIKE PRECURSORS WITH DIFFERENT Ni/Al RATIOS

Margareta Craiu, Eugenia Ivana, Mihaela Jitianu
Instit. of Physical Chemistry, 202 Spl. Independentei,77208 Bucharest, Romania

Ni-containing oxidic forms with high thermal stability were obtained using Ni-Al hydroxycarbonates as precursors /1/.

Three distinct phases were identified in the oxidic forms obtained by calcination between 400 and 900°C using a method of isothermal reduction followed by thermoprogrammed reduction (TPR) experiments: nickel oxide, easily reducible (aprox. 400 °C) but with a long induction period of the reduction (I), and two solid solutions corresponding to two TPR peaks at 500°C (II) and at 600°C (III).

Neither XRD nor IR spectroscopy were able to distinguish between these two phases. Only a more or less well formed NiO phase could be identified in samples calcined up to 900 °C. For the sample calcined at 900 °C, XRD, IR and diffuse reflectance spectroscopy revealed the presence of a small amount of an incipient spinel phase. Relative areas of the corresponding TPR peaks indicate that only aprox. 5% of the total Ni content is included in this latter phase.

Until recently, the existence of such a NiO phase having the mentioned reduction properties, was only infered from alkaline leaching experiments /2/.

Based on combined experiments of isothermal reduction followed by TPR, the relative proportions of phases I, II and III was found to depend on the Ni/Al ratio in the HT-like precursor. For low Al content, i.e. for high Ni/Al ratios, phase I is preponderent (up to 50 %) in the mentioned calcination temperature range. On the contrary, from HT-like structures with a high Al content having Ni/Al ratios near to an aluminate composition and calcined at low temperatures (400-450 °C), only phases II and III were obtained. Moreover, this structure is not thermally stable. A spinel structure develops starting with calcination temperatures of 600 °C, as shown by diffuse reflectance and IR spectroscopy. The identified phases I and II+II are supposed to present different adsorbtive and catalytic properties.

References

1. Clause O., Gazzano M., Trifirò F., Vaccari A. and Zatorski L., Appl.Catal. 73 (1991) 217-236
2. Clause O., Rebours B., Merlen E., Trifirò F. and Vaccari A., J.Catal. 133 (1992) 231-246

1.25 STABILITY RANGE OF HYDROTALCITE-LIKE COMPOUNDS

Rodica Marchidan and Eugenia Ivana
Instit.of Physical Chemistry, 202 Spl.Independentei, 77208 Bucharest, Romania

Various hydrotalcite (HT)-like structures having the general formula: $\left[M_p^{2+}M_q^{3+}(OH)_{2(p+q)}\right]^{q+}\left[(A^{n-})_r \cdot mH_2O\right]^{nr-}$ (where M^{2+} and M^{3+} are divalent and trivalent cations, respectively, and A^{n-} are n-valent interlayer anions) are known to exist within a wide range of M^{2+}/M^{3+} molar ratios. The limits of M^{3+} replacement for M^{2+} ions are usually established based on cell parameter data.

In the present paper, the causes of cation replacement limits and the accompanying structural changes in HT-like, double layered structures are discussed. Two aspects were taken into account in earlier studies, both concerning the main brucitic layer: (a) the mutual repulsion between M^{3+} substitutions, which causes them to place themselves as far as possible from one another and (b) the total cation charge admitted around any hydroxyl ion. But if another aspect, concerning the interlayer is taken into account, as revealed by our recent results, new conclusions concerning the causes of cation replacement limits can be drawn:

(1) With increasing M^{3+} substitution for M^{2+} ions, at $x_{M^{3+}} = 0.2$, a minimum anion density of 0.11 CO_3^{2-} groups per cationic position is attained, which proved itself necessary to switch from the close packed stacking of brucitic layers characteristic for $Mg(OH)_2$, to a HT-type stacking in which anionic interlayers assure the binding of the brucitic layers.

(2) One can speak of HT-like or double layered structures as long as the bond between the brucitic layers is assured by interlayer anions and hydrogen bonds intermediated by the oxygen atoms from the interlayer.

(3) In the M^{3+} substitutional range, $0.2 < x_{M^{3+}} < 0.44$, characteristic for pure HT-like structures, there is a point, $x_{M^{3+}} = 0.33$, beyond which a new type of charge compensation, characteristic for $Al(OH)_3$, develops gradually along with that assured by the anionic interlayer. Since the type of binding between brucitic layers remains unchanged, this point represents only the transition between stable and metastable HT-like structures.

(4) The switch to $M(OH)_3$ structures at the high substitution limit of the pure HT-like range and the mentioned switch to $M(OH)_2$ structures at the low substitution limit occur at nearly the same critical value of interlayer anion density.

I.26. THE DESIGN OF HETEROPOLYMETALIC SYSTEMS USING THE ANION $[Cr(bipy)(C_2O_4)_2]^-$ AS BUILDING BLOCK. CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES.

Marius Andruh[a] and Fernande Rochon[b]

a) University of Bucharest, Faculty of Chemistry, Dept. of Inorg.Chem., Dumbrava Rosie no.23, Bucharest 70254, Romania
b) Universite du Quebec a Montreal, Montreal CP 8888 H3C 3P8, Canada

The self assembly of the building blocks $[Cr(bipy)(C_2O_4)_2]^-$ with bivalent metal ions (Ba(II),Mn(II),Co(II) and Cu(II)) led to quite different structures: $[BaCr_2(bipy)_2)(C_2O_4)_4(H_2O)]_n\ nH_2O$ **(1)** , $[MnCr_2(bipy)_2)(\mu\text{-}C_2O_4)_4(H_2O)]_n$ **(2)**, $[CoCr_2(bipy)_2)(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2\ ]H_2O$ **(3)** and $[CoCr_2(bipy)_2)(\mu\text{-}C_2O_4)_2(C_2O_4)_2(H_2O)_2\ ]H_2O$ **(4)**. In addition, a complex derived from Ag(I) is reported: $[AgCrbipy(\mu\text{-}C_2O_4)_2(H_2O)_2\ ]$ **(5).**

The molecular and crystal structures of the above compounds were determined by X-Ray diffraction. The compound **(1)** is a scaffolding-like lattice with a unique three-dimensional structure. The compound **(2)** revealed a novel heterobimetallic chain with octacoordinated manganese(II) atoms, with stereochemistry of a flattened square antiprism. The molecular structures of **(3)** and **(4)** consists in discrete linear {CrMCr} trinuclear species with the divalent atom lying on an inversion center. In the case of {CrCuCr} complex, the copper atom exhibits a [4+2] axially elongated octahedral geometry, the axial sites being occupied by two oxalato- oxygen atoms. The compound **(5)** contains discrete metallacicles formed by two Cr(III) and two Ag(I) ions bridged by oxalato groups. The magnetic susceptibility data for **(1)** reveal an irregular spin state structure with S=5/2 groundstate and an antiferromagnetic interaction between the central copper(II) and the chromium(III) ions ($J=-18.8\ cm^{-1}$).

The $[Cr(bipy)(C_2O_4)_2]^-$ units retain their original environment and accomplish different coordination functions, acting as terminal and/or bridging ligands. The synthetic approach, namely the reaction of an aqueous suspension of the barium derivative, **(1)** , with a transition metal sulfate, seems to have a wide applicability in designing new heterobimetallic systems.

1.27. CRYSTAL STRUCTURE AND SOLID PHASE REACTIONS OF SOME COMPLEX CATION- COMPLEX ANION TYPE COORDINATION COMPOUNDS

Marius Andruh[a] , Fernande Rochon[b] and Marilena Cimpoesu[a]

a) University of Bucharest, Faculty of Chemistry, Dept. of Inorg.Chem., Dumbrava Rosie no.23, Bucharest 70254, Romania
b) Universite du Quebec a Montreal, Montreal CP 8888 H3C 3P8, Canada

This work is placed in the continuation of our studies concerning the solid phase rearrangements of ligands between cationic and anionic coordination spheres of the title compounds. A general process of the form,

$$[M(AA)_3][M'X_4]{-}{-}{-}{>}[M(AA)_2X_2] + [M'(AA)X_2], \qquad (I)$$

(where M,M'-3d metals , X halides, AA-aromatic diamine),
accompanied by thermochromism, was proved for a large variety of systems.

Here we report the molecular and crystal structures of the $[Fe(bipy)_3][ZnCl_4]$, the first compound of the $[M(AA)_3][M'X_4]$ series characterized by X-ray diffraction.

Another structurally characterized complex is $[Ni(phen)_2(H_2O)_2][ZnCl_4]$. This was obtained by a synthesis route that uses the $[Ni(phen)_2Cl_2]$ intermediate isolated from the solid phase reaction of type (I) in the $[Ni(phen)_3][PdCl_4]$ complexes.

This is a chemical evidence of the migration process (I), because otherwise, its products are not adequate for direct X-ray diffraction study.

Electronic spectra these complexes are discussed. The ligand-field electronic spectrum of the previous nickel complex is in accordance with the *cis* structure revealed by diffraction study. The spectral changes accompanying solid phase processes without weight-loss correspond to the modifying of the initial stereochemistry. The spectrum of iron complex is not of ligand field type, due to charge transfer effects, being then less sensitive to the structural changes promoted at heating.

1.28. THERMAL BEHAVIOUR OF COMPLEX CATION- COMPLEX ANION TYPE MIXED LIGAND COORDINATION COMPOUNDS

Marilena Cimpoesu[a] , Marius Andruh[a], Eugen Segal[b] , Aura Meghea[c] ,
Stefania Tănase[a], Gabriela Marinescu[a] and Titus Albu[d]

a) University of Bucharest, Faculty of Chemistry, Dept. of Inorg.Chem., Dumbrava Rosie no.23, Bucharest 70254, Romania
b) University of Bucharest, Faculty of Chemistry, Dept. of Physical Chemistry, B-dul Carol no.13 , Bucharest, Romania
c) Polytechnic University of Bucharest, Polizu no.1, Bucharest, Romania
d) Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest 77208, Romania

The reversible and irreversible thermochromisms of some complex cation-complex anion type coordination compounds are reported.

The colour change is caused by a thermally promoted solid state izomerisation of this type of compounds, namely the migration of ligands between the two coordination spheres.

This work deals with the influence of mixed ligand nature of cationic or anionic sphere of the title compounds complex cation and of complex anion in thermochromic process. The thermal stability and non isothermal decomposition kinetics of the compounds are discussed in this view. Two series, with mixed-ligand cation,

$$[Ni(phen)_a(bipy)_{3-a}][M'X_4]$$

(where, M'=Zn, Co, Ni, Cu; a=1-2; phen=1,10 phenanthroline; bipy= 2,2' bipyridine), and with mixed ligand anion,

$$[M(phen)_3][CuX_2Y_2],\ \text{(where M=Ni,Co, X= Cl}^-\text{, Y=Br}^-\text{)}$$

were investigated. The migration of ligands is proved by means of thermogravimetric and EPR studies, as well as by UV-VIS and IR spectroscopy techniques. The parameters obtained from these physical methods are correlated to the presumed structure of the compounds.

1.29. POLYNUCLEAR COORDINATION COMPOUNDS OF Cu(II), Ni(II) AND Zn(II) WITH SCHIFF BASES DERIVED FROM 3-FORMYLSALICYLIC ACID

Floriana Tuna [a], Luminita Patron [a] and M.Andruh [b]

a) Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest
b) Faculty of Chemistry, University of Bucharest, Dumbrava Rosie 23, Bucharest

Polynuclear transition-metal complexes are of great interest because they provide the opportunity to study the mechanism of superexchange interaction between paramagnetic ions, as well as the roles of the metal ions in multielectron redox reactions. The studies of these compounds have often been performed either in relation to the modeling of some metalloenzymes containing several kinds of metal ions or with the perspective to design novel molecular materials, in particular molecular-based magnets.

This report relates to the synthesis and characterization of some trinuclear complexes, $[M_3(fsaaep)_2X_2]$ (**1a**), $[M_3(fsaamp)_2X_2]$ (**1b**), $[M_3(fsaaba)_2].nH_2O$ (**1c**) ($M = Ni^{II}, Cu^{II}$ or Zn^{II}; $n = 0$ or 6; $X = ClO_4^-$ or NO_3^-), where H_2Fsaaep, H_2fsaamp and H_3fsaaba denote 3-(N-(2-pyridylethyl)formimidoyl)salicylic acid, 3-(N-(2-pyridylmethyl) formimidoyl) salicylic acid and 3-(N-(2-carboxyphenyl)formimidoyl)salicylic acid, respectively.

The bivalent transition metal complexes (**1a**) and (**1b**) were prepared by a template procedure. 3-Formylsalicylic acid (H_2fsa) used as a starting material was prepared after a method previously reported.The metal compounds (**1c**) were obtained by treating the ligand itself,H_3fsaaba,with the corresponding bivalent 3d metal salts.

Analitical data and conductance,spectral and magnetic studies support the trinuclear formulations of these complexes.The RPE spectra measured as a fonction of temperature for the copper(II) complexes confirmed also this structure.

1.30. COMPLEX COMPOUNDS WITH MACROCYCLES LIGANDS

Corina Onutu [a] *, Luminita Patron* [a] *, and Aurelia Meghea* [b]

a) Institute of Physical Chemisry , Splaiul Independentei 202 , Bucharest 77208, Roumania
b) Polytechnic University of Bucharest , Polizu no. 1 , Bucharest , Roumania

Polynuclear macrocyclic complex compounds of transition metal ions represent a helpful tool in the study of the mechanism governing metal - metal introductions or substrate activation by metal centers. The recognition that the accomplishment of several biological functions needs polynuclear metal centers has given a strong impulse to the study of multi - site macrocyclic complex compounds as model systems.

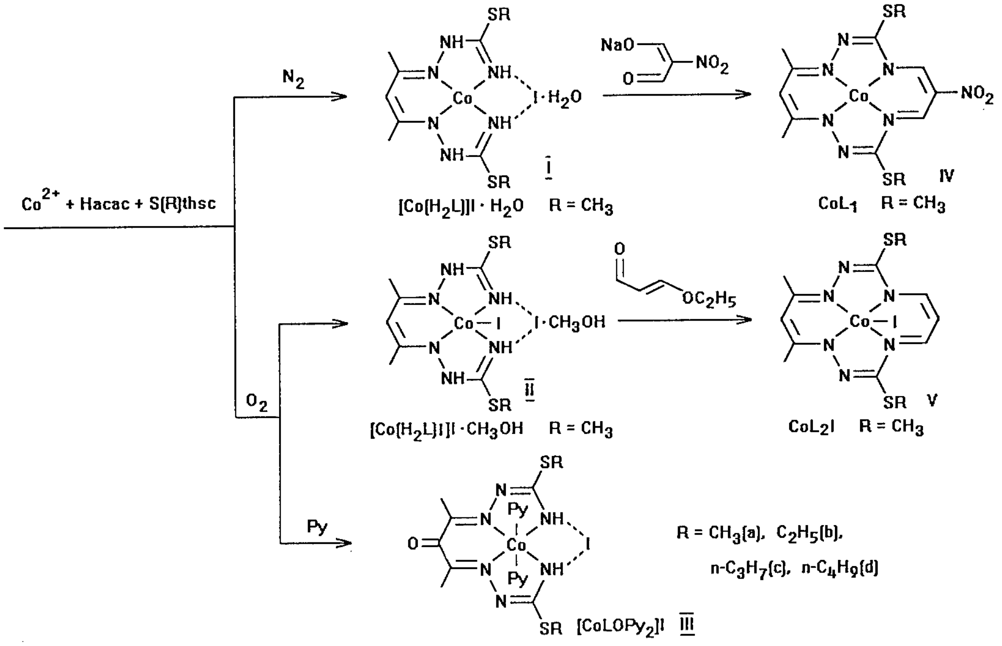
In this report we related to the synthesis and characterization of some binuclear or trinuclear complex compounds with the general formula : $[M_2L]X_2$ and $[M_3L'L'']X_6$ ($M = Ni^{II}$ or Cu^{II} ; $X = ClO_4^-$; L and $L' L''$ denoted the macrocyclic ligands) . The formula of these complex compounds was established on the base of elemental chemical analysis corroborated with both visibil , IR , and EPR spectral data and magnetical measurements .

1.31. SYNTHESIS AND STUDIES OF COBALT HEXAAZAMACROCYCLIC COMPLEXES

Julieta Gradinaru, Nicolae Gerbeleu
Institute of Chemistry, Moldova Academy of Sciences,
Academy str.3., Chisinau, Moldova

The template strategy was successfully used for building of Ni(II) macrocyclic complexes on the basis of S-alkylated thiosemicarbazides.

We have shown that Co(II) and Co(III) are also effective as a template centre. So, three types: planar, pyramidal and octahedral chelates were synthesized, according to the scheme:



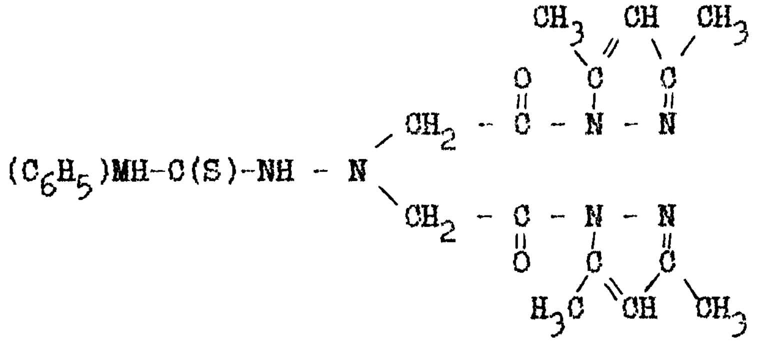
These complexes, due to their geometry and nature of donor atoms of the unclosed part of ligands, can be tailored into macrocyclic products. Indeed, on interaction of freshly prepared $[Co(H_2L)]I \cdot H_2O$ (I) with sodium salt of nitromalondialdehyde monohydrate, the macrocyclic complex CoL_1 (IV) is formed. In the mass spectrum the peak with m/z 412 corresponding to $[M]^+$ is present. This product is a low spin (μ =2,28 M.B. at 291K), but unlike the precursor is stable in air. Its ESR spectrum is characterized by $g_{\text{eff}} = 2,4$ in $CHCl_3$ solution.

If II was used as precursor in the condensation with ethoxyacroleine the five-coordinate macrocyclic species $[CoL_1I]$ (V) has been obtained. This assumption is confirmed by elemental analysis, IR (the absence of ν_{NH} and $\nu_{C=O}$), MS data (the presence of m/z corresponding to $[CoL_2I]^+$).

1.32. INTERACTION OF BIS-3,5-DIMETHYLPYRAZOL-1-YL-AMIDE OF 4-PHENYLTHIOSEMICAARBAZIDEDIACETIC ACID WITH COBALT(II) AND COPPER(II) SALTS

Olga A.Bologa, V.I.Lozan, N.V.Gerbeleu
Institute of Chemistry of Academy of Science of R.Moldova

The synthesis of the product of interaction between dihydrazide of 4-fenilthiosemicarbazidediacetic acid with 2,4-pentandione was realized. The product A of condensation of initial component in ratio 1:2 was obtained, as result of this reaction.



(A)

The obtained compound reprezent bis-3,5-dimethylpyrazol-1-ylamide of-4-phenylthiosemicarbazidediacetic acid.

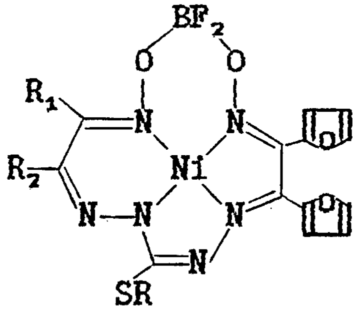
In the course of interaction of A with cobalt(II) and copper(II) salts there take place the hydrolysis of amide C(O)-N bond of A in each two equivalent branches of the ligand with the formation of the 4-phenylthiosemicarbazidediacetic acid $(C_6H_5)NHC(S)NHN(CH_2COOH)_2$ (H_2L) and 3,5-dimethylpyrazole (Pir). Such transformation of initial organic compound A is a result of coordination of pyrazole rings to metal ion, acompanyed by electronic density withdrawing from the N1 atom, with weakness of the C(O)-N bond and the subsequent nucleophilic attack of the later by water molecules and the hydrolysis of amide bonds. The final result of reaction are the complexes $[CuL\ Pir\ H_2O]\ H_2O$ and $[CoL\ Pir\ H_2O]\ 2H_2O$. The band of stretching vibrations of coordinated COO^--group appear in the IR spectra of these compounds at 1580 cm^{-1}, which is characteristic for metal complexes with H_2L. The data of thermogravimetric analysis permit to conclude, that the molecule of water and pyrazole are entered in the composition of final products.

1.33. ^{19}F NMR SPECTROSCOPY FOR STUDY OF NICKEL COMPLEXES OF BF_2^+ BRIDGED

Svetlana G.Baka, Lubov A.Nemchinova, Nicolae V.Gerbeleu
Institute of Chemistry of the Academy of Sciences of RM,
Kishinev, Moldova

Macrocyclic compounds have been the focus of considerable interest in recent years. Previously we have been exploring a new series of macrocyclic complexes of nickel in which original bridging proton of the precursor system have been replaced by BF_2^+ group[1]. These complexes have been characterized by microanalysis, visible, (^{1}H, ^{13}C) NMR and mass spectral data.

In this communication we present the results of ^{19}F NMR investigations of folowing Ni(II) macrocyclic complexes with ligands on the basis of S-alkylisothiocarbohydrazide (alkyl - CH_3, C_2H_5, $CH_2C_6H_5$) and monoximes (diacethyl-, α-furilmonoximes, isonitrosoacetone):



^{19}F NMR Spectral Data of I-VIII

	R	R_1	R_2	a	b
I	CH_3	CH_3	CH_3	−149.63	−149.16
II	C_2H_5	CH_3	CH_3	−149.47	−149.10
III	CH_3	H	CH_3	−149.83	−149.42
IV	C_2H_5	H	CH_3	−149.83	−149.48
V	$CH_2C_6H_5$	H	CH_3	−149.83	−149.24
VI	CH_3	C_4H_3O	C_4H_3O	−150.0	−149.57
VII	C_2H_5	C_4H_3O	C_4H_3O	−149.95	−149.58
VIII	$CH_2C_6H_5$	C_4H_3O	C_4H_3O	−149.83	−149.55

a-in CD_3CN; b-in DMSO; relative to C_6F_6 internal standard (δ −162.9)

The ^{19}F NMR spectra of I-VIII in CD_3CN, DMSO, $CDCl_3$ show several trends that assist in their identification and characterization (Table). In particular, the compounds have only one resonance as is expected for the two chemically equivalent fluorines and his value (−150 ppm) is typical for fluorine on tetrahedral boron compounds. The change of spectral characteristics of I-VIII from temperature (323-373K in DMSO) are disscussed.

[1] Nemchinova L.A., Baka S.G., Gerbeleu N.V. Journ. Neorg. Khim. (Russia) 1992, v. 37, No 11, p. 2473-2479.

1.34. NEW MANNICH BASES TYPE LIGANDS

Ramona Tudose, Otilia Costisor, Maria Mracec, Septimia Policec, Maria Brezeanu*
Academia Romana - Filiala Timisoara, Laboratorul de Chimie Anorganica
*Universitatea Bucuresti, Facultatea de Chimie

N,N'-Bis(salicylamidomethyl)-piperazine (SAP) has been obtained by the Mannich synthesis, starting from salicylamide, formaldehyde and piperazine clorhydrate. The nature of substance has been established by the elemental analysis. The compound has been characterized by UV, IR and ^{1}H-NMR spectra. In order to appreciate the ability of SAP to act as a ligand, the molecular modeling using MM^+ force field was performed. The obtained geometry was used to calculate net atomic charges and other electronic properties, by the EHT method. The spatial model of SAP suggests its capacity to act as a bis-bidentate ligand bridging two metal ions situated in the opposite sites of the piperazine moiety. This fact was confirmed by the successful in synthesis of the M_2LCl_4 type complexes, where $M = Cu^{2+}$, Co^{2+}. The obtained complexes provide the opportunity to be building units, through the salicylic group, leading to both homo- and heteropolymetallic systems.

1.35. ON THE HETEROMETALLIC Cu-Cr OXALATES

*Otilia Costişor, Monica Ihoş, Septimia Policec şi Maria Brezeanu**
Academia Română - Filiala Timişoara, Laboratorul de Chimie Anorganică
** Universitatea Bucureşti, Facultatea de Chimie*

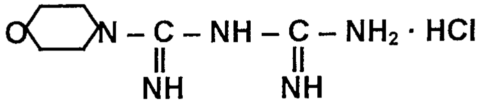
The following heterometallic complexes have been synthesized : $[Cu(bpy)_2]_3[Cr(ox)_3]_2 \cdot 4H_2O$ and $[Cu(bpy)_2][MCr(ox)_3] \cdot 4H_2O$, where bpy = 2,2'-bipyridine, $ox^{2-} = C_2O_4^{2-}$ and M = Na, Li. The nature of these compounds has been checked by elemental analysis and molecular electrical conductivities. Information about the structure of the above mentioned compounds has been obtained from electronic and IR spectra and from magnetic moment values at 20°C. The thermic stability has been followed by thermal analysis.

1.36. SYNTHESIS AND STRUCTURE OF ANTIVIRAL MONONUCLEAR COMPLEX COMPOUNDS OF BIGUANIDES

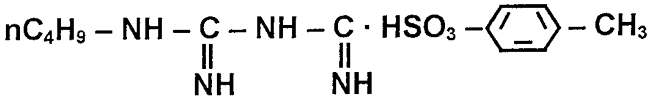
Sultana Niţă[a], Luminiţa Patron[b], Josette Weinberg[b],
Aurelia Meghea[c], and Constanţa Iliescu[a]
a - Chemical Pharmaceutical Research Institute, Bucharest
b - Institute of Physical Chemistry, Bucharest
c - University " The Polytechnic " Bucharest, Faculty of Chemistry

Literature data show the important therapeutic properties of biguanidine and its substituted derivatives. Numerous researches have utilised biguanides as ligands in complexing rections with a series of transition metals.

Among the substituted derivatives of biguanidines, morpholine biguanidine hidrocloride (I)(Morph·Big), known as moroxidine or virustat, and N,n-butilguanidin tosilate (II), known as bumorphin (II) (Buphorm), were the least tested as forming complex compunds:



(I)



(II)

The aim of the present paper is whole study from the synthesis, characterization and theoretical points of view of the following complexes:

$[M(II)(Morph \cdot Big)_2]Cl_2 \cdot 3H_2O$, where M (II): Cu, Co

$[Cu(Morph \cdot Big)Cl_2 \cdot 2H_2O]$

$[Cu(Morph \cdot Big)_2] \cdot (OH)_2$

$[Co(Morph \cdot Big)_2](OH)(Cl) \cdot 6H_2O$

$[Ni(Morph \cdot Big)(OH)_2] \cdot 2H_2O$

$[M(II)(Buphorm)_2]$, where M(II)=Cu, Co, Ni

$[Cu(Buphorm)(OH)_2]$

These complexes were obtained at ICCF Bucharest. Some of them were tested from the pharmacological activity point of view. It was evidenced the presence of important antiherpetic properties.

The complexes were obtained by an rigorously and well controlled synthesis as a function of the following parameters: the reaction temperature, the nature and pH of medium, the molar ratio M(II):ligand.

In order to characterize the complexes, the chemical analysis data were correlated with IR, electronic and RPE Spectra and magnetic measurements.

The theoretical study of these ones are obtained by Allinger' s molecular mechanics using an MM_2 force field; the program was running on a PC 486 computer.

It is important to emphasize that the molecular mechanics data indicate that the complex **$[Ni(Morph \cdot Big)(OH)_2] \cdot 2H_2O$** is the more easily to obtain, in a perfect agreement with the experimental data.

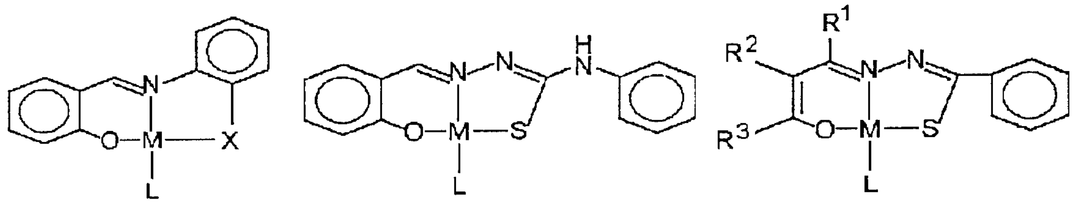
In the same time it is most to remark the useful theoretical information about the conformation of ligand around the metals. From the RPE Spectra it is very interesting to mention that the complex **$[Cu(Buphorm)(OH)_2]$** shows as an anomaly a paramagnetic dimer in the entire range at the liquid nitrogen temperature.

1.37. ELECTRONIC STRUCTURE AND CONFORMATIONAL ANALYSIS OF THE BIOLOGICALLY ACTIVE MIXED- LIGAND COORDINATIONAL COMPOUNDS OBTAINED ON THE BASE OF SOME AZINES AND HYDRAZONES

Dobrova B.N.*, Dimoglo A.S.*, Chumakov Yu.M.**

(*) Institute of Chemistry, Academy of Science, Kishinev.
(**) Institute of Applied Physics, Academy of Science,
Kishinev.

In the frameworks of the structure-antimicrobial activity investigations the conformational analysis in the series of mixed ligand compounds obtained on the base of three-dentate azines and hydrazones with some 3d and 4d metals was carried out for 25 complexes with the common skeletons.



where M = Ni, Cu, Zn, Pd
X = O, S
L = NH_3 , Py, H_2O, $(C_2H_5)_2NH$

R^1= H, CH_3; R^2= H
R^3= CH_3, C_6H_5
R^2+R^3= - $(CH=CH)_2$-

Bonds lengths, valent and torsion angles were calculated by means of the method of molecular mechanics (the force field, MMP2 approximation). According to the conformational analysis data all coordinational compounds are square-planar. Five- and six-membered melal-cycles are planar and almost coplanar. This fact agrees well with the data of X-ray analysis available for some compounds of Ni, Cu, Zn.

The quantum-chemical analysis of the electronic structure of the compounds under investigation was carried out on the base of the optimized structural data.

Structural and electronic characteristics found were used for the structure-activity relationships establishment. It was shown that the activity of a compound depends on the topology of the ligand, the nature of the metal and the distribution of the electron cloud in the system.

1.38. UV-VIS DERIVATIVE SPECTROPHOTOMETRIC STUDY ON THE INTERACTIONS OF CR(III) AND FE(III) IONS WITH BENZYLPENICILLIN IN AQUEOUS SOLUTIONS

Nicoleta Carp*, Victoria Aldea** and Mihai Carp*

*) - Romanian Academy, Institute of Physical Chemistry, Spl. Independentei 202,
Bucharest 77208, Romania
**) - Univ. of Medicine and Pharmacy, Faculty of Pharmacy, Traian Vuia 6,
Bucharest, Romania

The interactions of Cr(III) and Fe(III) ions with benzylpenicillin natrium salt (BP) in micellar and nonmicellar aqueous solutions (critical micellar concentration, c.m.c. = 0.26 $mol.L^{-1}$) by ultraviolet - visible spectrophotometry as a function of the molar ratio of the reactants and time have been studied.

The analysis of the electronic absorption spectra by derivative technique and with an original simulation spectra program emphasized that the most important process in aqueous solution below c.m.c. is the catalytic effect of the studied trivalent ions on the hydrolytic degradation reaction of BP and in time Fe(III) and Cr(III) ions form complexes with the degradation products.

The hydrolytic degradation reaction rate constant, obtained from UV absorption data, decreases with concentration of BP aqueus solution. In micellar solutions due to interactions between Fe(III) and Cr(III) with the BP autoassociates result colored slight soluble products, bright brown in the case of Fe(III) complexes and light-gray in that one of Cr(III) complexes. Because in aqueous solutions both Cr(III) and Fe(III) ions there are in one of their hydroyhydratated forms, the coloured solid products is supposed to be, in compliance with the elemental analysis, an octahedral binuclear complexes $Me_2BP_4(OH)_2$.

The interaction between Fe(III) and BP can explain the clinical observation that prolonged treatment with penicillin leads to anemia. The catalytic effect of Cr(III) and Fe(III) on the hydrolytic degradation reaction of BP may be one of the technological cause which can affect the quality of this drug.

1.39. THE INTERACTION OF AROMATIC DERIVATIVES OF PHOSPHINE, ARSINE AND STIBINE WITH BIOLOGICALLY ACTIVE COBALT DIOXIMATES

LIDIA PARUTA*, C.TURTA**, C.LEPADATU*, I.BULGAC**
AND V.SOFRANSKI**

*Institute of Chemical Physics, Sp.Independentei 202, Bucharest,Romania.

** Institute of Chemistry of Moldavian Academy of Sciences, Kisinev, R.Moldavia.

$[CoX(DH)_2(ER_3)]$, $[Co(DH)_2(ER_3)_2]Y$ complexes have been synthetized starting with aromatic derivatives ER_3(E : P,As,Sb and R: phenyl, tolyl) and $[CoX(DH)_2Lig]$ and $[Co(DH)_2Lig_2]Y$, where X:Cl,Br,I,NO_2,NCS; Y: NO_3, ClO_4; Lig: PyR, $NH_2C_6H_4R$, $NH_2C_6H_4SO_2$; DH: monoprotonated dimethylglyoxime or diphenylglyoxime.

Chemical analysis, IR and X-Ray spectroscopy were used to establish the molecular structure of the obtained compounds. They are trans isomers, the axial ligands being Lig-Co-ER_3, X-Co-ER_3, X-Co-Lig or ER_3-Co- ER_3.

The new complexes are crystalline, stable at the room temperature or heated up to 200^0 , brownish. In alcoholic solutions, an interaction between X^-, NO_2^-, NCS^- or organic ligands and the initial dioximates takes place, according to the following scheme:

$$[CoX(DH)_2(Lig)] \rightleftharpoons [CoX(DH)_2(H_2O)] \rightleftharpoons [CoX(DH)_2(ER_3)] \rightleftharpoons$$
$$\rightleftharpoons [Co(DH)_2(Lig)(ER_3)]X$$
$$[Co(DH)_2(Lig)_2]X \rightleftharpoons [Co(DH)_2(H_2O)_2]X \rightleftharpoons [Co(DH)_2(ER_3)_2]X \rightleftharpoons$$
$$\rightleftharpoons [Co(DH)_2(Lig)(ER_3)]X$$

1.40. THE MAGNETIC BEHAVIOUR WITH THE TEMPERATURE OF THE TRISNUCLEAR COMPOUNDS $\{M(II)[Cr(III)(AO)_3]_2\}Cl_2 . nH_2O$ WITH Zn(II) , Ni(II) AND AOH=3-AMMINO-1-PROPANOL .

N.STANICA* ,C.LEPADATU* and IOANA JITARU**
*Institute of Chemical Physics , Sp.Independentei nr.202 , Bucharest 77208,
Romania, **Polytechnical University of Bucharest, Faculty of Industrial Chemistry.

The complexes were characterized by variable temperature magnetic susceptibility in the range 80-300 K. Magnetic measurements were carried out with a Faraday-type magnetometer equipped with a continuous-flow nitrogen cryostat. The field strength was ≈6175 G . The data were fitted using Van Vleck's formula and the solutions of the spin Hamiltonian $H = -2(J_{12}S_1S_2 + J_{23}S_2S_3 + J_{13}S_1S_3)$. We performed the block diagonalization of the isotropic exchange Hamiltonian for a cluster of N spins where all the exchange constants are different. The technique , based on the rotation invariance of the system, leads to a considerable reduction of the total matrix. The symmetry-adapted spin functions were generated using Wigner coupling coefficients.The experimental data were simulated for several times, in general with two different least -squares fitting computer programs. The d-d transitions occurring in the electronic spectra of these complexes were analyzed using an Angular Overlap Model program(Inst.Theor.Chem.,Univ.Düsseldorf). They show that all metal ions are hexacoordinated, M(II) being in the middle bridged through Cl and O donor atoms. The Cr_2Zn complex is weakly antiferromagnetic and Cr_2Ni is ferromagnetic. The super-exchange mechanism is explained using MO-LCAO-EHT calculations.

1.41. PREPARATION AND PROPERTIES OF COPPER(II) COMPLEX WITH OXIMINOMETHYLETHYLIDENHYDRAZINDIACETAT ACID

Nelly N.Proschina
Institute of Chemistry, Academy of Sciences of Moldova,
Academiei Str. 3, Chisinau 2028, Republic of Moldova

Copper(II) with oximinomethylethylidenhydrazindiacetat acid has been synthesized by template condensation of isonitrozoacetone with hydrazin-I,I-diacetic acid in the presence of copper(II) ion. These compound was obtained also by interaction between $Cu(OH)_2$ and ligand in water.

The data of the elemental analysis show that the formula of compound corresponds to $KCu(Ligand\text{-}3H)(H_2O)_3$. The complex was characterized by electronic absorption, infrared, and EPR spectra.

The TG and DTA study have been showed that at heating to 130^0 observe the complexe losses 3 of molecules of water with destruction.

The spectroscopic analysis shows that the coordination of the organic ligand is realized by means of the NNOO atoms.Infrared spectra exhibits the absorbtions in the ν(COO), ν(NO) and ν(CN) regions.

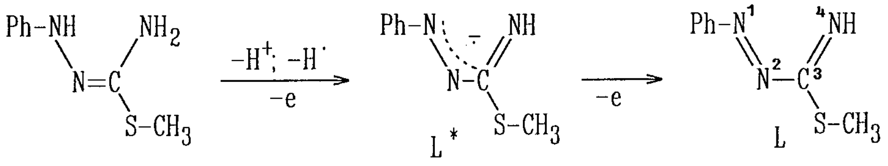
The compound has a low effective magnetic moment 0.66 MB. At the same time the EPR spectra show symmetrical singlet line g = 2,120±0,001; H_{pp} = 20,9 ± 0,2 mT (297 K) with form of line nears Gauss (M_4/M_2^2= 3,6). At low temperature to 120 K the lines narrow g= 2,120±0,001; ΔH_{pp}= 16,4 ± 0,2 mT, form of line near to Lorence (M_4/M_2^2= 4,4). Similar spectra are characteristic for mononuclear compounds of copper(II), where metal ions are found in near to octahedric crystalline field.

The coordination of atom central up to six is completed by two molecules of water.

1.42. CRYSTAL AND MOLECULAR STRUCTURE OF NICKEL COMPLEXES WITH PHENYLAZOTHIOMETHYLCARBOXIMIDES

M.Revenco[1], J.Lipkowski[2], Yu.Simonov[3]
J.Slowikowska[2], P.Bourosh[3], L.Timco[1]
[1]Moldova State University, Department of Chemistry
[2]Institute of Physical Chemistry, A.S., Poland
[3]Institute of Applied Physics, A.S., Republic of Moldova

During the interaction of nickel acetate with S-methyl-1-phenylizothiosemicarbazide in alkaline solution the initial ligand is oxidized by air oxygen and the formation of the complexes NiL_2^*(I) with free radical L^* takes place. This complexe represents the central neutral member of the electron transfer series (ETS)$[NiN_4]^{\pm z}$. The further oxidation of NiL_2^* by molecular iodine in organic noncoordinanting solvents gives rise to formation of the complexes with phenylazothiomethylcarboximides (L), which represents the last member of ETS $[NiN_4]^{2+}$. Thus by formation of L the complete two electron oxidation of initial ligand is finished and may be described as follows:



The direct synthesis of nickel complexes with L is impossible because of weak coordination ability of ligand. By oxidation with molecular iodine carried out in different solvents and with changable amount of oxidant we have prepared four types of the nickel complexes with L:
NiL_2I_2 (II); NiL_2I_6 (III); $NiL_2I_2 \cdot C_2H_4Cl_2$ (IV) and $NiL_2I_2 \cdot 2CHCl_3$ (V). The crystal structure of all the complexes types has been determined by X-ray difraction method. The compounds are octahedral. The equatorial plan is occupied by two trans-disposed L-molecules coordinated *via* marginal nitrogen atoms N(1) and N(4). In the other two positions of a little tetragonal distorted octahedron the ions I^- (for II, IV and V) and I_3^- (for III) are situated. Localization of the double bonds N(1)=N(2) (1.23-1.26Å) and C(3)=N(4) (1.24-1.29Å) is characteristic for all the compounds II-V. The solvent molecules occupy the cavities in crystal lattice assuring the best packing.

1.43. ELECTRONIC SPECTRA OF Ni(II) CHELATE COMPLEXES WITH PLANAR Ni(II)N_4 CHROMOPHORE

COMPLEXES SYNTHESIZED WITH LIGANDS FROM THE CLASS OF PHENYL-SUBSTITUTED 2-ACETYL-GLYOXALIMINO-(1)-PHENYLHYDRAZONES-(2)

Axente Constantin Banciu
Institute of Physical Chemistry of the Roumanian Academy,
77208 Bucharest, Spl. Independentei 202, Roumania

The diamagnetic title complexes are of 1:2 metal : ligand type and contain the planar Ni(II)N_4 chromophore. In their electronic absorption spectra within 220-600 nm range at least eight bands may be identified at ~230, 295, 345, 390, 420... 450, 470, 505 and 570 nm. The first three from these represent intra-ligand ($\pi \rightarrow \pi^*$ allowed) transitions, the next three charge transfer (CT) transitions of metal ⟶ ligand type, whereas the last two d-d allowed transitions. An another d-d allowed band is outlined in the electronic diffuse reflectance spectra of the complexes, at 710... 730 nm. In these complexes the b_{2g} (d_{xy}) orbital is the most stable from the "d"-type antibonding molecular orbitals, irespective of the accurate structure of the donor nitrogen atoms (whether they possess a structure close to the sp^2-hybridized or an intermediate one, between the sp^2- and sp^3- hybridized nitrogen atoms). In accordance with this and other considerations the d-d bands assignment is ${}^1A_{1g} \longrightarrow {}^1Eg = 13700\ cm^{-1}$ (730 nm); ${}^1A_{1g} \longrightarrow {}^1B_{1g} = 17540\ cm^{-1}$ (570 nm) and ${}^1A_{1g} \longrightarrow {}^1A_{2g} = 19880\ cm^{-1}$ (503 nm). The subsequent order of the "d"-type antibonding molecular orbitals is $b_{2g}(d_{xy}) < a_{1g}(d_{z^2}) < e_g(d_{xz}, d_{yz}) \ll b_{1g}(d_{x^2-y^2})$, with energy separations of $740\ cm^{-1}$, $4240\ cm^{-1}$ and respectively $17260\ cm^{-1}$ between these levels. The strongest from the CT bands is the first one, located at 470 nm, which represent the transition $e_g(d_{xz}, d_{yz})(\pi^*) \longrightarrow a_{2u}(\pi^*)$. The second CT band (~ 450 nm) represents the transition $a_{1g}(d_{z^2})(\sigma^*) \longrightarrow a_{2u}(\pi^*)$ whereas the third CT one (390 nm) the orbitally forbidden transition $b_{2g}(d_{xy})(\pi^*) \longrightarrow a_{2u}(\pi^*)$.

1.44. IR AND EPR SPECTROSCOPY IN CHARACTERISATION OF SOME COMPLEXES INHIBITORS OF CARBONIC ANHYDRASE

Dana Marinescu[a], Mihaela Badea[a], Mihaela Jitianu[b], C. T. Supuran[c], A. Jitianu[a], M. Ilies[a]

[a] Dept. of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest,
[b] Inst. of Physical Chemistry, Bucharest
[c] Lab. di Chimica Inorganica e Bioinorganica, Univ. degli Studi, Firenze

In the present work we tried to characterize using spectroscopic methods, especially IR and EPR spectroscopy, the structure of a class of Cu(II) complexes with 2-chloracetamido-5-sulfonamido-1,3,4-thiadiazole. The ligand was synthesised starting with the acetazolamide, which is the common inhibitor of carbonic anhydrase (CA).

The complexes were synthesised in a mixture EtOH/H_2O at different pH values, by using KOH or NH_3 as deprotonation agent.

Depending on experimental conditions, complexes of different composition and structure were obtained.

The chemical composition of the complexes was established by elementary analysis.

The structure was studied by IR and EPR spectral analysis.

The IR spectra did confirm the existence of M–L bonds.

The EPR spectra was used for determination of stereochemical distortion. The obtained data are in agreement with those of Kivelson and Neimann.

1.45. CHARACTERISATION BY IR SPECTROSCOPY AND THERMOGRAVIMETRY METHODS OF SOME Zn(II), Cr(III), Al(III) AND La(III) COMPLEXES CONTAINING A 5-SULFONAMIDO-1,3,4-THIADIAZOLE DERIVATIVE

A. Jitianu[a], Mihaela Badea[a], Marina Bălăşoiu[b], Mihaela Jitianu[b], C. T. Supuran[c], Dana Marinescu[a]

[a] Dept. of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest,
[b] Inst. of Physical Chemistry, Bucharest
[c] Lab. di Chimica Inorganica e Bioinorganica, Univ. degli Studi, Firenze

It was studied the thermal behaviour of some Zn(II), Cr(III), Al(III) and La(III) complexes with 2-chloracetamido-5-sulfonamido-1,3,4-thiadiazole.

The complexes were synthesised in a mixture methanol/water, using as deprotonation agent KOH or NH_3. Depending on the deprotonation agent complexes of different composition and structure were obtained.

The existence of the M–L bonds results on the basis of the IR spectral data.

The thermogravimetric study of the complexes emphasised different phases, appearing at well determined temperatures. The intermediates were isolated and characterised by chemical analysis and IR spectroscopy. The final products of the thermal decomposition in static air atmosphere were the oxides as indicated by x-ray diffractogramms of microcrystalline powders.

1.45. NOVEL COORDINATION COMPOUNDS OF LANTHANIDES WITH 1-(2'-BENZTHIAZOLIL)-3-METHYL-4-(o-CARBOXYPHENYLAZO)-PYRAZOL-5-ONE

D.NEGOIU* , A.EMANDI*, M.CALINESCU*, L.PARUTA** AND N.CARP**

*) University of Bucharest, Faculty of Chemistry, Dep. of Inorganic Chemistry,
Dumbrava Rosie 23, Bucharest, Romania
**) Romanian Academy, Institiute of Physical Chemistry, Spl. Independentei 202,
77208 Bucharest, Romania

The survey of literature revealed that hardly any data is available on the stereochemical properties of lanthanides complexes with 4-arylazopyrazol-5-ones, therefore, it was thought worthwhile to study the spectral and magnetic behaviour of some lanthanides complexes.

The present note describes isolation and characterization of Pr(III), Sm(III), Gd(III), Ho(III) chelates of 1-(2'-benzthyazolil)-3-methyl-4-(o-carboxyphenylazo)-pyrazol-5-one on the basis of the UV-VIS and IR spectral studies, magnetic properties, DTA and chemical analysis.

All the complexes are fairly stable colored solids and can be stored without any change for a long time. The purity of these complexes was checked by TLC. The molecular conductance values (116.2-120 mΩ) in DMF at the concentration 10^{-3} M show that these are uni-univalent electrolytes.

The analytical results show the general formula $[Ln(C_{18}H_{11}N_5SO_3)_2(H_2O)_2]Cl$, where Ln = Pr(III), Sm(III), Gd(III), Ho(III).

UV-Visible spectral studies by the derivative technique and spectra simulation underlined the electronic absorption characteristics of lanthanides complexes.

The IR spectra of lanthanides complexes emphasized the shifting on the frequencies of >C=O (1625 cm^{-1}) and -N=N- (1565 cm^{-1}) to lower region, 1600 and 1545 cm^{-1} respectively indicated the involvement of these two groups in complexation. Coordination of water molecules is indicated by the appearance of bands at 3300 - 3350 cm^{-1} in complexes. The disappearance of COOH group band (2600 cm^{-1}) and the appearance of new breathing frequencies at 1350 cm^{-1} and 800 cm^{-1} due to the symmetric stretching and bending mode OCO frequencies respectively indicate the participation of the -COOH group in complexation.

DTA data evidence that the complexes are stable until 110-120°C when they lose the coordination water, and then step by step the organic part. Ln_2O_3 is the finally compound.

1.47. SYNTHESIS AND CHARACTERIZATION OF SOME NEW COMPLEXES OF RUTHENIUM WITH BIPYRIDINE AND COLIGANDS

Ileana Serban*, Marilena Vasilescu**, Rodica Bandula** and Anca Emandi*

* Bucharest University, Faculty of Chemistry, Dumbrava Rosie 23
** Romanian Academy, Institute of Physical Chemistry, Splaiul Independentei 202

The synthesis of some mixed complexes of $[Ru(CO)_2Cl_2(bpy)]$ (2), $[Ru(CO)_2Cl(SnCl_3)(bpy)]$ (3) and $[Ru(SnCl_3)_2(bpy)]$ (4) type is reported. The elemental chemical analyses, molar electrical conductivity and IR spectra support the formulas advanced for the new complexes (3) and (4). The results of the characterization of these complexes by UV-vis absorption and luminescence emission were compared to those of $[Ru(bpy)_3]^{2+}$ (1) complex; thus the modification of the energy and intensity of the main absorption bands, ($d-\pi^*$ metal to ligand charge-transfer (MLCT) and $\pi-\pi^*$ ligand centered (LC)), was evidenced as function of the nature of the co-ligand and solvent. The luminescence emission of complexes 2 and 3 is considerably attenuated compared to complex 1, and that of complex 4 is absent.

1.48. STUDY OF SOME REACTIONS IN SOLID PHASE BY THERMOANALYTICAL AND SPECTROMETRIC METHODS

I. Dranca, V.Shofransky, T. Lupascu, V. Gorgos
Institute of Chemistry, Moldova Academy of Sciences,
Academiei Str. No 3,MD-2028, Chishinau , Republic of Moldova

The purpose of this study was the elaboration of a new method for synthesizing "dioximine" co-ordinative combinations $[CoX(DH)_2\ Lig]\ nH_2O$ and $[Co(DH)_2Lig_2]YnH_2O$ in solide state, where Lig - H_2O, NH_3 , Anilin, Py, p-aminobenzolsulfaguanidin (Sg). When the mixture $[Co(DH)_2\ (NH_3)_2]NO_3$ and Sg (1) is warmed up and the solvent is absent, a product is formed in whose IR spectrum the ν(NH) and (NH_3) ammonium bands disapper and bands of coordinated Sg apper after the NH_2 group of the benzene ring: $\Delta\nu(NH) = -(180\text{-}200)$, $\Delta\nu(NH_2) = +(10\text{-}20)$ cm^{-1}. In case of other guanidine derivatives the replasement of ammonia molecules occurs at a lower degree.

For instance, in the case of diphenilguanidine (Dfgu) there occurs the replacement of only on NH_3 molecule along with the formation of $[Co(DH)_2(Dfgu)(NH_3)]NO_3$.

If the $[CoCl(DH)_2\ H_2O]$ and Dfgu mixture is heated up to 110° C one can observe the change in the colour of the reactant mixture from green-greyish to light brown. In the IR spectrum of the obtained complex the intensity of ν(NH) absorption bands of HN=C group decreases and a ν(NH) band appears at 3100-3200 cm^{-1}. In the ν(NH) and ν(CN) absorption region the IR spectrum of the obtained complex is similar to that of $[CoCl(DH)_2\ Dfgu]$ obtained by the ordinary method with solvent-etanol, i.e. the following reactions occur in the solid phase:

$$[Co(DH)_2\ (NH_3)_2]NO_3\ + 2Sg \xrightarrow{110\ ^{\circ}C} [Co(DH)_2\ Sg_2\ ]\ NO_3 + 2\ NH_3 \qquad (1)$$

$$[CoCl(DH)_2\ H_2O]\ + Dfgu \xrightarrow{110\ ^{\circ}C} [CoCl(DH)_2\ Dfgu] + H_2O \qquad (2)$$

The investigation of $[CoX(DH)_2\ (NC\text{-}Gu)]\ H_2O$ applying thermoanalytical and IR methods has shown the presence of a regularity in the Cl^-, Br^- and I^-, NO_2^- chain. For derivatives of Cl and Br the intensity of ν(C≡N) and decreases at 2250 cm^{-1} and sharply increases at 2190cm^{-1}. Changes are also observed in the region of groups NH absorbtion. These changes are due to presence of isomers:
$[XCo(DH)_2\ \text{-}N{\equiv}CNHC(NH)NH_2]$ and $[XCo(DH)_2\ \text{-}NH{=}C(NH_2)\ NHCN]$.

1.49. POLYNUCLEAR COORDINATION COMPOUNDS WITH MIXED LIGANDS

Ioana Mandru[a],Luminita Patron[a], Adriana Gheorghe[b],Ana Lazarescu[c] and C.Turta

a- Institute of Physical Chemistry, Bucharest
b- University of Bucharest, Faculty of Chemistry
c- Institute of Chemistry, Chisinau, Republica Moldova

Recently, numerous studies have shawn that the anorganic polymers can be synthesized with different ligands and metalic ions.

One of these is $FeC_2O_4.2H_2O$, very well characterized and whose Mossbauer spectrum was intensively studied.

Moreover, a great number of polymers was obtained by the reaction $FeC_2O_4.2H_2O$ with different ligands : 1,10-phen, 2,2'-dipy, etc.

This work relates the synthesis, the characterization and Mossbauer studies of the polynuclear complex compounds with general formula $FeM^{(II)}(C_2O_4)_xL_y.nH_2O$ and $FeLn(C_2O_4)_xL_y.nH_2O$ (L = en). The oxidation state of iron was established as by chemical method as by Mossbauer spectroscopy.

1.50. SYNTHESIS AND STRUCTURE OF THE NEW METAL CARBOXYLATES

L.Singerean , G.Timco , N.Gerbeleu

Institute of Chemistry, the Academy of Sciencies of RM

The current interest in polinuclear carboxylate species stems from a desire (i) to futher characterize the rich fundamental coordination chemistry of this class of compounds, (ii) to investigate and to realise novel synthetic pathways of obtaining more developed architectures, (iii) to prepare synthetic model complexes for the active centres in the biological systems, (iv) to study the catalitical activity of this class of compounds, (v) to study the magnetic exchange interaction and so on.

We have obtained the different carboxylates of the metalls both of the "classical structure" (mono-, bi-, trinuclear) and with the unusual structures. Such compound may be separated into two classes:(i) complexes stabilized by oxo- and hydroxo- bridges, (ii) complexes stabilized by fluoride-bridges.

(i) Molecules of $Fe_6O_2(OH)_2Piv_{12}$ (I), where $HPiv=HO_2CCMe_3$, $Mn_6O_2Piv_{10}Py_4$ (II),$Cr_{12}O_{12}Piv_{15}$(III), $Fe_4(VO)_2O_2Piv_{10}(acac)_2$(IV), $Fe_3Mn_2O(OH)Piv_7(acac)_3$(V)are stabilized by oxo-bridges: μ_4-tetrahed ral in II and III, μ_3-trigonal planar in I and IV, μ_3-piramidal in III. The metal atoms form distorted planar hexagons in I and IV, a pair of tetrahedra with a common edge in II, and a body-centred pentacapped twisted trigonal prism in III. A μ_4-oxigen centred Fe_2Mn_2 tetrahedron and a μ_3-hidroxyl bridges $FeMn_2$ triangle share Mn...Mn edge (Mn...Mn3.015 Å) in V.

(ii)In the molecules of $(CrFPiv_2)_8$(YI) and $(FeFPiv_2)_8$ (VII) the nearly coplanar eight metal atoms are linked pairwise by one fluoride and two OCO bridges, forming a crown-ether like inorganic macrocycle with cavities accomodating different guest molecules (acetone, diethylamine, benzene or benzene and ferrocene). Thus these substances can be viewed as a clathrate coumpounds.

We have made the first attemt to create the bridge between oxo- and fluoro-carboxylates wich resulted only in synthesis of triiron μ_3-oxo-carboxylates with apical Fe-F bonds of general formula $[Fe_3(\mu_3-O)(OOCR)_6F_3]^{2-}(Et_2NH_2)_2^+$, where R=cyclo-$C_6H_{11}$and CH_2CHMe_2. We hope to continue researches in this direction to find out bridges between traditional and recently obtained "stability island" of carboxylates.

1.51. THERMOANALYTICAL INVESTIGATION OF SOME CHROMIUM AND IRON INCLUSION COMPOUNDS

I.Dranca, S.Grebenko, C.Timco, N.Gerbeleu
Institute of Chemistry of the Academy of Sciences of RM,
Kishinev, Moldova

Thermoanalytical investigation (TG, DTG, DTA, DSC) of inclusion compounds $[MeF(OOCCMe_3)_2]$ nA, where: for Me=Cr, A=$(CH_3)_2CO$ (I), C_6H_6 (II), Et_2NH (III), $Fe(Cp)_2$ (IV); Me=Fe, A=Et_2NH (V), Bu_2NH (VI), has been carried out. I-VI are macrocyclic systems having a dumb-bells-like cavity of 6A diameter in the middle part and up to 9A at the ends (surrounded by axial pivalate ligands).

Analysis of TG, DTG, DTA, DSC curves has shown that the loss of inclusion molecules occurs within the 40-290°C.

N	Compound	Loss of mass, %		Temperature interval °C
		found	calculated	
I	$[CrF(OOCCMe_3)_2]_8$ $2Me_2CO$	5.0	5.16	40-215
II	$[CrF(OOCCMe_3)_2]_8$ $2C_6H_6$	7.0	6.78	45-290
III	$[CrF(OOCCMe_3)_2]_8$ $2Et_2NH$	6.0	6.38	45-285
IV	$[CrF(OOCCMe_3)_2]_8$ $Fe(Cp)_2$	5.0	4.78	55-240
V	$[FeF(OOCCMe_3)_2]_8$ $2Et_2NH$	3.5	3.24	60-255
VI	$[FeF(OOCCMe_3)_2]_8$ $2Bu_2NH$	4.5	4.85	65-230

In the surveyed compounds there occurs the Wan-der-Walls interaction between the "guest" molecules and the "host" matrix. So, even in case of considerable loss of mass and high sensitivity the DTA peaks are poorly manifested. However, it is interesting to note that by means of DSC method the two-step loss of C_6H_6 for (II) has been established at 160.9°C and 218.7°C. The values of heat flows are 9.5 J/g and 2.6 J/g, respectively. The dependence of thermal properties of compounds on the nature of the metal and of inclusion molecules has been established.

2.1 PARTIAL RATES APPROACH IN CHEMICAL KINETICS

Oleg Pervukhin
Department of Chemical Thermodynamics and Kinetics
St.-Petersburg State University, St.-Petesburg, 198904, Russia

Kinetic treatment of the multistep chemical reactions in concentrated solutions without solvent is very important. Familiar theories such as Brønsted salt effect, Hammet acidity function, thermodynamic transition state theories are not the complete decision of the task. There are no reliable data about transition state and information about reaction mechanism. Such uncertainty encourages search of new approach. We suggest to use a concept of phase partial molar rate [1]: $\overline{W}_i \equiv (\partial W/\partial m_i)_{P,T,m_{j\neq i}}$, (s^{-1})...(1), where W-phase (extensive) rate (mol/s), m_i-moles of i substance. For P and T=const W concerning Euler theorem is a uniform function. For usual (intensive) rate J it is true $J = \sum_{i=1}^{n} \overline{W}_i c_i$...(2). Every term is an absolute reactivity $R_i \equiv \overline{W}_i c_i$...(3), it specifies an absolute contribution of i substance to reactivity. Relative reactivity equals $r_i \equiv R_i/J$...(4), it specifies a fraction of i substance [2, 3]. For reagent r and product p of irreversible reaction obeying Mass Action Law it is valid $\overline{W}_r=[\beta_r/c_r+(1-\beta)\overline{V}_r]J$, $\overline{W}_p=(1-\beta)\overline{V}_p J$...(5), where β_r and β-reaction orders by reagent and total, $\overline{V}_i$-partial volume [2, 3]. The role of the second term is great in the concentrated solutions. Dilution effect is taken here, it is conditioned by the volume growing for reagent addition. And starting from the second order reaction the volume growing can result in the rate decrease because of the concentration drop for all reagents exept of adding one. It leads to the unusual result when $\overline{W}_r$ together with R_r and r_r become negativ [4]! In dilute solutions these new values acquire highly transparent meaning. There are some formulae: $R_r^{\infty}=\beta_r J$ and $r_r^{\infty}=\beta_r$...(6) from which it is seen that R_r^{∞} equals to reaction rate for key reagent and r_r^{∞} equals simply to reaction order. The partial rate having the dimension of the inverse time is connected with the conversion time on 1/p part [5]: $\overline{W}^{\infty}_{r,0}=(1/(|\nu_r|(\beta-1))[(p/(p-1))^{\beta-1}-1]/t_{1/p}$...(7), partial rate is refered to the beginning of reacion. It is evident that for another kinetic approximation specific expressions for partial rates and reactivities (5)-(7) will be the others but general equations for them (1)-(4) will be unchanged.

1. *Первухин О.К.*//Вестн. ЛГУ. I988. № 25. С. 4I, 2. *Первухин О.К.*// Вестн. СПбГУ. I992. № II. С. 44, 3. *Первухин О.К.*//Вестн. ЛГУ. I990. № II. С. 58, 4. *Первухин О.К.*//Вестн. СПбГУ. I992. № I8. С. 48, 5. *Первухин О.К.*//Вестн. ЛГУ. I99I. № II. С. 42.

2.2 APPROXIMATION OF QUASIEQUILIBRATED STEP IN THE KINETIC TREATMENT OF REACTION NETWORKS

D.Oancea, Adina Raducan,
Department of Physical Chemistry, Faculty of Chemistry,
University of Bucharest, bd.Republicii no.13, Bucharest

The kinetic treatment of consecutive reaction networks makes use of several simpifying assumptions. Among them the approximation of a locally quasiequilibrated step allows the treatment of many consecutive reactions for both parameter identification and system temporal simulation.

Numerical solution of a consecutive reaction network, using a solver of a system of differential equations, can establish the limits of this approximation.

These limits are analysed for both single reactions coupled by active intermediates and consecutive reaction networks with normal intermediates.

2.3 CONSECUTIVE REACTIONS. THE DISCREET FORM OF THE MODEL

N. I. Ionescu, M. V. Freamăt
"I. G. Murgulescu" Institute of Physical-Chemistry of the Romanian Academy

The validity criteria of a mathematical model resulted from a kinetic model emphasize the impossibility of a complete characterization of a certain phenomenon by numerical analysis exclusively. In this case, the limits of the numerical methods and procedures usually used in the construction of an analytical expression of the system description are presented in a nonlinear form.

Thus, if in the case of the linear systems the simulation result is exactly proportional to the input signal, this fact is modified in the more natural cases of the nonlinear systems. In these cases the errors which appear due to the approximations introduced by the finite differences methods present a complex behavior, leading to additional solutions in the solution spectrum of the numerical problem. An unpredictable lack of similarity exists between the analytical and numerical solutions.

For a linear system, certain information that detail its solution behavior can be obtained from its variables using some new variables which however satisfy nonlinear equations.

As an example, a chemical consecutive reaction with an equilibrium step was chosen. Its mass balance takes the form of a homogenous differential linear equations system with two variables.

In order to obtain directly the trajectories from the system solutions in the phase space a new variable given by the concentration ratio was used. This variable leads to an equation of a logistic map form modified by an added constant. For this equation type, in a certain range, a chaotic evolution of the numerical solutions for the integrated form obtained by central difference scheme was calculated analytically and by numeric simulations. This behavior differs from those predicted by a continuous analysis.

The validity limits of numerical simulations of the mathematical models resulted from kinetical models are also discussed.

2.4 A NEW METHOD OF OBTAINING THE PERIODIC-CHAOTIC SEQUENCE IN THE BELOUSOV-ZHABOTINSKI REACTION

G. Bourceanu, M. Bourceanu and A. Bîrzu
Faculty of Chemistry, "Al.I.Cuza" University of Iaşi

Up to the present, the alternant sequence of periodic states with the chaotic ones, so called Texas sequence, in the Belousov-Zhabotinski (BZ) reaction, was obtained by modification of residence time.

We have realized experimentally the alternant periodic and chaotic states in the BZ - reaction by using a new reagent in the BZ base reaction system. The concentration of the new reagent is a controlling parameter.

If a periodic state is symbolized by P_n, where n is the number of oscillations in a compact group and the chaotic state is symbolized by C_n, then the then the alternating sequence is given as

$$P_1C_1,\ P_2C_2, \ldots, P_nC_n$$

Let us mention that among those n oscillations in a group, one of them has a higher amplitude and n-1 of them have lower amplitudes.

By modification of the controlling parameter, i.d. concentration of KIO_3, we have obtained the alternant sequence $P_1C_1, \ldots, P_6C_6$, while by modification of the residence time, the sequence $P_1C_1, \ldots, P_3C_3$ is obtained only.

2.5

CHARACTERISTICS OF THE EXPLOSION TRANSMISSION BETWEEN INTERCONNECTED VESSELS, FOR FUEL-OXIDANT GASEOUS MIXTURES

Domnina Razus*, D.Oancea**, F.Chirila* and N.I.Ionescu*
*ROMANIAN ACADEMY, "I.G.Murgulescu" Institute of Physical Chemistry,
Spl.Independentei 202, 77208 Bucharest, Romania
** UNIVERSITY OF BUCHAREST, Faculty of Chemistry, Department of Physical
Chemistry, Bd. Republicii 13, Bucharest, Romania

The effect of the initial pressure of a rich C_3H_6-air mixture on the characteristic parameters (maximum explosion pressure and maximum rate of pressure rise) of explosion propagation in vessels interconnected by a narrow cylindrical channel is reported and discussed.

At initial pressure ranging from MPT (the minimum pressure at which the transmission takes place) to 1 atm, 3 different types of explosion propagation were observed. The turbulence created both in the burned and in the unburned gas, at the flame passage through the channel, leads to significant pressure oscillations in the secondary vessel. A Fourier analysis of these oscillations allows the characterization of the 3 different regimes of flame propagation.

2.6 THE EFFECT OF INERT COMPONENTS ON THE SPARK IGNITION OF GASEOUS EXPLOSIONS

D.Oancea*, Domnina Răzuş**, N.Mitru*, F.Chirilă** and N.I.Ionescu**
* UNIVERSITY OF BUCHAREST, Faculty of Chemistry, Department of Physical Chemistry, Bd. Republicii 13, Bucharest, Romania
** ROMANIAN ACADEMY, Institute of Physical Chemistry, Spl.Independentei 202, 77208 Bucharest, Romania

The induction periods of ignition by electric sparks, predicted by several theoretical models, were measured using propylene-air mixtures at initial pressures between 400 and 800 mmHg, with or without CO_2 addition. The pressure change during the early stage of the explosion in a closed vessel was measured using a piezoelectric transducer and recorded by means of a TESTLAB 2505-Tektronix data acquisition system. The processing of the pressure-time curves allowed the measurement of the ignition delay as a function of the composition and initial pressure. The experimental data fitted the relationship $\tau \cdot p^n$=const, where **n** is the overall reaction order. The results are in reasonable agreement with the values obtained from other type of measurements. The induction period and the reaction order change with the CO_2 content in an expected manner.

2.7 KINETIC INVESTIGATIONS OF SOME HETEROGENEOUS REACTIONS UNDER CONSTANT RATE THERMAL ANALYSIS (CRTA) CONDITIONS

E.Segal[a], F.Rouquerol[b,c] J.Rouquerol[c], J.M.Fulconis[c] and O.Cerclier[b]

[a]Department of Physical Chemistry, Faculty of Chemistry,University of Bucharest, Bulevardul Republicii 13, Bucharest,Romania

[b]Université de Provence, Place Victor Hugo,13331,Marseille Cedex 3, France

[c]Centre de Thermodynamique et de Microcalorimetrie du CNRS, 26 rue du 141 eme RIA, 13331, Marseille Cedex 3, France

The occurence of heterogeneous chemical reactions, particularly heterogeneous decompositions in solid-gas systems under CRTA conditions provides some important advantages with respect to the classical thermogravimetric conditions characterized by constant heating rates. The main advantage from kinetic standpoints consists in the important diminution of the mass and heat transfer influences on the reaction rate.

This work is dedicated to the results obtained in the kinetic investigation of the calcium oxalate monohydrate decpmposition as well as of the gibbsite thermolysis in CRTA conditions at low pressures of the votalile evolved component.

A procedure to estimate the activation energy of solid-gas decompositions from CRTA curves modulated by a pressure jumps is equally suggested.

2.8 STUDY OF SOME REACTIONS IN SOLID PHASE BY THERMOANALYTICAL AND SPECTROMETRIC METHODS

I. Dranca, V.Shofransky, T. Lupashcu, V. Gorgos
Institute of Chemistry, Moldova Academy of Sciences,
Academiei Str. No 3,MD-2028, Chishinau , Republic of Moldova

The purpose of this study was the elaboration of a new method for synthesizing "dioximine" co-ordinative combinations $[CoX(DH)_2\ Lig]\ nH_2O$ and $[Co(DH)_2Lig_2]YnH_2O$ in solide state, where Lig - H_2O, NH_3 , Anilin, Py, p-aminobenzolsulfaguanidin (Sg). When the mixture $[Co(DH)_2\ (NH_3)_2]NO_3$ and Sg (1) is warmed up and the solvent is absent, a product is formed in whose IR spectrum the ν(NH) and (NH_3) ammonium bands disapper and bands of coordinated Sg apper after the NH_2 group of the benzene ring: $\Delta\nu(NH) = -(180\text{-}200)$, $\Delta\nu(NH_2) = +(10\text{-}20)$ cm^{-1}. In case of other guanidine derivatives the replasement of ammonia molecules occurs at a lower degree.

For instance, in the case of diphenilguanidine (Dfgu) there occurs the replacement of only on NH_3 molecule along with the formation of $[Co(DH)_2(Dfgu)(NH_3)]NO_3$.

If the $[CoCl(DH)_2\ H_2O]$ and Dfgu mixture is heated up to 110° C one can observe the change in the colour of the reactant mixture from green-greyish to light brown. In the IR spectrum of the obtained complex the intensity of ν(NH) absorption bands of HN=C group decreases and a ν(NH) band appears at 3100-3200 cm^{-1}. In the ν(NH) and ν(CN) absorption region the IR spectrum of the obtained complex is similar to that of $[CoCl(DH)_2\ Dfgu]$ obtained by the ordinary method with solvent-etanol, i.e. the following reactions occur in the solid phase:

$$[Co(DH)_2\ (NH_3)_2]NO_3 + 2Sg \xrightarrow{110\ ^{\circ}C} [Co(DH)_2\ Sg_2\ ]\ NO_3 + 2\ NH_3 \qquad (1)$$

$$[CoCl(DH)_2\ H_2O] + Dfgu \xrightarrow{110\ ^{\circ}C} [CoCl(DH)_2\ Dfgu] + H_2O \qquad (2)$$

The investigation of $[CoX(DH)_2\ (NC\text{-}Gu)]\ H_2O$ applying thermoanalytical and IR methods has shown the presence of a regularity in the Cl^-, Br^- and I^-, NO_2^- chain. For derivatives of Cl and Br the intensity of ν(C≡N) band decreases at 2250 cm^{-1} and sharply increases at 2190cm^{-1}. Changes are also observed in the region of groups NH absorbtion. These changes are due to presence of isomers:
$[XCo(DH)_2\ \text{-}N{\equiv}CNHC(NH)NH_2]$ and $[XCo(DH)_2\ \text{-}NH{=}C(NH_2)\ NHCN]$.

2.9 APPROXIMATION OF THE TG CURVE THROUGH A POWER SERIES OF TEMPERATURE IN ORDER TO EVALUATE THE NONISOTHERMAL KINETIC PARAMETERS OF SOLID-GAS DECOMPOSITIONS AND DEGRADATION

Alice-Luminita Petre*, P.Budrugeac** and E.Segal***
* "I.G.Murgulescu" Institute of Physical Chemistry of the Romanian Academy, Splaiul Independentei 202, 77208, Bucharest, Romania
**EUROTEST-S.A.,Splaiul Unirii 313, Sector 3, Bucharest, 73204, Romania
***Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd.Republicii,Nr. 13, Bucharest, Romania

A procedure to evaluate the nonisothermal kinetic parameters by means of a differential method which uses the TG curves was reported. The procedure is based on the approximation of the portion of the TG curve, corresponding to the investigated change, by a power series of temperature. From the known analytical form of the TG curve, one can evaluate the reaction rate for various degrees of conversion, α_i , and consequently the differential methods for the evaluation of the nonisothermal kinetic parameters can be applied.

In this paper we suggest another procedure to find the differential conversion function f(α).The first step of that procedure consists in the evaluation of the activation energy using an isoconversional method, like Friedman's one. In the second step the true form of f(α) is chosen using the plot $\left(\ln\left[\frac{d\alpha}{dT}/f(\alpha)\right] \text{versus} 1/T\right)$ as that which leads to a value of the activation energy close to the preview one.

The procedure was applied to the dehydration of calcium oxalate monohydrate, thermooxidative degradation of a stirenated unsaturated polyester resin and thermal degradation of polyvinyl chloride.

The proposed method for nonisothermal kinetic analysis leads to values of the kinetic parameters in fair good agreement with respect to those obtained using other methods (Flynn-Wall-Ozawa α=const.).

2.1o NEW EQUATIONS FOR HETEROGENEOUS KINETICS

E. URBANOVICI[a] AND E. SEGAL[b,*]

[a] Thermosis Ltd., P.O. Box 187, Sfântu Gheorghe 4000, Romania

[b] Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest,
Bulevardul Republicii 13, Bucharest, Romania

Abstract

In this paper, a number of new kinetic equations in order to describe heterogeneous reactions are presented.

A significant number of equations have been obtained on the basis of the general relationship

$$V(t) = \int_0^t v(t,y)\ (dN/dt)_{t=y} dy$$

by considering a new expression for v(t,y) which takes into account the nuclei overlaping during growth.

An equation involving an additional parameter, r, and describing sigmoid shaped α-t curves has been derived considering the following generalized form of the Avrami relationship

$$d\alpha/d\alpha_{ex} = (1 - \alpha)^r \qquad r>0$$

Finally, one has to mention a general equation involving four kinetic parameters (k, q, x and y)

$$d\alpha/dt = k(1 - \alpha)^{xq} \left[\frac{1 - (1 - \alpha)^{1-q}}{1 - q}\right]^y$$

This equation has been applied successfully to derive 40 reaction mechanisms known from literature.

---

* Author to whom correspondence should be addressed

2.11 CHARACTERIZATION OF SOME NODULAR CAST IRONS BY THERMAL ANALYSIS

Dumitru Fatu[*] and Maria Muscalu[**]
[*] Department of Physical Chemistry,
Faculty of Chemistry, University of
Bucharest, Bul. Carol No.13
[**] Hidrojet Breaza, str. Grivitei No.18

In this study thermal analisys was used to characterize thermal behaviour and oxidation resistance of some nodular cast irons. Generally nodular cast iron has a good oxidation resistance up to 650°C.

It has studied the thermal behaviour of the cast iron and some aspects concerning its oxidation in the air, using samples with different chemical composition and microstructures. The cast iron samples used were powders, resulted by breaking some plates with "white" microstructure (the cementite - Fe_3C is the main component). These plates are produced by a rapid solidification of some melts of nodular cast iron.

The cast iron powders were heated from room temperature up to 1000°C, with a linear heating rate of 10°C/min and the TG, DTG and DTA curves have been recorded.

The thermal curves show a continuous increase of weight and an exothermal effect up to 850°C. At high temperatures ($T > 850°C$), it can see a decrease of weight and an endothermal effect. When samples are heated a continuous oxidation takes place up to 850°C. The thermal peaks, recorded on DTA curves, correspond to iron oxides (Fe-O, Fe_3O_4, Fe_2O_3) formation.

The thermal effects and oxidation resistance are related to silicon content of the samples.

In the range of high temperatures, we also must take into account a superficial decrease of carbon content by carbon combustion ("decarburisation" effect). This effect goes to a loss of weight, which can exceed the increase of weight produced by oxidation of iron.

The combination of the two effects : iron oxidation and decarburisation are depending on structural changes of cast irons, which take place at high temperatures. To determine these changes, the powdered samples and the corresponding plates have been kept in a furnace, at the temperatures which are peaks on thermal curves. Then the samples have been examined by a microscope.

The kinetics of oxidation and decarburisation have been modeled. It has determined kinetical parameters for the process of carbon combustion using the model of a sphere which contracts.

The thermal analysis and miscroscopical observations give the possibility to point out some less studied features of nodular cast irons : thermal behaviour and oxidation resistance.

The study is an application of thermal analysis, based on heating curves

2.12 KINETICS OF THE $PbO-TiO_2-ZrO_2$ COMPOUNDS SYNTHESIS BY A SOL-GEL COLLOIDAL PROCESS

*Roxana Piticescu,**Aurelia Meghea, *Anca Drujescu
*Research Institute for Nonferrous and Rare Metals, 102 Biruintei str., Bucharest
**University POLITEHNICA Bucharest, 1 Polizu str., Bucharest

The paper presents the kinetics of the reactions in the system $PbO-TiO_2-ZrO_2$, in a sol-gel colloidal route, starting from soluble peroxyde precursors of Ti(IV) and Zr(IV).

The solid products obtained after controlled precipitation from the solutions were thermal treated in the temperature range 80 to 1000°C and then analysed by thermodifferential and thermogravimetric analysis, RX diffraction and also for the determination of chemical composition.

The phases presented in the thermal treated powders were detected and the mean crystallite sizes were calculated using the Scherrer formula. Crystals with tetragonal and orthorombic structures and mean crystallite sizes in the range 30-50 nm were obtained.

From the reactions mechanism it was seen that the structure and sizes of oxydic species of Pb in different valence states induce the structure and microcrystalline properties of the new phases formed in the $PbO-TiO_2-ZrO_2$ system.

In order to study the kinetics of the reactions involved, a quantitative method for detecting the lead oxyde species by diffuse reflectance spectroscopy, based on the Kubelka-Munk equation, was settled. For this purpose the diffuse reflectance spectra of PbO (litharge, yellow), PbO_2 (plattnerite, brown) and Pb_3O_4 (minium, red) were represented as a function of concentrations. These lead oxides are the probable intermediates in the reactions involved in the synthesis of PZT precursors.

The sensitivity of the method was aprox. 2% and the standard deviation ± 1.

The results obtained allowed for the calculation of speed constants and activation energies of the reactions involved.

The experimental data were fitted on a computer.

2.13 ON A CLASSIFICATION OF THE METHODS TO EVALUATE KINETIC PARAMETERS FROM THE NON-ISOTHERMAL EXPERIMENTS

C. Popescu* and E. Segal**
* LACECA Research Center, 95 Siret Str., RO-78308, Bucharest, Romania
**Department of Physical Chemistry, Faculty of Chemistry, The University of Bucharest

Much work has been dedicated to the methodology of evaluating the kinetic parameters from experiments carried out under non-isothermal conditions. New methods are published yearly.
These methods are usually compared using statistical tests, e.g. correlation coefficient, standard deviation, etc., and classified according to the form of the heating program and the kind of equation used (integral equation, differential equation, double-differential equation, etc.).
In this paper another point of view on the comparison of the non-isothermal kinetics methods is proposed. The number of principles and theoretical approximations used for deriving the equations which ground each method is considered as the comparison criterion and, subsequently, the methods are classified into classes of equivalence.
It is shown that, according to the proposed criteria, the most general method is the integral one, applied to data acquired from experiments carried out with various linear heating rates, and giving the activation energy as a range of values.
The classification of the methods suggests some new variants of those considered throughout the paper.
As a result of the analysis, it is also suggested that the value of the activation energy, as computed by non isothermal methods, should be given as a range of values instead of a unique value. One may, thus, notice that the increase of the generality leads to the decrease of the precision of the results.

2.14 STUDY ON THE CRYSTALLIZATION WATER´S NATURE IN SOME HYDRATES BY THERMAL METHODS

Lucia Odochian, Dana Ionescu and Irina Calugareanu
Dept. of Physical Chemistry , "Al.I.Cuza" University ,IASI

The nature of the crystallization water in $NiSO_4*7H_2O$, $CoSO_4*7H_2O$, $ZnSO_4*7H_2O$ and $MnSO_4*H_2O$ has been studied with the nonisothermal methods of thermogravimetry (TG) , derived thermogravimetry (DTG) and differential thermal analysis (DTA).

Analysis of the characteristic thermogravimetric data (T_i , T_m , W_{oo})and kinetic parameters (n , E_a) with $CuSO_4*5H_2O$ as control sample , provided evidence of the existence of coordination and anion water in these hydrates.

The analysis of the compensation parameters led us to the conclusion that the existence of the compensation effect is determined by the ionic bond´s strength in the studied hydrates.

2.15 KINETIC ASPECTS FOR REACTIONS ON POLYMERS CONTAINING PENDANT AMINE AND CHLOROMETHYLENE GROUPS

Cornelia Luca, Virgil Barboiu, Ecaterina Avram, Emilia Streba
"Petru Poni" Institute of Macromolecular Chemistry, Iasi-6600, Romania

The chemical reactions on polymers represent an efficient way to modify the chemical structure to get polymers with predicted properties.

An important aspect for the chemical modifications of polymers is to know how the reactivity of a functional group of a low molecular weight compound is changed when such a group belongs to a polymer chain.

To get an answer to this question, some reactions leading to structures with quaternary nitrogen atoms were kinetically studied.

Such reactions were the addition of poly(4-vinylpyridine) and poly(N-vinylimidazole) as well as their models, 4-methylpyridine and N-methylimidazole, to acrylic acid and the displacement reactions of chloromethylated polystyrene and benzyl chloride with tertiary amines as well as of poly(4-vinylpyridine) and 4-methylpyridine with halogenated compounds.

Kinetic models were formulated and kinetic parameters were determined for all these reactions. Some conclusions were the followings:

- generally, the reactivities of a group in a polymer and in its model are different;
- the displacement reactions follow a second order kinetics, as expected, while the additions show a third-order kinetics;
- the displacement reactions are highly dependent on the solvent that can produce modifications of kinetic model as well as phenomena of accelerations or decelerations.

2.16 THERMAL STABILITY AND NONISOTHERMAL DECOMPOSITION KINETICS OF SOME COORDINATION HETEROPOLYNUCLEAR COMPOUNDS OF Cu(II) WITH A LIGAND FROM THE CLASS OF THIADIAZOLS

MIHAELA BADEA, RODICA OLAR, ELENA CRISTUREAN,
DANA MARINESCU, MARIA BREZEANU
Department of Inorganic Chemistry, University of Bucharest, Dumbrava Rosie, 23, Bucharest, Romania
E. SEGAL
Department of Physical Chemistry and Electrochemical Technology, University of Bucharest, Bd. Republicii, 13, Bucharest, Romania

The results concerning the thermal behaviour of four heteropolynuclear compounds with the general formula [$CuML(CH_3COO)_3$] where M=Ni(II), Zn(II), Mn(II) and Co(II); LH=2-amino-5-mercapto-1,3,4-thiadiazole are reported. The main decomposition steps for this heteropolynuclear coordination compounds have been detected.

For the kinetically workable steps, the value of the kinetic parameters have been determined using three integral methods due to Coats-Redfern, Flynn-Wall (for constant heating rate) and Urbanovici-Segal who modified the Coats-Redfern method. These methods allow to obtain the values of the reaction order n, reaction energy E and preexponential factor A from the equation: $d\alpha/dt = k(1 - \alpha)^n$.

The solid product of the second decomposition step is a mixed sulfide $CuMS_2$ which is stable in a range of 30-40°C and can be consequently isolated.

The final residue obtained in the case of the compounds [$CuMnL(CH_3COO)_3$] and [$CuCoL(CH_3COO)_3$] contains besides CuO, the mixed oxides with spinel structure $CuMn_2O_4$ and $CuCo_2O_4$.

2.17 KINETICS OF SOME PSEUDOREACTIONS IN COBALT DOPED CADMIUM CHLORIDE

G. Munteanu[a] and E. Segal[b]

[a] Institute of Physical Chemistry "I.G. Murgulescu" of the Romanian Academy
202 Splaiul Independentei, 77208 - Bucharest, ROMANIA
[b] Bucharest University, Department of Chemistry, Chair of Physical Chemistry,
13 Bd. Republicii, 70346 - Bucharest, ROMANIA

Some of the absorption bands in the optical spectrum of cobalt doped cadmium chloride were previously assigned to various aggregates composed by two or more Co^{2+} ions. The temperature dependence of the integrated intensity of such a band has been analyzed. The intensity of this absorption band increases when the temperature decreases down to 77 K and, by contrary, when the temperature increases up to room temperature the intensity decreases down to zero.

This intensity variation was associated with the variation in concentration of the chromophore entities to which the studied band is assigned. We considered that the increasing of the chromophore concentration is due to a formation process and *vice versa.* We assumed that during spectral measurements the two processes are in equilibrium.

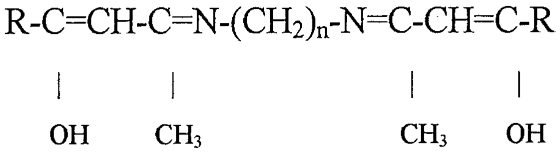
Taking into account the theory of the transition state both formation and decomposition of these chromophore entities were modeled and their formation energy was evaluated. Two reaction mechanisms were considered to model these pseudoreactions. The small value of the formation energy, of only 3.5 kcal/mole, suggests that the temperature dependence of the extinction coefficient could be due to a variation of the covalence degree of Co-Cl bonds.

2.18 THERMAL BEHAVIOUR OF SOME LIGANDS WITH NITROGEN AND OXYGEN

D.Fatu* and Viorica Popescu**.

* University of Bucharest, Dept. of Physical Chemistry Bd. Carol I, 13.
**University Ovidius, Bd. Mamaia, Constanta.

The thermal behaviour of some Shiff bases with the general formula :



$$R-\underset{\mathrm{OH}}{\underset{|}{C}}=CH-\underset{\mathrm{CH_3}}{\underset{|}{C}}=N-(CH_2)_n-N=\underset{\mathrm{CH_3}}{\underset{|}{C}}-CH=\underset{\mathrm{OH}}{\underset{|}{C}}-R$$

The thermal analysis methods have shown that the thermal decomposition of such compounds occurs after melting in two principal steps.The melting point increases with the molecular weight.

For the compound N , N$^{|}$ bis [4-hydroxy-3-penten-2 ilyden] ethylenedyamine the first decomposition step is controlled by the heat transfer even when using relatively low heating rates (2.5K/min).

The occurrence of the reaction is similar to a vaporisation as shown by the quite low value of the activation energy (E=64kj/mol).

The presence of the phenyl radical in N,N$^{|}$ bis [4-hydroxy-4-phenyl-3-buthene-2-ilyden] methandyamine determines the increase of the ntermal stability and the decomposition occurs in a kinetic regime being characterised by a higher value of the activation energy (E=160kj/mol).

The last decomposition step consists in the integral degradation of the compound which is characterised by strong exotermal effects.

2.19 THE EFFECT OF OXYGEN PRESSURE ON THE KINETICS OF THERMOOXIDATIVE DEGRADATION OF AN UNSATURATED POLYESTER RESIN

P.Budrugeac* , and E.Segal**

* EUROTEST S.A., 313, Splaiul Unirii, 73204 Bucharest 3 ,P.O.Box 4-77, Romania
** Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd. Republicii, Nr.13, Bucharest, Romania.

The results of nonisothermal kinetic analysis of thermooxidative degradation in air and oxygen of an unsaturated polyester resin are presented. It has been shown that thermooxidative degradation in oxygen occurs at lower temperatures than thermooxidative degradation in air. The kinetic parameters of thermooxidative degradation depend on heating rate and oxygen pressure. Two straight lines, *ln* A versus E (A is preexponential factor and E is activation energy), characteristic for compensation effect, have been obtained for thermooxidative degradation in air and in oxygen respectively. The difference between intercepts of these straight lines can be explained by dependence of preexponential factor on oxygen pressure.

~~2.21~~
2.20

COMPARATIVE NON-ISOTHERMAL KINETIC STUDIES CONCERNING "FULL AROMATIC" POLYETHERS AND POLYETHERS WITH THE OXETANIC RING IN THE MAIN CHAIN

Dana Ionescu[1], Nicolae Hurduc[2] and Natalia Hurduc[1]
1-"Al.I.Cuza" University of Iasi, Romania
2-"Gh. Asachi" Technical University of Iasi, Romania

The paper deals with the characterisation of thermal behaviour for some "full aromatic" polyethers and polyethers with the oxetanic ring in the main chain, using thermal analysis.

Thermal characteristics were correlated with kinetic and compensation parameters in order to obtain some information regarding the dependence between structure and thermostability.

2.21 KINETICS OF OXIDATION OF CYSTEINE BY HEXACYANOFERRATE(III) IN ACIDIC MEDIA. INBITION BY HEXACYANOFERRATE(II)

Ioan Bâldea and Maria Giurgiu
Faculty of Chemistry and Chemical Engineering. Babeş - Bolyai University of Cluj,
11, Arany Janos Street, Cluj - Napoca, 3400, Romania

The kinetics of oxidation of L-cysteine to cystine by hexacyanoferrate (III) has been investigated spectrophotometrically in $HClO_4$ solutions under various conditions. A first-order dependence on the oxidizing agent has been observed, when a large excess of cysteine and $HClO_4$ was used. The observed first-order rate constant exhibits a complex dependence on both the organic substrate and hydrogen ion concentration.

$$k_{obsd} = \frac{a[CysSH]^2[H^+]^{-1}}{1+b[CysSH][H^+]^{-1}}$$

CysSH stands for L-cysteine. Linear dependence of $[CysSH]/k_{obsd}$ as a function of $[H^+]/[CysSH]$ has been found.

Of a particular significance was the rate depression on addition of reaction product. A slight excess of hexacyanoferrate(II) was used to evidentiate its effect.

A reaction sequence involving a short-lived cyanide bridge complex $HFe(CN)_5(CN.SCys)^{3-}$ and a disulfide ion-radical $Cys_2S_2^{-\bullet}$ (cystine ion-radical) has been suggested to account for the kinetic data, free-radical detection and inhibition by Fe(II).

$$HFe(CN)_6^{-2} + CysSH \Leftrightarrow HFe(CN)_5(CN.SCys)^{3-} + H^+ \qquad k_1, k_2$$

$$HFe(CN)_5(CN.SCys)^{3-} + CysSH \Leftrightarrow HFe(CN)_6^{3-} + Cys_2S_2^{-\bullet} + H^+ \qquad k_3, k_4$$

$$Cys_2S_2^{-\bullet} + HFe(CN)_6^{2-} \rightarrow Cys_2S_2 + HFe(CN)_6^{3-} \qquad k_5$$

This mechanism leads to the following rate law :

$$r = \frac{\frac{2k_1k_3}{k_2}\frac{[CysSH]^2}{[H^+]}\left[HFe(CN)_6^{2-}\right]}{1+\frac{k_3}{k_2}\frac{[CysSH]}{[H^+]}+\frac{k_4}{k_5}\frac{[Fe(II)]}{[Fe(III)]}\left[H^+\right]}$$

Fe(II) and Fe(III) stand for protonated ferrocyanide and ferricyanide respectively. This rate law explains the dependence on CysSH, H^+ and $Fe(CN)_6^{4-}$ that has been found experimentally. Rate coefficient k_1k_3/k_2 $dm^3.mol^{-1}.s^{-1}$ has been determined as well as activation parameters :

$E_a = 39.5$ $kJ.mol^{-1}$, $\Delta H^{\#} = 36.9$ $kJ.mol^{-1}$ and $\Delta S^{\#} = -119$ $J.mol^{-1}.K^{-1}$.

From the inhibition effect of Fe(II), $k_4/k_5 = 0.67$ $dm^3.mol^{-1}$ has been calculated at 302.3 K.

2.22 THE CATALYTIC OXIDATION OF ALDEHYDES BY MEANS OF FERROPEROXIDE SYSTEMS

Sichiov A.Ya. Anikina Z.O
Department of Physical Chemistry,
Moldova State University,
Mateevici str. 60, Chisinau 2009 Md,
Republic of MOLDOVA

The oxidation of aliphatic and aromatic (such as formaldehyde, benzaldehyde, isobutyraldehyde, p-methoxybenzaldehyde) by means of Fenton's reagent and the influence of complexformation on the oxidation of formaldehyde by Fe^{2+}-ligand-H_2O_2 systems have been investigated. Tartric acid, citric acid, ethylendiaminetetraacetic acid, histidine, α,α'-bypyridil and 1,10-phenanthroline have been used as the ligands. It has been established that the effective oxidation of above-mentioned aldehydes takes place in the Fe^{2+}-H_2O_2 system. Aliphatic aldehydes are oxidized quicker and deeper than aromatic ones. The week dependence of the reaction rate upon pH testifying that the catalyst isn't changed at pH 1-3 occurs in all cases. The OH radical species generation has been established by means of the inhibitors method (the special inhibitor N,N-dimethyl-p-nitrosoaniline has been used as a $\overset{\circ}{O}H$ indicator). The $\overset{\circ}{O}H$ generation reaction is as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \overset{\circ}{O}H \qquad (1)$$

The carring out of the aldehyde oxidation under anaerobic condition has given the decrease of the rate and depth of the aldehyde oxidation. This fact shows the participation of dissolved oxygen in the mechanism of the process. As the Fe^{2+} ions forms according to the reaction (1), the addition of ascorbic acid (the reductant) regenerating Fe^{2+} -ions (the catalysts) gives the increase of the rate and depth of substrate oxidation. It has been established that the addition of ligands accelerates sharply the process of the oxidation of formaldehyde in the Fe^{2+}-ligand-HCHO-H_2O_2 systems. The increase of the oxidation rate of formaldehyde is connected with the change of the oxidation-reduction potential of the Fe^{3+}/Fe^{2+} couple resulting from the complexformation. The definite linear dependences observe in dependence on the nature of a ligand increasing or decreasing the redox potential.

2.23 SOLVENT EFFECT ON THE KINETICS OF THE BASIC HYDOLYSIS OF ISATIN

H.M. Abu El- Nader* and M.N.H. Moussa
Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

The kinetics of the basic hydrolysis of isatin in presence of ethanol and ethylene glycol has been investigated spectrophotowmetically. The changes in absorbance with time were followed at λ = 370 nm. the kinetis of the reaction were followed under pseudo first ander conditions with initial concentration of 4×10^{-4} and 4×10^{-3} mol l^{-1} for isatin and sodium hydroxide respectively. The rate of the reaction decreases with increasing the alcohol content and it passes through a minimum at about 30 wt % ethylene glycol. The effect of dielectric constant of the solvent mixture and the solvent composition on the reaction rate have been studied. solvation effects has been discussed from the study of the thermadynamic properties of the activated complex. A kinetic mechanism for the reaction was proposed to satisfy the obtained resalts.

2.24 THE KINETIC REGULARITIES AND THE MECHANISM OF THE DECOMPOSITION OF HYDROGEN PEROXIDE REACTION IN THE PRESENCE OF Fe(II) AND OF AN ORGANIC ACID

C.I.Tudoreanu
Department of Physical Chemistry, Moldova State University,
Mateevici Str.60, Chisinau 2809 Md, Republic of Moldova

The study of the kinetics of redox catalytic processes in the presence of transition metals' compounds indicates that the catalytic activity depends on the complexes composition and stability, and on the value of the redox potential of the respective metal in the presence of a ligand.

This paper studies the kinetic regularities and the mechanism of the hydrogen peroxide's decomposition in the presence of Fe(II,III) and the succinic acid (H_2L).

Measuring the redox potential at a constant pH and different concentrations of the H_2L, as well as at a consant concentration of the H_2L and different values of the pH, it was proved that in the pH=2-3 interval Fe(III) formes not only simple complexe, but also mixed, thus decreasing the value of the redox potential. The constant of the Fe(III) mixed compounds Fe(OH)L stability was found to be equal to $4.4 \cdot 10^{18}$.

The study of the kinetic regularities of the decomposition reaction of H_2O_2 in the presence of Fe(II) and H_2L proved the prevalent consumption of OH radicals in the reaction of H_2L oxidation. Keeping to the following condition

$K_{OH+H2L} \cdot [H_2L]/ K_{OH+H2O2} \cdot [H_2O_2] << 1$ there is no gas elimination in the reactant mixture what indicates that the decomposition of hydrogen peroxide in the system discontinues the moment Fe(II) compounds turn into Fe(III) compounds, which in this case are catalytically non-active. The actual achevement of the transformation

$LFe^{2+}(LFe^{2+}OH) \cdot LFe^{3+}(LFe^{3+}OH)$

takes place at the addition of an adequate reductor in the reactant mixture.

2.25 PHOTOBLEACHING KINETICS OF VIOLAMYCIN BI IN AQUEOUS SOLUTIONS, EFFECT OF IONIC STRENGTH

S. G. Ionescu, Tatiana Oncescu
Department of Physical Chemistry, Faculty of Chemistry,
University of Bucharest, R-70346 Bucharest, Bd Carol I nr 13.

Violamycin BI is an antracyclinic antibiotic isolated from fermentation cultures of Streptomyces violaceus. Löber et al. reported (1978, 1983) its absorption spectrum determined by the aglycone moiety, its ability to form aggregates solutions and its photochemical sensitivity, especially in diluted solutions. On this last aspect, we focused our studies in connection with the effect of ionic strength which influences the dimerization process.

One studied previously (1993-1994) the equilibrium between monomeric and dimeric violamycin BI at different ionic strengths I and determined the dimerization constant K_d.

The present study deals with the kinetics and quantum yields of V BI photobleaching on irradiation at λ =546 nm in the absorption band of both monomeric and dimeric species. By using diluted as well as concentrated solutions of violamycin BI at different ionic strengths, the dimerization equilibrium was shifted towards monomeric or dimeric form. Moreover, we studied the influence of ionic strength upon the rate constants and the reaction quantum yields of V BI photobleaching. In this respect we developed a kinetic model which takes into account both the presence of monomeric and dimeric violamycin and the equilibrium between them which depends strongly on the ionic strength. This model furnished plausible values of the photobleaching quantum yields.

We studied the same solutions in the presence of O_2 and in its absence by bubbling Argon into samples. The results obtained plead for a preponderent oxidative photobleaching of violamycin BI. New experiments are necessary to precise a comprehensive photochemical reaction mechanism.

2.26 SPECTRAL STUDY OF METALLO-TETRAPHENYLPORPHYRINS USED IN THE PHOTODYNAMIC THERAPY OF CANCER

Dr.Chim.Rodica-Mariana ION--ZECASIN S.A.,Photochem. Dept., Bucharest.

ABSTRACT

Due to their good singlet oxygen generation yield,the metalloporphyrins seems to be the most used chemical compounds in photodynamic therapy of cancer,(PDT) [1,2].

But ,in spiteof their singlet efficiency in PDT,the metalloporphyrins support one undesirable photooxidative degradation,producing cytotoxic species: peroxides, ketones,dioxetanes,etc,who enhance the applicability of these compounds in PDT,[3].

The present paper report on the photodegradation reaction parameters of metallotetraphenyporphyrins (Mg,Cd,Zn,Cu,Co, Ni,Pb,Pd),(reaction kinetic and mechanism,quantic yield).

Also,this paper present the results obtained from the spectral techniques (UV-Vis,emission,IR,NMR,ESR,masse) used to identify the photodegradation products.

References

1.R.M.Ion,EUROLIGHTS II,Belgium,1995.
2.R.M.Ion,G.A.Petre,Rev.Chim.,48,2,52(1996).
3.R.M.Ion,Ph.D.Thesis,Bucharest,1995.

2.27 *PHOTOLYSIS OF THE DICHLOROCYCLOBUTENEDIONE IN RARE GAS AT 10 K. INFRARED SPECRA ANALYSIS AND AB INITIO CALCULATIONS OF VIBRATIONAL FREQUENCIES*

I. Mincu*, A. Allouche, M. Cossu, P. Verlaque, M. Hillebrand*, J-P. Aycard, J. Pourcin

Laboratoire des Interactions Ioniques et Moléculaires, URA 773,
Université de Provence, Centre de Saint Jérôme, Case 232
13397 Marseille, CEDEX 20, FRANCE

* *University of Bucharest, Bd. Republicii 13, sector 1, cod 70034, ROMANIA*
E-mail: mincu@math.math.unibuc.ro

Abstract

The photochemistry of 3,4-dichlorocyclobutene-1,2-dione (A) embedded in solid argon matrix and irradiated by a filtered broad band source ($\lambda > 335$ nm) has been studied by FTIR spectroscopy. The new IR absorption bands were assigned to the photo-products by *ab initio* calculations of the theoretical vibrational spectra, at the SCF HF/4-31G* or 6-31G* level. A new highly intermediate bisketene, 2,3-dichloro-1,3-butadiene-1,4-dione ($O=C=CCl-)_2$ (B), was formed; the experimental infrared activities of (B) in the C=O spectral range corroborate its calculated twisted structure. (B) is decomposed by further irradiation and leads to the synthesis of carbon monoxide (D), dichlorocyclopropenone (E) and dichloropropadienone ($Cl_2C=C=C=O$) (F), by two concurrent pathways (branching ratios: 93% for (E), 7% for (F)). Photolysis of (E) and (F) by the full mercury lamp ($\lambda > 230$ nm) led to the infrared characterization of the dichloroacetylene (G) via a simple primary dissociation process. The study of the integrated absorbances versus time allowed us to characterize the kinetic behavior of the process and to establish the reaction mechanism.

Keywords: dichlorocyclobutenedione, cryogenic rare gas matrix, FTIR spectroscopy, photolysis, ab initio calculations, vibrational frequencies, infrared spectra analysis

2.28 PHOTOCATALYTIC ACTIVITY OF COLLOIDAL CdS FOR WATER CLEAVAGE TO GENERATE H_2

Tatiana Oncescu , M. Contineanu , Lucia Meahcov
Department of Physical Chemistry , Faculty of Chemistry
University of Bucharest , R-70346, Bd. Carol I , nr.13

Colloidal particles of CdS are produced by adding slowly $CdSO_4$ to an aqueous solution of Na_2S using Polyacrilyc acid 60 000 sodium salt as stabilizer.
CdS semiconductor particles generate electron-hole pairs on irradiation even with visible light , as follows :

$$\text{CdS} (h\nu) \rightarrow \text{CdS} (e^{-}_{CB} , h^{+}_{VB})$$

with photocatalityc activity for water cleavage.

Only donors or acceptors adsorbed onto particle surface can interven as h^{+}_{VB} or e^{-}_{CB} scavangers , respectively. In this purpose we employed S^{-2} as sacrificial electron donors to scavange photogenerated positive holes and a Pt redox catalyst to generate H_2 by reducing water . Its evolution was measured gas chromatographic.

We tested the role of K_2PtCl_6 concentration to establish the optimum one for H_2 evolution. One carried out experiments at various temperatures and observed that the higher temperature , the greater amount of measured H_2 . One investigated also the kinetic of H_2 evolution . We studied too the effect of CdS particles coprecipitated with ZnS on H_2 generation .

Our results permitted the calculation of turnover number TO for the partners of the investigated system .

REFERENCES

1.Kalyanasundaram K., Borgarello E., Duonghong D., Gratzel M., : Angew. Chem., 93 (1981), 1012
2. Hirai T., Shiojiri S., Komasawa I., : J. Chem. Engin. Jap. 27 (1994) 590

2.29 STUDY OF RADICAL SPECIES FORMED BY RADIOLYSIS OF POLYCRYSTALLINE $H_2TeO_4.2H_2O$

Mihai Contineanu

Department of Physical Chemistry, University of
Bucharest, Bd.Carol No 13, 7o346 Bucharest, Romania

EPR investigation of irradiated polycrystalline oxycompounds of tellurium has served for obtaining information on the nature of paramagnetic centers and ou changes in some properties of these compounds.

Polycrystalline samples of $H_2TeO_4.2H_2O$(Analer) irradiated at room temperature with doses around lo^{-3}Gy present rather complex EPR spectra. EPR signals having subaxial symetry were detected in all cases. EPR data compared with spectral parameters of Se oxyradicals known from literature lead to the conclusion that this spectrum belongs to the TeO_4^-, TeO_3^-, TeO_2^- species. Under higher amplifications the hyperfine structure due to the interaction of the unpaired electron with the ^{125}Te nucleus (7Y natural, abundance I=1/2) can be observed.

The spectral data allowed the calculation of spin densities v values on oxygen and tellurium orbitals.

The stability with temperature of TeO_3^- and TeO_2^- radicals with temperature has been studied by means of reactions isochronous. The kinetics of the thermal annealing of radical have been studied. The isothermal variation of the EPR signal in the interval 13o-15o^{o}C shows the disappearance proces of TeO_2^- radicals verifies a first order kinetics. On the basis of the EPR data a mechanism of formation of the TeO_4^-.TeO_3^-, TeO_2^- radicals in irradiated $H_2TeO_4.2H_2O$ crystals has been proposed.

2.30

CHEMILUMINESCENCE METHOD FOR STUDYING THE RADIO - AND THERMO - OXIDATIVE DEGRADATION OF POLYMERS

RADU SETNESCU, TANTA SETNESCU, SILVIU JIPA, MADALINA DUMITRU
ICPE - Research and Development Institute for Electrical Engineering, 313, Splaiul Unirii, 74204, Bucharest 3, Romania
ION MIHALCEA - *University of Bucharest, Faculty of Chemistry, Radiation Chemistry Laboratory, 13, Republicii, 70346, Bucharest 3, Romania*

The aim of this work was to test the capability of chemiluminescence (CL) technique, recently developed in ICPE, for studying of damaging effects produced in some polymeric materials (such as polyethylene or polypropylene) by thermo - or radio - oxidation.

Several works relating to the great sensibility of chemiluminescence both in antioxidant effectiveness assessement and in study of polymer degradation were reported .

We found a linear dependence between the iniatial chemiluminescence intensity and 1710 cm^{-1} absorbance for γ - irradiated unstabilized polypropylene ; a similar dependence is found for thermal oxidation of the unstabilized polyethylene .

Considerable differences in CL response between some stabilized polyethylene samples exposed to various thermal ageing conditions is found (Fig. 1) in spite of the fact that 1710 cm^{-1} absorbance is actually unchanged.

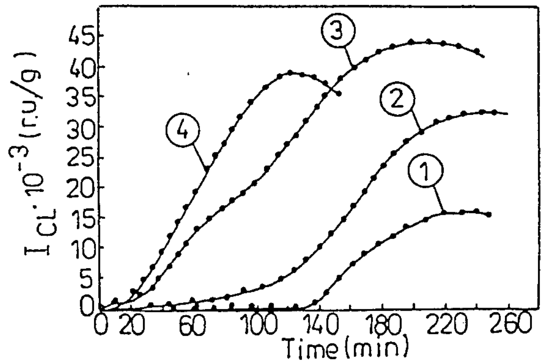


Fig. 1 - Chemiluminescence curves from poly - ethylene aged in various conditions
1 - unaged ; 2 - 1100 hours / 80°C in air (5 atm) ; 3 - 1758 hours / 80°C in air (5 atm) ; 4 - 7250 hours / 98°C in air (1 atm)

Using the oxidation induction time values and the formula of stress additivity the durability to various ageing conditions can be easily estimated, e.g. ~ 8500 hours at 98°C in air (1 atm) and 1900 hours at 80°C in air (5 atm) were determined for LDPE.

The specific shape of chemiluminescence curves can be correlated both with the crosslinking effect intensity in polyethylene and the strong radiation induced damage in polypropylene. The efficiency of Santonox - R in radiooxidative protection of polyethylene seems to be slightly greater than that of Irganox - 1010 although the efficiency in thermo - oxidative protection of Irganox - 1010 is considerably higher.

By mean of the oxidation profile obtained also from chemiluminescence data, the unhomogeneity oxidation of a γ - irradiated thick polyethylene sample is pointed out . In order to describe quantitatively the degradation level of the material an adequate parameter based on chemiluminescence is also proposed.

2.31 KINETIC STUDY REGARDING ZINC FERRITE LEACHING

Author: eng.Lucian MICLEA, IMNR Bucharest

Non-ferrous metals leaching represent one of the mains operations of hydrometallurgical processes.

This work aims to study the kinetics of zinc ferrite leaching in acid solutions and the factors which influence this process.

This information is used to optimize the actual hydrometallurgical processing of same materials that contain zinc ferrite, materials obtained from nonferrous metallurgy.

The leaching experiments have been done with high-purity zinc ferrite, synthetical obtained. As leaching agent was used sulphuric acid for the practical applicability reasons.

In this work there is shown the influence of following factors regarding the process kinetics:

- temperature, solution's acidity, velocity of agitation, initial concentration of Zn^{2+} and Fe^{3+} ions in solution.

Processing of experimental data has been based on kinetic equation of shrinking core model which describes in proper way the process.

Based on the experimental results, they have been calculated the values for activation energy and the reaction's order.

This work allows to establish the main directions for the intensification of the zinc ferrite leaching process in acid solutions.

ACADEMIA ROMÂNĂ

INSTITUTUL DE CHIMIE-FIZICĂ

2.32 THE REACTION OF SOME 5-HYDROXY-4H-PYRAN-4-ONE LIKE DERIVATIVES WITH THE STABLE RADICAL 2,2' DIPHENYL-1-PICRYLHYDRAZY

Emil Popa, Titus Constantinescu and Ştefania Rădulescu
Institute of Physical-Chemistry "I.G. Murgulescu"
Splaiul Independentei 202, Bucharest, 77202, Roumania

Researches upon the reaction of some derivatives of 5-hydrody-4h-pyran-4-one (3-hydrody-2-methyl-4h-pyran-4-one **1a**, 5-hydrody-2-methyl-4h-pyran-4-one **1b**, and 5-hydrody-2-(hydroxymethyl)-4h-pyran-4-one **1c**) with the stable free radical 2,2'-diphenyl-1-1picrylhydrazyl have evidenced the radicals scavenger properties of the three mentioned compounds; the reaction rate (k), measured in all three cases is significant ($k_{1a} < k_{1b} < k_{1c}$), with an order of reaction of 2 (in acordance with the order of the acidity constants, pK_a **1c** < pK_a **1b** < pK_a **1a**).

2.33 LABELLED POLYMERS, SYNTHESIYS AND SELFRADIOLYTIC EFFECTS

C. Postolache*, Carmen Postolache**, I. Mihalcea**
*Atomic Physic Institute; ** University of Bucharest

An alternative to glass tube technology that has the potential to produce higher light intensities is the use of a tritiated polymers. Such a polymer must be chemically stable with the attached tritium and remain transparent to the light emission from the contained phosphor. In this context, the presented studies have been focused on the synthesis of some tritium labelled polymers and their radiostability characterisation.

Labelled organic and siloxanic polymers containing phenyl radicals, which ensure high radiostability, were synthesised. Specific activities (Λ/m) obtained are between 7,4 GBq/mg and 51,8 GBq/mg (Ethyl-T_2 siloxane (I) = 22,2 GBq/mg; Ethyl-T_2 phenyl siloxane (II) = 11,1 GBq/mg; hydrogenated polyphenylacetylenes (III) = 37 GBq/mg; 1,4 dyphenylbutadyene-T_4 (IV) = 18,5 GBq/mg; 1,4 dyphenylbutane-T_8 (V) = 37 GBq/mg and N-phenylmaleinimide-T_2 (VI) = 74 GBq/mg).

Primary and secondary selfradiolytic effects were modelled by irradiation of unlabelled compounds using a 60 Co gamma irradiating source with rate of absorbed dose of 4 kGy/h, at absorbed doses between 0,5 and 2 MGy. Irradiated samples were analysed by IR spectroscopy, TLC chromatography and gel-sol ratio determination. The results did not show any structural modification of the studied compounds.

The contribution of the internal primary effects was identified on radioactive samples which present high selfabsorbtion. High instability of polysiloxanes was determined, the relative decreasing of the radioactivity being more than 30% for compound (I) and more than 20% for (II). Organic phenyl derivatives (III) - (VI) have a good stability ($-\Delta\Lambda \leq 15\%$). The results show a contribution of the primary internal effect to the selfradiolyses between 100% and 200% as compared with the other contribution effects.

Due to these studies, a new generation radioluminescente sources was realised at Radioisotope Production Centre of Atomic Physic Institute.

2.34 THE FATTY ACIDS DEUTERATION. DEUTERATION OF THE OLEIC ACID

VALER ALMASAN, MIHAELA LAZAR

Institute of Isotopic and Molecular Technology
P.O. Box 700, 3400 Cluj-Napoca, Romania,
Fax: 40-64-420042, Tel: 40-64-184037,
e-mail itimc@utcluj.ro

The deuteration of the fatty acids in preparative purposes is a more complex problem than the deuteration of other classes of organic compounds. For the preparation of deuterated oleic acid it was performed the kynetical type of the exchange reaction, the most active catalysts for it, and the exchange activity of different kinds of oleic acid's hydrogens. The main problem to be solved, is to pick out the most active catalyst for the exchange reaction heavy water (deuterium)/ oleic acid. This active catalyst is a transitional metal on oxidic support. The technology and the appropriate reactor for the deuteration of oleic acid represent the purpose of this work.

2.35 LABELLING WITH TRITIUM OF POLYACRYLIC ACID

C. Postolache , C. Ponta - Atomic Physic Institute

Polyacrylic hydrogels (PAA) were proved to be promising biomaterials with multiple applications in medicine and pharmaceutics: wound dressing, drapers, implants, controlled release sistems, microsphere. Biodegradability of polymeric material is an important characteristic in the use as implants of PAA or in other application which implies the hydrogel insertion in organisn. The usual determination of biodegradability is difficult and implies surgeries and high sensitivity analyses (e.g. HPLC). Labelling of polymer with radioisotopes followed by radiometric analysis of biodegradable products is an easier method.

The obtaining steps of tritium labelled polymeric hydrogel are presented:

(a) Labelling acrylic acid. Sodium acrylate (AANa) was labelled by isotope exchange technical (with Lindlar catalist Pd/C and quinolinum) in the presence of homopolimerizing inhibitores (Cu^{2+} ions). Total activities of 1,99 GBq for raw product and 1,66 GBq for purified compound were obtained. Specific activity obtained was 67 GBq/mmol and radiochemical purity was more 90%.

(b) Radioinduce polymerisation. Aqueous solution with a conc. of 30% of monomer (AA) was added to the labelled monomer (AANa-T- G), after the removal of solvent. Irradiation parameters were D = 4,5 kGy, d = 3 kGy/h, provided by an irradiation equipment IETI 1000 which consist in a gamma source of 60 Co with 185 TBq. The resulted product has a swolled degree in distilled water of 250 g/g, than 3% oligomers and undetectable monomeric products by Br^{-} - BrO_4^{-} analyse method.

2.36 MODELLING OF RADIOLYTIC PROCESSES IN TRITIUM LABELLED POLYMERS

C. Postolache[*], V. Fugaru[*], I.Mihai[*], Carmen Postolache[**]
[*] Atomic Physic Institute , Radioisotopes Production Centre
[**] Bucharest University, Faculty of Biology

Tritium incorporation in polymeric structures represents a technological alternative to beta light sources production, providing a high level of nuclear security. The main characteristic labelled polymers is the specific activity (Λ /m), but its increasing leads to significant selfradiolytic processes due to the selfabsorbtion of tritium beta radiation (secondary effects) as well as to the radioactive decay of chemically bound tritium (internal primary effect). The aim of the study was the identification of the polymeric structures which ensure a high capacity for tritium fixation and a good stability to selfradiolysis.

Absorbed doses due to selfradiolysis were calculated in accordance with the theoretical specific activities and thickness of polymeric layer. Absorbed doses situated in the range 35,3 MGy - 190 MGy were determined for thin layer of 0,03 - 0,05 μm and specific activities between 7,4 GBq/mg and 51,8 GBq/mg.

The modelling of radiolytic effects was accomplished by the analyses of monomeric and dimeric molecular structures providing the excited molecular states, the total bounding energy and extended molecular orbitals. A HyperChem computation programme was used for this purpose, phenylacetylene and phenylimidic derivatives being identified as high bounding energies on the principal chain of 333 - 494 kJ/mol and extended molecular orbitals with disipative effects of excitation energies. Siloxanic derivatives present a significant destabilisation of the bound Si-C (~ 199,9 kJ/mol), which implies high radiochemical yields (G_{-M}) and massive emissions of organic radioactive vapours.

The experimental results obtained for samples of labelled polymers have confirmed the superior stability of phenylacetylenic and phenylimidic compounds as compared to the instability of ethylsiloxanic derivatives.

2.37 FORMAL KINETICS OF CATALYTIC REACTIONS USING DIMENSIONLESS VARIABLES

CORNELIA IDITOIU*), NICOLAE DOCA**), DORINA CHAMBRE*)
*) " AUREL VLAICU " UNIVERSITY of ARAD
**) VEST UNIVERSITY of TIMISOARA

The paper presents some new kinetic models for omogeneous and heterogeneous catalytic reactions, in liquid media, using dimensionless reduced parameters. There are pointed out both the advantages and the limits of the proposed calculus method.

2.38 HETEROGENIZING OMOGENEOUS ACID - CATALYSIS OF SUCROSE HYDROLYSIS

DORINA CHAMBRE and CORNELIA IDITOIU
" AUREL VLAICU " UNIVERSITY of ARAD

The study presents the kinetic dependence of sucrose hydrolysis upon the acid catalysts nature and characteristics, both in omogeneous and heterogeneous system.

The influence of heterogenizing omogeneous catalysis on the catalytic constant, k_c, and on the kinetic parameters E_a and Z_α, is also emphasized.

3.1 VERIFICATION OF VAPOUR - LIQUID EQUILIBRIUM DATA IN QUATERNARY SYSTEMS WITH THE HELP OF THERMODYNAMIC INEQUALITIES

Alexander M. Toikka, Vitaly V. Kocherbitov
Department of Chemical Thermodynamics and Kinetics, Chemical Faculty, St.-Petersburg State University, Universitetsky pr. 2, Stary Petergof, 198904, St.-Petersburg, Russia.

We obtained some thermodynamic inequalities for verification of equilibria data. These inequalities are the results of stability conditions. For quaternary vapor the following inequality must be hold (P = const):

$$\sum_{i=1}^{3} x_i' RT \ln y_i \le \sum_{i=1}^{3} x_i' \left[\frac{L_i'}{T'}(T - T') + \tilde{c}_{p_i}' \left(T \ln \frac{T}{T'} + T' - T \right) + RT \ln y_i' \right], (1)$$

where y_i and T- molar fraction of component i in vapour and temperature in quaternary vapour; x_i', y_i', T' - molar fractions of component i in liquid and in vapour and temperature in ternary or binary subsystems; L_i' - partial molar heat of evaporation, c_{pi}' -average value of heat capacity for temperature range [T, T'} in ternary or binary subsystems. We suppose that nonideality of vapour can be neglected. In other case we use second virial coefficients or association constants.

The limit values of vapour concentrations y_i are the result of calculation by equality (1). For practical purposes we obtained the following form of formula (1):

$$\sum_{i=1}^{3} x_i' RT \ln y_i \le \sum_{i=1}^{3} x_i' \left[\frac{L_i^{\circ}}{T'}(T - T') + RT \ln y_i' \right], \qquad (2)$$

where L_i° - heat of vaporization for pure component i. The surfaces of limit values for planes y_i=const in concentration tetrahedron can be constructed. Formulae for other conditions (T = const) and parameters (temperature, pressure) also were obtained. The results of calculations for some quaternary systems and comparison with experimental data are displayed in concentration tetrahedron and triangles.

In conclusion, it can be said that the present method is one of few strict thermodynamics methods of equilibrium data verification for quaternary vapour - liquid systems.

This research was supported by Russian Foundation of Fundamental Investigations (N 96-03).

3.2 THE OPEN PHASE PROCESSES AND THERMODYNAMICS ISOLINES IN TERNARY SYSTEMS

Elena N. Rezanova, Alexander M. Toikka
Department of Chemical Thermodynamics and Kinetics, Chemical Faculty, St.-Petersburg State University, Universitetsky pr. 2, Stary Petergof, 198904, St.-Petersburg, Russia.

Regularities of displacement of equilibria along open evaporation curve and thermodynamic isolines in multicomponent heterogeneous systems are considered. Thermodynamic inequalities (consequence of conditions of stability) are in the basis of investigation.

We have obtained the following sequence of inequalities for processes of equilibria displacement under various conditions, imposed on parameters of the system:

$$\left(\frac{\partial Y_1}{\partial X_1}\right)_{X_2^{(1)}-X_2^{(2)},\ldots X_{n+2}^{(1)}-X_{n+2}^{(2)}} > \left(\frac{\partial Y_1}{\partial X_1}\right)_{X_2^{(1)}-X_2^{(2)},\ldots X_{n+1}^{(1)}-X_{n+1}^{(2)},Y_{n+1}^{(1)}} > \ldots$$

$$\ldots > \left(\frac{\partial Y_1}{\partial X_1}\right)_{X_2^{(1)}-X_2^{(2)},Y_3^{(1)},Y_{n+2}^{(1)}} > \left(\frac{\partial Y_1}{\partial X_1}\right)_{Y_2^{(1)},\ldots Y_{n+2}^{(1)}} > 0 ,$$

$$(Y_2, Y_3, \ldots Y_{n+2} = \text{const}), \qquad (1)$$

where X_i and Y_i - conjugate intensive and extensive thermodynamic parameters, upper indexes - indexes of phases; n+2 - total number of pairs of parameters. The inequalities (1) describe intensity of processes of displacement of equilibria in two-phase systems for different modes of condition changes. In indicated inequalities fastening of value $Y_i^{(1)}$ (at Y_i=const for system as a whole) specifies absence of phase transition for parameter i: entropies or volumes of phases, or the amount of substance in phases are constant. The condition $X_i^{(1)}-X_i^{(2)}$=const assumes phase transition, in particular, at $X_i^{(1)}-X_i^{(2)}=0$ - phase equilibria concerning parameter i (partial equilibria). The inequalities (1) can be interpreted as inequalities of Le Chatelier - Brawn principle.

On the basis of inequalities (1) and other similar ratio deduced in work an a mutual different thermodynamic curve arrangement is discussed; the specific examples are indicated for ternary systems (liquid - liquid, liquid - vapour, liquid - liquid - vapour).

This research was supported by Russian Foundation of Fundamental Investigations (N 96-03).

3.3 THEORETICAL BASIS AND GENERAL EQUATIONS OF A RECENT MODEL FOR MIXED ELECTROLYTES. NUMERICAL CALCULATIONS.

Rodica Vilcu*, Rodica Sirbu **

*** Prof. Dr. Doc. - Univesity of Bucarest**
****Lector - Ovidius University of Constanta**

Abstract

The authors presented a calculation method for the description of the thermodynamic properties of electrolyte mixture solutions using the Pitzer's model. This model proposed a set of equations for activity and osmotic coefficients and for the excess Gibbs free energy of an aqueous solutions of electrolytes. In these equations the first term is a modified Debye-Huckel contribution, the second term is a correction for short-range binary interactions between ions, which is a fonction of ionic strength and the third term correct the ternary interactions between ionic species and is assumed to be independent of the ionic strength.

The Pitzer's model constitutes an excellent contributions when compared to the Debye-Huckel's model and other models like Guggenheim's and Scatchard's model, because he utilised the virial coefficients which are symmetric and include short - range interactions between ions with same charges or opposite charges. For an excellent representation of experimental data of multicomponent solutions ternary parameters which can only be determined from experimental data on ternary or multisolute electrolyte systems are needed. For most engineering applications at ionic strength numbers up to about 6 molal, third virial coefficiens and interactions between ions of the same sign of charge can however be neglected.

Here demonstrated, the work achived using binary solutions: KCl - H_2O; KNO_3 - H_2O. Also using ternary solutions KCl - KNO_3 - H_2O. Results obtained by this callculation method are in a good accordance with those other experimental methods.

3.4 THE INFLUENCE OF THE METHOD USED FOR THE ESTIMATION OF THE SECOND VIRIAL COEFFICIENTS ON THE RESULTS OF THE EVALUATION OF THE THERMODYNAMIC CONSISTENCY OF THE V.L.E. DATA

Rodica Vilcu[1] , Luminita Simoiu[2]
[1]Universitatea Bucuresti, Facultatea de Chimie, B-dul Carol nr. 13, Bucuresti
[2]Universitstea din Craiova, Facultatea de Stiinte, str.A.I.Cuza, nr.13, Craiova

For the devlopement and design of the separation processes, accurate vapor-liquid equilibrium data are necessary.

In this order, thermodynamic consistency tests have been considered to be an important problem and by consequence last years there are reported many testing procedures.

The paper presents the study of the influence of the second virial coefficients on the results of the evaluation of the thermodynamic consistency of the binary vapor - liquid equilibrium data obtained under isobaric conditions.

The proposed method /1/ for evaluation of the data is a free-model procedure based on the numerical integration of the coexistence equation of the phases. The equation takes into account the nonideal behaviour of the vapor phase by the use of the coefficients from the virial equation of state.

For the proposed study there are considered three methods for the estimation of the second virial coefficients: the procedure of Tsonopoulos /2/, Hayden-O'Connell /3/, respectively, Vetere /4/.

Also, the experimental data for the virial coefficients, available from Dymond and Smith's /5/ collection are used for reference binary sustems.

The resuls of the study are appreciated by using the correlation analysis of the residuals of the vapor phase, calculated as differences between experimental and estimated values.

References

1. L.Simoiu, "Isobaric Test for trermodynamic consistency ";5-th CODATA Symposium., Liblice (1991)
2. G.Tsonopoulous, A.I.Ch.E.J. 20,263 (1974)
3. Hayden O'Connell, Ind.Eng.Proc.Des.Dev. 14, 3, 209 (1975)
4. R. C. Reid, J.M. Prausnitz, T.K. Sherwood: "The properties of Gases and Liquids", McGraw-Hill Book Company, Third Edition.
5. J.H.Dymond, E.B. Smith :"The virial coeficients of gases", Clarendon Press, Oxford 1969.

3.5 VAPOUR-LIQUID EQUILIBRIUM IN CYCLOOCTANE+ n-BUTHYLBENZENE BINARY MIXTURES

Mariana Teodorescu*,Alexandru Bârhala* and Ortansa Landauer**

* Institute of Physical Chemistry of Romanian Academy,202 Splaiul
Independentei,77208,Bucharest,Romania;
** Depart. of Applied Physical Chemistry,"Politehnica" University,313
Splaiul Independentei,77208,Bucharest,Romania

Abstract:

Isothermal vapour-liquid equilibrium data at 373.15,383.15 and 393.15 K in cyclooctane+n-buthylbenzene mixtures are reported.Use has been made of an ebulliometer which allowed sampling from both phases in equilibrium. The different expression for G^E suitable for correlation of these data are tested. The results evidenced a positive deviation from ideality of the system.

3.6 VLE AND EXCESS VOLUME DATA FOR CYCLIC AND AROMATIC BINARY MIXTURES

Dana Drăgoescu,Alexandru Bârhala,Adrian Crisciu,*Rodica Vîlcu* *

* Institute of Physical Chemistry " I.G.Murgulescu",202 Splaiul Independentei,
77208 Bucharest,Romania
* *Physical Chemistry Department, Faculty of Chemistry,University of Bucharest,
13 Carol Avenue,Bucharest,Romania

Isothermal vapour-liquid equilibrium data at temperatures between 303.15K and 328.15K in cyclohexane+ n-propylbenzene mixtures are presented. The vapour pressures of the mixtures were measured at 5 K intervals by a static method.
From these data the excess Gibbs free energy of the system was calculated and compared to those predicted by well-known method.

The excess volume was calculated from experimental densities of the mixtures, measured with a 10 cm^3 pychnometer at 298.15K. The excess volume have been fitted by an empirical equation ,whose coefficients were estimated by a non-linear regression.

The results evidenced a positive and small deviation from ideality.

3.7 THE THERMODYNAMIC RESEARCH OF THE BUFFER PROPERTIES IN THE MULTICOMPONENT HETEROGENEOUS SYSTEMS

IGOR G.POVAR

Institute of Chemistry, Academy of Sciences of Moldova, Kishinev

The concept of the "buffer" was introduced and developed only for homogeneous aqueous solutions, especially detailed for the acid-base conjugated pairs.

The present work has the aim to research the buffer properties of the heterogeneous systems that contain two phases: (a) the solid phase (sparingly soluble precipitate) and (b) the liquid one (saturated solution). Usually the real systems contain a great number of chemical species that interact with the precipitate components (the secondary reactions of the hydrolysis, protonization, complexation, etc.). It is shown, that the dissolution-precipitation process of a sparingly soluble salt M_mA_n (M - the metal ion, A - anion):

$$M_mA_n = m\,M + n\,A,$$

ensures the buffer stability of the system in respect to the components M and A. At the same time the secondary reactions that increase the solubility growth of the sediment intensifies their buffer properties of the examined systems. It was found that in case when the precipitate is a sparingly soluble hydroxide or acid, the system manifests the buffer in respect to pH of medium.

As a quantitative characteristic of buffer properties of the heterogeneous systems in respect to pM or pA there are $\beta_M = d\,C_M / d\,pM$ and $\beta_A = d\,C_A / d\,pA$, where C_M and C_A represent the total concentrations of the respective species.

The obtained expression are apt to be used in the field of the thermodynamic stability of the precipitates. Some of the peculiarities, characteristic for the heterogeneous buffer systems only are discussed. The usage of a number of concrete heterogeneous systems as a buffer system in different human activities is also put into discussion.

3.8 THE APPLICATION OF THE THERMODYNAMIC METHODS IN THE MODELING OF THE KIDNEY GALL-STONES FORMATION PROCESS

I. Povar[1], Iu. Barsan[2], V. Voroniuc[1]

[1] Institute of Chemistry , Academy of Sciences of Moldova, Kishinev
[2] The Clinic Republican Hospital, Kishinev

Usually the research of the physico-chemical processes of kidney gall-stones as well as the quest for new forms of the adequate treatment is realized an empirical way.

The formation-dissolution process of the gall-stones in form a sparingly soluble salts in the kidney cavity system is affected by the various simultaneous equilibria with the components from the kidney urine. A special influence on the nature and thermodynamic stability of the formed precipitates has the urine acidity that is its pH. At the same time, the presence of different complexing agents increase the growth of the solubility of a sparingly soluble precipitates.

In the present work the thermodynamic simulation of the heterogeneous equilibria in the systems of the kidney gall-stones (the solid phase) - the kidney urine (a multicomponent saturated solution) is proposed. As thermodynamic potential used for the determination of the direction and limits of the formation-dissolution process proceed of the kidney gall-stones, serves total change of the Gibbs energy (ΔG). The expression, obtained by one of the authors give as the possibility to calculated ΔG in the conditions of a definite chemical model of equilibria as well as to determine through an experimental way the value of total change ΔG and correspondingly, the definition of the proposed chemical model. In the process of thermodynamic modeling, the possibility of chemical species formation with a complex composition was taken into account.

The possibility of mutual transformation of various kidney gall-stones in function of the composition and concentration variables of the multicomponent heterogeneous systems that is researched. A special attention was payed to various complexing agents influence of a native and synthetic origin of the gall-stones solubility.

Following the idea of a correct evidence of the mass balance by the indirect polarographic method was determined the concentrations of the ions Ca^{2+} and Mg^{2+} in different urine samples and their contents in gall-stones.

3.9 ENERGETIC STUDY OF 1-PHENAZINCARBOXYLIC ACID DERIVATIVES

Viorica Meltzer[1], Anca Nicolae[2], Ion Ciocăzanu[1], Rodica Vîlcu[1]
University of Bucharest
Department of Physical Chemistry(1); Organic Chemistry Department(2)

In a previous paper both synthesis of 1-phenazincarboxylic acid hydrazide and its condensation with a number of aromatic aldehydes, in order to obtain new products, were presented. The new compounds, having active biological capacities, have been characterized by IR and NMR Spectra, the purity being studied by elementary analysis.

The purpose of this work is to realise an energetic study of the same compounds having phenazinic rings already studied:

*1-Phenazincarboxylic acid;
*1-Phenazincarbohydrazide;
*1-Benzylidene-2-Phenazinoilhydrazine;
*1-(2'-Nitrobenzylidene)-2-Phenazinoilhydrazine;
*1-(4'-Nitrobenzylidene)-2-Phenazinoilhydrazine;
*1-(4'-Methoxibenzylidene)-2-Phenazinoilhydrazine;
*1-(2'-Chlorbenzylidene)-2-Phenazinoilhydrazine.

The thermodynamic experimental and theoretical study, regarding these substances is oriented in the following directions: heats of combustion and formation enthalpies; thermal effects associated to phase transitions of first order (fusion enthalpies) and Cp=Cp(T) correlation. The accuracy of our data is a consequence of the performant applied thermochemical methods (DSC and combustion calorimetry).

3.1o HEAT CAPACITIES OF SOME AQUEOUS SOLUTIONS OF ALIPHATIC AMINO ACIDS

Dana Constantinescu,Dan Geană[*],Cristian Telea
"I.G.Murgulescu"Institute of Physical Chemistry,Spl.Independentei
202,77208 Bucharest,Romania
[*] University "Politehnica"of Bucharest ,Faculty of Industrial
Chemistry,Str.Polizu 1,Bucharest 78126,Romania

We have measured heat capacities for aqueous solutions of L-Alanine ,D-Alanine ,DL-alanine and β-Alanine ,using a heat conduction microcalorimeter. All solutions are prepared by weight on the molality concentration scale. The apparent molar heat capacity data were analyzed by weighted least-squares method using an equation of the form:

$$C_{p,A}(app)=C_{p,}{}^{\infty}{}_{A}+C_{AA}m$$

where $C_{p,}{}^{\infty}{}_{A}$ is the standard state (infinite dilution) partial molar heat capacity of the solute and C_{AA} is the heat capacity pairwise interaction coefficient.
We have explored several group additivity schemes for aqueous amino acid systems.Our analysis are based on a multiple regression procedure that uses matrix mathematics to produce estimates of the required group contributions.
We compare experimental standard state heat capacities with those which can be calculated for our data set of four amino acids.

3.11 CALORIMETRIC MEASUREMENTS ON THE GROWTH OF THE YEAST SACCHAROMYCES CEREVISIAE IN STATIC CONDITIONS

M. Freamat, Aurora Costache, Cr. Telea

Institute of Physical-chemistry "I. G. Murgulescu" ,Splaiul Independentei 202,
77 208, Bucharest, Romania

The main purpose of this paper is to establish the correlation between the power-time curves on one side and growth and metabolic characteristics of the yeasts on the other side. On the power-time curve three areas have been differentiated:

- the initial phase corresponding to the lag phase;
- the yeast population growth phase, described by an exponential equation of Malthus type;
- the final phase, while the thermal flux decreases down to the base line in correlation with a Michaelis-Menten kinetic equation.

The considered factors towards the thermogram characterization belong to the following categories:

- factors depending on the biological material (species, strain, inoculum growing phase);
- factors depending on the cultivation conditions (culture medium type, its composition, absence or presence of the growth factors, pH, oxygenation);
- finally, factors depending on the concrete conditions the experiments were accomplished in (the total volume of the sample, the volume ratio between sample and inoculum, the substrate initial concentrations, the initial amount of biomass, the temperature, the inoculation method).

The cultures have been carried on using a complex medium with glucose as carbon source, Yeast Extract and Tryptone as nitrogen source. In the given experimental conditions the anaerobic degradation of the glucose towards ethanol and CO_2 has been registered; this process is mainly responsible for the thermal flux. A value of 33 kJ/mol has been found for the catabolic average enthalpy. There have been used culture media with a substrate concentration varying between 1.5 g and 6 g per 100 mL of medium. The substrate does not explicitly appear but in the expression of the used Michelis-Menten kinetic equation for the final phase, but it determines the exponential phase duration as well as the maximal thermal flux value. A comprehensive approach has been used, in attempt to modeling the whole process.

3.12 CALORIMETRIC TITRATION OF BOVINE SERUM ALBUMIN WITH UREA

Gabriela Chilom, Ovidiu Chilom, Teodor Vişan, Cristian Telea
Institute of Physical-Chemistry "I.G. Murgulescu"
Splaiul Independentei 202, Bucharest, 77208, Roumania

The interaction of urea with protein has been studied calorimetrically by titrating protein solutions with denaturant at 35°C and at different pH. Protein studied was bovine serum albumin (BSA) and the concentration of the solution was about 10^{-5} M. The concentration of denaturant (urea) has been varied form 0-M to 9.5-M. In case of protein solution with pH=7, without buffer solution, has been no conformational transition, even on great concentration of urea. From this reason has been titrated in identical conditions a protein solution thermal denaturated previously. The difference between global thermal effects represents just the heat of denaturation. In case of protein solution with pH = 5 in acetate buffer, has been observed an conformational transition at urea concentration accessible experimentally. In this case the heat of denaturation has been measured directly. It has been shown that the observed heat effects can be described in terms of a simple binding model with independent and similar binding sites.

3.13 THERMODYNAMICS AND KINETICS OF DECOMPOSITION PROCESSES FOR THE ISOMERS OF AMINOBUTYRIC ACID

Sofia Călin and Cristian Telea
Institute of Physical-Chemistry "I.G. Murgulescu"
Splaiul Independentei 202, Bucharest, 77208, Roumania

The thermal properties of amino acids, has been extensively investigated by various thermal analysis techniques. It is well known that solid α-amino acids melt at high temperatures because of hydrogen bonds between COO^- and NH_3^- groups bonded the same α carbon atom. This dipolar ion structure could account for the general thermal behavior; however it is beyond doubt that the side chain as well as the nature and position of the functional groups determine the distinct thermal behavior between amino acids classes and within the same class.

The amino acids studied belong to the " apolar or hydrophobic chain" class.

The thermal stability of aminobutyric acid isomers (α, β , γ, iso) was studied simultaneously by TG, DTG and DTA measurements. The influence of the amino group position and the side chain upon the thermal decomposition and thermal stability was investigated.

The parameters employed in the characterization of compounds are: the initial temperature of decomposition, T_i, the temperature at maximum decomposition rate, T_m, final decomposition temperature, T_f, the temperature range of thermal effect (DTA) and the kinetic parameters E_a and lnA.

Various scales of the thermal stability as function of T_i, T_m and E_a were developed.

3.14 EXPERIMENTAL AND THEORETICAL ASPECTS OF PROTEIN-WATER INTERACTION. CALORIMETRIC STUDY

Ovidiu Chilom, Gabriela Chilom and Cristian Telea
Institute of Physical-Chemistry "I.G. Murgulescu"
Splaiul Independentei 202, Bucharest, 77208, Roumania

An microcalorimeter Calvet has been used to obtain water sorbtion isotherms for bovine serum albumin (BSA) at 35°C and normal pressure. Protein was previously treated so as the initial content of water was zero and protein remain on native state. Simultaneously with calorimetric studies, has been made gravimetrical measurements for determining the quantity of water adsorbed on BSA in solid state and its time variation. The measurements has been made on identical samples placed in an external thermostat, at the same temperature as the calorimeter. From the analysis of experimental determination results three domains of linear dependence of differential heat of hydration of the quantity of water adsorbed. This leads to the idea of water heterogeneity in hydration sphere of globular proteins, determined by the interactions with ionic groups, polar and non-polar groups.

3.15 DETERMINATION OF THE ENTHALPIES OF COMBUSTION BY MEANS OF A MICROBOMB

Iulia Contineanu, Cristian Telea
Institute of Physical Chemistry, "I.G.Murgulescu",Bucharest
Spl.Independenţei 202, 77208, Romania

A microbomb of combustion was built up, inteneded for measurements of the heat of combustion of organic sustances. The dimensions of the microbomb are as follows: 16 mm diameter, 8,5 mm height and 4,5 cm^3 internal volume. The two ends of the microbomb served as the inlet and autlet of oxygen. Combustion pellets, 2,5 mm in diameter, have obtained in a special press. The weight of samples was about 6mg.

Two such devices, as similar as possible, were placed in a Calvet type conduction calorimeter which ensured the overall integration of the calorimetric cell. The error of measurements was 0,52%.

All details regarding microbomb construction, working procedure and experimental difficulties of the method are supplied.

Experimental results of the chemical standardization with benzoic acid (SRS 39i) and of combustion runs with urea are presented.

3.16 THE ENTHALPIES OF COMBUSTION AND FORMATION OF L-, D- AND DL-ASPARTIC ACIDS

IULIA CONTINEANU AND D.I.MARCHIDAN
„I.G.Murgulescu" Institute of Physical Chemistry,
Splaiul Independenţei 202, Bucharest 77208, Rumania

Standard energies of combustion of L-, D- and DL-aspartic acids have been determined in an oxygen bomb combustion calorimeter. Derived standard enthalpies of formation at 298.15 K are as follows:

$$C_4H_7NO_4\ (s) + 3.75\ O_2\ (g) \longrightarrow 4\ CO_2\ (g) + 3.5\ H_2O\ (l) + 0.5\ N_2$$

L-aspartic acid

$\Delta \underline{cH}^{o}(298.15\ K) = -\ 378 \pm 2.7$ kcal/mol

$\Delta \underline{fH}^{o}(298.15\ K) = -\ 236 \pm 2.7$ kcal/mol

D-aspartic acid

$\Delta \underline{cH}^{o}(298.15\ K) = -\ 379 \pm 2.6$ k cal/mol

$\Delta \underline{fH}^{o}(298.15\ K) = -\ 235 \pm 2.6$ kcal/mol

DL-aspartic acid

$\Delta \underline{cH}^{o}(298.15\ K) = 374.1 \pm 2.5$ kcal/mol

$\Delta \underline{fH}^{o}(298.15\ K) = 240.4 \pm 2.5$ kcal/mol

3.17 THE STANDARD ENTHALPIES OF FORMATION OF SOME DIBENZO-CYCLOHEPTANE ALCOHOLS

[a]Stefan Perisanu, [b]Mircea Banciu

[a]Laboratory of General Chemistry, Polytechnic University of Bucharest, 76206 Bucharest, Romania.
[b]Laboratory of Organic Chemistry, Polytechnic University of Bucharest, 76206 Bucharest, Romania.

The heats of combustion of four monoalcohols (5-hydroxymethyl-5,6-dihydro-7H-dibenzo [*a,c*] cycloheptene , 6-hydroxy-methyl-5,6-dihydro-7H-dibenzo [*a,c*] cycloheptene, 5H-dibenzo [*a,d*] cyclohepten-5-ol, 10,11-dihydro-5H-dibenzo [*a,d*] cyclohepten-5-ol) were measured by means of a Gallenkamp adiabatic bomb calorimeter..

The synthesis and purification of some of them was described elsewhere, by one of the present authors , the other ones were synthesized after literature data. Uncertainties in the determination of the heats of combustion ranged between 0.2 and 0.5 %.

A typical example is given, namely that of 5H-dibenzo [*a,d*] cyclohepten-5-ol. Its molar enthalpy of combustion is ΔH_c^o = -7484.8 kJ/mol and its standard enthalpy of formation is ΔH_f^o= -132.9 kJ/mol We obtained, by means of the latter value, the enthalpy of atomization of this compound, i.e. ΔH_{exp}^a= 13723.6 kJ/mol , while the corresponding value, calculated by means of the Allen-Skinner bond energy scheme, for the liquid state is ΔH_{calc}^a= 135916 kJ/mol. The required parameters for this calculation and details about the determination of heats of combustion may be found in previous paprs of the first author. As the latent heat of melting of this compound should be in the range 30-50 kJ/mol, it results, from the difference between the experimental and calculated enthalpies of atomization, that a considerable resonance energy (of at least 70 kJ/mol) is stabilizing this structure (the resonance energy of the benzenoid rings not included). This observation is, at least in qualitative agreement, with a similar one, about the corresponding ketone, investigated in a previous paper.

Conclusions were drawn about the stability of dibenzo-cycloalcane systems. Comparison was made with a six membered ring diol, namely 9,10-bis-hydroxymethyl-9,10-dihydro-phenantrene (trans isomer) for which the thermochemical properties were also measured. For diols, the possibility of building internal hydrogen bonds was investigated toa.

3.18 THERMOCHEMICAL STUDY OF SOME POLYCYCLIC HYDROXI-KETONES

Ion Ciocazanu

Department of Chemical Thermodynamics, University of Bucharest, Bd. Republicii 13,
Bucharest 70031, Romania.

The thermochemical characterisation of some derivatives of 8-R-tricyclo [7,3,1,$0^{2,7}$] tridecan-2-ol-13-one series has been performed, where R is: hydrogen, methyl, ethyl and n-propyl.

The experimental determinations of the enthalpies of combustion were obtained using a Gallenkamp adiabatic bomb calorimeter. The experimental values of the combustion heats in the solid state were compared with those calculated using a contribution group method.

The enthalpies of formation for the studied compounds were derived.

By sublimation calorimetry, using a Tian-Calvet calorimeter equipped with a Knudsen. effusion cell, the heats of sublimation were determined.

The differential scanning calorimeter (DSC) has been used to determine the heats of fusion and the phase transition temperatures.

3.19 THERMODYNAMICS OF ADSORPTION AND FOAM SEPARATION FOR HEAVY METALS

Olga Lobacheva

Department of Colloid Chemistry, Sankt-Petersburg State University,
Universitetsky pr., 2, Stary Petergof, Sankt-Petersburg,198904, Russia

In this report we discuss the results of our theoretical and experimental investigation of thermodynamics of foam separation for heavy metals (copper, cobalt, nickel). The technique of foam separation shows some promise for the removal of certain classes of inorganic compounds from water. Method is based on adsorption of cations of heavy metal at the air-liquid interface in aqueous solutions which contain anion active surfactants. In spite of practical value of foam separation, the thermodynamic foundation of this technique has been elaborated insufficiently. We present here a simple method for estimating the adsorption isotherm parameters of cations of heavy metal at the air-water interface. As the basis for calculation of relative adsorptions, the adsorption equation is used for an aqueous solution contains electrolytes including ionic surfactant (A.I.Rusanov //Colloid J., V.49, N.4, P.688-692, (1987) RUSSIA).

The concentration-dependence of surface tension in the mutual system containing sodium dodecylsulfate and heavy metal sulfates and relative adsorptions of bivalent metals were found from adsorption equation. In addition, in the presence of anion active surfactants the adsorption of cations of heavy metal is positive as determined in our experiment. It allows removing these heavy metal cations from water with the use of anionic surfactants. Foam separation method permits cleaning water from heavy metal cations up to the limiting permissible concentration. Heavy metal cations are substituted by sodium cations in the process of foam separation.

This research was supported by Russian Foundation of Fundamental Investigations (N 96-03).

3.20 THE STUDY OF THE THERMODYNAMIC PROPERTIES OF SOME NONSTOICHIOMETRIC COMPOUNDS WITH PEROVSKITE STRUCTURE

Speranta Tanasescu, N.D. Totir and D.I.Marchidan
Romanian Academy, Institute of Physical Chemistry
Splaiul Independentei nr. 202, Bucharest, 77208, ROMANIA

The thermodynamic properties of $LaMnO_{3+x}$ and $La_{0.7}Sr_{0.3}MnO_{3+x}$ perovskite-type compounds with the oxygen nonstoichiometry ranging for 2.981 to 2.947 have been studied by the solid electrolyte galvanic cells method coupled with the solid state coulometric titration technique.

The partial molar free energies, enthalpies and entropies, as well as the equilibrium partial pressures of oxygen in the temperature range of 1073-1373 K have been determined.

The measurements put into evidence the variation of the thermodynamic data both with the temperature and the oxygen nonstoichiometry. A comparative study of the undoped and strontium doped compounds allowed us to make some observations regarding the effect of the strontium presence on the thermodynamic properties in the lanthanum manganite.

For some compositions, the obtained values of the partial molar quantities and of the pressures of oxygen were compared with the thermogravimetrical data founded in the literature [1,2].

1. N.Kamegashira, Y.Miyazaki and H.Hiyoshi, Mat. Letters,2,194 (1984)
2. J.H.Kuo, H.H.Anderson and D.M.Sparlin, J.Solid State Chem. 83,52 (1989).

3.21 INCORPORATION OF A MANGANESE(III) CHIRAL COMPLEX INTO THE CHANNELS OF MCM-41 ZEOLITE SAMPLES. THERMAL ANALYSIS

Ligia Frunza[1], H.Kosslick[2], E.Hoeft[2], R.Fricke[2], Rodica Vilcu[3]

[1]Institute of Physics and Technology of Materials, Bucharest
[2]Institute of Applied Chemistry, Berlin-Adlershof
[3]Faculty of Chemistry, University of Bucharest

TG and DTA curves were obtained for a free manganese(III) complex of salen type, namely [[(R,R)-N,N'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato(-2)]] manganese(III) chloride (hereafter designed as Jacobsen complex) as well as for some MCM-41 samples loaded with this complex. In addition, the free ligand behaviour in thermal analysis was also performed for comparison. The maxima for weight loss and heat flow curves suggest the decomposition and desorption of the complex. The melting of the pure ligand takes place at ca. 200°C, whereas that of Jacobsen complex, at ca. 324°C.

The highest and narrowest exothermic peak in the manganese complex case is that at 412°C, followed by a smaller one at 426.6°C; each of these corresponds to a certain (large enough) mass loss. Above 450°C, the residue fails to undergo appreciable mass variation. The exothermic peaks became very broad and structureless by embedding the complex into the zeolite channels.

Isomorphous substitution of Si with Ga, Fe, Al, Ti into the zeolite framework is expected to strongly influence the reactivity of the embedded complex: Therefore, the thermal analysis curves show the differences among the loaded samples. Taking into account the highest exothermic peak at ca. 400°C, the decomposition stability decreases in the sequence: Al-MCM-41 ≈ Ga-MCM-41 > Ti-MCM-41 > free complex > Fe-MCM-41 > Si-MCM-41. We supposed that this decomposition peak should give a measure of the thermal stability of the embedded complex and thereby, of the guest-host interaction between Jacobsen complex and the zeolite walls.

These conclusions are supported onto data obtained spectroscopically /1/.

/1/ L.Frunza, H.Kosslick, E.Hoeft, R.Fricke sent to publication

3.22 SOME THERMODYNAMIC ASPECTS OF SALTS DISSOLUTION

Ana ONU, Mircea APOSTU
"Al. I. Cuza" University of Iassy, Faculty of Chemistry

We had studied the thermal dissolution effect of $K_2Cr_2O_7$ in water, using a DIRECTHERMOM-D calorimeter. The measurements of thermal dissolution effect had been made in the whole solubility range. The concentration dependence of thermal dissolution effect had been showed by the empirical polinomial equations versus $\sqrt{m}$ or $\ln(m)$: ${}^{i}\Delta H_{diz}(m) = \sum_{i=0}^{r} a_i m^{i/2}$ and ${}^{i}\Delta H_{diz} = \sum_{i=0}^{r} a_i (\ln m)^i$.

Based on this dependence it had been calculated the integral thermal dissolution effect for infinite dilution, and the partial molar enthalpies of the components. The polinomial fitting of experimental data was performed using the Gauss criterion for choosing between two or more representations of the experimental data and to decide if the data should be fitted in more separated concentrations intervals or in the whole range.

The determination of ${}^{i}\Delta H_{diz}$ based on the calorimetric record T=T(t) had been made using a theoretical model of the calorimetric experiment mainly based on the Newton's cooling law and assuming the dissolution process is a first order pseudo-reaction.

References:

1. V. Vacek, V. Pekarek, Chemicky Prumysl, 32, 178, (1982).
2. Dinh Dang, D. P. Tassios, Ind. Eng. Chem. Process. Des. Dev. 25, 22-31,(1986).
3. Nathalie Hubert, M. Bouroukba, L. Schuffenecker, Thermochimica Acta 259, 41-48, (1995).

3.23 FACTORIAL MODELS FOR THE EXCESS GIBBS FREE ENERGY

M. Stan
Institute of Physical Chemistry,
Spl.Independentei 202, Bucharest, 77208, Romania

The factorial models are already in use for solidus-liquidus equilibria calculations. They are based on a regular approximation for the solutions. In that case all of them give the same results but significant differences appear in calculated thermodynamic values when a subregular approximation for an actual solution is employed.

In this paper, the equations used in phase diagram calculation are written in a form that emphasizes the three-factor model dependent part of each function. A systematic investigation of the values of the partial excess Gibbs free energy of the components, as predicted by a large class of factorial models, in the subregular approximation, is then possible.

This form of the equilibrium equations accentuates the contribution of the factorial models by separating a ternary interaction part that is specific to each model. A general form that includes most of the ternary models is presented.

The symmetric Colinet, Muggianu and Kohler models, the asymmetric Hillert and Toop models and many other new models are discussed in order to emphasize the problems that occur when using the subregular approximation for the solutions.

The aim of the work is to show that even an infinite collection of factorial models can be derived from the above described formalism, the predicted values of the partial excess Gibbs free energy derivatives at some special points are not always acceptable for phase diagram calculations.

4.1 SELECTIVE ACTIVATION OF CHEMISORBED MOLECULES BY VIBRATIONAL INTERACTIONS - INTERPRETATION OF KINETIC DATA

Nicolae Doca
University of Timişoara, Department of Chemistry
str. Pestalozzi 16, 1900 Timişoara.

The most important problem for the dinamics of a heterogeneous catalyzed reactions is to estabilish the mechanism of the adsorbed species. One of the possibilities is due to an energy transfer from the catalyst to the adsorbed species, by means of vibrational interactions.

The selectivity of heterogeneous catalyzed reactions can be well explained by the resonance condition of this transfer and the active site of the catalyst is considered as identified. Examples are presented for hydrogenation and hydrogenolysis reactions.

It is possible a less - speculative interpretation of the kinetik data, but only for surface rate limited reactions. Considering the compensation effect, a new interpretation of the isokinetic temperature is proposed.

The Nature of Protons on Oxide Surfaces : A Bridge between Surface Chemistry and Chemical Kinetics

James A. Schwarz[1], V.T. Popa[2] and C.I. Contescu[2]

1. Department of Chemical Engineering and Materials Science
Syracuse University, Syracuse, NY 13244, USA
2. "I.G. Murgulescu" Institute of Physical Chemistry
Bucharest, Romania

The equilibrium binding properties of protons at the solid oxide/aqueous interface have revealed the heterogeneous nature of this class of materials as reflected by their proton affinity distributions (PAD_s). The results can be considered a (quasi) equilibrium acid-base fingerprint of the interface viewed as a continuous distribution of sites with different equilibrium constants for proton binding.

We now explore the dynamic response of the interface. Oxide materials have been studied at two levels. Perturbation methods are described that reveal the transfer rates of protons, which are a function of pH, to (from) the substrate from (to) the aqueous medium. The ratio of these rate constants corresponds to the equilibrium acidity constants of specific surface sites on the oxide. Proton transfer rates to reactants which undergo isomerization have also been determined. Here only specific sites are catalytically active. Surface non-uniformity at the oxide surface is thus corroborated by equilibrium and kinetic measurements.

As a model system we apply the developed procedures to a series of Al_2O_3-SiO_2 mixed oxides. PAD_s provide the starting point for establishing the experimental conditions for proton transfer as well as quantitative analysis of kinetic data to establish rate constants for catalytic reactions for one type of surface acidic site.

4.2 DYNAMIC SCALING OF ADSORBATE-ADSORBENT INTERFACE

GIANINA DOBRESCU AND MIHAIL VASS
Institute of Physical Chemistry, Spl.Independentei 202,
Bucharest, 77208, ROMANIA

Dynamic Scaling Method was developed in the last decade for describing the time evolution of rough interfaces. Till now, it was applied to a great number of models that lead to rough surfaces: random deposition, ballistic deposition, random deposition with surface diffusion, Eden model, restricted solid-on-solid model. Dynamic Scaling Method was used to determine universality classes and phase transitions for the studied models.

In this work we applied the Dynamic Scaling Method for a simple model of physisorption on a homogeneous, respectively non-homogeneous fractal substrate. The substrate has fractal dimension D=2.26. For homogeneous substrate, all adsorption sites are equivalent, having the same adsorption probabilities. For the non-homogeneous substrate we computed the adsorption probability for every site using Van der Waals interaction potential substrate-adsorbate. We also consider the influences of diffusion and restructuring on the adsorbate-adsorbent interface. There was computed the Hurst exponent α that describes surface roughness and the exponent β that describes time correlations of the surfaces. As an important result we mentioned that when adsorption occurs on a fractal substrate, β depends on time and there is a strong dependence of Hurst exponent and fractal dimension of interface on substrate fractal dimension.

4.3 EFFECTS OF THE CRYSTALLOGRAPHIC ORIENTATION IN THE POTENTIODYNAMIC BEHAVIOR OF THE Cu(hkl) ELECTRODES

V. Lazarescu, N. Totir and M.F. Lazarescu*
Institute of Physical Chemistry "I.G. Murgulescu" -Bucharest
*Institute of Physics and Technology of Materials - Bucharest

The potentiodynamic behavior of the three basal orientations of the Cu(hkl) single crystalline electrodes have been investigated in $NaClO_4$, Na_2SO_4 and NaCl solutions with concentrations between 5 and 100 mM, in a potential range limited by the hydrogen and oxygen evolution reactions. The electrode processes in the double layer region as well as those in the region of the anodic oxidation of the metal were found to be highly sensitive to the crystallographic orientation of the surface.

The adsorption of the anions ($ClO_4^- < SO_4^{2-} < Cl^-$) on the surface of the single crystalline Cu(hkl) electrodes has been observed to interfere strongly with that of the OH groups. Although the strength of the interaction increases from perchlorate to chloride, as for other metal surfaces, the geometric factors appeared to be decisive in the competition of these electrode processes. For Cu(111), the adsorption of OH that takes the form of a reversible process, is prevailing in perchlorate solutions, occurs simultaneously with that of the sulfate anions but it is inhibited by the higher concentrations of chloride anions. Instead, for Cu(110), the OH adsorption gives rise to two distinct electrode processes, both irreversible, that let no available sites for the adsorption of perclorate and sulfate anions, while Cu(110) exhibits all the characteristics of an ideal polarizable surface in all the three electrolytes.

The first step of the anodic oxidation of Cu(0) to Cu(I) was also found to be very sensitive to the crystallographic orientation of the electrode surface. In case of Cu(111), this step has been observed to yield a *surface* and a *subsurface* oxide layer while for Cu(100) only the formation of a single phase could be discerned. Cu(110) exhibited, in its turn, another particular phenomenon, namely, a structural transition. It is worth to mention that such a structural transition has been noted too in the investigations on the oxygen adsorption from the gas phase. The anions were found to influence this step of the anodic oxidation of the metal only when they were strongly adsorbed on the electrode surface.

4.4 AN XPS STUDY ON SiO_x/Si INTERFACE.

P. Osiceanu
Institute of Physical Chemistry, Spl. Indep. 202, Code 77208, Bucharest, Romania

The detection of the stoichiometry of SiO_x / Si interface is of great importance for the formation of high quality ultra - thin thermal oxides, epitaxial growth, pre-gate oxidation, etc.

The monocrystalline Si wafers used in this XPS experiment were 125 mm (100) p-type wafers. The surface sensitivity of the XPS measurements can be enhanced by means of the Angle Resolved XPS. Since the escape depth in XPS is given by $\lambda\sin\theta$, it is possible by varying the take-off angle θ to get a signal from the first atomic monolayers in a layer-by-layer manner.It must be emphasized that the ARXPS technique is a nondestructive method for the measurements of thin surface layers (< 10 nm) with an abrupt interface between the layer and the substrate.

Photoelectron spectra excited by monochromatic AlK_α radiation were measured at photoelectron take-off angles of 10,15,25,35,50,70 and 90 degrees using an SSX - 100 instrument . The spectrum is decomposed into Si 2p1/2 and 2p3/2 spin - orbit partner lines. The intermediate oxidation states consist only of Si^{1+}, Si^{2+} , and Si^{3+} called suboxides. The full oxidized state Si^{4+} denotes a silicon atom bonded with four oxygen atoms. In the native stage the oxidation on the Si(100) surface does not occur uniformly, but the chemical states are localized. Thus, the suboxides are mostly localized at the interface SiO_x/ Si while the 4+ oxidation state is spread over the entire range of the oxide (the thickness of the native oxide measured "in situ" by ARXPS was estimated to 10 Å). In these circumstances an abrupt interface between the layer and the substrate was detected if, after the cleaning procedures, the silicon surface is atomically flat and terminated with hydrogen.

4.5 ESCA - AUGER : WHERE TO ?

P.Osiceanu
Institute of Physical Chemistry, Spl. Indep. 202, Code 77208, Bucharest, Romania

In practical surface analysis we generally seek the answers to three fundamental questions: (i) what elements are present at the surface, (ii) how much of each is present, and (iii) what is their chemical state? In ESCA - Auger, question (i) is readily solved by reference to Handbooks. Question (iii) is tackled by tabulations of precise line positions of many elements as a function of chemical state, but question (ii) is still the subject of some debate. A new development allow us to measure the variation of composition as a function of position (both parallel or normal to the surface) - called depth profiling in both ESCA and AES.

The nature of the problem to be solved and the available resources(instrumental availability and capability, cost, time) both define and/or limit the experimental strategy in particular situations. An analytical strategy is required involving a sequence of steps that represents the most efficient means to solve a problem. In present, such a strategy is proposed and supervised by the ISO' TC -21 (Surface Chemical Analysis - SCA) covering all the aspects of ESCA - Auger analysis. We can notice a huge effort towards standardization of these methods starting with definitions of the terms, then measurement principles, precision and accuracy of surface analysis, sources of uncertainty in AES and XPS analysis, data aquisition, processing and format transfer, qualitative and quantitative analysis, sample handling, quality of results and detection limits.

Both ESCA and AES have evolved and progress is clear and effective. Accurate reference data and materials are now being established together with procedures and written standards. However, many problems remain to be addressed such as the major problem of reliable experimental data for escape depth, preferential sputtering and the sputtering yields of nonelemental materials.

4.6 SIMULATIONS OF COLLISIONS OF THE HYDROGEN WITH THE GRAPHITE SURFACE (0001) USING SEMIEMPIRICAL MOLECULAR DYNAMICS.

VIOREL CHIHAIA, COSTINEL LEPADATU and MIHAI VASS
Institute of Physical Chemistry, Spl. Independentei 202,
Bucharest, 77208, Romania.

Semiempirical molecular dynamics are used to study the collision of hydrogen with surface (0001) of graphite.

Hydrogen is classically propagated using forces calculated from the Modified Neglect of Differential Overlap (MNDO) Hamiltonian.

The surface (0001) of the graphite crystal is simulated by means of a cluster composed of one layer containing 120 atoms of carbon arranged in graphite structure. The cluster is surrounded by Capped Bond fictive atoms.

By assigning different collision velocity (v_H) and impact angles (α) to the hydrogen, we simulated two sets of collision events: one collision at $v_H = 1$ au and one at $v_H = 10$ au. Parameter α varies between 10 and 90 degree with one step of 15 degree.

In the paper we present various parameters related to collision.

4.7 Modelling of competitive adsorption of phenolic derivatives on activated carbon

*Aurelia Meghea *, Romina Mihalache **, Ion Peleanu**

*University "POLITEHNICA" Bucharest
**Environmental Engineering and Research Institute, Bucharest

The experimental measurement of multicomponent adsorption isotherms is time consuming, so the problem of predicting binary and multicomponent equilibrium from single-component adsorption data has attracted much attention. Our task is to predict equilibrium of competitive adsorption of some phenolic derivatives - as main organic pollutants in water sources - on activated carbon (CF_3 – type).

The adsorbed studied bisolute systems were: phenol / p-nitrophenol, phenol / p-chlorphenol, p-nitrophenol / p-chlorphenol, p-nitrophenol / p-chloraniline.

In order to apply the Ideal Adsorbed Solution theory for predicting multi - solute adsorption equilibria reliable single - solute data are required.

In this respect it is desirable that these data be represented accurately by a relatively simple mathematical equation (adsorption isotherm). To fit experimental single-solute data we considered several equations : Freundlich, virial, generalized (from corresponding states), Dubinin-Radushkievitch isotherms. The best fitted representation for all monosolute data was Dubinin isotherms which also allows a semiempirical interpretation, and virial equation which provides a more theoretical background.

A number of correlations of both mono- and bisolute data were obtained using extended Langmuir, Freundlich-Langmuir and Fritz-Schlunder models; the last provided the best representation for all systems although the goodness-of-fit is not strongly different from that obtained with other equations.

A new four-parameter adsorption isotherm (sigmoidal in shape) is presented, which might also be extended to systems deviating from normal behaviour, as in the case of couple: p-nitrophenol / p-chloraniline.

4.8 CONCURRENT GAS-LIQUID - REPARTITION AND ADSORBTION ON CARBOWAX-20M GLASS CAPILLARY COLUMNS.

Ecaterina Tudor

Institute of Physical Chemistry "I.G.Murgulescu", Splaiul Independentei 202, 77208 Bucharest.

It is known that **G/L repartition** of nonpolar and some of polar solutes in polar stationary phase films coated on gas chromatographic supports or capillary column walls is more or less accompanied by the **adsorbtion at G/L interface.** The G/S adsorbtion is negligible, except for very thin films. The net retention volume is:

$$V_N = K_L V_L + K_{GL}^{a} A_L \qquad (1)$$

where K_L, K_{GL}^{a} -are **G/L repartition and adsorbtion constants**; V_L, A_L - volume and superficial area of the liquid stationary phase. For glass capillary columns, a more convenient expression used in this work to determine the constants K_L and K_{GL}^{a} (by measuring the **capacity ratio k** on a number of columns with known **film thickness d_f** and column radius r_c) is:

$$k = a + b\, d_f \quad ; b = (2/r_c)\, K_L \quad ; a = (2/r_c)\, K_{GL}^{a} \qquad (2)$$

The approximate values of the constants were determined for 33 acyclic, alicyclic and aromatic alcohols, esters, ketones, Grob's test compounds and for n-C11-n-C19 -alkanes, at 120 ° and 150° C. We used four statically coated, barium carbonate treated Carbowax -20M glass capillary columns, $d_f = 0.1$-0.4 µm. **The two series of constants are linearly interrelated**, but differently for the following groups of compounds, i.e. at 120°:

n-alkanes: $K_L = 12.786\, K_{GL}^{a} + 124.7 \qquad n = 8 \qquad r^2 = 0.9961$ (3)

polar compounds: $K_L = 27.692\, K_{GL}^{a} + 224.6 \qquad n = 33 \qquad r^2 = 0.9766$ (4)

For the same solubility, the n-alkanes are more adsorbed. The two lines is possible to correspond to **different adsorbtion mechanisms**, based on **poor solubility for n-alkanes** and respectively on **preferential orientation** for specific interactions on the liquid surface, **for the polar compounds**.

The **contribution of the adsorbtion mechanism to retention** (as capacity ratio k) was calculated for investigated compounds, columns and temperatures. This contribution:1) increases with molecular mass, e.g. on the 0.3 µm column, from 11 to 21% for C11- C19 n-alkanes; 2) increases for thinner films, e.g. at 120° for n-C14, from 11 to 34% using 0.4 to 0.1 µm columns; 3) decreases with column temperature, e.g. for dimethylbenzylcarbinol on 0.4 µm column, from 7% at 120° to 1% at 150°.

Coexistence of the two distribution phenomena, produces a **dependence of the relative retention and retention index, I, from d_f.** We refined the theory for this dependence, giving-up some simplifying hypotheses. Instead of a previously reported linear relationship retention index versus $1/d_f$, the following equation results, describing well the data for 11 columns with $d_f = 0.45$- 0.08 µm:

$$I = a + b/d_f + c/d_f^2 \qquad (5)$$

Eqn.5 is supported also by simulation of I- d_f dependence for some hydrocarbons on tiodipropionitrile, using R.L.Martin's equilibrim constants data (Analyt.Chem.,1961, 33, 3471).

4.9 ADSORPTION OF OXYGEN ON COPPER FILMS BY WORK FUNCTION MEASUREMENTS

Antonina Guţu, M. Anastasescu and M. Vass
Institute of Physical Chemistry "I.G.Murgulescu" - Bucharest

The interaction of oxygen on the copper was the object of many research and they concluded that oxygen adsorbs atomicly, at 80 - 300 K for surface coverage up to 0.7 ML and there is no conclusive evidence for existence of molecularly chemisorbed oxygen on this surface.

On copper, unlike the other noble metals, oxygen adsorption is not reversible. At high temperatures the oxygen atoms dissolve into the bulk, rather than recombining and desorbing into the gase pase. This probably reflects the high stability of the copper oxide, $\Delta H_f = -169$ KJ mol^{-1} for Cu_2O comparated to - 29 KJ mol^{-1} for Ag_2O or +172 KJ mol^{-1} for PtO, for example.

We have investigated the adsorption of oxygen on copper films by work function measurements.

The experiments were performed in a UHV system equipped with a turbomolecular and tanium pumps. The base vacuum was at $\leq 10^{-9}$ Torr after bake-out at $180^0 - 200^0$.

The copper films were preparated by evaporation above a polycrystalline tungsten ribbon.The films were annealed at 600 K for 15 min.

Oxygen was adsorbed by dosing with 100 L to 20×10^4 L.

The adsorption of oxygen on copper films results in an increase of the work function.It can be seen that the work function increases rapidly with oxygen exposure. When the copper surface is exposed up to 1000 L, further exposure would change the work function very little, which indicates that saturation coverage is achieved.

4.10 STUDIES ON THE ELECTRICAL BEHAVIOUR OF Sn-Sb-O COMPOUNDS

D. Sprînceana, Monica Caldararu, Angela Ovenston*, J.R. Walls*,
N.I. Ionescu.
"I.G. Murgulescu" Institute of Physical Chemistry of the Romanian Academy,
Spl. Independentei 202, Sector 6, 77208 Bucharest, Romania
* University of Bradford, Department of Chemical Engineering, W. Yorks.,
BD7 1DP, England

Electrical analysis of the behaviour of polycrystalline semiconductor oxide materials under different temperature and ambient conditions provides valuable information on the processes occurring in the solid state. The dynamic evolution of oxide materials (in general nonstoichiometric), used as catalysts and/or chemical sensors, can be followed by electrical measurements when adsorption or reactions take place with the surrounding atmosphere. It is possible to model by the method of equivalent circuits the comportment of the samples and to determine the changes which happened in the bulk and/or on the surface. In the studied Sn-Sb-O compounds the alterations observed are the result of a complex set of overlapping phenomena: modifications in the concentration of charged species (vacations, ions, free carriers), variations in their mobility, creation of new types of charged carriers and disappearance of other ones, reversible/ irreversible phase transitions, surface reconstruction and shifts of energy levels of solid under the interaction with adsorbed and reacting species; all these in connection with the history of the sample (preparation, pre-treatments, former experiments).

Using this kind of analysis it is possible to understand some of the fundamental processes occurring in the electronic and ionic conducting materials and to predict with satisfactory accuracy the behaviour under certain conditions met in practical applications.

4.11 PREPARATION AND PHYSICO-CHEMICAL CHARACTERIZATION OF SOME Cu AND Cr CATALYSTS

1. I. Dranca1), V. Popa2), V. Pocol2, V. Georgescu2),
T. Lupahscu2), V. Shofransky1), M. Vass2)

1) Institute of Chemistry, Moldova : Academy of Sciences,
Academiei Str. No. 3, MD-2028, Chisinau, Republic of Moldova

2) Institute of Physical Chemistry "I.G. Murgulescu", Romanian
Academy of Sciences, Spl. Independentei No. 202, Bucuresti
77208, ROMANIA

The present investigation is devoted to the synthesis and study by IR spectroscopy and thermoanalytical methods (TG, DTG, DTA) of some mixed compounds of the following type : 4Cu : 1Cr/Tartrate/ $-Al_2O_3 + SiO_2$ (1), 4Cu : 1Cr/Tartrate (III) and the suports $Al_2O_3 + SiO_2$; Al_2O_3.

The mixed compounds have been obtained by extraction with ethylic alcohol and NH_4OH (with 1:1 ratio) after complete precipitation at pH = 6-7 of aquaeous solutions of corresponding metals nitrates and of the d-tartric acid. After drying in open air the precipitates were dried in vacuum. IR spectra were measured in KBr. Thermoanalytical investigations were carried out by means of derivatograph OD-102, derivatograph-C thermoanalyzers and Du Pont 1090

D-tartric acid (HOOC-CHOH-CHOH-COOH) forms with 3d - metals various salts which have useful properties[1].

IR spectra of synthesized mixed compounds, were analyzed by comparison with tartric acid IR spectra. Also investigated were the IR spectra of the support consisting of $-Al_2O_3$, $Al_2O_3 + SiO_2$, as well as of catalysts. Catalysts eliminate the crystalization water up to 120°C, thermic oxidation occurs between 160-540°C and the total mass loss is 20-50 %.

Reference :

1 . I. Dranca, T. Lupashcu, V. Shofransky, V. Popa, M. Vass // J. Thermal Analysis, 1996, N. 46.

4.12 CATALYTIC POTASSIUM - MODIFIED ALUMINA : ADSORPTION OF CO

A. R. IORDAN[a], C. KAPPENSTEIN[b], M. I. ZAKI[c], C. GERON[b], M. PALAMARU[a]
a) University "Al. I. Cuza", Faculty of Chemistry, B-dul Copou N° 11, 6600 Iasi, Romania
b) LACCO, URA CNRS 350, Catalyse en Chimie Organique, Facultè des Sciences F-86022, Poitiers, France
c) University El Minia, Faculty of Science, Department of Chemistry, El-Minia, Egypt

The acidity of the surface of such supports plays an important role in catalysis as well as for the preparation of supported catalysts ; this acidity may be modified and lowered by alcalinization with potassium and such alkaline additions influence favorably the catalytic control of atmospheric pollution.

The present investigation aims basically to explore the alumina sutface consequences of the alcalization.

Adsorption of CO followed by in-situ IR spectroscopy on K-modified and unmodified samples after different in-situ pretreatments is currently undes investigation. The formation and stability of different species - polydentate carbonates, bidentate hydrogenocarbonates and formate - will be discussed.

4.13 THE INFLUENCE OF SOME FACTORS TO IRON (III) SORPSION BY THE HIGHER BASIC ANION EXCHANGER

V.Gutsanu, R.Drutsa, M. Cherdivarenco,
Technical University of Moldova, 2004. Chisinau,
Bl. Stefan cel Mare, 168

The higher basic anion exchangers and membranes which are used in different branches of industry are often contaminated by iron (III) compounds. The process of iron (III) compounds formation in the phase of exchanger is irreversible relatively to anion exchange process that is the why the classic methods of anionits regeneration based on using of alcali treatment aren't efficient for regeneration of iron (III) contaminated higher basic exchangers. Contamination of higher basic exchangers by iron (III) compound involves the decreasing of the efficiency of its using.

This report lists the rezults of the investigations of iron (III) sorption on higher basic exchanger AV-17x8(Cl) contained R_4N^+ functional groups and some the factors influencing the sorption. Sorption took place in static conditions from 0-0.02 M $Fe_2(SO_4)_3 \cdot 9H_2O$ solutions having equilibrium pH 2.0+0.1.

The essential and unusual influience of temperature on sorption of iron (III) is demonstrated in this raport. In dependence of temperature the value of sorption passes through maximum ot 50 °C. We also stadied the influence of ionic force of solutions on sorption of iron (III) at 30 and 50 °C. The values of ionic force were formed by adding necesary amount of Na_2SO_4, $NaClO_4$, $NaNO_3$ or KNO_3 to 0.02 M $Fe_2(SO_4)_3 \cdot 9H_2O$ solution. The rezults showed the decreasing of iron (III) sorption with growing of ionic force of solutions.

But the values of iron (III) sorption also depend on nature of salts added to solution.

The investigation demonstrated that the iron (III) restrainting by higher basic exchanger is not an ordinary sorption process. The posible mechanism of the process of iron (III) sorption on exchanger AV-17x8 is discussed.

4.14 EQUILIBRIA AND KINETICS OF URANIUM EXTRACTION WITH SOLVENT IMPREGNATED RESINS

N. Petrescu - University "Polytechnica", Bucharest
Lucia Ganovici - Institute of Physical Chemistry, Bucharest

The extraction of uranium (VI) from sulphuric acidic solutions by using solvent impregnated resins method has been studied.

Two types of polystyrene/divinylbenzene resins having different particle size have been investigated. Impregnated resins containing di(2-ethylhexyl) phosphoric acid (DEHPA) and mixtures of DEHPA and tributyl phosphate (TBP) were prepared by direct adsorption of both extractants into the macroporous support.

The work in this paper was aimed at an investigation of the most important features of solvent impregnated resins - their capacity for adsorbing uranium under different conditions and the time dependence of uranium sorption in order to obtain informations about the kinetic model of uranium extraction process.

4.15 Investigations on the unsupported and supported catalysts Co - Cr , Cu - Cr and Ni - Cr using thermoprogrammed reduction (TPR) and thermoprogrammed desorption (TPD)

M. Teodorescu[a] **, I. Sitaru**[a] **, V. Georgescu**[a] **, A.C. Banciu**[a] **, M.I. Vass**[a] **and E. Segal**[b] .
a. Institute of Physical Chemistry " I.G. Murgulescu" of the Romanian Academy,
Spl. Independentei 202, Bucharest 77208, Romania .
b. Departament of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bulevardul Republicii 13, Bucharest, Romania.

Abstract

The thermoprogrammed reduction (TPR) method is widely used in order to characterise various kinds of catalysts unsupported or supported, zeolites with metallic cations, etc. It consists in flowing a carrier gas with a known content of hydrogen through a layer of catalyst while the temperature increases in time according to a linear heating programme. The TPR curve is obtained by ploting the hydrogen consumption versus temperature.

A TPD experiment consists in recording the carrier gas (initially pure) flowed through the layer of catalyst versus temperature a linear heating programme.

The unsupported catalysts Co-Cr an Cu-Cr have been prepared through precipitation at pH=7 a mixture of respectively nitrates in aqueous solution mixed with tartaric acid.

As far as the supported catalysts are concerned these have been prepared by help of two methods :

1. The precursor deposition through impregnation on two kinds of supports namely tableted alumina and granulated alumosilica.

2. The solution of tartaric acid and the mixture of nitrates has been deposited through sucsesive impregnations on the two supports above mentioned.

The hydrogenation catalyst Ni-Cr in the oxidic form with atomic ratio Ni : Cr of 2,3 :1 was prepared through precipitation of a mixture containing basic nickel carbonate and hydrated chromium (III) oxide form a solution of nickel and chromium (III) treated with a concentrated natrium carbonate.

The TPR method is sensitive to the composition chages, method of preparation, supporting and prereduction while the TPD is not sensitive to these factors.

4.16 INFLUENCE OF METAL-SUPPORT INTERACTION ON ACTIVITY OF NICKEL/CHROMIA CATALYSTS

P. Mãrginean
Institute of Isotopic and Molecular Technology, P.O. Box 700,
3400 Cluj-Napoca 5, Romania

Nickel black and three samples of Ni/Cr_2O_3 catalysts with different nickel content (60, 70 and 85 at.% Ni) were prepared by precipitation method and heat-treated at temperatures between 350 and 1050 ^{0}C in hydrogen atmosphere. The BET surface area (by krypton adsorption), metal dispersion (by hydrogen chemisorption) and catalytic activity for deuterium exchange reaction between hydrogen and water vapour were measured. The effect of the heat treatment on the catalyst properties depends on the catalyst composition: for nickel black sample the metal dispersion is lowered but does not affect the intrinsic activity while for Ni/Cr_2O_3 samples the metal dispersion, as well as the intrinsic activity, are severely affected. In the case of the sample containing 85 at.% Ni heat-treated at 1050 ^{0}C, the intrinsic actvity decreases, tending to that of the nickel black. This behaviour of the heat-treated Ni/Cr_2O_3 catalysts is due to the weak metal-support adhesion and, at the same time, to the collapse of the chromia surface area during the thermal treatment. The experimental data provide arguments for the model invoking the creation at the nickel-support interface of new highly active sites for an interfacial sensitive reaction like that of deuterium exchange between hydrogen and water vapour.

4.17 DEUTERATION OF AROMATIC COMPOUNDS BY ISOTOPICAL EXCHANGE WITH HEAVY WATER

VALER ALMASAN, MIHAELA LAZAR
Institute of Isotopic and Molecular Technology
P.O. Box 700, 3400 Cluj-Napoca, Romania,
Fax: 40-64-420042, Tel: 40-64-184037,
e-mail itimc@utcluj.ro

The deuterated aromatic compounds (benzene, toluene) are obtained by heterogeneous catalyzed isotopical exchange H/D, the deuterium source being heavy water. It was studied and picked out the most efficient catalysts for this isotopical reaction. They are the transitional metals (*Ni, Pt, Pd*) on oxidic support (Cr_2O_3, Al_2O_3, etc). The conditions of the isotopical exchange reaction in to the system heavy water - aromatical compound are influenced by the reactivity of different types of hydrogen atoms from organic molecule (aromatic or alifatic). This work proposes an installation (reactor) without mechanical elements that can apply the optimal technology for the preparative purposes of these perdeuterated products. The technology is completed with the appropriate high purification methods for obtaining the spectroscopic grade deuterated compounds.

4.18 TRANSIENT PROCESSES ON Pt/Al_2O_3 CATALYST CAUSED BY TRACES OF WATER AND OXYGEN.

Mariana Stoica, Monica Caldararu, D. Sprînceana and N.I.Ionescu
"I.G.Murgulescu" Institute of Physical Chemistry of the Romanian Academy,
Spl. Independentei 202, 77208 Bucharest, Romania

The transient surface behaviour on oxidation and reduction of a partial oxidised alumina - supported platinum catalysts containing residual water have been observed by AC electrical conductance (G) measurements. A standard Sinclair Becker 0.5% Pt/Al_2O_3 catalyst was used. Two identical samples (2.6 g, BET surface area 195 m^2g^{-1}) were pretreated in two different ways, namely: (1) five successive cycles of temperature-programmed heating (20 K/min) up to 673 K, followed by cooling up to the room temperature, in Ar-O_2-Ar-H_2-Ar flows (the argon contained about 1% air) and (2) pretreatment (1), followed by flushing with humid argon (2.5 mg of water/L and 1% air) at room temperature up to the surface saturation with water.

On the partially dehydrated catalyst surface and partially oxidised, the O_2(inc.,0)-G transient response was characterised by a slow increase of conductance up to a stationary value. When the catalyst surface was partial oxidised and saturated with water, it was found an exponential decrease of conductance. This decrease of conductance is also coincident with a sharp and a sudden increase of the content of water in the effluent.

The results can be interpreted by participation of Lewis acid sites and by contribution of electron deficient platinum sites at vicinity of the metal - support interface. Some polarisation effects also can play a role.

In both cases, the transient responses during of the oxygen - hydrogen titration were of the overshoot type (more intensive for the later). This behaviour is, very probably, due to the increased contribution of protonic conductivity facilitated by the presence of residual adsorbed water on the catalyst surface.

4.19 INVESTIGATION OF 5% K/BaO$_2$ CATALYTIC SYSTEM IN METHANE OXIDATIVE COUPLING REACTION

Authors: **I. Balint, G. Dobrescu and M.I. Vass**

Romanian Academy
Institute of Physical Chemistry "I.G.Murgulescu"
Splaiul Independentei 202, Bucharest 77208, Romania

The paper is dealing with the oxidative coupling of methane to C$_2$ hydrocarbons over potassium doped barium peroxide catalyst in the 973 K-1113 K temperature range. The 5% K/BaO$_2$ catalyst was able to give 8-17% conversion with selectivity to C$_2$ hydrocarbons of ~ 80%. The oxygen pressure increase in the feed mixture lead to the increase of CO$_2$ generation rate while the rate of C$_{2+}$ formation remains practically constant. A remarkable tendency for a higher amount of C$_2$H$_4$ formation compared with C$_2$H$_6$ has been observed above 1048 K. The C$_2$H$_6$ generation rate depends markedly on the space time (W/F) while the CO$_2$ and C$_2$H$_4$ formation rate is independent on W/F. It is also likely that the C$_2$H$_6$ formation rate, which is considerably affected by the mass transfer limitation, is higher than CO$_2$ formation rate. Three models (power-law rate, Mars van Krevelen, and Eley-Rideal) have been used to fit the experimental data. The power-rate expression gave the best fit for the experimental data. The experimental and kinetic results are suggesting different pathways for C$_2$H$_6$ and CO$_2$ formation, directly from methane or having a common intermediate (i.e CH$_3$ ·), on different catalytic sites.

4.20 STUDY OF ISOBUTYRALDEHYDE OXIDATION ON MOLYBDOPHOSPHORIC AND MOLYBDOVANADOPHOSPHORIC ACIDS BY MEANS OF THE REACTANT PULSE TECHNIQUE

V.Sasca, N.Doca, Gabriela Suru and A.Popa
Romanian Academiy - Branch of Timişoara
Bd. Mihai Viteazul 24, 1900 - Timişoara

The study of isobutyraldehyde transformation to methacrylic acid, on heteropolyacid catalysts, shows some fundamental aspects: it needs two reactions, an oxidative dehidrogenation in the aliphatic chain and a carbonyl - carboxyl oxidation, respectively; this processes take place on different sites, needed for C-H bond breaking and surface hydroxyl formation, respectively for the insertion of surface oxigen into the organic molecule.

The two catalyst functions were estimated by the reactant transformation in isobutyric acid (oxigen insertion), respectively in methacrylic acid (oxigen insertion and oxidative dehydrogenation); the variation of these two functions vs. pulse number and reaction temperature was studied.

Also the regeneration ability of the surface oxigen was studied by taking again the experimental procedure on reoxidized catalysts.

4.21 ENANTIOSELECTIVE HYDROGENATION OF β-DIKETONES ON Ru/SUPPORT CATALYSTS: KINETIC ASPECTS OF THE RATE ACCELERATION INDUCED BY CHINCONIDINE

S.Coman[1], Em.Angelescu[1], C.Radu[2] and V.I.Pârvulescu[1]

[1]- *University of Bucharest, Faculty of Chemistry, Department of Chemical Technology and Catalysis, B-dul Republicii 13, Bucharest 70346, Romania*

[2]- *University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, B-dul Republicii 13, Bucharest 70346, Romania*

Pt/Al_2O_3 are the most investigated metal-supported catalysts in enantioselective hydrogenation of β-keto-esters [1]. In such case it was very well proved the rate acceleration as an effect of the presence in the reaction environment of a chiral modifier [2,3]. Recently, it was showed that this behaviour is not typical for platinum, other metals being also sensible to the presence of a chiral modifier. Ruthenium is one of these [4].

Nevertheless, an evident explanation of this effect has not yet been done. Two are the problems that are still not clear and both refer to the nature of the interactions which are responsible for the rate acceleration and the induction of the enantioselectivity. These processes seem to be controlled by two factors: i) interaction between the modifier and the metallic phase and ii) interaction modifier-substrate that occurs in the liquid phase.

Our contribution also deals with these questions. In such an order a kinetic investigation of the enantioselective hydrogenation of acetylacetone using as catalysts ruthenium supported on different molecular sieves has been followed.

Catalytic tests were performed in liquid phase using a stainless steel autoclave, under vigorous stirring and in a temperature range between 30-80 °C and pressures between 2-10 bar. Evolution of the reaction has been checked using chromatographic analysis and the enantioselectivity by polarimetry.

Kinetic measurements were carried out considering the separate introduction of the modifier (chinconidine) and the substrate (acetylacetone) in the reaction environment. These experiment revealed that catalytic performances strongly depend on the way of introduction of these components. The higher reaction rate were obtained considering the chinconodine introduction after a certain time from the start of the reaction. Contrarily, simultaneous introduction of these components before the introduction of hydrogen determined the lowest values of the reaction rate.

Strong influence of the substrate concentration upon the enantiomeric excess seems to suggest that even the reactant play a key role in the control of the enantiodifferentiating step.

In the presence of acetic acid an increase of the enantiomeric excess has been observed too. These data clearly indicate that the interactions between the modifier and substrate are strongly influenced by the characteristics of the solvent.

These observations lead us to the conclusion that the explanation of the enantioselectivity as well as of the increase of the reaction rate in these systems can be done only after consideration of all interactions that could be generate in the liquid phase.

References

1. Y.Orito, S.Imai and S.Niwa, J.Chem.Soc.Jpn., (1979) 1118.
2. H.U.Blaser, H.P.Jalett, D.M.Monti and J.T.Wehrli, Stud.Surf.Sci.Catal., 41 (1988)153
3. J.T.Wehrli, A.Baiker, D.M.Monti and H.U.Blaser, J.Mol.Catal., 61 (1990) 207.
4. G.Bond and P.B.Wells, J.Catal., 150 (1990)329.

4.22 CO_2 HYDROGENATION ON CATALYSTS OBTAINED FROM HYDROTALCITE-LIKE PRECURSORS WITH DIFFERENT Ni/ Al RATIOS

Eugenia Ivana, Lucia Bejan, N. Georgescu, Margareta Craiu and Veronica Lăcătuşu
„I. G. Murgulescu" Institute of Physical Chemistry
202 Spl. Independenţei, sector 6, 77208, Bucharest, ROMANIA

The compounds with hydrotalcite-like structures are used both in obtaining catalysts, and the preparation of catalyst supports. Hydrotalcite-based catalysts generally have better activities and selectivities than catalysts obtained by other methods. Moreover, they have better stabilities and longer lives in reactions produced under hydrothermal conditions. These characteristics are related to the existence of thermally stable oxidic forms (1). Such a phase was identified only after experiments of alkaline leaching of calcinated hydrotalcites (2).

The results presented in this paper are an attempt to correlate the activity of catalysts from hydrotalcite-like precursors with the concentrations of nickel-containing, thermally stable phases.

CO_2 hydrogenation was performed on two catalysts with a concentration of approximately 13% Ni, obtained from two Ni-Al hydrocarbonates prepared by coprecitation at constant pH = 7 and 80°C. These have the atomic Ni/Al ratios of 3 and 0.93 respectively. The precursors were calcinated at 450°C, then mixed with cement, graphite and Al_2O_3, pressed into tablets and hydrothermally treated as to increase their mechanical resistance.

The reduction temperatures were those corresponding to the maximum hydrogen consumption in the TPR profile of the two calcinated hydrocarbonates.

The hydrogenation reaction was investigated at atmospheric pressure for a H_2 / CO_2 reactant ratio of approximately 4.2.

TPD spectra show an important increase in CO_2 adsorbtion in the presence of preadsorbed H_2.

Data suggest that in the CO_2 hydrogenation reaction on the two catalysts formiate-like and carbonate-like species were formed; the quantities of these species depended on the Ni concentration in the catalyst sample.

Catalytic tests performed on catalysts reduced at temperatures corresponding to the TPR peaks of the phases identified in the oxidic forms of the two precursor hydrocarbonates, suggested the dependence of catalytic activity on the relative proportion of these phases.

Bibliography

1. Clause O., Gazzano M., Trifiro F., Vaccari A. and Zatorski L., Appl. Catal. 73 (1991), 217
2. Clause O., Rebours B., Merlen E., Trifiro F. and Vaccari A., J. Catal. 133 (1992), 231

4.23 Cu - Cr and Co - Cr oxide catalysts for the complete oxidation of aromatic hydrocarbons

V. Georgescu and M.I.Vass

Institute of Physical Chemistry " I. G. Murgulescu ", Romanian Academy, Spl. Independentei 202,
77208 Bucharest, Romania.

Abstract

Complete oxidation of hydrocarbons or of different waste gases containing hydrocarbons on platinic catalysts is a well developed procedure. However, for evident reasons searching for conventional efficient oxide catalysts is at present the scope of many investigations.

The aim of the present paper is to check the catalytic activity and stability of a set of mixed oxides on supports prepared, starting with complexes of Cu - Cr and Co - Cr with tartaric acid. The idea behind this preparation was to improve the dispersion of the oxide clusters on the supports and eventually obtain egg - shell type catalysts.

The precursors complexes were obtained by precipitation at pH =7 a mixture of Cu - Cr and Co - Cr nitrates in aqueous solution mixed with tartaric acid .

In order to prepare the supported catalysts two procedures have been used :

- The first one consists of the binding of the precursor on the support by succsesive impregnation of the solution of tartaric acid and of the nitrate mixtures.
- The second consists in the synthesis of the precursor, its solubilisation and deposition on the support by impregnation . Two types of supports were used for impregnation : Al_2O_3 tablets ($\phi = 6$ mm) and a mixture $Al_2O_3 + SiO_2$ grains ($\phi = 3\text{-}5$ mm). The supported catalysts prepared by the two above mentioned procedures, have been dried for 12 h at 90°C and calcinated at 700°C for 6h.

The transformations of the complexes into oxides were checked by TGA analysis.

The samples were subsequently submitted to IR spectrometry, magnetic measurements, UV - vis and XRD analysis.

The catalytic activity of the samples was measured in a flow reactor at the complete oxidation of benzene, toluene and isopropilbenzene.

Egg - shell type catalysts were obtained by impregnating the supports with precursor complexes.

Better activity and stability of this catalysts as compared to some older results obtained by simple impregnation of $\gamma - Al_2O_3$ with corresponding nitrates was evidenced.

4.24 PHOTOCATALYTIC REDUCTION OF Cu^{2+} IONS OVER TiO_2 CATALYSTS

D. Dumitriu and V. I. Pârvulescu
Institute for Nonferrous and Rare Metals, Bd. Biruinţei 102, Bucharest, 73951

Semiconductors activation under the incidence of a UV-vis light beam makes possible new reaction paths in catalytic processes; photodeposition of metallic ions from solutions on semiconductor supports is an application of this principle.

The aim of this study is the photoinduced reduction of Cu^{2+} ions from aqueous solutions over TiO_2. To this purpose, TiO_2 catalysts, prepared by thermal hydrolysis of $TiCl_3$ or by sol-gel method from $(EtO)_4Ti$ precursors, have been investigated. TiO_2-anatas has been tested for comparison. Deposition of TiO_2 highly dispersed on silica supports has been also realised.

Catalysts have been characterized by electronic microscopy and atomic absorption.

Photocatalytic process evolution has been evidenced by Cu^{2+} ions disparition in time, expressed as ion-g Cu^{2+}/ atom-g Ti×min. Results evidenced the influence of preparation method and nature of the precursor on catalytic properties of TiO_2.

Irradiation intensity influenced also the reduction rate of Cu^{2+} ions from solutions.

Photocatalytic purification of waste waters from metallurgical industries is envisaged as practical application.

4.25 INTERPHASE PROCESSES IMPLYING CROWN ETHERS , 2,2-DIPHENYL-1-PICRYLHYDRAZYL AND THEIR DERIVATIVES.

C. Luca[a], Petre Ionita[b], T. Constantinescu[b], M.T.Caproiu[c], H. Caldararu[b] and A.Caragheorgheopol

a. "Polytechnica" University, Faculty of Chemistry, Str. Polizu 1, Bucharest
b. Institute of Physical Chemistry, "I.G.Murgulescu", Spl.Independentei 202, Bucharest
c. Institute of Organic Chemistry, "C.D.Nenitescu", Spl. Independentei 202B, Bucharest

By implying the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) in the biphase processes mediated by crown ethers (CE) the selective synthesis of 2-(p-nitrophenyl)-2-phenyl-1-picrylhydrazyl (NO_2DPPH) and 2,2-(p-nitrophenyl)-1-picrylhydrazyl ($(NO_2)_2DPPH$) was optimized (η= 50-70 %) and two new compounds , 2,2-diphenyl-1-(2,4-dinitro-6-cyano-phenyl)hydrazyl and 2,2-diphenyl-1-(2,4,6-trinitro-3-cyano-phenyl)hydrazyl (η = 40 %) was obtained.

The applied procedures allows for easily obtaining of the derivatives $^{15}NO_2DPPH$ and $(^{15}NO_2)_2DPPH$ marked with ^{15}N.

All compounds were characterized by NMR, ESR and UV-Vis analysis.

Because DPPH , NO_2DPPH and $(NO_2)_2DPPH$ are hydrophobic and have oxidant properties, they are used in interphase processes of electron transfer (ET) type , mediated by CE (i.e. , for obtaining the reactive free radicals $HO^{\bullet}$, $HOO^{\bullet}$, $NO_2^{\bullet}$, $\Phi^{\bullet}$ etc.); the mechanisms of these processes were elucidated by capturing the formed free radicals and isolating the reaction products which were characterized (including GC and TLC).

The hydrophobic acidic derivatives $DPPH_2$, NO_2DPPH_2 and $(NO_2)_2DPPH_2$ were succesfully employed as pair anions for the L-L CE mediated interphase transfer of the cations and aminoacids (amphionic species).

.26 OXIDATION REACTIONS WITH HYDROGEN PEROXIDE IN BI AND TRIPHASIC SYSTEMS -CATALYSIS AND PHASE TRANSFER PROCESSES

Viorica Pârvulescu*, M.Vass* and C.Luca**

* Institute of Physical Chemistry "I.G.Murgulesu", Splaiul Independenţei 202, Bucharest
** Polytechnic Univerity of Bucharest, Faculty of Industrial Chemistry, Str.Polizu 1, Bucharest

Oxidation with $H_2 O_2$ and phase transfer agents are not always considered as typical phase transfer catalytic reactions. We present some experimental evidences indicating the effect of the phase transfer precesses and of the catalytic reactions in such reactions.

Experimental data show the results obtained in oxidation of toluene and benzylic alcohol with $H_2 O_2$ in bi and triphasic systems. In the first case quaternary ammonium salts, crown ethers and polyethylenglycohols (PEG's) were used as phase transfer catalysts. For the second one, the transfer agents were immobilized on innorganic supports like SiO_2, Al_2O_3 and ZSM-5.

Phase transfer processes were followed by measuring the extraction degree of the $H_2 O_2$ into organic phase. For the phase transfer agents investigated, the best results were obtained in the presence of PEG's. In spite of the best extraction degree of $H_2 O_2$ with PEG's the best results concerning the oxidation activity of toluene and benzylic alcohol are obtained with guaternary ammonium salts.

The effect of the nature and quantity of the catalysts and of the pH of the aqueous phase upon the extraction degree and upon the reaction turnover were also investigated.

For the triphasic system, the effect of the acidity as well as basicity of the support on the selectivity of the oxidation reactions of toluene was supplementary investigated.

Differences between the values of the extraction degree of the phase transfer catalysts and the oxidation activity of the same catalysts evidence the key role of the catalytic reaction in the organic phase upon the oxidation reactions with $H_2 O_2$ by phase transfer catalysis.

Experimental data allowed us to present an integrated phase transfer-catalytic reaction mechanism.

4.27 KINETIC ASPECTS AND CATALYTIC PERFORMANCES OF SOME IMMOBILIZED GLUCOSIDASE ON ANION EXCHANGER

POPA IULIANA- INSTITUTE OF MACROMOLECULAR CHEMISTRY
"PETRU PONI" IASI

Some enzymes of glucosidase type were immobilized on weak basic acrylic or styrene supports with amine functional groups.

The influence of the functional group on the featuring of the enzymes immobilization and on theirs catalytic activities has been evaluated.

The Michaelis-Menten and thermodynamic parameters of the immobilized enzyme preparates, in correlation with the chemical structure of the support and affinity to the functional groups were established.

4.28 A COMPARATIVE STUDY REGARDING THE PARTITION OF CERTAIN SULPHONAMIDES IN LIQUID/LIQUID BIPHASE SYSTEM

C. Luca[a], Daniela Oana Popescu[b] and T. Constantinescu[b]

a. "Polytechnica" University, Faculty of Chemistry, Str. Polizu 1., Bucharest
b. Romanian Academy, Institute of Physical Chemistry, "I.G.Murgulescu", Spl. Independentei 202, Bucharest

The liquid/liquid biphase partition of certain sulphonamides, HS, and their alkaline salts, M^+S^-, (were $M^+= Na^+, K^+$) was studied in two different situations: **i.**) unmediated transfer; **ii.**) mediated transfer involving crown ethers (CE). Where HS are:

4-amino-N-(4,6-dimethyl-2-pyrimidinyl)benzensulphonamide,
4-amino-N-5,6-dimethoxy-4-pyrimidinil)benzensulphonamide,
4-amino-N-(5-methyl-3-isoxazolyl)benzenesulphonamide,
4-amino-N-(3,4-dimethyl-5-isoxazolyl)benzensulphonamide;

and CE are: 15-crown-5 (15C5), 18-crown-6 (18C6), Dicyclohexyl-18-crown-6 (DCH 18C6) and Dibenzo-18-crown-6 (DB18C6).

The obtained results were correlated with: certain structural characteristics of the sulphonamides (hydrophobicity, acidity constants, isoelectric points); certain properties of the organic solvents (dielectric constants, polarity, density, viscosity, surface tention, dipole moments, hydrogen bond acidity and hydrogen bond basicity); certain aqueous phases characteristics (pH and ionic strength); some properties of the crown ethers (cavity dimentions and hydrophobicity).

The experimental results allowed a future tackle of certain correlation criteria of above mentioned characteristics which might be reasoning the biphase transport process optimisation.

4.29 ESTRONE NITRATION WITH $NaNO_2$ IN THE PRESENCE OF CROWN ETHERS

Constantin Luca[a], Dana Nourescu[b], Titus Constantinescu[b] and Miron Teodor Caproiu[c]

a. Polytechnic University Bucharest, Department of Analytical Chemistry, Str. Polizu 1, Romania.
b. Institute of Physical Chemistry, Spl. Independentei 202, 77208, Bucharest, Romania.
c. Institute of Organic Chemistry, NMR Department, Spl. Independentei 202 B, Bucharest, 15 PO Box 258, Romania.

The folicular hormone ESTRONE (3-hydroxyestra-1,3,5(10)-trien-17-one) **1** is nitrated in a biphasic system S/L or L/L in the presence of $NaNO_2$ and ionophores of crown ether type (CE), yielding two isomers : 2-NITROESTRONE (3-hydroxyestra-2-nitro-1,3,5(10)-trien-17-one) **2** and 4-NITROESTRONE (3-hydroxyestra-4-nitro-1,3,5(10)-trien-17-one) **3** (where the amount of **2** is higher than **3**, according to TLC analysis).

The process is of phase transfer catalysis type and it is facilitated by CE according to a mechanism which develops in several steps. The studied process of nitration is new and it can be interesting because :

- proves that nitration also occurs with the NO_2^- anion in the case of same substrates of phenol type, under certain experimental conditions ;

-proves that physiologically active natural steroidic folicular derivatives of **1** type (ex: estradiol , estriol) can be involuntarily nitrated in organism, in the presence of nitrites (originated from foods) and through a membranary process facilitated by hydrophobic ionophores, yielding the corresponding nitroderivatives, which are less active for physiological purposes but more toxic.

4.30 REGIOSELECTIVE IODINATION OF TYROSINE IN A LIQUID MEMBRANE SYSTEM IN THE PRESENCE OF CROWN ETHER TYPE, MACROCYCLIC LIGANDS

Constantin Luca [a], Adriana Zarna[b], Dan Anghel[b] and Titus Constantinescu[b]

[a]University "Politehnica" Bucharest, Analytical Chemistry Department, str. Polizu 1
[b]Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei, 77208 Bucharest

The regioselective iodination of tyrosine **1** (β-[4-hydroxyphenyl]alanine) in a "liquid membrane system" - aqueous phase source (containing $I_2 + I^- \rightleftharpoons I_3^-$) // dichloroethane (containing crown ethers) // aqueous receiving phase (containing **1**) - in view of obtaining preferentially, *first, monoiododerivative* **2** *of tyrosine (β-[4-hydroxy-3-iodo-phenyl]alanine) and then diiododerivative* **3** *of tyrosine (β-[4-hydroxy-3,5-diiodo-phenyl]alanine)* is controlled by the exclusive existence in the "liquid membrane" of the complex species **$[CE...I]^+I_3^-$** (where CE=12-crown-4, 15-crown-5, 18-crown-6, benzo-15-crown-5, 4'-nitro-benzo-15-crown-5). The highest yield (100%) of derivative **2** is obtained with 18-crown-6. The process is considered to be of the electrophilic substitution type (through "phase transfer catalysis") to the aromatic nucleus; the experiments suggesting that the reactive iodine species results from the $[CE...I]^+I_3^-$ complex decomposition at the "membrane"//aqueous receiving phase interface.

4.31 THE EVOLUTION OF HYDROGEN FROM WATER OVER FeH-MORDENITES

Gr. Pop*, Ecaterina Pop* and Magdalena Momirlan**

*Zecasin S.A., Spl. Independentei 202, P.O.Box 121304,
Bucharest, Romania

**Institute of Physical Chemistry, 202 , Spl.Independentei,
Bucharest 77208, ROMANIA

Hydrogen can be evolved by thermocatalytic decomposition of water over zeolites.

Zeolites and zeolite-like materials comprise a broad range of porous crystalline solids. The structures of zeolite type materials are based essentially on tetrahedral networks which encompass channels and cavities. Mordenite is one of the siliceous zeolites and the typical formula of synthetic mordenite is:

$$Na_2O \cdot Al_2O_3 \cdot 9\text{-}10\ SiO_2 \cdot 6\ H_2O$$

The evolution of hydrogen from water over mordenites-H with different contents of Fe_2O_3 was investigated, using a thermal dissociation method. The experimental device for the evolution of hydrogen over zeolites consisted of a quartz reactor introduced in an electric adjustable furnace and connected to a vacuum line. The reactor was equipped with a tube for the evacuation of the resulted gases and water steam. The noncondensable collected gases were periodically analyzed.

The ability of hydrogen generation from water was noted over the mordenite with Fe_2O_3 content of about 11 p.c.

The quantity of hydrogen evolved was 0.39 ml/thermocycle.

5.1 ORGANIZED COLLECTIVE MOTIONS OF DENSE MONOATOMIC AND COULOMB FLUIDS

Şerban-Dan Cartianu
Institute of Physical Chemistry of the Romanian Academy
Splaiul Independenţei 2o2, Bucureşti, Romania

Propagating collective modes of dense fluids arise as side-peaks in a three-peak Lorentzian structure of the dynamic structure factor, versus the energy transfer and are described by a dispersion relation relating the energy transfer to the momentum transfer variables for which the dynamical structure factor is side-peaked which is characteristic of the respective collective mode. The collective modes for monoatomic dense fluids are phonon-like, or sound-like excitations. The collactive dynamics arises through the backflow and renormalization vertices (mode-coupling effects) in the memory functions of the linear non-Markovian Langevin equations governing the Newtonian evolution of dense fluids. The mode coupling approximation projects the non-Markovian Langevin equation also onto bilinear products of hydrodynamic (slow)modes. The selfconsistent mode coupling theory truncates the hierarchy of Langevin equations for the successive memory functions until a smooth memory function is reached and amounts to solving by iteration a coupled system of integral equations. Charge-density fluctuations do not lead to a hydrodynamical mode but to a plasma interspecies relaxation mode or propagating optic mode whose dispersion relation has a nonzero ordinate at the origin. The spectrum of collective modes is being studied for one-component plasmas, liquid metals, molten salts, plasmas, ionic mixtures and superionic conductors (half-frozen ionic liquids). The collision kernel of the non-Markovian kinetic equation is separated into a connected part due to recollision effects and a disconnected (mode-coupling) part which is factorized and which determines solely the long-time behaviour of the self-energy or memory function. The accompaning paper presents the memory functions for binary ionic systems. The mode-coupling approximation results in a coupled set of integral equations solved by iteration.

5.2 NEW MODELS FOR ELECTRICAL CONDUCTIVITY IN MOLTEN SALT SYSTEMS WITH COMMON ION

Mircea Olteanu and Petrică-Mircea Pavel
Romanian Academy
Institute of Physical Chemistry "I. G. Murgulescu"
Spl. Independenței No. 202
Bucharest – Romania

The basics of some new models for describing the electrical conductivity in binary molten salt systems with common ion are presented. The models discussed in this contribution are all based on two main assumptions of different natures: i) chemical, the possibility of an incomplete dissociation of the two salts, depending on temperature and composition, and ii) physical, an analogy between an equivalent circuit of electrical resistors and the melt overall electrical resistance, the latter being calculated as a sum of contributions of the individual components of the mixture, each of then placed within separate imaginary cells that may be linked together either in series or in parallel.

At constant temperature, the dissociation degrees of the two pure salts change on mixing depending on concentration and accordingly, the real number of "free ions", considered to be the only charge carriers, changes too.

All these changes are reflected by the evolution of the molar conductivity vs. concentration isotherms and thus, calculated conductivities may be weighed against the experimental values.

An analysis of validity of the proposed models was made using our own data for electrical conductivity and molar volume: there is a maked difference between the behaviours of common anion and common cation systems, respectively.

A comparison with previously reported models for electrical conductivity in molten salt mixtures is also presented.

5.3 A SUMMARY OF THE CALCULATIONS AND ERROR ANALYSIS FOR VISCOSITY MEASUREMENTS USING AN ABSOLUTE OSCILLATING CUP VISCOMETER.

D.Tolbaru, Rodica Borcan, Stefania Zuca.
Romanian Academy, Institute of Physical-Chemistry"I.G.Murgulescu",
Spl.Independentei nr.202,77208,sector 6, Bucuresti, Romania.

Recently, in our laboratory a plane bottomed oscillating cup viscometer was built up for viscosity measurements in molten salts ($\eta \leq 10$ mPa.s) up to 1400 K. For the set up and method, an error analysis was developped in terms of polynomial equations for viscosity deduced from Beckwith and Newell's general solution. From practical viewpoint it is useful to consider the relative error in viscosity as the sum of the following two terms:

- accuracy, imposed by uncertainty in determining the calibration constants (inner crucible radius, free period of oscillation of empty crucible and moment of inertia of oscillating ensamble);

- precision, as resulted from the errors in determining the experimental parameters (the logarithmic decrement of amplitude, oscillation period of the filled crucible, liquid column height and density of the melt).

Therefore, both terms were calculated and the minimising limits for each parameter were established. For the viscometer in question, these values are of ± 0.21% and ±0.33% respectively.

In order to obtain a self-consistent and more accurate set of data, the viscosity of molten KNO_3 and NaCl (both of spectral purity) was measured over ~ 373 K temperature range. The standard error is used for data analysis. The calculated standard deviation ammounted to ± 0.39% for η_{KNO_3} and ± 0.37% for η_{NaCl} .

This error analysis shows that the principle of the oscillating crucible seems to be the best suited and accurate amoung the methods used for viscosity measurements at high temperatures.

5.4 STUDY OF THE SOLUBILITY OF LANTHANIDE OXIDES IN FLUORIDE MEDIA

Vasile Soare , Anca Drujescu
Research Institute for Nonferrous and Rare Metals,
102 Biruintei str., Bucharest

The solubilities of cerium oxide (CeO_2) and the lanthanum oxide (La_2O_3) in the following flouride media : Al-Na-F and Li-Ba-Ln-F were studied .

The solubility of rare earth oxides was determined by two methods .

According to the first method , small amounts of oxides were added into the fluoride melts under continuous stirring and the solubilization process was visualy observed .

In the second method , the termodifferential analysis was used for the monitoring the melting poits of the mixture fluoride media - rare earth oxides as a function of the oxides content .

It was concluded that the solubility of La_2O_3 is greater than that of CeO_2 , being in the range from 1,9% to 4,5% .

5.5 PHASE DIAGRAM OF THE $Na_2B_4O_7$-Na_3AlF_6 SYSTEM

Elena Maria Anghel, Maria Zaharescu, Stefania Zuca
Romanian Academy,Institute of Physical Chemistry,
Splaiul Independentei 202,Bucharest,77208, Romania

The melts of the NaCl-$Na_2B_4O_7$-Na_3AlF_6-TiO_2 system are very important in the electrosynthesis of TiB_2, a new material applied in the advanced technologies. The binary NaCl-Na_3AlF_6 eutectic mixture of the quaternary system above mentioned represents the solvent melt while the other two components are the electrochemically active species in the electrosynthesis of TiB_2. Therefore their interactions with the solvent melt supplies data of interest for mechanism of electrochemical process.

The most accurate information on the components resulted in the melt, due to the interaction between the constituents, is supplied by phase diagrams. This contribution presents such results obtained in $Na_2B_4O_7$-Na_3AlF_6 binary system. The whole concentration range was investigated by differential thermal analysis, X-ray diffraction and IR spectroscopy.

Regarding the single components, the DTA data evidenced a polymorphous transformation at 559°C in Na_3AlF_6 ; X-ray studies confirmed the vitreous character of $Na_2B_4O_7$ melt while Na_3AlF_6 exhibited a typically ionic structure.

Regarding the $Na_2B_4O_7$-Na_3AlF_6 system, X-ray diffraction studies has not evidenced the presence of any new compounds; the DTA liquidus curve showed the characteristics of a binary system with a melting temperature of 642^{0}C and an eutectic composition of 83% $Na_2B_4O_7$ (wt. %). The aditional IR spectroscopy data confirmed the cristalline structure of all mixture over the 0-80% (wt%) $Na_2B_4O_7$ concentration range, while at higher concentrations vitreous mixtures were formed. Because the eutectic composition lies within this range it is obvious that such melt with glass characteristics are not interesting for utilisation in electrosynthesis.

5.6 Electrosynthesis of TiB_2 in molten electrolyte $NaCl - Na_3AlF_6 - Na_2B_4O_7 - TiO_2$

N.Ene, A.M.Popescu and S.Zuca
Romanian Academy, Institute of Physical Chemistry " I.G.Murgulescu "
Spl. Independentei 202, 77208, Bucharest Romania.

The electrosynthesis of intermetallic compound TiB_2 was studied in molten $NaCl - Na_3AlF_6 - Na_2B_4O_7 - TiO_2$ electrolyte, which offers some chemical and electrochemical advantages.

The experiments were carried out on a wide range of compositions of the electroactive species, TiO_2 and $Na_2B_4O_7$, at temperature ranging within 850 - 900 °C. It was found out that Ti/B optimal ratio is » 4 and the cathodic deposit consist. mainly of high powder whose granulometry depends on the current density and electrolyte composition.

Cyclic voltametry measurements were performed on cathodic deposition of titanium and boron as well as on their codeposition to form TiB_2. The electroreduction potentials and peak currents were determined and the corresponding electrokinetic parameters were evaluated. A mechanism for the cathodic reactions was advanced.

5.7 ELECTROCHEMICAL REDUCTION OF ZIRCONIUM IN FLUORIDE-CHLORIDE MOLTEN SALTS

Vasile Vasilescu
Institute of Physical Chemistry I.G.Murgulescu, Splaiul Independentei 202, 77208 Bucharest

The electrochemical reduction of zirconium in chloride-floride molten salts has been studied by cyclic voltammetry.

The experiments were carried out in a stainless steel electrolysis cell which ensured the melting of the electrolyte, the adequate positioning of the electrodes and the unfolding of electrolysis in controlled conditions: purified argon atmosphere with less than 10 ppm of N_2, O_2 and water vapour.

Platinum cathode of known surface area, platinum reference electrode and spectral carbon anode were utilized.

The electrolyte was equimolar mixture of KCl and NaCl eutetic as supporting component and various concentrations of K_2ZrF_6 as electroactive component.

It was shown that catodic electrodeposition of zirconium is directly influenced by the concentration of K_2ZrF_6 and implicitely by concentration of fluoride ions resulted from dissociation which influences the thermodynamic stability of $ZrCl_6^{2-}$ complex.

At lower K_2ZrF_6 concentration, reduction consists of two reversible processes with two electrons each, while at higher concentration reduction may occur in one four electron process.

5.8 AN EXPERIMENTAL INVESTIGATION OF THE SOLIDIFICATION OF A BINARY MOLTEN SALT SYSTEM AROUND A HORIZONTAL PIPE.

Petrică-Mircea Pavel and Mariella Constantinescu
Romanian Academy
Institute of Physical Chemistry "I. G. Murgulescu"
Spl. Independenţei No. 202
Bucharest – Romania

Experimental measurements are presented for the transient outward solidification of a binary, molten salt system around a horizontal pipe. The system is selected to avoid the eutectic composition so that solidification takes place over a large range of temperatures. Transient liquidus front progressions and temperature measurements are used to characterize the solidification with "mushy" zone of system.

The two-regions models predicts the time for radial formation of mush-solid region around of the pipe, based upon the assumptions of negligible diffusion and convection of liquid region during solidification. The dependence of the position of mush-liquid interfaces on the time and Stefan number were also determined.

Experimental results are compared with presented model predictions and discrepancies are used to critically assess model assumptions and limitations.

5.9 THE BEHAVIOUR OF SOME AMINO ACIDS AT THE TRANSFER ACROSS THE INTERFACE BETWEEN TWO IMMISCIBLE ELECTROLYTE SOLUTIONS

Tanta. Spătaru, Alexandra Popovici and N. Bonciocat - ICECHIM Bucuresti

The interfaces between two immiscible electrolyte solutions (ITIES) are recently among the most studied (from the electrochemical stand point) liquid-liquid interfaces. Two are the main reasons for the great interest arisen by these interfaces. The first reasons consist in the similarities existing between the ionic transport across the ITIES and the charge transfer processes occurring at the interface metal (semiconductor)/electrolyte, usually associated with redox processes. The second one is the fact that ITIES represent very suitable models for the study of those substances which exert therapeutic effects at the membrane level.

In the present work an experimental method is reported which allows the measurement of the potential drop variation at ITIES during the transfer of an electrolyte, CA, through the interface. The experiments were carried out by using the following electrochemical cell:

$$\mathrm{Pt}\ |\ W_B,\ O/R\ \underset{\text{ITIES}}{||}\ B_W,\ O/R\ |\ \mathrm{Pt}$$

where W_B and B_W represent water saturated with butanol and butanol saturated with water, respectively and O/R stands for the redox couple (in this case O = $[Fe(CN)_6]^{3-}$ and R = $[Fe(CN)_6]^{4-}$). The experimental glass cell had a vertical configuration containing the B_W and W_B phases into the upper and lower compartments of the cell, respectively. The establishment of the partition equilibrium for the O and R species in the two phases results in a voltage across the cell, U = 0.

A drop of W_B, which contains an appropriate amount of electrolyte (the concentration of CA has to be much higher than that of the O and R species), crosses the upper B_W layer, reaching the ITIES. At this very moment, a jump of the voltage across the cell was observed, from zero to a value depending on the nature of the electrolyte. A correlation has been found between the height of the voltage jump and the relative standard transfer free enthalpies of the C^+ and A^- ions. It is to be noticed that the electrolyte reaching the ITIES must cover the entire area of the interface.

A comparison was made between the shape of the $\Delta U(t)$ curves associated to the transfer of the CA electrolyte across the ITIES, and those obtained for some amino acids. In this later case, the influence of the pH was also studied. A decrease of the initial voltage jump was put into evidence for the amino acids in the amphionic form, for which ΔU tends to zero as the pH value approaches that of the amino acid isoelectric point.

5.1o THE POLAROGRAFIC INVESTIGATION OF ELECTROREDUCTION KINETICS AND THE COMPLEXFORMATION THERMODYNAMICS OF Zn(II)

Tsipleakova V.A., Anikina Z.O
Department of Physical Chemistry,
Moldova State University, Mateevici str. 60,
Chisinau 2009 Md, Republic of Moldova

Zinc(II) electroreduction in formate, thiocyanate, lactate,tartrate, salicylate, thiocyanate-tartrate and acetylthiocarbamide media has been investigated by means of polarography. In each case the quasi-reversible mechanism of zinc(II) electroreduction has been established; the rate constants calculated by the Koryta's method are of the order of 10^{-3}cmxsec. The rate of the electrode reaction increases with increase of ligand concentration. This might be due to the formation of zinc(II) and ligand intermediates in solution or on Hg-surface. Such intermediates make the electron transfer process easier. In all investigated complexing media with the exception of acetylthiocarbamide it has been observed that the $E_{1/2}$ values are shifted to more negative potentials indicating the formation of complexes. So far as the reduction of zinc(II) on Hg drop has the quasi-reversible nature, the composition and stability constants of homogeneous and mixed complexes have been calculated by the DeFord and Hume's and Schaap and McMasters' methods respectively. The effect of ligand nature on the stability of homogeneous complexes has been discussed. The statistical and coporportion constants have been calculated with the purpose to establish the mutual effect of the ligands and their compatibility in the coordination sphere of zinc(II) ion. The values of these constants indicate the compatibility of thiocyanate and tartrate ions. The comparison of the stability of zinc(II) and manganese(II) personal and mixed complexes shows that in all cases the stability of Zinc(II) complexes is more than stability of manganese(II) ones. This fact coordinates with the Williams and Irving's row for nitrogen- and oxygen-containing ligands. The kinetic parameters of the electrode process and Leden's functions for homogeneous and mixed complexes have been calculated by special computer programm.

5.11 A KINETIC STUDY OF THE HYDROGEN EVOLUTION REACTION ON RuO_2 BY IMPEDANCE SPECTROSCOPY

N. Spătaru - *Roumanian Academy, Institute of Physical Chemistry, Bucharest, Romania*

Transition metal oxides represent electrode materials which arose great interest especially in the chlor-alkali industry because of their good electrocatalytic properties for the chlorine evolution reaction. Nevertheless, recent patents have also claimed good performances for such kind of electrodes in the cathodic evolution of hydrogen. In spite of this there are few papers in the literature dealing with kinetic aspects of the hydrogen evolution reaction at oxides.

The present work is a study of the hydrogen evolution reaction in alkaline media on the RuO_2 coated nickel electrodes, both by d.c. and a.c. measurements, in order to obtain new experimental results concerning the mechanism and the kinetic parameters of the reaction.

The electroactive RuO_2 coatings were prepared by thermal decomposition of a $RuCl_3$ solution at 450 °C in air.

The real surface area of the cathodes was estimated from cyclic voltammetric measurements as well as from the double layer capacitance (evaluated by impedance measurements). A roughness factor between 651 and 683 was found for an amount of 4.2 mg cm^{-2} RuO_2.

The Tafel slope and the transfer coefficient estimated from the polarization studies were $b = 37$ mV $decade^{-1}$ and $\alpha = 1.57$ in the low overpotential range and $b = 70$ mV $decade^{-1}$ and $\alpha = 0.83$ at overpotentials higher than 70 mV. Thus, it was concluded that, in the in the low overpotential range, the surface coverage is low and the Heyrovsky step must control the reaction. The increase of the Tafel slope at higher overpotentials indicates that, in this case, it is not possible to neglect the effect of the Volmer reaction.

The impedance measurements allowed us to estimate (by a nonlinear fitting procedure) the rate constants of the forward and backward reactions of the two steps (Volmer and Heyrovsky) involved in the overall hydrogen evolution reaction.

5.12 ELECTROCHEMICAL STUDIES OF SOME PROPERTIES INVOLVING CHARGE-TRANSFER FOR 2,5 CYCLOHEXADIEN - 1,4 - DIONE - 2,3,5,6 - TETRACHLOR (CHLORANYL)

CRISTINA MANDRAVEL, *Chemistry-Physics Department, Faculty of Chemistry, University of Bucharest*

ION IOSUB, *Chemistry-Physics Department, Faculty of Sciences, University of Piteşti*

We investigated the electrochemical behaviour of chloranyl in potentiodynamic regime in order to estimate its oxidation-reduction ability in some organic solvents on differents working electrodes.

The cyclic voltammetry measurements were carried out by using an Electrochemical Analysis System - Model 273 Princeton with an IBM - PS2 data acquisition.

One of the purposes we had in view in our researches, was the study of the electrochemical behaviour of chloranyl in organic solvents such as dimetylformamide, dimetylsuplhoxide and dioxan, where the tetraphenylborate (TFB) was used as supporting electrolyte.

The Ag/AgCl electrode was used as reference electrode. The experiments were proceeded at room temperature and at various scanning rates.

We tried to improve the conditions for emphasize the ability of chloranyle in being involved in charge-transfer phenomena. The number of involved electron reversible reduction waves was shown by the cyclic voltammetry data.

There were also advanced some assumptions about the processes in solid/organic solvent layer .

5.13 CYCLIC VOLTAMMETRIC STUDY OF HEMIN IN WATER AND IN DIMETHYLSULPHOXIDE

Elena Constantinescu,Herbert Storch,Monica Andrei
Department of Physical Chemistry,Faculty of Chemistry
University of Bucharest. R-70346 Bucharest,Bd.Carol I
nr.13

Hemin is a widely distributed metabolite found in all cells in a protein bound form serving as a prostetic group. Under patological conditions it may be released as a free molecule.In the present study we investigated the electrochemical behaviour of hemin in dimethylsulphoxide and also in water by cyclic voltammetric technique.

The investigated potential range was +0.5 V -(-1.4)V, the hemin concentrations being: 2.5×10^{-4}M, 5.0×10^{-4}M and 1×10^{-3}M. Several sweep rates were used : 20; 50; 100; 200 and 500 $mV.s^{-1}$.

In dimethylsulphoxide the voltammograms exhibit two successive reduction waves located at -0.1 V and -1.3 V respectively. Only the first reduction wave is reversible. It was registered also in the restricted potential range +0.1 - (-0.25 V) in order to be subjected to the usual electrochemical tests.

The values of the peak current ratio i_{pa}/i_{pc} calculated by the Nicholson semiempirical procedure are close to unity. The slope values estimated for the liniar dependence $E_p=f(\lg v)$ were smaller than 30 mV/decade showing the existance of a reversible monoelectronic charge transfer step.

The standard rate constant k_s for this step calculated using the Nicholson correlation between peak potential separation ΔE_p^{ac} and function Ψ lead to a value of about 1×10^{-2} cms^{-1}. Additionally,the rotating disk electrode data attested that only one electron is involved in the first step.

In water (buffer solution pH = 8),the voltammograms exhibit only one irreversible peak,the reduction mechanism being different in water and in noaqueous solvents.

5.14 ELECTROCATALYTIC REDUCTION OF DIOXYGEN ON CHEMICAL MODIFIED ELECTRODES

N.D. TOTIR and St. POPOVICI
Romanian Academy, Institute of Physical Chemistry
Splaiul Independentei nr. 202, Bucharest, 77208, ROMANIA

Electroreduction of molecular oxygen using derivative porphyrins as electrocatalysts in aqueous solutions has been intensively investigated [1-4].

In this paper, a study of electrocatalytic properties of (Ru, Rh, Pd)-derivative porphyrins modified graphite electrodes, by using cyclic voltammetry method, has been performed.

The experimental cell was made of Teflon, with a teflon holder for the working electrode; a platinum wire was used as counter electrode. All experimental measurements were reported versus saturated calomel electrode. A NaOH 0,5M aqueous solution, was used as supporting electrolyte. The aqueous solution were prepared with tetradistiled water and p.a. chemicals. Highly purified argon was used to remove the oxygen from solution by bubbling for 30 minutes. Molecular oxygen was obtained by electrolysis of a 30% KOH aqueous solution. The other chemicals of analytical purity were used without further purification. (Ru, Rh, Pd)-derivative porphyrins were prepared according to Adler's method [5) by heating the porphyrin with metal-ligand-acetate in dimethylformamid.The modified electrodes were obtained by placing a few drops of a (Ru, Rh, Pd)-derivate porphyrins solution in benzen onto the highly polished ordinary pyrolytic graphite electrodes. Cyclic voltammetric measurements were performed by using a TACUSSEL instrumentation. A mechanism for electrocatalytic reduction of dioxygen using graphite electrodes modified with Ru, Rh, Pd derivative porphyrins are presented.

REFERENCES

1. J.F. Roland and F.C. Anson, J.Electroanal. Chem. 1992, 336, 245-261.
2. R.Holze, Electrochimica Acta, 1991, 36, 999-1007.
3. F.Arifuku and H.Kurikawa, Fukuoka University Science Reports, 1990, 20, 77-82.
4. N.D.Totir and St.Popovici, Conf. de Chim. si Ing. Chim.1995,405

5.15 ELECTROREDUCTION OF AROMATIC DINITRO DERIVATIVES

Virginia Danciu*, Veronica Coşoveanu*, Anne-Marie Martre**, Maria Jitaru*,
B.C.Toma*, Mariana Toma*

* *"Babeş-Bolyai" University of Cluj-Engineering*
Chemical Research Group
Str. Arany Janos, nr. 11
3400 Cluj-Napoca

***Blaise Pascal University of*
Clermont-Ferrand
Laboratory of Organo-Electrochemistry
24, Av des Landais
63 177, Aubiere Cedex,France

The reduction of the 4,4'-dinitrodibenzyl(DNDB) was studied in the H_2SO_4 5N / EtOH 50/50 medium either by electrochemistry or in the presence of the Ti^{3+}/Ti^{4+} or Sn^0/Sn^{2+} redox couples. The analitical study of $TiOSO_4$, $SnCl_2$ and dinitrodibenzyl has been realized on a mercury electrode. In the presence of $TiOSO_4$, the 4,4'-diaminodibenzyl is obtained with 90% yield. When $SnCl_2$ is used as mediator, hydroxy or ethoxy derivatives are characterized in the reduction products. The use of Ti^{3+} for the chemical reduction allows the obtaining of the amino-nitrodibenzyl with 70% yield for a Ti^{3+}/dinitroderivative ratio of 6/1 while the diamine, accompanied by hydroxy or ethoxy derivative is formed in 50% yield in the presence of Sn^0. These last results are quite similar to those obtained with an Sn electrode or with the mercury electrode and adding of $SnCl_2$.

The reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid (DNSS) was studied in H_2SO_4 2,5N at 30°C and in HCl 10% by electrochemistry and in the presence of Ti^{3+}/Ti^{4+} or Sn^0/Sn^{2+} redox couples. The results are similar for both supporting electrolytes. The used electrodes were: mercury, lead, monel and tin. The 4,4'-diaminostilbene-2.2'-disulfonic acid (DASS) was obtained with 90% yield.

The use of Ti^{3+} for the chemical reduction allows the obtaining of diaminoderivate or aminonitroderivate (ANSS) as a function of the ratio Ti^{3+}/DNSS. In the presence of Sn^0 the reaction mixture contains: 48% ANSS, 32% DASS and 20% DNSS.

The products are characterized by RMN ^1H, TLC - photodensitometry, mass-spectrometry, gas-chromatography, for DNDB, and HPLC, for DNSS.

5.16 ELECTROHYDROGENATION OF SOME NITROSO DERIVATIVES

Maria Jitaru*, Virginia Danciu*, D.A.Lowy**, B.C.Toma*,
Veronica Coşoveanu*,Mariana Toma*

* *"Babeş-Bolyai" University of Cluj-Napoca*
Department of Chemistry and Chemical Engineering
Chemical Research Group
Str. Arany Janos, nr. 11
3400 Cluj-Napoca

** *Department of Chemistry*
West Virginia University
Morgantown, WV 26506-6045
USA

The electrochemical reductibility of some nitroso compounds of two differents classes : A. N-nitroso derivatives - nitroso piperidine (I), nitroso piperazine (II) and N-methyl-N-nitroso piperazine (III)

B. C-nitroso derivatives - acid 4-hidroxy 2-nitroso-1 naphtalin sulfonique (III) were studied. The pH - dependence of the polarographic half-wave potentials is addressed. A preparative scale electrochemical method for the reduction of N=O group is described.

The half -wave potentials corresponding to the reduction of compounds (I-III) are located between the aliphatic compounds ($\varepsilon_{1/2} > -0{,}7$ V vs Ag, AgCl) and the aromatic ones ($\varepsilon_{1/2} < -0{,}55$ V vs Ag, AgCl).

The influence exerted by the pH of the supporting electrolyte and by the temperature on the electroreduction of compounds (I-IV) was also explored. According to our previous results [1,2], in agreement with data reported by other authors, the charge consumption at pH<5 is equal to 4 faraday/mole, corresponding to a four-electron reduction. In the pH range from 8 to 10 the two electron reduction mechanisms can be assessed (the charge consumption is of 2 faraday/mole).

The optimum pH range for amines preparations is the acidic domain (from pH 1 to 4.5), where the nitroso derivative is present in the protonated form. At pH values greater than 5, the limiting current decreases abruptly, due to the deprotonation of the substrate molecule. Thus, the neutral molecule of the nitroso derivatives is more difficult to reduce than its protonated form.

Give the linear dependence of the limiting current with the concentration in the range from 10^{-3} to 10^{-5} mole/L, the polarographic method can be used for analytical purposes.

References:

1. Maria Jitaru, B.C. Toma, Mariana Toma and D.A. Lowy
   Bull. of Electrochem., vol. 11, nr. 12, dec. 1995, pp.573-577
2. Maria Jitaru, Dora Smarandache
   Journees d'Electrochimie 95, 29 mai-1 iun. 1995, Strasbourg (Franţa), CA 8-18

.17 CYCLIC VOLTAMMETRY OF THE ANODIC OXIDATION OF POTASSIUM ETHYL XANTHATE ON GALENA ELECTRODE UNDER FLOTATION CONDITIONS.

ANTONIO HUERTA, JUAN GENESCA, F. RAMON COTA, H. HERNANDEZ. DEPARTAMENTO DE INGENIERIA METALURGICA, FACULTAD DE QUIMICA EDIFICIO D, UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO. CD. UNIVERSITARIA, MEXICO. CP 04510

Froth flotation on sulphide ores is one of the more important concentration process in the mineral benefication. This process has been utilized in different mexican plants with the purpose to achive selective separations from complex ores such as lead-zinc, copper-lead-zinc.

Until now this process has been studied by many people to wordl level trying to understand the phenomena in search of better grades and recoveries. However there is not a good control at present time bacause of the complexity of the mineral reactive interactions.

The objects of this investigation were: a) Obtain a better understanding of the electrochemical interactions galena-collector-depressor (PbS-KEX, PbS-$K_2Cr_2O_7$) system,. It has been been proved that the process is electrochemical type in nature. b) To detect by electrochemical studies the influence of the collector and depressor concentrations on galena electrode and to find possible correlations between rest potential, oxidation potentials and flotation potentials. c) To find the favorable conditions to abtain high galena recoveries by electrochemical studies.

Experimental work.- It consisted of the following studies: characterization ore, cyclic voltammetry studies, rest potential and flotation potential determinations and flotation tests.

Experimental conditions.- The galena was characterized by X-Ray and atomic Absortion Technics. The ore used for voltammetry, rest potential and flotation potential performed a 86.5% Pb. The ore used for flotation test performed a 44.8% Pb. It was prepared a galena electrode (work elctrode) attached to copper wire using an araldite resin for the electrochemical determinations.

The voltammetry determinations were carried out on a PAR 173 potentiostat and VIMAR GB-02 signal generator, from -1300 to 0 mV. vs SCE in anodic direction.

Two sweep velocities were applied, 5 and 10 mV/sec. A Buffer solution (boric acid/sodium borate) was used to obtain the pH flotation.

The concentrations used on each experimental work were te following: KEX 0.01, 0.001 and 0.0001 M, concentrations of $K_2Cr_2O_7$ .001 .0001 and 0.00001M.

Reults will be discussed.

5.18 Synthesis of pinacol by electrochemical reductive coupling of acetone

Dr. N.D.TOTIR and C. LETE
Romanian Academy, Institute of Physical Chemistry
Splaiul Independentei nr. 202, Bucharest, 77208, ROMANIA

Pinacols are very important intermediates with wide aplicability in synthetical rubber industry, obtaining of pesticides or synthesis of drugs.

Coupling of acetone by electrochemical reduction have been performed taking into account some parameters as: the type of the cell, the temperature, current density, the nature of the electrodes.

All the measurements have been performed by using galvanostatic method. As working electrode, a zinc electrode was used . All experimental measurements were reported versus saturated calomel electrode. A platinum wire was used as counter electrode.

As supporting electrolyte a NaOH aqueous solution at different concentrations was used. The acetone of technical purity was used without further purification. The temperature of the cell was precisely controlled by using a Ultra Kryostat MK 70.

Gas chromatograph analysis showed the only products formed were isopropanol and pinacol and that the decrease in acetone was accounted for by the appearance of these two products.

Recovery of pinacol is a fairly simple procedure. Excess sodium hydroxyde is added to the already alkaline electrolyte to get a strong phase separation with almost all the pinacol going into the acetone phase. The two phases are split by means of a separatory funnel and the acetone evaporated at low temperatures leaving the pinacol in a concentrated aqueous solution. The solution is then frozen with dry ice and filtered. The solid product was obtained as a white pinacol hydrate ($C_6 H_{14}O_2\ 6H_2O$), which proved to be 99% pure.

Between 5 and 15^{0}C the pinacol was obtained with 30-76% efficiency. The best results were obtained using a NaOH 2 N aqueous solution at 5^{0}C for a time of electrolysis of about 16 hours and 40-60mA/cm^2 current densities. Bellow 5^0 C the efficiency in pinacol decrease.

5.19 Electrochemical Synthesis and Characterization of Polypyrolle Films Based on Amide Ferrocene Pyrolle Derivatives

T.Vişan[1], M.Ungureanu[1], E.Saint-Aman[2] and J.-C.Montel[2]

[1]Department of Applied Physical Chemistry & Electrochemistry, "POLITEHNICA" University, Bucharest, Romania

[2]Laboratoire d'Electrochimie Organique et de Photochimie Redox, Universite "Joseph Fourier", Grenoble, France.

We found that the electrochemical polymerization of pyrolle derivatives is a simple, effective and versatile method for carrying out the coating of Pt, glassy carbon and ITO (indium tin oxide) electrodes. In the present paper we report the synthesis of modified electrodes by electrochemical oxidation of 1,1'-bis-(N-ethyl-1(2 amino ethyl-pyrolle)-formamide)-ferrocene (denoted as compound **2**) and (N-ethyl-1(2 amino ethyl-pyrolle)-formamide)-ferrocene (denoted as compound **3**) in 0.M TBAP/CH_3CN solution.

During the continuous growth of the film by potential cycling, gradual appearance of the redox wave of incorporated ferrocene, together with elimination of the original ferrocene/ferricinium ion couple in solution was observed. The formal potential of ferrocene couple in poly(**2**) films (from CVs) was about 100 mV more positive than the reversible couple in solution. The behaviour of **3** during the polymerization is somewhat different: an extended anodic scan limit (0.95 V, at least) was required to start the film deposition and after 20-25 cycles the new redox wave drew until a constant shape.

The films were tested in 0.1M $TBABF_4/CH_3CN$ and 0.1M $TMABF_4/H_2O$ or $LiClO_4/H_2O$. The immobilised ferrocene was well characterized in acetonitrile solution, showing a symmetrical shape signal ($\Delta E_p = 0$ or few mV on CVs) and has also a satisfactory electrochemical response in aqueous solution. The influences of monomer concentration, as well as synthesis charge, on the performances of modified electrodes were discussed. The observed linear dependencies of the peak current on scan rate and electropolymerization charge agree well the power law:

$$i_p = A\times(vQ)^m \qquad (1)$$

charge.

where i_p is the current in the transfer solution, v - scan rate, and Q, A and m are constant parameters. The constant A is a function of the physical (homogenity, permeability, content of doping anions) and electrochemical (value of transfer coefficient) properties of the film. According to the model, the exponent m should be unity if the electrochemical process is charge transfer controlled. As expected, m= 1-1.04 in acetonitrile for poly(**2**) and poly(**3**), whereas in aqueous solutions m = 0.86 for poly(**2**) in 0.1M $TMABF_4$ at constant Q, and m= 0.3-0.37 in both 0.1M $LiClO_4$ and 0.1M $TMABF_4$ using variable Q (constant scan rate).

5.20

ELECTROCHEMICAL BEHAVIOUR OF POLYPYRROLE FILM SYNTHESIZED IN THE PRESENCE OF DODECYLBENZENESULFONATE

V.BRANZOI* FLORINA IFTIME**,MIHAIELA BAIBARAC***,D.ANGHEL**
*)UNIVERSITY POLYTEHNICH OF BUCHAREST,STR.POLIZU 1.
ROUMANIA
**)INSTITUTE OF PHYSICAL CHEMISTRY,SPL.INDEPENDENTEI203,
77208,BUCHAREST,ROUMANIA,
***)INSTITUTE OF PHYSICAL AND TECHNOLOGY OF MATERIALS,PO
BOX MG-6,R-76900,MAGURELE,ROUMANIA

The electrochemical properties of polypyrrole films electrosynthesized from aqueous solutions containing sodium dodecylbenzenesulfonate as "doping" electrolyte were studied by cyclic voltammetry.The results indicate that the mechanism of the redox process is complex and may be governed by the diffusion of the cations and anions of the electrolyte.The kinetics of the processes can be monitored by changing the nature of the electrolyte and this may allow modulation of the electrical and optical properties of PPY/DBS.

The cyclic voltammograms of PPY films synthesized in solutions having different sodium dodecylbenzenesulfonate concentrations indicate that the concentration of the surfactant indeed plays a very relevant role in the electrochemical response of the PPY/DBS films.The broad peaks observed in the voltammograms suggest a complicated redox process for PPY/DBS.We have observed that PPY doped with amphiphilic anions presents an electrolyte-dependent redox process.Contrary to what is observed for PPY doped with common low molecular weight inorganic anions,the amphiphilic anion does not diffuse out from the polymeric matrix.This fact is partially assigned to its size and partially to the compatibility of the polar end with the charged matrix and of the unpolar end with the neutral (reduced) matrix. The reduction process produces the neutral polymer chain,however,the presence of the remaining DBS$^-$anion leads to the insertion of the cation in order to equilibrate the charge.The cation participation in this process was illustrated by the cyclic voltammograms of the PPY films in solutions of NaCl,KCl and LiCl.The electrochemical response of the PPY/DBSfilm was indeed dependent on the nature of the cation .

5.21 Electrochemical Studies of Diffusion of Perchlorate and Sulphate Counterions During Doping-Undoping Processes in Polyaniline Films

T.Vişan[1], M.Sima[2], M.Buda[1] and G.Marin[3]

[1]Department of Applied Physical Chemistry & Electrochemistry, "POLITEHNICA" University, Bucharest, Romania

[2]Institute of Physics and Technology of Materials, Măgurele, Bucharest, Romania

[3]Research and Development Institute for Electrical Engineering, Bucharest, Romania

Cyclic voltammetry, chronoamperometry and impedance spectroscopy were used for study of electrodeposited polyaniline. Polyaniline (PANI) films were formed under galvanostatic conditions onto Pt foil (50 mC cm^{-2} synthesis charge in each experiment) either in 0.2M aniline, 1M $HClO_4$ solution, or 0.055M aniline 1M H_2SO_4 solution.

It was shown by cyclic voltammetry that PANI electrodes with incorporated perchlorate or sulphate ions can be repeatedely cycled in the corresponding solutions. Redox PANI films have been mainly studied by electrochemical impedance spectroscopy in 1M $HClO_4$ and 1M H_2SO_4 aqueous solutions, respectively, at potentials corresponding to the first redox process and electronic conducting state.

A 5mV constant amplitude of applied sinusoidal signal was maintained and the data were collected in the frequency range of 10^{-1} - 10^{-5} Hz. Impedance spectra were presented both as Bode diagrams and Nyquist representations. The capacitive charging behaviour and diffusion of counterions (ClO_4^-, HSO_4^-) into/out the polymer film were discussed on the basis of a simplified Randless circuit model. The examined scanning electron micrographs have also shown that the nature of dopant anion changes the structure and morphology of films.

All results indicate that the counterion incorporated into the PANI film during synthesis step plays an important role in determining the electrochemical properties of conductive PANI layers.

5.22 THE STUDY OF MODIFIED ELECTRODES IN ALKALINE ELECTROLYTE WITH ADDITION OF REDOX COUPLE

N.D.Totir[x] and Maria Ileana Ioniţă[xx]

x)Institute of Physical Chemistry,Spl.Independenţei 2o2,782o8,
Bucharest,ROMANIA
xx)S.C."ZECASIN"S.A.,Spl.Independenţei 2o2,782o8,Bucharest,
ROMANIA

New types of high performances electrodes,based on an oxidized nickel support and metalloporphyrines derivatives in aqueous alkaline electrolyte with addition of a redox couple,Fe^{2+}/ Fe^{3+};HQ / Q HQ- hydroquinone,Q-quinone, in dark and under illumination, have been investigated by using cyclic voltammetry method.

The best behaviour have been noticed for the modified oxidized Ni / NiTPP electrode in 0.5 M NaOH as electrolyte with addition of 0.5 mM HQ / Q under illumination up to 650 nm, reaching a high value for the peak current density.

The role of modified oxidized Ni / NiTPP as well as the benefical influence of the aromatic structure of HQ have been reported.

5.23 OSCILLATING ELECTROCHEMICAL PHENOMENA ORIGIN AND PHYSICAL SIGNIFICATION

G. Semenescu
Univ. Piteşti, Facultatea de Ştiinţe

There exists numerous examples of oscillating electrochemical phenomena obtained at equilibrium potential, at controlled potentials and in potentiodynamical regime.

There is accomplish a complex analysis of the oscillating electrochemical phenomena according to the double mixed layer electrod model which allows a global treating of the solide/electrolyte interface, generally speaking, and especially of the metallic oxide/electrolyte interface.

There are shown some considerations regarding the origin and the physical signification of the oscillating electrochemical phenomena, as well as some implications of them, in interpretation of the cyclic voltammogrames that should be interpreted on their characteristical fields, sometimes described by totally different phenomena as has been demonstrated.

It is considered that at the equilibrium potential, the electrochemical oscillating phenomena could give interesting data in conections with adsorbtion - desorbtion phenomena of the solid / electrolyte interface.

At cotrolled potentials, according to the value of the imposed potential and to the selected system, there can be obtained interesting informations from electrolyte in adjacent electrode area.

There are made some evaluations on the origin and physical meaning of the oscillating electrochemical phenomena in prepassive, passive and active area of cyclic voltammogrames both at direct and inverse scan of the potential.

It is analysed the importance of the imposed potential, of preelectrolyse time and of the scan rate on the oscillations.

It is shown the role and the importance of potentiostat in maintaing these phenomena.

5.24 MATEMATICAL MODEL OF THE ELECTROCHEMICAL OSCILLATIONS IN THE ANODIC DISSOLUTION

G. Bourceanu and J. Vatamanu
Faculy of Chemistry "Al. I. Cuza " University of Iasi

Based on the electrochemical reactions found experimentally in both surface of iron electrode and in omogeneous volume , a mathematical model able to describe the behaviour of the real electrochimic system , has been elaborated .

For this reason , the function describing the acrons of the changed species through potential barrier , has been taken into consideration .

By numerical integration of the system of diferential equations , the temporal evolution is obtained , that is aproximately identical with that obtained experimentally.

Taking a convinient controlling parameter , the entire sequence of tranzition from periodical behaviour to that chaotic one , has been realized .

For each behaviour , the phases portret has been given too , and the fractal dimension has been calculated .

5.25 MECANISM OF ELECTROCHEMICAL OSCILATIONS IN THE RANGE OF ANODIC DISOLUTION

R.Vasiliu , G. Bourceanu , V.Melnig and J.Vatamanu
Faculty of Chemistry "Al. I. Cuza " Iasi

In order to determine exactly the range of appearance of electrochemical oscillations firstly the caracteristic $j=f(E)$ was ploted .both, frequence and duration of oscilationsdepend on stirring of the studied system .

Taking into consideration these remarcs and possible reactions in volume of solutions as well as , on surface of working electrode , a mecanism being responsable for apperance of electrochemical osscilations have been proposed .

Indeed , it was found experimentaly that for the system under study within the anodic range the $Me^{Z+}$and $HCrO^-_4$ ions have a controlling rol for appearance and mentienance of oscilations .

Disspearance of oscilations may be explained by coating the Fe electrode surface and therefore blocking of the reaction.

5.26 MODELLING OF ZIRCONIUM OXIDE/ELECTROLYTE INTERFACE BY EQUIVALENT CIRCUITS

M.Radulescu, I.Pirvan
Institute of Nuclear Research 0300 Pitesti

ABSTRACT

Kinetics of Zirconium alloys oxidation in specific nuclear reactor environment constituted the research aim of numerous investigators.

Oxidation mechanism and implicitely the physico-chemical characteristics of oxides formed under several conditions represent a result of a number of factors such as: microstructure, intermetallic precipitates presence, stress present in the oxide, etc.

A.C. Impedance technique (Electrochemical Impedance Spectroscopy - E.I.S.) is adequate for determining electrical characteristics of oxide and implicitely it can supply experimental data in view of modelling the zirconium oxide/electrolyte interface.

Experimental data obtained by E.I.S. may by presented in the following modalities : Bode curve (log-Z-/log w), Nyquist curve (Z_{real}/Z_{imag}) and phase angle δ/log w.

E.I.S. data presented in format Bode are adequate to determine quantitatively the components of equivalent circuits for several interface types of zirconium oxid/solution.

Generally, the principal components of an equivalent circuit for a coated zirconium alloy electrode are : C_c-capacitance of film (or of coating present on the electrode), Rp- resistance of pores and Z_i-general impedance which characterizes the reactions of metal/solution interface.

In the case of zirconium alloy, Z_i may by described by charge transfer resistance (R_t) coupled in parallel with double-layer capacitance or, in another way by one resistance R_t in series with a Warburg impedance.

Being known our interest for the films formed on the electrodes, we paid a special attention to high frequency region, in which the response of the system is preponderently determined by the film capacitance.

We performed experimental measurements on the samples of the following zirconium alloys: Zy-2, Zy-4 end Zr-2.5 Nb alloy.

E.I.S. determinations done on the electrochemical system -Princeton Applied Research Model 273 interfaced with an Apple IIe computer - in the frequency range 10-1 v 10fHz.

The films formed on the electrodes were of two types : perfect and, respectively, imperfect.

The perfect films - corresponding to nonstoichiometric zirconium oxide (ZrO_2-x) - were uniform, black, lustrous, adherent.

6.1 ELECTRODEPOSITS OF DISPERSE PARTICLES WITH METALS

Lidia Benea[1], **Magda Lakatos Varsanyi**[2] and **Geta Cârâc**[1]
[1] Department of Metallurgy and Materials Science, “Lower Danube” University
47 Domneascã St., R-6200 GALATZI, Romania
[2] Department of Physical Chemistry , Eötvös Lorand University,
BUDAPEST 112, P.O. 32, H-1518 Hungary

The paper presents the experimental results from the electrodeposits of insoluble disperse phases (zirconium oxide and silicon carbide) with nickel.

In order to study the influence of disperse particles on the metal electrocrystallization mechanism, use was made of a cylindrical electrochemical cell. The anode which was cylindrical too was placed at 20 mm from the cathode surface. Composite layers (metal + disperse particles) were electrochemically deposited on the cathode (metal support) having an active surface area of 10 cm^2 .

The curves of cathodic polarisation in electrolytes with and without particles were plotted to identify their influence in the process of metal electrodeposits.

Taking into account the intermediate steps in metal electrodeposition, the equivalent circuit corresponding to the electronic transfer stages was established by using the method of electrochemical spectroscopy impedance.

The effect of the operating parameters (current density, concentration of the disperse phase in the electrolyte) on the concentration of the disperse phase in the composite layer is correlated by means of simple mathematical equations.

6.2 EXPERIMENTAL RESULTS CONCERNING RECOVERY OF COPPER IONS USING FLUIDIZED BED ELECTRODES

Mihai Mihaela - University of Baia Mare

Contact surface electrodes-solutions, in case of bi-dimensional electrodes (planar electrodes) is low and that determine a low recovery of metallic ions from dilute solutions.

Improvement of process efficiency is realised using tri-dimensional electrodes. These electrodes are characterised by large surface contact between them and solutions and that allow high efficiency in recovery processes of metallic ions from dilute solutions.

Fluidized bed electrodes are represented by conductive particle (made by metal or graphite) which are keep in suspension by electrolyte flow. Those particles represent the cathode and are polarised by contact with a current feeder.

The paper present experimental results obtained to copper recovery from dilute solutions using fluidized bed electrodes. The particles are made by copper and are studied the influence of a few parameters (size of particle, electrolysis time, form of current feeder) on current efficiency.

6.3 TRASPORT PHENOMENA OF INERT PARTICLES IN ELECTROLYTES USED FOR COMPOSITE LAYERS

Arpiar Sachian - ICTCM Bucuresti
Marioara Blidariu - ICTCM Bucuresti
Carmen Raducanu - ICTCM Bucuresti

The paper presents the study of transport phenomena which occurs in suspension-electrolytes used for obtaining of composite electrodeposit.

The study of these phenomena permits the control of codeposition processes in order to obtain protective composite layers with improved properties.

6.4 INFLUENCE OF COMPOSITION OF ANIONIC SURFACTANTS ON THE PROCESS OF ELECTRODEPOSITION OF IRON COATING

J.I.BOBANOVA, O.A.BOLOGA, V.I.LOZAN, N.V.GERBELEU

Institute of Apllyed Physics and Institute of
Chemistry of Academy of Science of Republic Moldova

The influence of additives containing organic and inorganic ligands on the stability of iron(II)/iron(III) system, rate of iron (II) oxidation, electrochemical characteristics of iron coating obtained from cloride and sulfate electrolytes of iron, was investigated by assistance of a series of electrochemical and physico-chemical methods. The thermodynamic analysis demonstrates that the stability of iron(II)/iron(III) is determined by redox system and also by stabilization energy of the ligand field. Rational utilisation of electrochemical active additives for increasing the stability of iron electrolyte was argumented on the basis of application of fundamental regularity of electrochemical kinetics in the limits of the formal theory of inhibitors.

The dependence between the rate of iron(II) oxidation, physico-chemicals composition of iron coating and the structure of employed inhibition additives was studied. The correlation between the inhibitors redox potential of dioxibenzones in this case was found and the iron(III) content in solution. It was determined that the order of reaction relative to iron is equal to 1. The activation energy is equal to 8 ccal/mol. The additive which posses the reduction properties stabilizes the oxidation-reduction processes in the iron electrolytes and the additives which contain sulphur compounds influence on the discharge process of the iron and hydrogen ions. It established, that the stabilization of irom(II)/iron(III) takes place on addition of the additives which contain -COOH, -OH groups into the electrolyte as result of chelate type formation of mixed complexes. The dependence between the iron(III) content and the microhardness of iron coating was determined.

6.5 SEMICARBAZIDDIACETIC ACID DERIVATIVES UTILIZED AS BRIGHTERING ADDITIVES IN ELECTROPLATING

Cecilia Vass,E.Roman,V.Lozan*,N.Garbalau*

"I.G.Murgulescu" - Institute of Physical Chemistry,Romanian Academy,Bucharest
* Institute of Chemistry - Academy of Sciences of The Republic of Moldavia, Kishinew

The possibility of the utilizing of some semicarbaziddiacetic acid derivatives (dihydrazide and dimethylester and dihydrazide and dimethylester of the 4-phenylthiosemicarbaziddiacetic acid, as well) as brightening additives has been investigated. The influence of the compounds in question upon the structure of copper electrodeposits from the acid baths has been studied.

The measurements effected with Hull cell indicated the optimum current densities ranges to realize bright electrodeposits.

The obtained data, on plane electrodes, have been correlated with the cyclic voltammetry measurements, the surface coverage of the cathodes being appreciated.

6.6 INFLUENCE OF THE QUATERNARY AMMONIUM COMPOUNDS ON THE ELECTRODEPOSITIONS

Liana Roman - ICTCM Bucuresti
Emilia Barbulescu - ICTCM Bucuresti
Gh. Andoniant - ICTCM Bucuresti
Dana Radoi - ICTCM Bucuresti
Rodica Stancu - ICTCM Bucuresti

The paper presents the study of some quaternary ammonium compounds used as additives in electrochemical deposition baths in order to establish relations between chemical structure and efficiency. The effect of the following elements on the improvement of depositions and brightness is specified: quarternary ammonium compound concentration, organic cation structure, hidrocarbon chain length, anion type.

6.7 PHYSICO-MECHANICAL CHARACTERISTICS OF THE CHROMIUM PLATING FROM ELECTROLYTES BASED ON Cr(III)

Aurica Borcea S.C. Aerostar S.A. Bacău
Camelia Beldie Univ. "Al. I. Cuza" Iaşi
Phys. Chem. Dept.

It was studied the physico-mechanical characteristics of decorative chromium plating obtained from electrolytes based on Cr(III). These characteristics were compareted with those obtained from chromium anhydride electrolytes, in order to replace the highly toxic Cr(VI), process curently employed.

6.8 STUDY OF SOME SPECIFIC ADDITIVES EFFECT ON CHROMIUM ELECTRODEPOSITIONS

Liliana König - ICTCM Bucuresti
Eugen Roman - The Physical Chemistry
Center of the Academy, Bucharest

Emilia Barbulescu - ICTCM, Bucuresti

As a result of the excellent corrosion and wear-resistance properties of chromium electrodeposits, researches have been made to improve the performances of depositions obtained from conventional baths (Cr^{6+}).

The effects of some specific additives on deposits quality and cathodic current efficiencies were investigated.

6.9 Anodic behaviour of zinc in cyanide solutions

Daniela Bughiu*, M.Buda**
* ICPE S.A., Splaiul Unirii 313, 74204, Bucharest, Romania
** "POLITEHNICA" University of Bucharest, Faculty of Industrial Chemistry, Applied Physical Chemistry&Electrochemistry, Calea Grivitei 132, 78122, Bucharest, Romania

Anodic behaviour of zinc was studied by means of potentiodynamic polarization curves (500 mV min^{-1}) in cyanide electrolytes with and without $Zn(CN)_4^{2-}$ complex, in a wide range of cyanide and complex concentrations (0.5M - 2M cyanide concentration and 0 - 1M zinc complex concentration) at three temperatures (20, 40 and 60°C).

The obtained data indicate a weak correlation of electrochemical parameters (peak potential, peak current, passive current, etc.) at low cyanide concentrations (up to 0.75M, at different complex concentrations), and a better one for high cyanide concentrations (1M and 2M, for different complex concentrations) for all studied temperatures. The results show that at low cyanide contents the Zn dissolves directly and then complexing in solution (Tafel slope corresponding for two-electron charge transfer), while at high cyanide contents (1M and 2M) the cyanide is adsorbed at the zinc electrode (Tafel slope corresponding to one-electron charge transfer).

Also, for high cyanide concentrations (1M and 2M) the system exhibits clearly current osscilations in a ~100 mV potential range (the osscilation potential range depends on the complex concentration), ressembling those obtained in literature for Zn in alkaline solutions. However, the relatively low pH for cyanide concentrations (~11.2) indicates that the current osscilations are not due to system's alkalinity.

6.10 MECHANISM OF THE ACTION OF AN ADDITIVE IN ZINC ELECTRODEPOSITION

M. Eyraud, M. Andrei* and J. Crousier

Laboratoire Phisico-Chimie des Materieux, Universite de Provence, 13331 MARSEILLE cedex 3, FRANCE.
* Depart. of Physical Chemistry, Faculty of Chemistry, University of Bucharest, 70346 BUCHAREST, ROMANIA.

This paper reports on a though process starting from a commercially available additive, ZETA PLUS 410 BASE provided by " Societe Continentale Parker ", which is recognised to produce smooth and bright zinc deposit. The influence of this additive on the kinetics of the deposition, its morfology and texture was tested.

The voltammetry study shows the presence of a small peak in the potential region for zinc deposition without additive, which precedes the large peak, at more cathodic potential, for zinc deposition under additive influence. Potential changes with time curves during zinc formation show that for small applied currents, in presence of additive, the potential stabilises in the potential region for zinc deposition without additive.

However, the morfology of the deposit corresponds to the one obtained in presence of additives, with small crystallites. The determination of double layer capacitances, by E.I.S., for both with and without additive, gives indications on the adsorbtion processes.

6.11 MULTILAYER ELECTROCHEMICAL ZINC DEPOSITION USED TO REPLACE CADMIUM DEPOSITIONS

Liana Roman - ICTCM Bucuresti
Valentina Filippi - ICTCM Bucuresti
Gh. Andoniant - ICTCM Bucuresti
Rodica Stancu - ICTCM Bucuresti

As a result of harmful cadmium prohibition, several alternatives were used including zinc alloys depositions. However, these alloys could not replace cadmium as to corrosion resistance in various environment conditions.

The paper presents research studies on obtaining electrochemical zinc multilayer deposition and their corrosion resistance compared to that of cadmium depositions.

6.12 CONTRIBUTIONS TO THE ESTIMATION OF STRUCTURAL FEATURES OF THE ELECTROCHIMICAL Ni-Co ALLOYS CARRIED OUT BY COMPUTER ASSISTED ANALYSIS OF THE XRD SPECTRA

Catalin Cristescu - ICTCM Bucuresti
Liana Roman - ICTCM Bucuresti
Cristian Soviani - Univ.Politehnica Bucuresti
Marioara Blidariu - ICTCM Bucuresti

The paper shows the estimation of the main structural features of Ni-Co electrochemical platings by analysing the real diffraction line profile of the samples, in order to optimise the codeposition technology.

The XRD diffraction spectra are analysed through an original software, resulting in information, concerning the structure and the quality of the electroplated alloys.

6.13

STUDY ON THE INFLUENCE OF TEMPERATURE AND CONCENTRATION OF THE COMPOUNDS ON THE DEPOSITION RATE FOR THE ELECTROLESS NICKEL PLATING BATHS

Maria Dinescu - ICTCM Bucuresti

The study presents the influence of temperature and concentration of the compounds, on deposion rate of Ni-P alloy.

The experiments were done using electroless nickel acid electrolytes having hypophosphyte base, under the influence of special additives (stabilizers, accelerators, buffers and complexing agents).

6.14 THE INFLUENCE OF TANTAL ALLOYING ON THE ELECTROCHEMICAL PROPERTIES OF NICKEL BASE SUPERALLOYS

Prof.Dr.Doc.O.Radovici*, **I.Roman****
*Universitatea "POLITEHNICA". Bucuresti, Facultatea de Chimie Industriala, St.Gh.Polizu 1
**Departamentul de Cercetare al S.C.METAV S.A. Bucuresti, St. Zapada Mieilor 16-18

The high heat resistance and electrochemical corrosion resistance of the superalloys make them useful for the aircraft and chemical industry. This special behaviour is due to the pasivization capacity of nickel itself and of the other alloying elements like aluminium, titanium, cobalt and especially chromium.

Tantalum is less studied from this point of view, of increasing the anticorrosion characteristics of the superalloys.

The present paper analyses the role of tantalum in the anodic oxidation-pasivization processes in NC20Nb and NC19Nb nickel base superalloys.

The electrochemical tests have been performed in sulphuric acid 1N, at 25°C, on cylindrical samples obtained from as cast alloys with a tantalum content between 1.12 and 4.01 percents.

The analysed electrochemical parameters was corrosion potential, critic passivation potential, critic passivation current and passivity current.

Regarding the NC20Nb superalloy, a typical electrochemical passivation can be observed only at the samples with a small tantalum content. This behaviour is due to chromium. For the sample without tantalum a 0.02mA/dm^2 passivity current has been measured. The other samples have not show such low passivity current.

The NC19FeNb superalloy has show the same aspects regarding the tantalum influence on the anticorrosion characteristics. The increase of the passivity current, a movement of the corrosion potential toward negative value and a modification of the shape of the reverse curve are due to the tantalum content.

The electrochemical analyses of the nickel base superalloys NC20Nb and NC19FeNb have shown a detrimental influence of tantalum on the anticorrosive characteristics: the passivity current has increased with the tantalum content, the mixed corrosion potential has moved toward negative values and the reverse current curves have had a tendency to come near the direct ones.

The evolution of the reverse current curves under the direct ones has demonstrated a relative stability of the passivity films.

Tantalum promotes a spontaneous passivation of the superalloys in H_2SO_4 1N, at 25°C and a lower quality possivation state.

6.15 The study of tube- tubesheet crevice corrosion in the steam generator CANDU

Authors: Dumitra Lucan, Maria Radulescu, Ioana Pârvan, Alice Dinu,
Valeria Cotolan.

ABSTRACT

Corrosion is the major problem affecting the reliability of steam generator. Many corrosion problems can be attributed to local concentration effects of aggressive solutes and/or impurities in restricted regions, such as tube-tubesheet crevices. The concentration effect in these restricted areas is of great importance and interest in the design and operation of steam generators.

In this study are presented the results of corrosion testings performed in secondary circuit under specific conditions of Nuclear Power Plant operation (temperature 260°C, pressure 5.1 MPa) on crevice simulated devices manufactured from carbon steel (SA 508 class 2) and Incolloy 800. The following testing environments were utilized: demineralized water (pH=9.5 all volatile treatment), raw water (pH=9.5) from the Danube river, used for condenser cooling, NaCl solution 100g/l (pH=10.5).

The examination of corrosion behaviour of these materials have been realized by metalography and X-ray difraction. The results are presented as micrographies distinguishing the appeareance of pitting corrosion firstly on the tubesheet material and then, eventually in the presence of a verry aggressive environment, on the tubes material.

The purpose of this paper was to develop a good understanding of mechanism of corrosion and oxide growth on carbon steel in simulated crevice devices.

6.16 **Influence of thermal treatment on the corrosion behaviour of Zy-4 alloy**

by I.Pirvan, M.Radulescu, L.Velciu, L.Nedelcu

Corrosion resistance of metals and alloys under corrosion environment depends also on their mettalurgical characteristics such as: macrostructure, microstructure, cristalytes orientation, composition and grain limits state, crystalline lattice, distribution of intermetallic compounds precipitates.

Also, these characteristics depend on thermal treataments parameters such as : thermal treatment temperature, ageing period at a certain temperature and cooling rate after thermal treatment.

Generally, an increasing in corrosion resistance can be obtained as follows :

- α-phase sufficient finish;
- homogenization treatment of ß-phase followed by a quenching and α-phase finish.

To underline the influence of thermal treatments and of cooling rates post-treatments on the corrosin behaviour of zircaloy-4 samples, there were executed the following corrosion tests:

- corrosion tests in demineralized water at 360°C (17 MPa) on zircaloy-4 samples thermally treated in the range (400-600°C);
- corrosion tests executed in water and steam at 350-450°C on zircaloy-4 samples, thermally treated in the ß, (α+ß) ranges and as-received ;
- corrosion tests in superheated steam at 400, 450 and 500°C on the zircaloy-4 samples, thermally treated in the ß range and cooled with 50°C/sec. and 200°C/sec.

The evaluation of corrosion behaviour of the respective samples was done by gravimetric determinations, metallographic examinations and X-rays diffraction analyses.

The parameters followed in the thermal treatment influence study were:

- oxidation kinetics, thickness and oxide layer aspect;
- metal hydriding (morphology of hydrides, hydrogen amount absorbed);
- structural modifications and intermetallic precipitates development.

6.17 STUDIES OF SACRIFICIAL ANODES ALTERNATIVE MATERIALS.

J. RAMÍREZ, A. HUERTA, T. ROBERT, M.E. NOGUEZ, G. SALAS.
DEPARTAMENTO DE METALURGIA, FACULTAD DE QUIMICA, UNIVERSIDAD
NACIONAL AUTÓNOMA DE MEXICO, CIUDAD UNIVERSITARIA, MÉXICO, D.F. 04510

Since the past century (about 1820), when Sir Humphrey Davy suggested to protect the British Naval Ships with cathodic protection with Zinc, several materials have been studied and used as sacrificial anodes in order to protect structures, ships, pipe lines, etc. Four properties are important for validating the material to be used as a sacrificial anode: the corrosion potential (steady state potential), the efficiency, the polarization and the homogenous corrosion of the material. Zinc, Magnesium and Aluminium are typical anode base materials. Comparing this three metals, Zinc has the smallest theoretical current capacity, 0.094 A-year/kg, while those for Al and Mg are 0.340 and 0.251 respectively, nevertheless Mg shows the lowest efficiency (50 % when Al and Zinc have 90 %). From these electrochemical point of view, aluminium could be the ideal material for being used as sacrificial anode. However as Al presents anodic passivation, which makes it corrosion resistant, its use as galvanic anode is relatively recent. Therefore, alloying elements must be used in order to minimise the anodic passivation. Typical alloying elements used for Al commercial anodes are: Zn, Sn, Hg and In. Hg use has been reduced due to its high toxicity. The other elements have a negative environmental impact too so, the purpose of the work is to substitute them by others less detrimental. This substitution is based on the hypothesis that they must form ternary compounds or eutectics, to show very low solid solubility and to have an specific position in the electromotive force series, related to the base metal. In this work samples were cast an solidified using commercial alloys as well as the proposed alloys with Ag and Mg. Their potential, efficiency and polarization were measured. The kinetic parameters of the corrosion reaction mechanisms were determined and the types of corrosion evaluated. Results are discussed.

6.18 NEW ELECTRODE MATERIALS FOR ANTICORROSIVE CATHODIC PROTECTION

I.Roman*, Corina Vlad*, Carmen Dolea*, P. Nita*, A.Buzaianu*, M.Z. Dumitrescu**
*Departamentul de Cercetare al S.C.METAV S.A.Bucuresti, St.Zapada Mieilor 16-18
**PETROSTAR S.A. Ploiesti, Bdv. Bucuresti 37

The paper contains electrochemical investigation data on some new anodic materials aimed for cathodic anticorrosive protection.

Two magnesium base alloys (for sacrificial anodes), Mg1Mn and Mg6Al, containing manganese and aluminium respectively as main alloying elements and a silicon cast iron (for impressed current installation), containing 3 ÷ 7 percent chromium, were tested.

For the magnesium alloys the tests included mix corrosion potential time evolution aswell as the dissolution rate, with or without a charge, evaluations.

The silicon cast iron investigation included anodic dissolution rate evaluation as a function of chromium content, for a current density of $35 A/dm^2$.

All tests were carried out in 3% NaCl solution, at room temperature. Anodes polarization was made coupling them with a steel cathode (OL-37 grade).

The mix corrosion potential of the tested magnesium alloys varies in a reduced range of values, less than 50mV, under the value recorded when immersed into solution, -1600mVs.c.e., approximately. The time evolution is determined by an initial activation of the samples surface, followed by a pseudopassivization due to a film of corrosion products, formed on the surface.

In the NaCl solution the two tested magnesium alloys don't generate compact and adherent films, their activity being maintained continuously. The materials have the tendency to regain the initial potential value. The Mg1Mn alloy regains quicker. After 18 days immersion the mix corrosion potential was -1595mVs.c.e. for both alloys.

Under charge the magnesium anodes potential has the same evolution between -1300 ÷ -1375mVs.c.e. Under charge the magnesium anodes current densities were stabilized at $16 mA/cm^2$ and $14 mA/cm^2$ for Mg6Al and Mg1Mn respectively.

The gravimetric losses of the two magnesium base alloys, as immersed in 3% NaCl solution, for 18 days showed the dissolution rates of Mg6Al to be higher than those of Mg1Mn; this was confirmed by the samples surface aspect, as analyzed by scanning electron microscopy.

The two magnesium alloys don't passivate in the tested environment and their activity is due to some local cells working on their surface, whose electrodes (limited areas on the material surface) continuously change their position.

The mass losses of the silicon cast iron aimed for impressed current anodes production were evaluated gravimetricly as well as by atomic absorption analysis of the used electrolyte. Both methods evidenced that a chromium concentration increase leads to an increase of the anodic dissolution rate, for the applied experimental conditions.

6.19 CATHODIC PROTECTION OF REINFORCEMENT STEEL IN CONCRETE: ELECTROCHEMICAL REACTIONS AND TRANSPORT MECHANISMS

I. Pepenar - Building Research Institute, INCERC,
Sos. Pantelimon 266, sector 2, 79614 Bucharest, ROMANIA

The paper presents the main electrochemical reactions, able to take place at the surface of the reinforcement steel embedded in concrete and the transport mechanisms in the interstitial solution in the case of cathodic protection of the steel.

There are analysed two types of (primary) electrochemical reactions:

- the discharge of cathions existing in the interstitial solution in the neighbourhood of the metallic electrode (Fe^{2+}, H^+, K^+, Na^+, Ca^{2+});
- the reduction of dissolved species (O_2, Fe^{3+}).

The transport process within the interstitial solution, expressed by the Nernst-Planck relationship, is stated as a total of three components : diffusion+migration+convection. The paper describes the transport mechanisms which take place in the concrete, both at the interface steel-concrete, as well as in the electrolyte solution present in the concrete mass.

6.20 THE INFLUENCE OF CHLORIDE IONS UPON THE ELECTROCHEMICAL BEHAVIOUR OF THE ZINC COATED STEEL IN CONCRETE

Elena Pepenar and I. Pepenar - Building Research Institute, INCERC,
Sos. Pantelimon 266, sector 2, 79614 Bucharest, ROMANIA

The paper presents the results of researches, performed by electrochemical methods, on the behaviour of zinc coated reinforcement in saturated solutions of $Ca(OH)_2$ and in cement paste in the presence of chloride ions.

In order to establish the limiting value of the chloride ions concentration in the electrolyte solution, beneath which the passivity state of the zinc coated steel is preserved, i.e. the passivity is not destroyed and the steel does not corrode, there have been drawn up the anodic potentiodynamic curves in electrolytes with various amounts of chloride ions. At the same time, the influence of the state of the zinc coated steel surface and of the time of its immersion in the electrolyte solution on the anodic corrosion process have been studied.

There has been pointed out that the presence of a passive layer of calcium hydroxizincate on the zinc surface provides a decrease of the corrodability of the zinc coated steel in the saturated solution of $Ca(OH)_2$ with admixtured chloride ions, i.e. the growth of the limit of chloride ions concentration at which the passivity of the zinc is no more affected, from 0.05 M to values over 0.1 M.For comparison, this limit value for uncoated reinforcement steel is of 0.01 M.

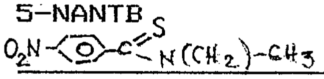
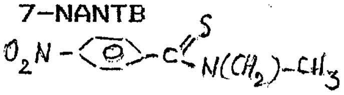
6.21 INHIBITION AND POLARIZATION STUDIES OF SOME ORGANIC COMPOUNDS FOR CORROSION ZINC IN NH_4Cl SOLUTIONS.

Maria Nicola, Teodora Badea si Angela Lupu
POLITEHNICA University of Bucharest

The inhibition of zinc corrosion in chloride media recently attracted great interest in reletion to the manufacture of primary bateries using mercury-free zinc anodes, named "green piles".The present paper report the reults of our investigations on effect of some organic compounds on zinc (99,97% puritty) corrosion in 10% NH_4Cl solution.

The corrosion rates of zinc have been determined by means of the hydrogen evolved ($cm^3/cm^2.h$) and electrochemical -by extrapolation of cathodic Tafel line to the corrosion potential.In table 1 are given some results of the experimental studies for maximum concentration of the inhibitor.

Table nr.1. Electrochemical parameters of the zinc corrosion in 10% NH_4Cl without and with 0.01M inhibitor.

Inhibitor .	$V\text{-}H_2$ $cm^3/cm^2.h$	ε_{cor} V/enh	b_c V/decada	i_{cor} $\mu A/cm^2$	E %
without	0.04	-0.845	0.119	100	-
ANILINE	0.0069	-0.802	0.120	14.7	85.3
4-PICOLINE	0.0053	-0.805	0.125	13.2	86.8
PYRIDINE	0.0078	-0.813	0.118	19.5	80.5
SALICYLALDEHYDE	0.0037	-0.801	0.123	9.3	90.7
5-NANTB 	0.0034	-0.803	0.122	8.4	91.6
7-NANTB 	0.0027	-0.795	0.127	6.4	93.2

6.22

THE INFLUENCE OF ANION STRUCTURE OF QUINOLINE DERIVATIVE SALTS UPON THE VALUE OF INHIBITION COEFFICIENT IN CORROSION PROCESSES

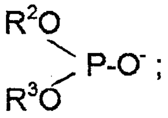
N.Luta*,E.Roman**,C.Crangus*,M.V.Popa**,Sanda Velea*,
Maria Grigorescu*

* Chemical Research Institute. Research Institute for Pesticides.
Spl.Independentei 202 A, 77208, Bucharest, Roumania
** Institute of Physical Chemistry "I.G.Murgulescu"
Spl.Independentei 202 A,77208, Bucharest, Roumania

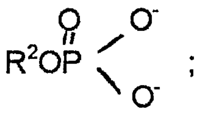
In order to obtain new corrosion inhibitors with polyvalent action (which ensure an efficient protection against electrochemical corrosion as well as microbiologic corrosion), a series of products were synthesized whose cation consists of quinolinic nuclei (I). The synthesis was based on some hypotheses regarding the relation between the molecular structure of organic chemical compounds and their ability to reduce the rate of electrode processes. The cation structure was, in its turn, selected according to the relations between the chemical structure and the microbiocide activity.

(I) where: R=alkyl and R^1=alkyl or various organic functions.

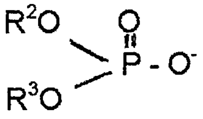
Structures of phosphorous acid organic esters were employed as anions: dialkyl phosphites (II), mono (III) and dialkylphosphates (IV), dialkyldithiophosphates (VI) as well as derivates of carbonylic acids (VII).



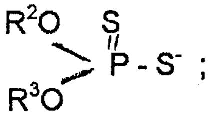
(II)



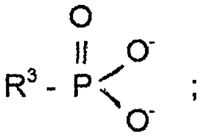
(III)



(IV)



(V)



(VI)

R^4COO^-

(VII)

where:

a) $R^2=R^3$ or $R^2 \neq R^3 =$ $-CH_3$, $-CH_2-CH_3$, -iPr, $-(CH_2)_3-CH_3$

b) R^4 is alkyl or aryl in whose structure halogen atoms and various organic functions are present

6.23 ON THE CHARACTERIZATION OF ORGANIC FILMS USED IN ROMANIAN RAILWAYS SYSTEM

O.Radovici*, Belarisa Popescu*, Ioana Demetrescu* and Florica Ghiță**

***) "Politehnica" University, Bucharest, General Chemistry Department**
****) Refer SA Bucharest**

A comparison between the behaviour of various organic protective systems used in railways system is presented, based on capacity, resistance and electrode potential measurements.

Individual alchydic, alchydo-melaminic, acrylic and combined systems were examined as a function of chemical nature of organic resins, film thickness and exposure time in NaCl solution (1.5%, 0.015% and 0.00015%).

The change of electric capacity in the first 30 minutes gives information about the water distribution and penetration way in the protection films. From the variation of capacity and electric resistance in 30-90 days the breakdown time of protective films was determined.

6.24 THE DEPENDENCE OF THE ANTICORROSION ELASTOMERIC COATINGS PERFORMANCES BY THE PLASTIFICATION SYSTEMS

M.V.Popa*,Ecaterina Vasilescu*,Paula Drob*,Cristina Catana**,N.Epure**,
Maria Anghel*

* Institute of Physical Chemistry "I.G.Murgulescu",
Spl.Independentei 202, 77208,Bucharest,Roumania
** ANTICORROSIV S.A.- Co,B-dul Theodor Palladi 313,Bucharest,Roumania

The behaviour of three chlorosulphonated polyethylene rubbers, reticulated with epoxy resin and with esther plastifier (PESC-E and CS4 types) and polymer plastifier (CS5 type) in comparison with a chlorosulphonated polyethylene rubber reticulated with litharge (PESC-L type) and not included plastifier was carried out in oxidizing chemicals.

The rubbers were experimented under laboratory conditions as simple vulcanizing sheets in the following corrosion media: sodium hypochlorite NaOCl with 12-13% Cl active, pickling and chroming solutions, all at 23^0,40^0 and 60^0C.

Assessment of the protective properties were made from qualitative (visual observations) and quantitative measurements: percentage modification of weight $\Delta W(\%)$, weight loss W_l (%), liquid absorption A(%), hardness, tractional-tearing resistance $\Delta R_t(\%)$, tractional-tearing length $\Delta L_t(\%)$.

The rubbers performances were determined by the correlation of the variations of all those six quantitative characteristics in time and with temperature; these performances were estimated as being respectively: good (+), moderate (0), poor (-). In case of the good performances, all the properties present slow variations with small slope over time, within acceptable limits, reflecting a reduced reactivity of the materials to the aggressive media; the temperature changes the slopes of the curves, the latter becoming steeper with increasing temperature, but the curves themselves tend to a constant level denoting a good stability. For poor performances a variation of the main properties (which exceed acceptable limits) with even steeper slope is observed; the curves do not tend to a constant level; the temperature effect is more remarkable than for good performances; these facts reflect a increased reactivity.

The kind of the plastifier influences the anticorrosion performances of the elastomeric coatings; for the same plastifier, the protective properties of the coatings depend on its content.

6.25 THE PIGMENTS INFLUENCE ON THE CORROSION BEHAVIOUR OF PAINT FILMS

O.Radovici*,Paula Drob**,Ecaterina Vasilescu**,M.V.Popa**,R.Serban***

* "Politehnica" University of Bucharest,Faculty of Chemistry,
Str.Polizu 1-5, 77126 Bucharest, Roumania
** Institute of Physical Chemistry "I.G.Murgulescu",
Spl.Independentei 202 A, 77208 Bucharest, Roumania
*** Research Institute for Anticorrosive Protection,
Bdul Theodor Pallady 49 A, Bucharest,Roumania

The protective properties of paint films can be increased by the use of a suitable pigment. This improvement of the anticorrosive paint performance is depending of the kind, the fineness, the dosage of pigments and their compatibility with the film binder.

This paper presents the results regarding the pigments influence on the corrosion behaviour of alkyd films in 3% NaCl solution. The protective films were realized on carbon steel substrate using seven pigments of metallic, mineral and organic types. Dry films thickness in the range 20-25 μm were obtained.

The NaCl solution penetration in tested paint films have been investigated by capacitance, resistance and stepwise polarization measurements (the total immersion time - 60 days). The corrosion behaviour of coated steel depends on the coating capacitance and resistance, which are related to uptaked water amount, conductive pathways and the state of degradation of the paint film.

The water uptake (calculated from capacitance measurements) permitted to establish the permeability of the paint films; it was resulted that the metallic pigment-Al powder and the mineral pigment-TiO_2 decrease the water permeability of alkyd film.

The total area of conductive pathways (obtained from resistance measurements) presents the minimum values for the paint films with the Al powder and TiO_2 pigments, demonstrating a reduced movement of ions through these films and respectively an improvement of protective properties.

The efficiency and porosity values of the paint films (calculated by comparing the dissolution current density of painted and bare substrate) show that the Al powder and TiO_2 pigments increase protective performances of alkyd coatings. The polarization curves present a good correlation with the capacitance and resistance measurements and the visual assessment.

7.1 Surfactant self-assembly in simple and complex systems. Micelles, microemulsions, adsorption and polymer-surfactant solutions.

Lindman, B., Piculell, L., Thuresson, K., Olsson, U. and Tiberg, F.
Physical Chemistry 1, Chemical Center, P O B 124, S-221 00 Lund,
Sweden

Surfactant self-assembly in simple binary aqueous solutions is compared with that in more complex systems, like ternary systems with an oil or a polymer or the behaviour at solid surfaces. The ubiquity of surfactant self-assembly is underlined and an overview is made using nonionic surfactants for illustration. For the nonionic surfactants the spontaneous curvature of the surfactant film varies with temperature which leads to a marked effect of temperature on aggregate structure.

Topics discussed include microstructure of microemulsions, phase separation of segregative and associative type and mixed polymer-surfactant solutions and surfactant adsorption at hydrophobic and hydrophilic surfaces. Microemulsions can depending on temperature be of the droplet or bicontinuous type. Mixed polymer-surfactant solutions are compared with mixed polymer and mixed surfactant solutions and the marked difference in behaviour between hydrophilic homopolymers and amphiphilic polymers is stressed. Regarding surfactant adsorption, the role of interfacial aggregation is shown and consequences are discussed.

7.2 SYNTHESIS AND CHARACTERIZATION OF FLUORESCENTYL-LABELED POLYACRYLIC ACIDS

D. F. Anghel and Francoise M. Winnik[(a)]

Department of Colloids, " I. G. Murgulescu" Institute of Physicsl Chemistry, Spl. Independentei 202, 79611 Bucharest, Romania
[(a)]Department of Chemistry, McMaster University, 1280 Main St. West, Hamilton, Ontario, Canada L8S 4M1

Studies on fluorescently-labeled polymethacrylic or polyacrylic acids were reported by Chu and Thomas [1], and Turro and Arora [2], respectively. In both cases they obtained the polymers by copolymerization of methacrylic or acrylic acid and a dye-substituted monomer. We report here the synthesis and characterization of labeled polyacrylic acid (PAA) obtained by post-modification of a commercial sample (PAA of M_w ~150,000). The polymer was prepared by a simple amide formation procedure, modeled after a technique previously used to prepare PAA-based associative thickeners. The reaction between the polyacid and an arylalkyl amine was performed in an aprotic solvent, N-methypyrrolidone, in the presence of dicyclohexylcarbodiimide. Polyacrylic acids labeled with pyren, naphthalene, and with both chromophores, were prepared starting with 1-pyrenylmethyl amine, 4(1'-pyrenyl)butyl amine, and 1-naphthylmethyl amine. Characterization by GPC and NMR confirmed that the dye was linked covalently to the polymer. The amount of fluorophore incorporated was determined by UV spectroscopy, and it ranged between 0.5 and 3.0 molar %. Photophysical properties of the labeled polymers were determined in aqueous and nonaqueous media. In water, the labeled polymers exhibit characteristic polyelectrolyte properties, their behavior being strongly dependent on pH and ionic strength. However, the incorporation of hydrophobic chromophore induced subtle changes in polymer properties which will be emphasized during the presentation.

---

1. D. Y. Chu and J.K. Thomas, Macromolecules, 17(1984)2142

2. N. J. Turro and K. S. Arora, Polymer, 27(1986)783.

7.3 INTERACTIONS OF POLY(ACRYLIC ACID) WITH POLYETHYLENE GLYCOL MONO-NONYLPHENYL ETHERS: EFFECTS OF THE LENGTH AND POLYDISPERSITY OF THE HYDROPHILIC GROUP

D.F.Anghel, Francoise M. Winnik[a], and Nicoleta Galatanu

Department of Colloids, "I.G.Murgulescu" Institute of Physical Chemistry, Spl. Independentei 202, 79611 Bucharest, Romania,
[a)] Department of Chemistry, McMaster University, 1280 Main St. West, Hamilton, Ontario, Canada L8S 4M1

The solution behavior of polymeric acids in the presence of ethoxylated nonionic surfactants with normal distribution of the poly(ethylene oxide)(PEO) chain-length has been studied extensively, but only little attention was paid to systems based on surfactants homogeneous in PEO chain-length. Some recent data collected on systems containing poly(acrylic acid)(PAA) and homogeneous ethoxylated (n=6 and 8) dodecanols ($C_{12}E_6$ and $C_{12}E_8$) [1] have given evidence for the existence of several critical points in the interaction: the onset of surfactant aggregation onto the polymer chain (i.e., the critical aggregation concentration, CAC or T_1), the polymer saturation by surfactant molecules (T_2'), and the appearance of free micelles into solution (T_2). Subsequent investigation of these systems by dynamic fluorescence probe experiments [2], gave further evidence for the existence of surfactant clusters wrapped around by the polymer. The aggregation numbers of free micelle are lower for $C_{12}E_8$ than for $C_{12}E_6$ and they decreased by a factor of about 20% by polymer addition.

The main objective of the work described here is to quantify the effect of the hydrophilic moiety of ethoxylated nonylphenols on the interaction with PAA. To this end, a PAA of MW ≅ 150,000 and both homogeneous (n=9 and 14) and polydisperse (n ≅ 9.5, 13.3 and 29) PEO chain nonylphenols were used. Static fluorescence probe experiments with pyrene were carried out to determine the critical micelle concentration (CMC) and CAC values. The CAC values were always smaller than the corresponding CMC's. For polydisperse ethoxylated nonylphenols, the static fluorescence data were correlated with results obtained by surface tension, viscometry and pH measurements. In the corresponding polymer/surfactant systems, the three interaction points T_1, T_2' and T_2 were detected on surface tension isotherms. A characteristic of the polydisperse ethoxylates was the narrowing of the surfactant concentration range for the interaction with the increase of ethoxylation degree. The viscosity and pH had visible changes in the vicinity of T_1 and T_2. The results were discussed taking into account the interaction of both ethoxylated and hydrophobic moieties of the surfactants with PAA (i.e., hydrogen bonding and hydrophobic bonding, respectively).

1. D.F.Anghel, S.Saito, A.Iovescu and A.Baran, Colloids Surf.A, 90(1994)89.
2. M.Vasilescu, D.F.Anghel, M.Almgren, P.Hansson and S.Saito, paper in preparation.

7.4 Interactions in nonionic surfactant-nonionic polymer systems

Nicoleta Galatanu and Dan Florin Anghel

Institute of Physical Chemistry "I. G. Murgulescu", Department of Colloids,
Spl. Independentei no. 202, 79611 Bucharest

It is well known that nonionic polymers interact with anionic surfactants, whereas the ionic polymers influence the surfactants of oposite charge [1]. For a system with nonionic components the interaction is faible and more difficult to detect. The aim of this work is to investigate the interaction between a nonionic surfactant and a nonionic polymer. In this respect the association behaviour of polydisperse ethoxylated octylphenol (OP_8) and its interactions with polyethylene glycol (PEG) and polypropylene glycol (PPG) in aqueous solutions were studied. The methods used to reveal the presence of interactions in the systems were surface tension, viscosity, pH and clouding point. The measurements were performed for surfactant concentrations between 10^{-5} and 10^{-1} M at constant polymer concentration. Although the surface tension method fails to detect an interaction in the OP_8-PEG system, the other methods reveal a clear difference between the behaviour of surfactant alone and that in the presence of PEG. For the OF_8-PPG system the effects of interaction were detected by all methods and some critical points were determined, too. The interaction mechanisms appear different for each system and the interaction strength can correlate with the polymer hidrophobicity.

[1] E.D. Goddard and K.P. Ananthapadmanabhan, Interactions of Surfactants with Polymers and Proteins, CRC Press, Boca Raton, FL, 1993.

7.5

Polarity Profiles in Reverse Micelles of Triton X-100, as Studied by Spin Probe and Absorption Probe Techniques.

Agneta Caragheorgheopol, Rodica Bandula and Horia Caldararu
Romanian Academy, "I.G.Murgulescu" Institute of Physical Chemistry
Splaiul Independentei 202, 77208 Bucharest, Romania

Heikki Joela
Department of Chemistry, University of Jyvaskyla, PO Box 35, SF-40351 Jyvaskyla, Finland

The microenvironment characteristics – polarity, viscosity and order degree – in Triton X-100 reverse micelles (RM) in cyclohexane and benzene - *n*-hexane 30 : 70 (v/v), were investigated with the aid of a homologous series of cationic spin probes, CAT *N* (4 - (N,N - dimethyl - N- alkyl)ammonium - 2,2,6,6 - tetramethyl - piperidine - 1 - oxyl iodide), of 5 - and 16 - doxyl stearic acids and of a new absorption probe, 4-nitropyridine-N-oxide (NP). The spectral parameters were related to local hydration values by means of a series of poly(oxyethylene) (PEO)/water calibration mixtures. All results regarding the polarities in RM and calibration mixtures have been expressed in terms of Kosower's Z values, by determining the linear dependence of the transition energies of NP, E_{NP}, on Z, for a series of polar solvents: $Z = 3.008E_{NP} - 178.4$ (in kcal mol^{-1}). Thus, the relative radial positioning of all probes was established and could be compared with those of 1-methyl-8-oxyquinolinium betaine (QB) and methyl orange (MO), previously used in the same systems.

A continuous variation of the polarity in the RM was evidenced with different probes, from the most polar region in the center, with the polarity of ethanol/water mixtures (CAT 1, CAT 4 and QB) to a region corresponding to tetraethylene glycol (TG)/water mixtures and triethylene glycol monoethyl ether (TGME)/water mixtures (NP and CAT 8), to a region at the limits of the core, with the polarities of the triethylene glycol dimethyl ether(TGDE)/water mixtures (MO) and to still lower values, found with the 16 doxyl probes, in the corona. Also, the different hydration dynamics at various depths in the micelles were followed, showing earlier saturation in the outer regions of the core as compared to the central regions.

The spin probes evidenced the compacting and ordering effects of water on the surfactant chains in the polar core and corona. From this point of view the RM in benzene-hexane appear to have a much lower viscosity in the polar core (over the whole range of water contents) as compared to those in cyclohexane. The order degree of the surfactant chains is lower too and the corona appears to be penetrable by an oil-soluble Cu complex, at variance with the cyclohexane system. All this data can be consistently explained by the loosening effect of benzene, solvating the surfactant chains in the corona.

7.6 A SPECTROFLUORIMETRIC STUDY OF PROTEIN-SURFACTANT INTERACTION IN BSA-SDS AQUEOUS SOLUTIONS

Marilena Vasilescu, Daniel Angelescu and Laura Tugulea*
Institute of Physical Chemistry I.G.Murgulescu, Splaiul Independentei 202, 77208 Bucharest
* Bucharest University, Physics Department, Magurele

The interaction of bovine serum albumin (BSA) - sodium dodecylsulfate (SDS) and the resulted complex were investigated by spectrophotometric measurements at two pH values: close to the isoelectric point of the protein or to the physiologic conditions. The specific interaction brings about a denaturation of the protein which is evidenced by changes in its fluorescence intensity. It was found out that the CMC of the surfactant and solubilization temperature decrease in presence of the protein. The aggregation number of SDS, determined by the method of static quenching of pyrene fluorescence, is smaller than the number corresponding to free micelles and varies with the increasing of the protein over surfactant concentration ratio; the values agree to those obtained by other methods.

The variation of aggregation number as well as of pyrene fluorescence lifetime support the "necklace" complex structural model which suggests that along the unfolded protein micelle-like clusters are formed.

7.7 INTERACTION OF POSITIVELY CHARGED NON-DENATURED COLLAGEN IN GEL STATE WITH ANIONIC SURFACTANTS AT DIFFERENT pH

Minodora Leca[a] and Viorica Trandafir[b]
[a]University of Bucharest, Faculty of Chemistry, Department of physical Chemistry
[b]CERPI SA, Bucharest

The following mechanism was given for the interaction of positively charged collagen from hide powder (cid medium) with anionic surfactants: a *primary interaction* by ionic and hydrophobic forces, the electrostatic attraction facilitating the approach of the surfactant to the peptide chain of the protein, which could provoke a strengthening or a development of the hydrophobic regions neighbouring the bonding sites; a *secondary interaction* by direct interaction of the surfactant with the hydrophobic regions of the protein through its hydrocarbon chain.

To verifie the proposed mechanism a collagen-surfactant system with pH=2.5 (pH of collagen gel) was prepared, its pH was increased progresively adding 5 M natrium hydroxide solution, to maintain the component concentrations practically constant, and rheological measurements were performed using a Rheotest RV. Viscosities of gels containing surfactant must be higher than those of gels without surfactant over the whole pH range and must preserve even at isoelectrical point (IEP) if secondary interactions really take place.

Previous studies, carried out by rheological measurements, shown that at pH=2.5 the greatest interaction is obtained for collagen(C)-sodium dodecyl sulphate (SDS) systems, regardless of the SDS/C ratio and C concenration. C-SDS system with a C concentration of 0.35 and a SDS/C ratio 1/20 g/g or 0.173 mmol/g (SDS concentration 0.606 mmol/l) was selected and its pH modified within the range 2.5-11.5. To compare gel viscosities, they were calculated at zero shearing rate, by linearization of rheograms and extrapolation, and η_0 were obtained.

Very high constant η_0 values were obtained both in the presence and the absence of SDS for pH ranging between 2.5 and 3.3, but SDS increases it about 7 times. A drastical decrease of η_0 is observed with increasing pH for gel containing SDS and a less pronounced one for C gel, the values become equal at pH=4.5 and gels destruct at IEP. A new increase of η_0 takes place at pH passing the value 6, reaches a maximum at pH=8.3 and a constant value is obtained for pH=10.5 and higher; the values for both kind of gels lies on the same curve. This demonstrates that interaction between C and SDS exists only at pH lower than IEP and increasing of viscosities produced by SDS are due to the interaction of hydrocarbon chains attached to different collagen molecules and fibrils as the only secondary interaction existing.

7.8 INTERACTION OF CATIONIC SURFACTANTS WITH BIOLOGICAL MEMBRANE. THEORETICAL AND EXPERIMENTAL APPROACH

Dan Niţă, Valerică Raicu, Cristian Gusbeth and Dan F. Anghel

Romanian Academy, Institute of Physical Chemistry, Spl. Independenţei 202, 79611 Bucharest

The pourpose of this paper is to model the absorption of cationic surfactants on surface of biological membranes. The Stern theory was used to treat the absorption of such surfactants by phospholipid membranes, assuming that functional form for absorption isotherm is a Langmuir one. Comparison between theory and experimental data obtained from surface tension, cell radius optical absorption measurements on suspensions of cetyltrimethylammonium bromide - treated yeast cells was made for various medium pH's.

7.9

DIELECTRIC BEHAVIOUR OF SURFACTANT - TREATED BIOLOGICAL MEMBRANES

*Valerică Raicu, Cristian Gusbeth, Dan Niță, Dan F. Anghel and Grigore Turcu**

Romanian Academy, Institute of Physical Chemistry, Spl. Independenței 202, 79611 Bucharest
**University of Bucharest, Physics Faculty, Biophysics Department, Bucharest*

Complex permittivity of yeast cell suspensions has been measured over the 0.1-100 MHz frequency range. The cells were treated with solutions of cetyltrimethylammonium bromide (CTAB) in the 0 - 1.2 mM concentration range. A reduction of the dielectric dispersion was observed as the concentration of surfactant increased. The results were interpreted in terms of the two-shell dielectric model, analyzed in a previous work[1]. The model allowed to evaluate the influence of CTAB upon the specific conductance and capacitance of the plasma membrane. Previous works reported in the literature on the interaction between cationic surfactants and biological membranes supported the assumptions that the surfactant molecules are strongly absorbed into membranes by electrostatic and other cohesive forces. Our results allowed to determine the surfactant-induced changes of the intrinsic physical properties of the membranes.

---

[1] V. Raicu, G. Raicu and Gr. Turcu, Dielectric properties of yeast cells as simulated by the two-shell model, *Biochim.Biophys.Acta*, in press

7.10

THE CONDUCTIVITY BEHAVIOUR OF POLYELECTROLYTE SOLUTIONS: THEORETICAL MODEL AND EXPERIMENTAL VERIFICATION

*V. Raicu, Adriana Baran, Alina Iovescu, D. F. Anghel, S. Saito**

Department of Colloids, Institute of Physical Chemistry,
Spl. Independentei 202, 79611 Bucharest, Romania
*Momotani Juntenkan Ltd., Minatoku, Osaka 552, Japan

A theoretical model was proposed to describe conductimetric behaviour of polyelectrolyte solutions. The model yields a mixture equation which relates the intrinsic properties of dissolved polymer and continuum water phase to those of solution regarded as a whole.

The model was experimentally verified on aqueous poly(acrylic acid) systems having the concentration within the 2 - 15 mM range. To this end, both conductivity and pH measurements were employed. Electrical conductivity is given by the mobility of the macroion or the polymer coil and the proton. By fitting the theoretical equation of conductivity with the experimental data it was found out that the polymer coil could be depicted as an oblate ellipsoid. Furthermore, the determined values of the polymer coil semiaxes were in good agreement with those reported in the literature.

7.11 HYDROPHILE - LIPOPHILE PROPERTIES OF NONIONIC SURFACTANTS AND THEIR STUDY BY RP-HPLC

M. Balcan, D. F. Anghel, D. Donescu*, V. Raicu and N. Galatanu
Department of Colloids, Institute of Physical Chemistry, Spl. Independentei 202,
79611 Bucharest, Romania;
**Center for Plastic Materials Research, Spl. Independentei 202, Bucharest,Romania*

The properties and applications of nonionic surfactants depend on the equilibrium existing between the hydrophile and lipophile moiety of the molecule. This equilibrium is usually called the hydrophile-lipophile balance (HLB). The HLB concept allows an empirical classification of the surfactants according to their affinity towards the lipophilic or hydrophilic media [1,2]. It is well known that HLB depends on weight percentage of the hydrophilic portion of the surfactant molecule [2]. At the same time, the HLB value depends on various factors. For estimating the degree and direction of HLB modification under the influence of these factors, different methods such as clouding point (CP), critical micelle concentration (CMC), phase inversion temperature (PIT), emulsion inversion point (EIP) were proposed[3]. Chromatographic methods such as gas chromatography [4] and reverse-phase thin-layer chromatography [5] were also used to evaluate the HLB. An attempt to determine the HLB value by means of RP- HPLC was made in the case of cholesterol and stearic acid derivatives [6], but no data are available yet on alkylphenol-based nonionic surfactants.

This study has been carried out to verify the applicability of RP-HPLC to determine the HLB values of some polyethoxylated alkylphenols. The stationary phase and the eluents tested were C_{18} modified silica, and mixtures of methanol-water and acetonitrile-water, respectively. A relationship between the HLB value and the retention time obtained by extrapolating to 100% water content of the eluent was established. RP-HPLC is a suitable chromatographic technique to study the hydrophile-lipophile properties of nonionic surfactants. The chromatographic retention of these compounds is the result of interactions between the two moieties of molecule (lipophile and hydrophile) and the two immiscible phases (stationary and mobile). The chromatographic behavior of the surfactants for the two elution systems used was correlated with the eluent physical properties (i.e., viscosity, density, dielectric constant and refractive index).

1. W.C. Griffin, J.Soc.Cosmet.Chem., 1(1949)311.
2. W.C. Griffin, J.Soc.Cosmet.Chem., 5(1954)249.
3. L. Marszall, Yukugaku , 32(1983)135.
4. V.M. Nace and J.C.Knoell, JAOCS, 72(1995)89.
5. G.Trapani, C.Altomare, M.Franco, A.Latrofa and G.Liso, Int.J.Pharm.,116(1995)95.
6. L.Lahn and H.Sucker, Tenside Surf.Det., 26(1989)192.

7.12

POLYELECTROLYTE ADSORPTION IN HIGHLY TURBID SYSTEMS

Oswald L. Hörer
"Ştefan S. Nicolau", Institute of Virology, Bucharest

New insight in the polyelectrolyte-adsorbent interactions resulted, using an improved theoretical model for heterogeneous photon distribution in highly turbid media, based on Multiple Light Scattering Enhanced Absorption (MLSEA) bichromatic spectrophotometry and a great number of experimental data obtained on nucleic acids adsorbed on chromatography paper celluloses.

From $\mathbf{A_d}$ absorbances of nucleic acid polyelectrolytes on chromatography paper disks, measured using MLSEA bichromatic spectrophotometry, the adsorbed nucleotide **X** mole fraction was determined in various experimental conditions, leading to following main inferences:

- The adsorption of polyelectrolytes on electrically charged surfaces, which is a result of the balance of electrostatic long-range and dispersive and hydrogen bond short-range forces, is shown in an obvious manner using the adsorbed structural unit **X** mole fraction, in terms of the **I** ionic strength, below and beyond the Manning counterion condensation (CC) edge, depending upon the **P** degree of polymerization;
- A new type of conformational transition from a statistical isometric to a statistical anisometric coil resulted within the 0.3-0.9 mol/l **I** ionic strength range for flexible polyelectrolyte chains, when adsorption on a surface with dissociated ionic groups occurs; a diffusion controlled process is considered to be the determinant element of the shown phenomenon;
- The change in static dielectric constant of the polyelectrolyte solutions used in adsorption experiments on charged surfaces, does not modify in a regular way the adsorbed structural unit mole fraction (**X**), the interactions at the interface being influenced mainly by molecular effects on both the polyelectrolyte and the adsorbent;
- Some thermodynamic parameters are expressed using the **X** values determined experimentally and the **ΔG** free enthalpy values are found to be consistent with dispersive and hydrogen bond forces;

A framework of conditions for a computational modelling of the polyelectrolyte adsorption is presented, using the experimental data and the proposed adsorption model based on the heterogenous photon distribution MLSEA theory.

7.13 SYNERGETIC EFFECTS IN MIXED SOLUTION OF SURFACTANTS IN AQUEOUS MEDIUM

Otilia Cinteza, Mihaela Olteanu, Manuela Dudau

University of Bucharest, Physical Chemistry Department,
13 Republicii Blvd., 70346, Bucharest, ROMANIA

The behaviour of lauryl polyglucose (LPG) in mixed aqueous solution with other surfactants (sodium lauryl sulphate, polyoxyethylene sorbitan monooleate, cetyl dimethyl benzyl ammonium chloride) was studied.

LPG is a nonionic surfactant from a new generation synthesised by reacting corn starch glucose with fatty alcohol. It is compatible with all classes of surfactants and also offers a very high degree of biodegradability.

Some properties of mixed systems at liquid - air interface and in bulk solution were investigated at various molar fractions.

In aqueous solutions LPG forms ideal mixed micelles, with both ionic and nonionic surfactants.

At liquid - air interface LPG in mixed solutions produces strong synergetic effects, surface tension of mixture showing minimum values at certain molar fractions, depending on HLB of the nature of the surfactant.

As compared to an other nonionic surfactant with equivalent polyoxyethylene group, LPG itself and in mixture presents higher surface activity.

Some parameters of adsorption at liquid - air interface (free standard energy of adsorption, molecular surface area at CMC) have been calculated in order to explain the behaviour of LPG.

7.14

DETERMINATION OF LIFSHITZ - VAN DER WAALS AND ACID - BASE COMPONENTS OF SURFACE TENSION FOR SOME POLYMERIC SURFACES

Manuela Dudau, Mihaela Olteanu

University of Bucharest, Physical Chemistry Department,
13 Republicii Blvd., 70346, Bucharest, ROMANIA

The possibility to forward the wettability was studied modifying the polar-apolar character of the solid surface by Langmuir - Blodgett film deposition.

The surfaces have been described by solid - gas surface tension values and them Lifshitz - Van der Waals (γ_S^{LW}) and acid-base (γ_S^+ and γ_S^-) components, calculated on the basis of modern theory of contact angles, from Young - Good -Girifalco - Fowkes and Newmann equations of state.

The values γ_S^{LW}, γ_S^+ and γ_S^- have been calculated using contact angle measurements with three different liquids for each of polymer surfaces.

The pH dependence of contact angles confirm the values of γ_S^+ and γ_S^- (apolar or polar character of polymeric surface).

The change of acid - base surface properties as a result of the deposition of cationic detergent mono- or multilayer by Langmuir - Blodgett technique has been proved by contact angle variation.

7.15

ULTRA LOW INTERFACIAL TENSION OF OIL CARBOXYLIC ACID/ALKALI SYSTEMS

Pablo Contreras, Mihaela Olteanu

University of Bucharest Faculty of Chemistry
Laboratory of Colloids / Bucharest - Romania.

Carboxylic acids are identified as responsible of the ultra low interfacial tension (ULIT), in crude oil alkali solution systems. Apparently there is a synergetic effect due to the presence of these acids and the soaps formatted in the oil/alkali solution interface. In some conditions, the interface free energy reduction is so big that also produce spontaneous emulsification. Nowadays all these phenomenona are not clear and the most common technique to measure the ULIT, the spinning drop, it is not reliable. This work is a contribution to understand a little bit more such type of systems.

We use pure carboxylic acids like oleic, stearic and cyclopentane carboxylic, their sodium salts and decane like oil; in order to mimic the behavior of the crude oil/alkali solution systems. In all cases the ionic strength was kept constant with sodium chloride. We studied the alkali solution/air surface, and alkali solution/oil surface measuring the surface tension with the Wilhelmy plate. The alkali solution/oil surface was analyzed too with some rotating devices, to put in evidence the ULIT values. The different states of monolayer were studied.

Changes in the solution's pH with soap concentration show that according with the theory of hydrolysis and precipitates in carboxylate soap solutions, of Lucassen, there is a complex formation with a characteristic slope of 3,0 . The concentration in which the slope change, coincide with the values of superficial (solution/air) and interfacial (solution/oil) minimum. We suppose that the complex is present in the interface and it is responsible of ultra low interfacial tension. The results confirm, the application of the theory of hydrolysis and precipitates, of Lucassen, made for saturated carboxylic acids; and extend the applicability for unsaturated chains.

7.16 CADMIUM SULFIDE NANOPARTICLES PREPARED IN MICROEMULSIONS

Sandu Peretz, Mihaela Olteanu* and Otilia Cinteza*

Institute of Physical Chemistry, Department of Colloids,
202 Spl.Independentei, 77208, Bucharest, ROMANIA
* University of Bucharest, Department of Physical Chemistry,
13 Republicii Blvd., 70346, Bucharest, ROMANIA

The preparation of nanoparticles of various metals, oxides and sulfides is very important for industrial application, such as drugs, ceramics, catalysts and photographic emulsions. The size of particles in AOT/water/isooctane system was controlled by changing the water/AOT ratio (w_0=[H_2O]/[AOT]), and this was almost independent of the ions concentrations (Cd^{+2}, S^{-2}). Among these nanoparticles, the semiconductors are very interesting. The nanometer-sized particles have larger band gaps than the bulk semiconductor owing the quantum size effects.

The kinetics of cadmium sulfide nanoparticles formation has been studied by UV-spectroscopy.

The particles was prepared by mixing equal volumes of reverse micelle solution containing $6x10^{-5}$ - $6x10^{-4}$ mol/l Cd^{+2} and S^{-2} respectively, and 0.1 mol/l AOT in isooctane at different pH conditions. The investigations showed that, the particles increases in the first 24 hours and then their spectrum remains essentially unchanged for days. These systems which contain CdS particles have an photocatalytic activity.

7.17 MECHANO-CHEMICAL RECLAIMING OF ELASTOMERS
A TECHNOLOGY FOR FUTURE

Minodora Leca and I. F. Runcan
University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry

Elastomers are ideal systems for conversion and dissipation within the space of directioned mechanical stresses. Such structures impart exceptional mechanical strength but, as a reverse, produce great difficulties regarding the reclaiming.

Reclaiming process supposes breaking of a part of crosslinks, until the plastic character and viscous flowing required for processing are regained. Mechanical forces are high enough to break chemical bonds even when elastomers are subjectet to “mild” processing. Energy for bond breaking is relatively low compared to that dissipated.

Non-conventional energies were used in our works to reduce the cohesion energy of elastomers and to make them brittle. Advanced swelling - close to equilibrium - using solvents with solubility parameters ranging between 16.8 and 19.4 $(MPa)^{1/2}$ produces the following phenomena: induces great stresses within the elastomer network due to volume increase (about 3 times); reduces cohesion force and elongation at break at 5 and 20 %, respectively; the liquid present into the network, being incompressible, favours propagation of mechanical waves with a supersonic speed, amplifying thus the breaking of chemical bonds by resonance; controlled desactivation of radicals can be achived introducing adequate compounds. As a consequence impact mechanical forces required for destruction of swollen networks are much lower than those for cryolitic grinding. This suggests that destruction of swollen elastomers is very similar to that of solid bodies.

Swelling processes correlated with destruction forces required for a standard grinding as a function of the degree of swelling are presented. Mathematical models were suggested and the relations describing these phenomena for the usual sorts of elastomers were established.

Solvent is removed as an azeotrope by sudden heating with process steam, a pseudo-expansion of particles takes place and a powder with high specific surface is obtained. The environment protection was taken into account: adding chlorinated alkanes a density higher than unity can be obtained and swelling can be realized using a water seal (swelling solvent has a subunitary density).

A new system of grinding is presented, which assure total environment security.

7.18

DISTRIBUTION OF NEUTRALIZING AGENTS BETWEEN DISPERSION AND AQUEOUS PHASES FOR CATAPHORETICALLY APPLICABLE FILM-FORMING RESINS

Minodora Leca and Marin Micut
University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry

The most stable dispersions of electrophoretically applicable resins are obtained by stirring water containing the desired quantity of neutralizing agent with resin concentrated solutions in coupler solvents. The degrees of neutralization for which stability of dispersions and film-forming properties are most favorable must be established. Completely neutralized resin dispersions(solutions) are not convenient for electrodeposition because of very thin films they give.

The degree of neutralization for which a resin can be completely dispersed into water depends of the content of ionogenic groups and of molecular weight. The higher the degree of neutralization, the lower the time for complete dispersion for a given resin.

Kinetics of dispersion of a resin containing tertiary amine ionogenic groups and a number average molecular weight of 3800 was studied as a function of the degree of neutralization to obtain 15% aqueous dispersions as required for industrial electrodeposition. Acetic acid was used as neutralizing agent and pH and conductivity measurements to determine the distribution of hydrogen ions between aqueous and polymer phases.

The lowest degree of neutralization for which a dispersion can be obtained is 0.4. Kinetics of dispersion was determined for degree of neutralization ranging between 0.4 and 0.9. Acetic acid consumption, determined by pH measurements, indicates a first order kinetics with neutralizing rates increasing with degree of neutralization. Equilibrium pH of dispersions neutralized to different levels show smaller values compared to those of the amine monomer dispersions having the same content of amine groups and degree of neutralization. This is also valid for equivalence point, which is well bellow 7 (~5.4) and shows that a part of acid is present into water. In two phase systems the pH values characterize only aqueous phase and this demonstrates that the largest part of the neutralizing acid is present into the disperse phase retained by the amine groups.The neutralized amine groups prevail on the surface of particles and the free amine groups in the interior. This conclusion is supported by other properties like conductivity, turbidity and viscosity.

7.19 INFLUENCE OF SOME ALCOHOLS ON STABILITY OF SOME FATLIQUORING EMULSIONS

Minodora Leca[a] and Gh. Coara[b]

[a]University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry
[b]S.C.I.P.P.A. SA, Bucuresti

The influence of some alcohols, added 3% by volume into oil phase, both soluble (n-butanol and ethylene glycol) and insoluble (n-hexanol and dodecanol) into the dispersion medium, on stability to aggregation of some O/W emulsions used for fatliquoring of leather was studied.

The fatliquoring compositions were obtained as W/O emulsions with an oil phase content of 60-70 per cent by sulphation of two mixtures of animal and vegetal triglycerides (a ratio 4/1 for Cerpiol SPS2 and 1/4 for Cerpiol VG), of an animal triglyceride esterified with ethanol (Cerpiol E), of castor oil (Ricinol) and of triolein (Sulphated oil CH) with sulphuric acid 92-96 % at temperatures ranging between 20 and 30^0C.

The five W/O emulsions were inverted by dilution and increasing of temperature at 60^0C (fatliquoring temperature) and O/W emulsions with 10% dispersion phase were obtained.

The stability was measured visually during 1 h (oiling time) at 60°C in water of 20^0d hardness using glass tubes with inner surfaces of 1 cm^2. The height of emulsions were 20 cm.
In the absence of alcohols Ricinol has the the highest stability, followed by Cerpiol SPS2 and Cerpiol VG; the lowest stability was obtained for Cerpiol E; Sulphated oil CH is a bit more stable.

n-Butanol and ethylene glycol have very close action on stability of emulsions and, in some cases and for certain periods, even identical: they increase significantly the stability of Cerpiol SPS2 and slightly that of Cerpiol E and Sulphated oil CH, but decrease a little the stability of Ricinol and highly that of Cerpiol VG.

n-Hexanol produces a great stabilization of Ricinol and Cerpiol SPS2 emulsions, a slight stabilization of Cerpiol E one, has no influence on stability of Sulphated oil CH emulsion, and decreases greatly the stability of Cerpiol VG one.

Dodecanol stabilizes Ricinol emulsion, has no effect on stability of Cerpiol E and Sulphated oil CH emulsions, and decreases stability of Cerpiol SPS2 and VG emulsions.

The influence of the four alcohols on stability of fatliquoring emulsions can be explained by their different solubility into dispersion and continuous phases and thus by their different capabilities to act as coemulsifiers: n-butanol and ethylene glycol are soluble in the both phases and distribute between them in quantities depending on their relative solubility; n-hexanol and dodecanol are soluble only in oil phase, excepting for Cerpiol E and VG in which dodecanol is less soluble.

7.20 STABILITY OF AQUEOUS DISPERSIONS OF SOME POLYESTER-IMIDE OLIGOMERS

O. Segarceanu[a], Minodora Leca[b] and Mariana Voinea[a]
[a]Anticorrosive Protection Varnishes and Paint Research Institute, Bucharest
[b]University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry

Polyester-imides (PEI) are electrical insulators with high thermal resistance, belonging to the isolation class H(180). PEI oligomers are usually comercialized as cresol solutions. As it is known, cresol is a carcinogenic compound and it is very desirable to replace it with less dangerous solvents or to use PEI oligomers as suspensions.

The most convenient dispersion medium from all points of view - environment protection, economic and fire prevention - is water, but PEI oligomers are not water-soluble. This is why their suspending in water was realized using different stabilizers.

Suspensions with a content of PEI oligomers of 33% and 3% crosslinking agent (blocked isocianate) were prepared, to be applicable by conventional methods. PEI oligomers crashed in a mortar were introduced into a ball mill (ball diameters 15-20 mm) for 24 h and the obtained powder was sieved using a 100 μm mesh sieve. The sieved part was introduced within a ball mill for wet grinding (ball diameters 7-15 mm), together with the crosslinking agent and water, for 48 h. Two types of stabilizing agents were added to the obtained suspensions, 0.2-1.0% reported to the whole content of solids: nonionic surfactants and polymers. The systems were stirred vigorously for 30 min. 20 cm^3 from every sample were introduced into glass tubes and the heigth of deposits measured until constant values were obtained by free settling at 20-25^{0}C (about 7 days). The results were expressed as percents from the total volume.

The following stabilizing agents were used: ethoxylated nonylphenol (EO = 8), poly(vynil alcohol) and some water-soluble acrylic oligomers (SP-424, SP-425, SP-426, SP-441, SP-442, SP-443, SP-446, SP-447, SP-448).

It must be specified that even the suspension without stabilizer is quite stable, due to a structuration phenomenon which takes place producing a gel which can be easely destructed by gentle stirring. The best results were obtained for SP-424, which stabilize completely the suspensions, and also for SP-424, SP-425 and SP-426 which increase stability, while all the other compounds reduce suspention stability.

The above suspensions were applied using a spray gun. The obtained films, crosslinked at 240^{0}C for 4 h, have good film-forming and insulating properties.

7.21 THERMAL STABILITY OF ETHYLENE-PROPYLENE ELASTOMERS AFTER ONE YEAR OF STORAGE

Traian Zaharescu, ICPE SA, 313 Splaiul Unirii, 74204 Bucharest; Rodica Vîlcu, University of Bucharest, 13 Carol Av., 70346 Bucharest

Ethylene-propylene elastomers, EPDM and EPR, in the presence of Topanol OC were prepared and stored at room temperature in order to evaluate the antioxidant capacity for thermal stabilization of polymers. Oxygen uptake measurements were performed on the polymer films at three temperature. Activation energies for oxidation were calculated on different stages of thermal degradation (induction period, half period of oxidation and maximum time of the process). The greatest values of this energy were obtained using oxidation induction time, because phenolic antioxidant hinders thermal degradation of elastomers. A comparison of activity of the tested antioxidant in fresh and aged samples emphasizes that, after one year of storage, the compounded polymers are less stable than they are immediately after preparation. The presence of diene (ethylidene norbornene) in the structure of EPDM decreases its thermal stability. In spite of the addition of the stabilizer in the case of ethylene-propylene-diene terpolymer, the rate of oxidation is very high.

It is known that Topanol OC is a light stabilizer for polyolefins. For this reason, it was easierly evaluated the change of thermal stability by calculation of Gibbs potentials. Their time dependences point out that the two elastomers show unlike behaviour. A continuous increase of ΔG for ethylene-propylene copolymer describes an unique mechanism of oxidation, i.e. the attack of molecular oxygen on the tertiary carbons. A double stage dependence of ΔG on degradation time proves that during the initial period of oxidation, double bonds and tertiary carbons were the most reactive sites, while on the second step, when double bond content was consumed, the thermal degradation proceeds similarly for both materials. The rates of oxygen uptake calculated for the second part of each isothermal experiments are different for EPDM and EPR at the same temperature, because peroxyl radical content does not reach the same level. It can be assumed that ethylene - propylene terpolymer is degraded with higher rate, because the concentration of oxidation positions is greater than in ethylene-propylene copolymer.

The present communication can be considered as an exemple of practical study, which can describes the loss of stabilization ability of light antioxidants during the storage period of techical products manufactured with low content additives provided against thermal ageing (even at room temperature). It can be noted that the chemical structure represents an important factor, which has to be taken into account for evaluation of product durability relative to aggresive conditions of applications.

7.22

POLYAMIDIC MATERIALS CONTAINING CROWN-ETHERS, USED IN THE FIELD OF MEMBRANES

Authors: M Barboiu, Camelia Barboiu, Georgeta Popescu
Research Center for Macromolecular Materials and Membranes
206, Splaiul Independentei, Bucharest

This paper presents the synthesis of new polyamidic materials containing crown-ethers grafted in the polymeric matrix, used for membranes preparation.

The obtaining procedure of these materials was the interfacial polymerisation, by varying some parameters:

- nature and concentration of reagents (5-10%);
- solvents (C_6H_6, $CHCl_3$);
- type of catalyst (Py, MeOH).

All synthetised materials were characterized by I.R. spectroscopy, ^1H,^{13}C-NMR and elemental analysis.

7.23

ORGANIC-INORGANIC MIXED MATERIALS CONTAINING CROWN-ETHERS INCLUDED IN A PHOSPHAZENIC MATRIX

Authors: M. Barboiu, Ancuta Moldoveanu, Georgeta Popescu
Research Center for Macromolecular Materials and Membranes
206, Splaiul Independentei, Bucharest

In this paper we report the synthesis of new mixed materials which contain crown-ethers grafted by chemical bonds on the phosphazenic matrix, used for membranes preparation.

The polymeric fibers were transformed by complexation with different transitional metals and lanthanides, in order to obtain new materials with better physical and chemical properties.

All synthetised polymers were characterized by I.R. spectroscopy, ^{1}H, ^{31}P-NMR and elemental analysis.

7.24 WATER/ORGANIC SOLVENT EMULSIONS USED IN LIQUID MEMBRANES

Mihaela Sandu and Gheorghe Nechifor
Research Center for Macromolecular Materials and Membranes
Spl. Independentei 206 POB 15-143 Bucharest Romania

The analytical and technological separations that imply the emulsion membranes have as main stage the obtaining of water/organic solvent stabile emulsion.

In this work the influence of the nature of organic solvent, surfactant respectively, of water/organic solvent ratio on emulsion stability is presented. By use of organic solvents from the saturated alcohol class with 5 and 6 carbon atoms, halogenated derivatives and esters, emulsions with an adequate stability in liquid membrane processes were obtained.

The efficiency of the obtained emulsions is exemplified on removal of the barbituric acid derivatives from aqueous solutions.

7.25

THE REMOVAL OF NOBLE AND RADIOACTIVE ELEMENTS FROM NATURAL WATERS BY USE OF LIQUID MEMBRANES

Georgeta Constantinescu, B. Mitraşca, Gh. Nechifor, Georgeta Popescu

Research Center for Macromolecular Materials and Membranes S.A.
Splaiul Independenţei nr. 206, Bucureşti

The selectivity and efficiency of membrane processes allowed to develop some separation methods of useful elements from poor sources.

In this work it is presented experimental data concerning separation of Ag, Au, Ra and U from natural and surface sources using supported liquid and emulsion membranes with classical carriers.

Ion carriers composed from 8 - hydroxi quinoline and dibenzo - 18 - crown - 6 ether were introduced in liquid membranes based on esters of dicarboxylic acids or aromatic hydrocarbones.

In a single step it was obtained a separation efficiency of about 50 - 75%.

The optimum working system have the composition: membrane from dioctylsebacat containing 10^{-4} - 10^{-3} mol/L carrier, pH = 5.5 in source phase and 10^{-2} mol/L NH_4SCN in acceptor phase.

7.26

ORGANIC-INORGANIC COMPOSITE MEMBRANES

Brăduț Mitrașca, Gheorghe Bătrînescu, Georgeta Popescu

Research Centre for Macromolecular Materials and Membranes S.A
Splaiul Independenței nr. 206, București

The organic-inorganic composite membranes are made of polysulfone network and inorganic powder (ZrO_2, TiO_2, Al_2O_3) as an inorganic filler.

These composite membranes are actually being used for a variety of ultrafiltration purposes and as separator material in different types of electrochemical cells.

The membranes which are being discussed in this paper are formed by the phase-inversion process. In this phase-inversion technique a polymer is dissolved in a suitable solvent. This solution which is called the casting dope is poured onto a substrate (e.g. glass plate) and the porous film is formad by extraction of the solvent with a non-solvent (water or isopropanol).

As a major result is has been observed that the amount of the inorganic powder which is present in the membrane plays a dominant role: the structure of a composite membrane is completely different from the structure of a pure polysulfone membrane. The membrane becames denser with increasing amounts of inorganic powder.

7.27 DETERMINATION OF THE MICROPOROUS MEMBRANE PORE SIZES BY USE OF GAS PERMEATION

Bujor-Gabriel Albu and Gheorghe Nechifor
Research Center for Macromolecular Materials and Membranes
Spl. Independentei 206 POB 15-143 Bucharest Romania

Use of microporous materials in the enhanced filtration processes of disperse systems require a fast and relevant characterization of pore size.

The gas permeation method through porous media, initiated by Phys.Nicolae Luca was improved by testing a large amount of membrane type microporous materials.

Track-etching, asymmetrical and composite membranes obtained from polymers such as: polyethyleneterephtalate, polycarbonate, polysulfone, polyamide was characterized, the results being compared with the scanning-electron microscopy, bubble-point and mercury porosimetry data.

A calibrating function of the method based on Adzumi equation was found.

7.28 ULTRAFILTRATION MEMBRANES

Siegfried STÖCKEL, Carmen MANEA,
Liliana TEODORESCU, Livia IVAN
Research Centre for Macromolecular Materials and Membranes
Splaiul Independenţei 206, Bucharest, Romania

Ultrafiltration allows the recovery, the concentration and the demineralization, without heat, of the useful components from whey.

The most important component is not lactose, but lactalbumin; the amino acids sequency of this protein is alike, or even richer than that of egg proteins.

The denaturated form of lactalbumin was prepared by cheese whey heating, with the purpose of protein precipitation. Therefore, polymeric membranes on nonwaven and textile support were prepared.

The hydrodynamic tests of these membranes led to permeat fluxes in the range of 8 - 16 l/m^2hbar for the membranes with nonwaven support and 1.3 - 1.8 l/m^2hbar for the membranes with textile support. For the protein concentration process the retention values were ranging between 92 - 94 % for the membranes with nonwaven support and 95 - 96 % for the membranes with textile support.

7.29

SEPARATION OF METALLIC IONS BY POLYELECTROLYTE ULTRAFILTRATION

Cristina Cirlan, Gheorghe Nechifor, Bujor Albu and Georgeta Dumitrescu

Research Center for Macromolecular Materials and Membranes
Spl. Independentei 206 POB 15-143 Bucharest Romania

Separation of metallic ions by ultrafiltration from aqueous solutions is feasible when molecular or macromolecular additives are introduced in the medium to be separated.

In this work some obtained results regarding removal of Cu^{2+}, Zn^{2+} and Ni^{2+} ions by ultrafiltration in the presence of synthetic and natural polyelectrolytes (lignosulphonates, sulphosuccinates and polyacrylates) are presented.

The polyelectrolyte ultrafiltration experiments were carried on in a cross-flow ultrafiltration cell with polysulfone asymmetrical membranes having pore sizes in the active layer below 0.1 μm.

A retention ranging between 60 - 85 % for solutions containing 10^{-4} - 10^{-3} ion.gram/L and a flux between (1 - 1.5)10^{-2} $cm^3/cm^2.s$ were obtained.

30

MICELLAR-ENHANCED ULTRAFILTRATION OF AQUEOUS PHENOL SOLUTIONS

Georgeta Dumitrescu, Bujor-Gabriel Albu and Gheorghe Nechifor
Research Center for Macromolecular Materials and Membranes
Spl. Independentei 206 POB 15-143 Bucharest Romania

Usually, the organic solutes with small molecules (bellow 1000 Da) are retained from aqueous solutions by reverse osmosis, by use of membranes with diffusive active layer. In the last 10 years the membrane separation processes were developed in which the system subjected to be separated is pretreated with colloidal systems so that the small size solutes may be retained with ultra- and nanofiltration membranes.

In this work new arguments regarding the removal of phenols from aqueous solutions by micellar enhanced ultrafiltration is presented. By use of cetyltrimethylammonium bromide, potassium oleate and alchylbenzyldimethylammonium chloride as test surfactants, the β-naphtol was removed with polysulfone membranes.

7.31

INFLUENCE OF POLYETHYLENE GLYCOLS ON THE PROTEIN ULTRAFILTRATION

Loredana Moise, Luminita Andrei and Georgeta Popescu

Research Center for Macromolecular Materials and Membranes
Spl. Independentei 206 POB 15-143 Bucharest Romania

The ultrafiltration of protein systems is studied in view to recover the proteins or the continuous phase. The recent researches were focused on protein retention by ultrafiltration using microporous polymeric membranes without any modifications in the system to be separated.

In this work some results concerning protein ultrafiltration (bovine serum albumin) in the presence of polyethylene glycols with molecular weights ranging among 300 - 40000 Da, by use of polysulfone and cellulose acetate asymmetrical membranes are presented. The influences of molecular weight, ionic strength and pH on protein retention and permeate fluxes are evidenced.

7.32

ASYMETRIC MEMBRANES FOR WATER DESALINATION BY REVERSE OSMOSIS PROCESS

Authors: Luminiţa Andrei, Nicoleta Udrea, Bujor Albu, Georgeta Popescu
Research Center for Macromolecular Materials and Membranes

Reverse osmosis is a process that tranforms an unusable water supply into a usable resource. It is capable of renovating a broad spectrum of feedwaters from municipal water supplies that need polishing for industrial purposes to sea water that is refined into a potable water supply.

The paper presents the results for desalination by reverse osmosis, with an improved membrane prepared from a blend of cellulose diacetate and cellulose triacetate:

- it is more stable than the cellulose diacetate membrane;
- it has a better flux and rejection than the cellulose diacetate;
- it is more resistant to compaction then either the diacetate or triacetate;

The tests were made using standard solutions:

- for brackish water, the flux and rejection of the membrane is determined when the membrane is tested on a feed water of an aqueous NaCl solution with the concentration of 2,000 mg/l at 30atm. with a temperature of 25°C;
- for sea water, test is similar except that the feed water is an aqueous NaCl solution with a concentration of 35,000 mg/l and the test pressure is 43atm.

7.33

HEMODIALYSIS HOLLOW-FIBER MEMBRANES. PREPARATION AND CHARACTERIZATION

Authors: Luminiţa Andrei, Nicoleta Udrea, Georgeta Popescu,
Aurelia Lăcătuşu*, Alexandra Ciupiţoiu**

C.C.M.M.M.S.A., *ROMPROCEF-Brăila, **ICECHIM-C.C.M.P.

Hemodialysis is the most important synthetic membrane application. Hemodialysis is applied to the treatment of patients which suffer from chronic or acute kidney failure to remove toxic metabolic wastes like urea, uric acid and creatinine from their blood.

Synthetic polymeric membranes for hemodialysis must have the following properties:

- good compatibility with blood
- good mechanical properties;
- good permeability and selectivity.

Our research was carried out on a pilot spinning instalation, with a special spinneret. The polymeric solutions are prepared from cellulose diacetate (10 - 15% by weight), in solvent mixtures (dioxane, acetone). In order to obtain the lumen are used several tips of central liquides. Membranes characterisation was accomplished by optical microscopy in cross section and along the fiber to determine the inner and external diameter and by thermoporometry tehnique to determine the pore size distribution and porosity of meso-pore membranes.

7.34

ENZYMES IMMOBILIZATION ON POLYMERIC MEMBRANES

Bătrînescu Gh. Garganciuc Dana, Stöckel S., Manea Carmen, Cuniţă A.

Research Center for Macromolecular Materials and Membranes S.A.
Splaiul Independenţei nr. 206, Bucureşti

Insoluble enzymes are repeatedly used in biocatalytic processes and they maintain their activity. Insolubilization is achieved through a large number of immobilization methods; among them, a great importance has covalent binding on macromolecular supports.

In this paper, we present the experiments carried out in order to select polymeric materials able of accomplishing two functions: to support the enzymes molecules and to form microporous structured membranes.

As polymeric materials, we have studied polysulphone and its functionalized derivatives, polyphenilen oxide and its derivatives. The recovery of the enzymatic activity of about 50% confirm the enzyme binding on the macromolecular supports.

7.35

ENZYMES SEPARATION, PURIFICATION AND CONCENTRATION THROUGH ULTRAFILTRATION TECHNIQUE

Garganciuc Dana, Bătrînescu Gh., Cuniţă A.

Research Center for Macromolecular Materials and Membranes S.A.
Splaiul Independenţei nr. 206, Bucureşti

Enzymology, field of study recently developped, uses a great number of separation, purification and concentration techniques; among them, a particular interest is given to ultrafiltration, as:

- it diminishes the loss of enzymatic activity - no use of organic solvents, only low temperatures;
- it allows us to obtain high purity products.

Our paper presents new data concerning processing of biosynthesis media with enzymatic activity through ultrafiltration through polymeric membranes.

We test enzymatic solutions containing proteases, catalase, alcohol oxidase, amylases. The recovery of enzymatic activity after ultrafiltration was 60%.

7.36

COLLOIDAL ROAD - BITUMUM - POLYMER SOLUTIONS. RELATIONSHIPS BETWEEN THEIR COMPOSITION AND PROPERITIES

Authors: Boris Hlevca, Georgeta Grisic, Georgeta Popescu, Constantin Romanescu*
Resarch Center for Macromolecular Materials and Membranes
*Tehnical Building University, Bucharest

Experiments are presented on the relationship between several suppliers road-bitumum compositions and the polymer structure as regards the characteristics of the road-bitumum which has been modified with polymer, in order to obtain a homogenous compound that has to get the necessary qualities for use both in road works or hydro-instalations.

They present the influence of the aromatic hidrocarbons on the road-bitumum polymer system's compatibility and the modification of the road-bitumum characteristics by the colloidal balance displacement of that one through a polymer adding.

7.37

INVESTIGATIONS OF THE SOLUTION PROPERTIES OF STYRENE/ ACRYLONITRILE COPOLYMERS

Ana Onu - University "Al.I.Cuza", Iassy, Faculty of Chemistry
Ig.C.Poinescu - Institute of Macromolecular Chemistry "P.Poni", Iassy

SAN copolymers produced by suspension polymerization were investigated by means of viscosimetry, light scattering and turbidimetric titration. The values of structural-thermodynamics obtained parameters have been correlated with composition of copolymers.

8.1 Anomalous behaviour of some dilute solid solutions

Ion Teoreanu and Adrian Volceanov
University "POLITEHNICA" of Bucharest , Faculty of Industrial Chemistry

The phenomenological representation in thermodynamics of solid solutions uses a large variety of models that describe in a satisfactory way their behaviour for "usual" compositons range.

In the case of some isovalent solid solutions from $M_{1-X}M'_XO$ family, in the range of low and very low concentration, certain pecularities, i.e. strong non-ideal behaviour, were observed when magnetic cations are involved. To study such behaviour, the continuous solid solution phase diagram of NiO-MnO system was tested. The experimental data obtained by electron spin resonance method outlines local magnetic interactions with possible formation of clusters. A correct thermodynamic description has to take into account these aspects, including them in thermodynamic modelling of phase diagrams. Different models are tested to describe the thermodynamic behaviour of such dilute solid solutions.

8.2 ABOUT REACTIONS MECHANISMS AT THE CONVENTIONAL SYNTHESIS OF BARIUM POLYTITANATES.

Ion Teoreanu, Antoaneta Folea
University "POLITEHNICA" of Bucharest

The X-ray diffraction, in correlation with thermal analysis, offered more information about the processes that take place at the synthesis of barium polytitanates, and also about the evolution of phase composition and thermodynamic stability of the intermediary phases. Thus, the hypothesis regarding the mechanisms of solid-state reactions which yield to the stable compounds could be established.

Ceramic samples having barium titanates compositions with different concentrations (80.0 - 83.3 mol% TiO_2) and conventionally synthesized were investigated.

The samples were treated at temperatures between 650 and 1300°C, then rapidly quenched in air.

A global mechanism for the solid-state processes could be considered, taking into account the primary formation of a metastable phase including TiO_2 and $BaCO_3$. Its thermal decomposition started at 710 - 760° C (depending on the type of barium titanate). The decomposition of this phase is followed by the formation of certain intermediary phases having different stoichiometries. Their interractions (at temperatures between 800 - 1000°C) yield to the intermediary compounds ($BaTiO_3$, $BaTi_4O_9$ or $BaTi_5O_{11}$), and, finally, to the stable compounds.

The X-ray patterns for the samples treated as mentioned above indicated the presence of intermediary compounds (such as $BaTi_4O_9$ or $BaTi_5O_{11}$), but also showed the presence (at low temperatures) of some peaks that could not be attributed to any known barium titanates. We suggest that this peaks could belong to the TiO_2-rich phases, their composition being different from that of the stoichiometrically barium titanates compounds.

8.3 FORMATION AND ELECTRICAL PROPERTIES BEHAVIOR OF (Ba, La) (Ti, Nb)O_3 SOLID SOLUTIONS

I. Teoreanu, Ecaterina Andronescu, Adelina Ianculescu*
University"Politehnica" Bucharest, Faculty of Chemistry, Department of Materials Science and Engineering, 313 Splaiul Independentei, Bucharest, Romania
*Institute of Physical Chemistry, 202 Splaiul Independentei, 77208 Bucharest,Romania

In this paper, phase composition and electrical behavior of (Ba, La) (Ti, Nb)O_3 ceramics were investigated.

The compositions taken into account were classically prepared, starting with raw materials such as: $BaCO_3$, TiO_2, La_2O_3 and Nb_2O_5 of high purity (99.9%).

After being batched and homogenized, the mixtures were shaped as plates and thermally treated at temperatures between 800-1400°C, being kept at these temperatures for 3, 7 hours, respectively.

The compositions under discussion were obtained as ceramic materials, on which specific characteristics were determined (apparent density and porosity). Not depending on the dopant type and content, one can find the increase of the apparent density and the decrease of the porosity, at the same time with the temperature increase, due to the progress of the sintering process.

The estimation of the dielectric properties was carried out by capacity and dielectric losses measurements at 1 kHz frequency. The experimental results point out the influence of the composition and thermal treatment temperature (by means of the microstructure) on the relative permittivity and on the tangent of the losses angle.

The electrical behavior of the investigated ceramics depends on the defect chemistry and on the phase compositions of these materials.

8.4 STUDY OF ELECTRIC CONDUCTIVITY OF SOME CERAMIC MASSES : $SnO_2 + Sb_2O_3 + CuO$ WITH THE DOPANTS CONCENTRATION.

IOAN GALASIU, RODICA GALASIU
INSTITUTE OF PHYSICAL CHEMISTRY BUCHAREST
NICULAE POPA, VASILICA CHIVU
UNIVERSITY OF BUCHAREST, FACULTY OF CHEMISTRY

The following ceramic pellets were prepared :

1. 98 % SnO_2 + 1 % Sb_2O_3 + 1 % CuO
2. 96 % SnO_2 + 2 % Sb_2O_3 + 2 % CuO
3. 92 % SnO_2 + 4 % Sb_2O_3 + 4 % CuO
4. 95 % SnO_2 + 1 % Sb_2O_3 + 4 % CuO
5. 95 % SnO_2 + 4 % Sb_2O_3 + 1 % CuO

which were sinterised for 4 hours at 13oo°C. The apparent density and electric resistivity in direct current of these pellets were neasured.

It was found that the recipe nr. 2 has the greatest apparent density.

The electric resistivities decrease with the current density and temperature increase. The recipe nr. 2 has the lowermost values of electric resistivities. The activation energies for electric conductivity were calculated and it was noticed that these decrease with the current density increase.

Likewise the ceramic masses prepared with recipe nr.2 have the lowermost values for the activation energies for conductivity.

Therefore, the excess or small quantity of dopants by comparation with the optimum concentration (2 % Sb_2O_3 + 2 % CuO) increases the electric resistivity and activation energy for conductivity of these ceramic masses.

8.5 IR STRUCTURAL CHARACTERIZATION OF THE CERAMICS IN THE Sn-Sb-Cu-O SYSTEM

Oana Ionescu, Rodica Marchidan, Susana Mihaiu, D.Crisan and Maria Zaharescu
Institute of Physical Chemistry, 202 Splaiul Indepedentei, 77208-Bucharest, Romania

In the Sn-Sb-Cu-O system large domains of SnO_2 based solid solutions as well as the presence of two binary compounds, $CuO\cdot Sb_2O_5$ and $4Cu_2O\cdot Sb_2O_5$, have been identified. In certain conditions $CuO\cdot Sb_2O_5$ can also form solid solution dissolving SnO_2. The mechanism of the solid-solutions formation is complex and takes places in certain compositions, stepwise.

Most of the compositions exhibit a poor sintering ability; dense ceramic materials can be obtained only in certain composition in which the initial ratio $CuO:Sb_2O_3 \geq 1$.

In order to bring more information about the structure of the SnO_2-based dense ceramics in mentioned system, the present work reports the results of their IR structural investigations.

The IR spectrometry data yield additional information of the phase compositions determined by X-ray diffraction.

8.6 SUBSOLIDUS EQUILIBRIA IN THE Sn-Sb-Cu-O SYSTEM

M. Stan, Suzana Mihaiu, D.Crisan and Maria Zaharescu
Institute of Physical Chemistry, Splaiul Independentei 202
77208, Bucharest, Romania

Sn-Sb-Cu-O system contains ceramics with specific electrical and magnetic properties, employed as sensors, electrodes and catalysts. Studies covering the whole concentration range of compositions emphasize the complexity of processes that occur during the formation of several phases in these systems.

The aim of the work was to study subsolidus phase equilibria in the Sn-Sb-Cu-O system. Samples of various composition were thermally treated in the 450°C-1000°C range of temperatures at a normal atmospheric oxygen content.

The obtained results were as follows:

- At high temperature Sb_2O_3 presents a strong tendency to oxidize to Sb_2O_4 and Sb_2O_5, while CuO reduces to Cu_2O.

-Large domains of solid solutions with SnO_2 or $CuO\cdot Sb_2O_5$ structure were identified in the studied compositions

- Using the X-Ray diffraction, the presence of $CuO\cdot Sb_2O_5$ and $4Cu_2O\cdot Sb_2O_5$ binary compounds was also observed.

Taking into account the Sb_2O_3 oxidation and the CuO reduction, a model for oxygen content calculation was proposed and used for calculating composition diagrams. The variation of the oxygen content was compared with the sample loss or gain of weight.

Subsolidus phase diagrams were drawn in ternary and quaternary representations.

8.7 PHASE FORMATION AND THERMAL STABILITY OF THE COMPOUNDS IN THE Bi_2O_3-PbO SYSTEM

Ana Brăileanu[a], Maria Zaharescu[a], D.Crisan[a] and E.Segal[b]
[a] Institute of Physical Chemistry, 202 Spl.Independentei, 77208 Bucharest, Romania
[b] University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry,
13 Blv.Republicii, Bucharest, Romania

The scientific interest for the Bi_2O_3-PbO system has increased due to the importance of the PbO in high-T_c superconducting phase formation in the Bi_2O_3-SrO-CaO-CuO system.

Previously, several low melting defined compounds have been identified in the system: $6Bi2O_3.PbO$, $3Bi_2O_3.2PbO$, $4Bi_2O_3.5PbO$, $4Bi_2O_3.6PbO$ and $Bi_2O_3.3PbO$.

This work deals with the phase formation and thermal stability of the mentioned compounds.

Under non-isothermal conditions, up to 823 K, in all mixtures, regardless of the Bi_2O_3/PbO molar ratio, a mixture of phases was identified.

At 873 K, in the mixtures corresponding to the composition of the compounds with Bi_2O_3 in excess, $6Bi_2O_3.PbO$ is preferentially formed. In the mixtures corresponding to the composition of the compounds $4Bi_2O_3.5PbO$ and 4Bi2O3.6PbO the stoichiometric compounds are identified, while in the case of the compound with PbO in excess a solid solution with litharge structure has been observed.

Under isothermal conditions, in the same temperature range, the tendency to form the stoichiometric compounds increases. All compounds are melting at temperatures ranged between 873K and 1023 K.

8.8 NEW TYPES OF STARTING PRODUCTS FOR HIGH T_C SUPERCONDUCTORS(II)

G. D. Cismaru and Lidia Paruta
Institute of Physical Chemistry, 202 Splaiul Indepedentei, 77208-Bucharest, Romania

The research we developed aims the synthesis and the thermogravimetric study of some coordination complexes with organic ligands containing the OH group and N in the molecule.

There were synthesized coordination complexes with molecule derived from hydroxyquinoline.

The complexes have been used as starting products in synthesis of some high T_c superconductors from Bi-(Pb)-Sr-Ca-Cu-O system establishing the formation and the treatment temperatures.

8.9 THE STUDY OF THE OXALATE COPRECIPITATION CONDITIONS FOR THE SYNTHESIS OF Bi-Sr-Ca-Cu-O SUPERCONDUCTORS

Liana MARTA[a], Ossi HOROWITZ[a], Maria ZAHARESCU[b] and Costel SARBU[c]

[a] Technical University Cluj-Napoca, Department of Material Science
[b] Institute of Physical Chemistry, Roumanian Academy, Bucharest
[c] "Babes-Bolyai University", Chemistry Department, Cluj-Napoca

The oxalate coprecipitation is a practical method for the synthesis of superconducting materials especially for the Bi-Sr-Ca-Cu-O system. The quantitative coprecipitation of the metal oxalates is a very important procedure but has not received detailed attention.

In this work, a systematic analytical study of the oxalate precipitation conditions has been performed, for obtaining superconducting materials in the Bi-Sr-Ca-Cu-O system. For this purpose, the formulae of the precipitate solubility as a function of pH and oxalate excess were established. The possible formation of hydroxo-complexes and soluble oxalato-complexes was taken into account. A BASIC program was used for tracing the precipitation curves, using a logarithmic scale. The theoretical curves were confirmed by experimental results.

From these diagrams, the optimal conditions for the quantitative oxalate coprecipitation can be deduced.

The superconducting oxide materials were prepared from the oxalate precursors obtained by this method., by an appropriate thermal treatment. The formation of the superconducting phases in the system was identified by X-ray diffraction analysis.

8.10 THERMAL ANALYSIS OF IODINE DE-INTERCALATION FROM BiSrCaCuO-I SUPERCONDUCTOR COMPOUNDS

N. Dragoe*, E. Segal*, Jocelyne Jegoudez** and A. Revcolevschi**

*Faculty of Chemistry, University of Bucharest, B-dul Carol I 13, Bucharest, ROMANIA

**Laboratoire de Chimie des Solides, U.R.A. 446 - CNRS, Université Paris Sud, Orsay 91405, FRANCE

The superconductor compounds from BiSrCaCuO family have structures formed by (oxygen deficient) perovskite type blocks. These blocks (alternated with Bi-O planes) are separated by a distance of 3.5Å. The weak interactions between these blocks determine a platelet-like microstructure, the cleavage and the anisotropy of electrical properties also (the electrical resistivity along the Bi-O planes is metallic-like whereas perpendicular to the Bi-O planes is semiconducting-like).

The intercalation of foreign atoms and molecules increases the distance between Bi-O planes (to about 7Å in the case of iodine intercalation) and might change the charge transfer processes in the structure. A change in the electrical anisotropy upon intercalation is usually observed.

We performed a thermal analysis study of the iodine de-intercalation from $Bi_2Sr_2CaCu_2O_8$-I compound by constant heating rate and constant decomposition rate methods. Our results suggest that there are two types of intercalated iodine (or activity sites) in $Bi_2Sr_2CaCu_2O_8$-I: one part (of about 60%) is physically adsorbed, the other one is chemically bent (the actication energy for the second process is about 100 kJ/mole).

These measurements pointed out a difference in the intercalated iodine species: the previous supposition of chemically equivalency of I_3^- molecules must be modified accordingly.

8.11 STRUCTURAL AND SUPERCONDUCTING PROPERTIES OF $Sm_{0.6}Pr_{0.4}Ba_{2-K}Sr_KCu_3O_7$ $(0 \leqslant k \leqslant 1)$

L. Samson-Colonescu[1], J. Berthon[2], R. Suryanarayanan[2] and A. Revcolevschi[2]
[1] Universitatea “Al.I.Cuza” Iași, Facultatea de Chimie, Catedra de Chimie Fizică
Bd. Copou nr. 11, Iași - 6600, România
[2] Laboratoire de Chimie des Solides, CNRS, UA446
Bât. 414 Université de Paris-Sud, 91405 Orsay, France

Abstract

It has been well established that the compounds $LnBa_2Cu_3O_{6+z}$ (z~1) are all superconductors ($T_c = 92$ K) except for Ln = Ce, Pr and Tb . Whereas Ce and Tb based cuprates cannot be prepared in a single phase form, $PrBa_2Cu_3O_{6+z}$ is a single phase compound that has an orthorhombic symmetry for z = 1 very much like the well studied $YBa_2Cu_3O_7$ but is not a superconductor. In fact, Pr destroys superconductivity in $Y_{1-x}Pr_xBa_2Cu_3O_{6+z}$ when x reaches a critical concentration, $x_c = 0.55$. Further, the critical concentration of Pr (x_c) depends on the ionic size of Ln . In particular, for Ln = Sm, the value of x_c was found close to 0.4. In spite of considerable theoretical effort, these results have not been understood well. In order to examine the effect of Sr substitution on structural and superconducting properties, we report here on the preparation, X-ray diffraction (XRD), ac susceptibility and thermogravimetry of $Sm_{0.6}Pr_{0.4}Sr_kBa_{2-k}Cu_3O_{6+z}$. An insulator to superconductor transition was observed for k = 0 by heating the sample in argon followed by oxygen annealing, T_c increased from 0 to 14 K. An orthorhombic to tetragonal transition was observed for k = 0.8, with a maximum in $T_c = 37$ K, after this heat treatment. It is proposed that excess hole density brought into the CuO_2 planes both by Sr substitution and the heat treatment, is responsible for changes observed in T_c. The results will be discussed in the light of recent theoretical models.

8.12 CRYSTALLIZATION PROCESS OF THE GLASSES OBTAINED IN THE DOPED Bi-Sr-Ca-Cu-O SYSTEM

I.Teoreanu[1], V.Fruth, Maria Zaharescu, Geta Tanase and Z.Hegedus[2]
Romanian Academy, Institute of physical Chemistry, Bucharest 77208, Spl.Independentei 202, Romania;
1-University Politechnica Bucharest, Str.Polizu 1, Romania
2-Stockholm University, Inorganic Chemistry, Arrhenius Laboratory, 106 91 Stockholm, Sweden.

We have investigate the glass formation ability and crystallization process in the doped Bi-Sr-Ca-Cu-O system.

The starting compositions were around the 2223 stoichiometry and as dopants Pb, Sb and B, single or associated in different molar ratio, were used.

The crystallization process was carried out in two different ways: (1) the glasses were heated from the room temperature up to the annealing temperatures and (2) the glasses were melted again and cooled down to the annealing temperatures.

The temperatures and sequences of formation of the superconducting phases within the investigated compositions were determined using simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA), X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The structural investigation of the glasses was carried out by IR spectrometry. Superconducting properties were confirmed by the recording of the electrical resistivity and magnetic susceptibility versus temperature.

One can note that the presence of dopants oxides with low melting points, acted as network-forming, but in a narrow range of composition. Furthermore, it should be pointed out that the association of dopants benefits the promotion of high-Tc phase.

One may also emphasize that the crystallization process is strongly influenced by the schedule of the applied treatment as regarding the mechanism and the reaction kinetic.

8.13 Bi-BASED SUPERCONDUCTORS OBTAINED BY OXALATE COPRECIPITATION, CONTAINING Fe

Monica Popa, Maria Zaharescu, Liana Marta[a] and D.Crisan
Institute of Physical Chemistry, 202 Splaiul Independentei, 77208 Bucharest, Romania
[a]Technical University Cluj-Napoca, Romania

It is well known that Bi-based superconductor exists in two main superconducting phases identified as the 2212 low-T_c phase and the 2223 high-T_c phase.

Some strategies were employed to obtain the high-T_c single phase, which is known to be very difficult to obtain. Substitution of various ions in cuprate oxide superconductors represents an important experimental technique in the study of high-T_c superconductivity.

Several groups have reported that partial replacement of Bi by Pb facilitates the formation of the higher-T_c material but the lower phase is generally present as a minor impurity. It was also observed that substitutions of Cu ion by 3d transition metal ions like Fe, for Bi based superconductors is not beneficial to the superconductivity behavior. Fe dopant has a beneficial role to the low-T_c phase formation and disadvantageous to the 2223 phase.

This paper reports the observation of the substitutional effect of Pb for Bi and Fe for Cu. We present a comparison of the influence of the mentioned dopants on the formation mechanism and structure of the superconducting phases in the Bi-Sr-Ca-Cu-O system. We used in the preparation of high temperature ceramic superconductors a wet chemical technique - the oxalate coprecipitation - which offers the possibility of close control of the chemical and physical characteristics of superconducting oxide powders.

The superconducting phases formation process and the properties of the resulted samples have been studied using simultaneous DTA/TGA, XRD, ceramic properties measurements, electric resistivity investigations and Mössbauer spectra measurement.

8.14 INFLUENCE OF THE TRANSITION METAL ON THE MeY HEXAGONAL FERRITE FORMATION

Marina Balasoiu, Maria Zaharescu, Georgeta Tănase and N.Drăgan
Institute of Physical Chemistry, 202 Splaiul Independentei, 77208 Bucharest, Romania

The hexagonal ferrites are oxide compounds having feromagnetic properties with high values of saturation magnetization and magneto-crystalline anisotropy. The hexagonal ferrites are also ternary compounds in the BaO-MeO-Fe_2O_3 system, where M^{2+} may be Zn, Co, Cu, Ni, etc.. It is generally accepted that in these systems five different compounds may appear, which are conventionally denoted by X, W, Y, Z, U and have a hexagonal stratified structure. It was observed that small variation of their composition or/and the existence of defects of packing of the component structural blocks determines, for a given compound, an enlargement and a shift of the X-Ray characteristics diffraction lines and has a high negative influence on its magnetic properties.

Previous studies have established that no matter the transition metal in the composition is, the MeY hexagonal ferrite ($BaO.MeO.3Fe_2O_3$) has the higher rate of formation and that it is obtained as a pure phase at lower temperature compared with the other hexagonal ferrites.

In the present work, systematic studies performed on the MeY type hexagonal ferrites (Me = Zn, Co, Cu, Ni), in isothermal and non-isothermal conditions emphasized the influence of the transitional metal on the rate and the temperature range of formation and also on the network parameters of the considered ferrites.

8.15 NEW METHODS FOR OBTAINING FINE PARTICLES OF HEXAFFERITES

Oana Carp[a], Maria Brezeanu[b], E.Segal[b], Ruxandra Barjega[c]

a- Institute of Physical Chemistry, Splaiul Independentei Nr.202, sector 6, Bucharest
b- Faculty of Chemistry, University Bucharest, Bd. Carol nr.13, sector 2, Bucharest
c- ZECASIN S.A., Splaiul Independentei Nr.202, sector 6, Bucharest

Fine particles of hexaferrites $MFe_{12}O_{19}$ (M= Ba,Sr,Pb) have been synthesized by nonconventional methods.

The methods consist in the synthesis of the precursors with high homogeneity, in which the metal ratio necessary for the mixed oxides stay in the range $1/12 < M/Fe < 1/10.5$.

It was established foe every synthesis method, the influence of the precursors' features (metal ratio, homogeneity, crystalinity, dispersion) on the final mixed oxides' characteristics' (phase composition, crystalinity, magnetic properties).

The thermal analysis performed on the hexaferrites precursors, shows in the case of barium and lead precursors an exothermic phase transformation at ~750°C, which can be associated to the ferritization or to the crystallization of the hexaferrite. The activation energy associated with this change was evaluated using Kissinger's method.

Taking into account the phase composition of the calcination residia (600-1000°C, 1-8 hours) found by using X-Ray diffraction determinations we suggest two different ferritization mechanism : one for barium hexaferrite ($BaFe_{12}O_{19}$) and another for lead hexaferrit ($PbFe_{12}O_{19}$).

8.16 ON THE CORRELATION BETWEEN THE TYPE OF WATER FROM THE FERRITIC POWDERS PREPARED BY WET METHOD AND THE STRUCTURE OF THESE POWDERS.

Viorica Muşat, Laurenţiu Frangu - "*Universitatea Dunărea de Jos*" din Galaţi, Domnească 111, 6200 Galaţi,
Oana Carp - *Institutul de Chimie Fizică "I.G. Murgulescu" al Academiei Române*, Spl. Independenţei 202, 77208 Bucureşti,
Eugen Segal - *Catedra de Chimie Fizică, Facultatea de Chimie, Universitatea Bucureşti*, Bd. Republicii 13, 70346 Bucureşti.

The development of ferritic phases in alkalinised solutions of Fe^{3+} or (and) Fe^{2+} and M^{2+} (M=Mn, Zn,Co, Ni, etc) is correlated to the removal of the various types of water to be found in the initial coprecipitates. Among the various form of water one has to mention: physically adsorbed at the outer surface water, physically adsorbed water in the pores, coordination water and constitution water. These types of water are rather difficult to discriminate due to the superposition of their removal processes.

Based on the thermogravimetric measurements, the paper presents and investigation on the correlation betweem the different types of water to be found in the powders obtained from the solution of Fe^{3+}, Fe^{2+} and Mn^{2+} (pH $\simeq$12) at various temperatures and ageing times, on the one hand, and the structure of these powders, on the other hand. This correlation provides information on the process of ageing in solution of the initial coprecipitates. The identification of the types of water in the powders have been made by deconvolution of the overall water loss process by means of a specially developed computer programme.

8.17 ORTHOFERRITES OBTAINED BY UNCONVENTIONAL METHODS

Silvia Plostinaru, Luminita Patron, Ioana Mîndru and *Dorel Crisan*
Institute of Physical Chemistry

During the past years the rare earth oxides with transition metals have been in the highlights because of their physical properties (piezoelectricity , pyroelectricity, magnetism, electro-optical effects, etc.) as well as of their applications , among which the most interesting are their use in catalytic processes or as superconductors.

Bearing in mind the importance of these mixed oxides , it seems interesting to study the different synthesis ways. A special focus will be the preparation and study of Ln(III)FeO_3 ,where Ln(III)=La-Tb ,with perovskite structure.

The first reports, recommend for perovskite preparation the methods usually used for ceramics , i.e. pyrolysis of stoichiometric amounts of the corresponding oxides or transition metal carbonate with Ln_2O_3 . The method is difficult and expensive. It requires high purity oxides, high calcination temperatures (1200-1400°C), a long processing time.

In the last years, the diversification of preparation methods was achieved. Unconventional methods have been thus been used with obvious advantages against the ceramic method.

This works deals with a comparative study on the most important unconventional methods used: hydrolysis and forced hydrolysis methods (wet methods) , thermal decomposition of alkoxides and polynuclear coordination compounds respectively. Both the precursors and perovskite oxides are characterized by physico-chemical measurements.

8.18 SYNTHESIS OF CO(II) AND CO(II)-MN(II) FERRITES FROM POLYNUCLEAR COORDINATION COMPOUNDS AND METAL ALKOXIDES

Ioana Mîndru[a], *Luminita Patron*[a], *Dorel Crisan*[a], *Maria Brezeanu*[b] *and Cristiana Bercu*[c]
a-Institute of Physical Chemistry
b-Romanian Academy
c-Institute of Chemical Research

The chemical and physical properties of oxidic materials with spinelic structure (especially ferrites) depend on the preparation method and the thermal treatment which affects the interdispersion of components and the defining of morphology. Therefore, considerable efforts have been made to develop synthesis methods which yield precursors in which two or more metals are includes in the same crystalline structure and which, after calcination, are dispersed according to requirements.

Among these methods, the thermal decomposition of polynuclear coordination compounds and metal alkoxides have been taken into account. The application of these methods requires a detailed study of their formation , in order to establish the parameters that influence the synthesis (the combination ratio of elements, the nature of the ligand, the pH of reaction medium, the temperature, etc.) and a study regarding the mechanism of their thermal decomposition accompanied by the characterization of mixed oxides resulted.

In the present work we report about the possibility of obtaining the Fe_2CoO_4 and $Fe_2(Co_{0.5}Mn_{0.5})O_4$ ferrites from the following systems:

$2Fe(III) : (M(II)_{1-x} M'(II)_x) : L$
$x = 0 - 0.5$
$L = C_2O_4^{2-}$; $HCOO^-$; CH_3COO^- ; $CH_2(OH)COO^-$; $C_4H_4O_6^{2-}$; $C_4H_4O_5^{2-}$; $C_6H_{11}O_7^{2-}$
$2Fe(III) : (M(II)_{1-x} M'(II)_x) : L'$
$x = 0 - 0.5$
L'=1,2,3 propanetriole

The precursors and the ferrites are characterized by physico-chemical measurements.

8.19 POLYNUCLEAR COORDINATION COMPOUNDS AS PRECURSORS FOR Al^{III} MIXED OXIDES.

Camelia Suciu - Research and Engineering Institute for Environment , Bucharest
Luminita Patron , Dorel Crisan , Maria Brezeanu - Institute of Physical Chemistry , Bucharest

In recent years , special attention has been awarded to the succesfull utilization of Al-mixed oxides in atmosphere cleaning . Oxides based on Al^{III} ion are the main component of catalytical supports used in the exhaust gas treatment .

The same oxides may , also , be used , in the manufacturing of filters for pollutants resulted from Diesel exhaust gases.

Industrial utilization of mixed oxides requires the obtaining of samples of reproductible composition (i. e. reproductible properties and structure) . These requirements determined the diversification of the preparation methods, improvement of classical methods and development of non-conventional methods, as e.g. thermal decomposition of polynuclear coordination compounds.

This work deals with the results of an exhaustive study concerning the utillization thermolysis in the obtaining of:

Al_2MO_4 **M^{II}=Cu,Co,Ni**
$Al\ MO_3$ **M^{III}=La - Er**
and **$Al_5Ln_3O_{12}$** **Ln=Er**

Therefore , the coordination compounds in the systems :

Al (III) : M (II) : Carboxylic acid where **M (II) = Cu,Co,Ni**
$RCOO^- = C_2O_4^{2-}$; $C_4H_4O_6^{2-}$; $C_6H_6O_7^-$,

Al (III) : Ln (III) : Carboxylic acid where **Ln (III) = La,Nd,Er**
$RCOO^- = C_2O_4^{2-}$; $C_4H_4O_6^{2-}$; $C_6H_6O_7^-$

and **Al (III) : Er (III) : Carboxylic acid** where **$RCOO^- = C_4H_4O_5^{2-}$; $C_6H_6O_7^-$**

were isolated and characterized by physico-chemical measurement (IR , UV - VIS spectra , magnetic susceptibilities) .

The oxidic products resulted from the decomposition of complex compounds were analyzed by X-ray diffraction.

8.20 Polynuclear complex compounds, precursors of the chromites of lanthanoides.

Petru Spacu*, Maria Brezeanu*, Luminița Patron**,
Valerica Pocol*, Oana Carp**, N.Stănică**, D. Crișan**.
* - Romanian Academy
** - Institute of Physical Chemistry "I.G.Murgulescu", Bucharest, Romania.

The polynuclear complex compounds obtained from Ln(III)-Cr(III)-tartric acid system, were studied in order to obtain $LnCrO_3$ oxides (Ln(III) = La - Tm) used as catalysts in depolluation reactions.

The studies had the purpose of :

- establishing the optimal conditions for obtaining the mixt complex compounds in the Ln(III)-Cr(III)-tartric acid system precursors of mixt oxides,
- describing the complex compounds by means of elemental analysis, electronic spectra, IR, magnetic measurements and therogravimetric analysis,
- characterisation of the oxidic phase by difraction with X rays and physico-chemical methods.

8.21 CERAMICS PIGMENTS BASED ON CHROMIUM

Maria Preda, Aurelia Meghea
Universitatea POLITEHNICA Bucuresti

Chromium is one of very often used in obtaining the ceramics colours and helps to their diversification. The multiple possibilities of colour variation can be result of chemical reactions with the formation of different compounds which can lead to the apparition of the most various colours as a direct consequence of their structure. In the some time, there is the possibility of forming solid solutions which takes to very stable colours in the melting silicates which constitutes the glazes. In this case, an important role is played by polieder deformation of chromium coordination which leads to d-d additional level of transition. Another possibility of colour diversification is formed by the variation of the chromium valence which can be in one or more valence states and therefore multiple possibilities of accomplishing the electronic transition. Because of these large possibilities of variation, using the chromium as chromofor, a very large colouring palette can be obtained (yellow, orange, light-brown, pink,black,etc.).

In the present paper have been synthesized masses in which the only cromofor is the chromium with the more simple or more complex composition. Beside this ther oxides have been introduced in the masse composition as for example calcium oxide, tin oxide sillicium dioxide, etc. The above mentioned oxides can react with the chromium oxide and lead to the formation of coloured compounds, as for example calcium chromate, calcium tinate, tin sphene, etc.The raw materials and the work conditions have been choosed in an advantageous way of forming either one colouring compound that gives a specific colour and it is easy to be controled or two colouring compounds that are reciprocally completing themselves. Also, other raw materials joined the composition as folowing: oxidating raw materials, raw materials that gives gloss to the colour, fluxes which create of small quantity of liquid phase that goes to the intensification of the reactions at a relative low temperature. The raw material mixture were briquetted and thermical treated at 850-1350°C temperatures.The mineralogic composition of the samples has been determinated in two ways from which the first one analytic through integration in the thermic equilibre diagram and the second one by X-ray analysis. Taking in consideration the composition and the temperature of thermic treatment it came out throught RES spectrums the valence modifications of the chromium, which can be Cr^{3+}, Cr^{4+} and Cr^{6+}. Also for an objective characterization of the colours were made the visible absorption spectrums.

3.22 HYDRATION AND HARDENING PROCESSES IN $CaO.Al_2O_3$ - SILICA FUME - H_2O SYSTEM

Maria GEORGESCU, Alina BĂDĂNOIU, Nicoleta NICHITA

University POLITEHNICA Bucharest
P.O. BOX. 12-134 Bucharest

Information about the influence of different amounts of silica fume (5-20%) and temperature on hydration and hardening processes which occur in $CaO.Al_2O_3$ - H_2O system, are presented.

The kinetic of the above mentioned processes, as well as the nature and proportion of formed hydrocompounds were studied using X-ray diffraction analysis, complex thermal analysis, chemical bound water and mechanical strengths determinations.

The presence of silica fume in the $CaO.Al_2O_3$ - H_2O system, increase the rate of $CaO.Al_2O_3$ conversion and modifies the amount of formed hydrocompounds in correlation with the temperature at which hydration occurs (23°C and 45°C).

It can be obtained increases of the mechanical properties by adding 5% silica fume, especially when the hardening is made at 45°C.

8.23

THE INFLUENCE OF CATALYST TYPE ON THE SOL-GEL PROCESS, STUDIED BY GC-MS

Maria Zaharescu[a], A. Vasilescu[a], V.Badescu[b] and M.Radu[b]
[a]Institute of Physical Chemistry, 202 Spl. Independentei, 77208 Bucharest, Romania
[b]ICECHIM, 202 Spl. Independentei, Bucharest, Romania

Sol-gel process is based mainly on the hydrolysis - polycondensation of alkoxides. Hydrolysis is most rapid and complete when catalysts are employed. Although mineral acid or ammonia are most generally used in sol-gel processing, other known catalysts are acetic acid or HF.

The effect of a variety of catalysts on the overall hydrolysis and condensation rates, as judged by the times required for gelation have been summarized by Pope and Mackenzie.

In the present work the influence of four catalysts (HCl, HF, CH_3COOH and NH_4OH) on the hydrolysis - polycondensation of TEOS is presented. The molecular species formed in the initial stages of process have been investigated by GC-MS. In all cases the reaction mixture was : TEOS/ H_2O/ EtOH = 1/1/ 1.75.

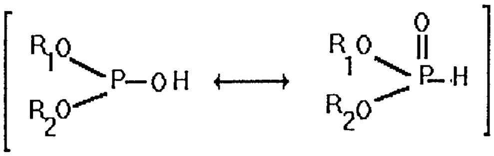
The method lets direct observation of the process, underlying that different catalysts change not only the reaction rate, but also the reaction mechanism.

The HCl catalysis leads to preferential formation of linear polymers , while in the presence of NH_4OH and HF the gelation of the samples takes place in the same time with a large amount of unreacted monomer, suggesting that the role of OH^- and F^- is similar.

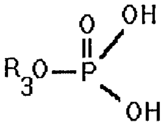
8.24 THE REACTIVITY OF THE DIALKYLPHOSPHITES AND OF THE MONO AND DIALKYLPHOSPHATES IN SOL-GEL SYSTEM

Maria Zaharescu*, N.Luta, A.Vasilescu*, Maria Grigorescu**, Ligia Todan****
***Institute of Physical Chemistry, Bucharest**
****Research Institute for Pesticides, Bucharest**

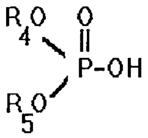
Dialkyl phosphites (I), mono (II) and dialkylphosphates (III) were synthesized and some experiments were elaborated in order to optimize the relation between the molecular structure of the organophosphoric compounds and their reactivity in sol-gel systems with TEOS:



(I)



(II)



(III)

where $R_1 = R_2 = R_3 = R_4 = R_5$ or $R_1 \neq R_2 \neq R_3 \neq R_4 \neq R_5$: $-CH_3$, $-CH_2CH_3$ etc.

The alkyl groups in the phosphite and phosphate compounds chosen had the fewest carbon atoms : $-CH_3$ and $-CH_2CH_3$.

The phosphites were synthesized by the esterification of PCl_3 with methanol and ethanol and the phosphates by partly esterification $POCl_3$ with corresponding alcohols.The esterchlorides that were obtained, gave by hydrolysis the esteracids (II) and (III).

The reactivity of the alkylphosphites and phosphates in the gel systems was studied for molar ratios P_2O_5 / SiO_2 of 0.1 /1 to 1 / 1.

The methylphosphites and phosphates had the greatest reactivity. Their gelling time decreased three times compared to that of the compounds with ethyl groups.

The gels obtained using hydroxylated precursors for P_2O_5 have a tendency to crystallize, while those obtained with un-hydroxylated precursors have the tendency to sustain a vitreous structure.The gels obtained were analyzed using physical-chemical methods (DTA/TGA, IR spectrophotometry, RX diffraction).

8.25 INTERMEDIATE-RANGE ORDER IN SILICA GELS

R.Popescu[a], R.Manaila[b], M.Zaharescu[a], A.Vasilescu[a] and G.Catana[b]
a) Institute of physical Chemistry, Spl.Independentei 202, Bucharest, RO-77208 ROMANIA
b) Institute of Physics and Technology of Materials, Bucharest-Magurele, P.O.B. MG-7, RO-76900 ROMANIA

Fresh silica gels prepared by the sol-gel route with acid (A) and base (B) catalysis display typical alteration of the X-ray diffraction (XRD) pattern in comparison with vitreous (v) silica.

The position and width of the first sharp diffraction peak (FSDP) are shown to be phenomenological quantities, permitting to follow the intermediate-range order (IRO) evolution in gels.

A positive shift of the FSDP at k_1 is noticed in fresh gels, which also shows an excess broadening. These changes can be accounted for by the alteration of the IRO in gels, in comparison with v-SiO_2. Thermal annealing causes a gradual decrease in the shift and broadening of the FSDP, suggesting that the evolution of the vitrification can be followed on the basis of XRD data. Two types of IRO alteration were explored within simulated XRD patterns. They account quantitatively for the experimental observations, using a phenomenological disorder parameter b. The evolution of b values with annealing temperature reveals well-defined stages in the vitrification process. Base-catalyzed samples show a retarded thermal evolution in comparison with the acid-catalyzed ones.

8.26 EFFECT OF ANNEALING TEMPERATURE ON THE CRYSTALLIZATION BEHAVIOUR OF AMORPHOUS PZT THIN FILMS

C.Parlog[1], M.Gartner[1], F.Vasiliu[2], A.Ianculescu[1], A.Arnautu[3], C.Cobianu[3]

[1] Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest 77208,Romania
[2] Institute of Physics and Technology of Materials, PO-BOX MG-7, R 76900, Bucharest-Magurele, Romania
[3] Institute of Microtechnology, P.O.Box 27-17, 77550 Bucharest, Romania

There is a renewed interest in the deposition of ferroelectric $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) thin films for their potential applications in non-volatile memories, pyroelectric detectors, electro-optic devices and sensors.

In this paper we analyse the influence of the technological parameters and annealing temperature on the microstructure, optical and electrical properties of PZT thin films deposited by sol-gel technique on a multilayer $Si/SiO_2/Ti/Pt$ substrate.

XRD studies of PZT indicate the coexistence of both tetragonal and rhombohedral phases for which the lattice parameters were calculated.The axial ratio c_T/a_T, indicating the degree of tetragonality, increases weakly from 1.014 to 1.023 in the 650-750^{0}C temperature range but decreases to the initial value in the last annealing step (800^{0}C). The same strange variation was also observed for the refractive index (determines by ellipsometry) which increases from 1.923 to 2.049 in the 650-750^{0}C and decreases to 1.939 for 800^{0}C. The variation of the degree of tetragonality and of the refractive index is followed in the same manner by the resistivity too.

All these facts could be correlated with the dependence of titanium diffusion rate upon the annealing temperature and thus can be explained by the titanium diffusion through the platinum layer. A {011} titanium-rich layer is formed at the Pt-PZT interface. The titanium-rich layer supplies titanium in excess for the nucleation of the tetragonal phase with either a {011}, or a {110} texture .

Thus, the annealing temperature is an important technological parameter, which by microcompositional fluctuations can determine the width of the phase coexistence range.

8.27 TIN DIOXIDE SOL-GEL DERIVED THIN FILMS OBTAINED FROM DIFFERENT PRECURSORS

C. Cobianu[1], C. Savaniu[1], Maria Zaharescu[2], Constanta Pirlog[2]
[1] Institute of Microtechnology, P.O.Box 38-160, 72225 Bucharest, Romania
[2] Institute of Physical-Chemistry, 202 Splaiul Independentei, 77208 Bucharest, Romania

In order to control air pollution and to detect toxic, flammable and smelling gases at low levels in air, efforts toward the development of simple and inexpensive semiconductor oxide gas sensors such as tin dioxide have been increased. It is well known that the sol-gel technique has several advantages such as excellent homogeneity, easy control of coating thickness, ability to coat large and complex shapes and simple and low cost processing.

In the present work tin dioxide thin films had been obtained by the sol-gel method starting from three precursors: Tin (IV) ethoxide, Tin (IV) isopropoxide and Tin (II) 2-ethylhexanoate. Starting with the three mentioned precursors, the Sb-doped SnO_2 films were also prepared. The films have been deposited by spin-coating method on three types of substrates: Si, Si/SiO_2 and porous Si wafers.

Transparent, homogenous and crack-free SnO_2 films have been obtained in all cases. The thickness of the solid films as well as the other physical properties of the starting solutions, strongly depend on the used precursors. The microstructure of the obtained films was characterised using XRD, IR spectroscopy, TEM, ED-XTEM analyses. For all substrates, preliminary X-ray diffraction measurements indicated that the initial films are amorphous.

The thin films deposited on porous silicon were analysed by XTEM and RBS techniques. The results confirmed the presence of SnO_2 in the pores. This fact leads to the increasing of the specific area and improves the surface properties of the substrate, that is convenient for its applications in gas sensing field.

A test device for determination of the sensing properties of this structure - Si/porous Si/SnO_2 - has been realised. Preliminary experiments in detection chamber with controlled atmosphere are under way.

- The research is performed in the frame of the European COPERNICUS program (Project CP 940963), coordinated and financed by the European Union.

8.28 VANADIUM DOPED SOL-GEL TiO_2 COATINGS.

Maria Zaharescu[a], Maria Crisan[a], Rodica Ion[b], Mihaela Manolache[c].

[a] Roumanian Academy, Institute of Physical Chemistry, 202, Spl.Independentei,
77208 Bucharest.
[b]ZECASIN S.A., 202, Spl.Independentei, Bucharest.
[c]Chemical Research Institute ICECHIM, 202, Spl.Independentei, Bucharest.

TiO_2 sol-gel films have found wide applications for various optical coatings, porous coatings, photocatalysts, photoelectrochemical coatings and sensors. During the last decade, TiO_2 films doped with transition metal ions have been suggested as electrochromic materials for display devices. In the case of vanadium doped TiO_2 films these exhibit high electrochemical conductivity and have been suggested for potential application as antistatic coatings or switchings.

In the present work a study of the experimental conditions of the obtaining of vanadium doped sol-gel TiO_2 coatings has been carried out. Tetraethyl orthotitanate was employed as TiO_2 source and VCl_3, $VOSO_4 \cdot H_2O$ and $VOSO_4$ solution in H_2SO_4 where employed as vanadium sources.

Supported materials have been obtained by dip coating method on silicon wafers, carbon spectral electrodes and titanium electrodes. The presence and valency of vanadium ion has been evidenced by UV-VIS absorption spectra, IR spectroscopy and X-ray diffraction, both on supported and unsupported coatings. The measurements have been made on initial and thermally treated samples at temperatures ranged between 100-300°C. The thermal treatment temperatures have been established according to the DTA/TGA results.

The vanadium doped sol-gel TiO_2 coatings have been used as sensors in electrochemical processes. The influence of both the thickness of films and the nature of substrate has been investigated.

8.29 STUDII ASUPRA MICROSTRUCTURII XEROGELULUI DE Al_2O_3 OBTINUT DIN ISOPROPOXID DE ALUMINIU MODIFICAT CU ACID ACETIC

Luminița Nimară*, Aurel Iovi, Iuliu Menessy**, Ana Nimară*****
***- Institutul de Electrochimie Timișoara**
**** - Universitatea "POLITEHNICA"Timișoara- Facultatea de Chimie**
*****- Academia Română - Filiala Timișoara**

ABSTRACT

Microstructure of Al_2O_3 xerogels prepared from aluminium isopropoxid $Al(O^iPr)_3$ modified with glacial acetic acid (Acac), was investigated for controlling the microstructure of Al_2O_3. The specific surface area and the pore size distribution of these gels heat-treated at various temperatures are measured. From the results obtained, the effects of Acac contens, heating temperatures, and the drying process on the microstructure of the gels are discussed.

8.30 ASPECTS OF THE IMMISCIBILITY IN GLASSES OF THE $PbO-B_2O_3-SiO_2$ SYSTEM

Petru Baltă
University "Politehnica", faculty of Industrial Chemistry,
department Science and Engineering of Oxidic Materials

The system $PbO-B_2O_3-SiO_2$ is of interest both for very extended immiscibility area and for low melting temperatures of many compositions. Thus the system is convenient for studying different features of glass melts immiscibility.

Were synthesised some glasses in the binary system $PbO-B_2O_3$, then adding SiO_2 up to the rise in melting temperature above 1100 °C. The kinetics of the microphases dissolution and melt demixing have been followed using an own method. The expansivity determination on some glasses evidenced the interesting phenomenon of the presence of two T_g temperatures corresponding to the two separated glasses.

Using Cu^{2+} as an indicator ion the glasses basicity was experimentally determined. It was possible to follow the basicity modification of both separated glass phases. By comparing the experimentally determined basicity values with the calculated ones some hypotheses were drawn, concerning the compositions and structures of separated glasses. The results are in good agreement with the existing in the specialised literature data.

The presented data seems to allow the use of the theory of Flory elaborated for immiscibility of organic polymer solutions for understanding the causes of the apparition of this phenomenon in borate and silico-borate glasses.

The studied glasses have some useful properties too.

8.31 CHEMICALLY RESISTANT GLASSES TO BE USED FOR RESIDUE INERTIZATION.

—Mariella Constantinescu, Georgeta Jitianu, Chiamiran Vuap and Mircea Olteanu.
Romanian Academy, Institute of Physical Chemistry "I.G.Murgulescu",
Splaiul Independentei Nr.202, 77208 Bucharest, Romania.

The total amount of industrial and domestic waste, only in western Europe, is about 2.2 billion tones/year and that made it necessary to find the means to turn it into some stable, inert materials.

Incineration followed by a vitrification of the solid compounds thus obtained is a world widely employed procedure to produce glasses which immobilize the heavy metal compounds within the silica network in order to avoid the re-circulation back into the environment, by "free water" solubilization, of the highly pollutant substances.

The solid residues (flue ashes, slags and electro-filter dusts) obtained at waste incineration contain mainly SiO_2,Al_2O_3,CaO,K_2O (components common for most usual glasses) and also a large number of heavy metal oxides. The possibility to controll the "immobility" of heavy metal oxides is an important task for environmmental protection.

A series of "synthetic residues" of compositions similar to those of the real materials were prepared on laboratory scale. They were polyoxidic compounds obtained by melting together up to 12 components at 1400-1450°C and then the mixture quenched quickly in cold water. In order to obtain highly chemically resistant materials, several adjustments of the glass composition were made, that is compounds such as SiO_2, Al_2O_3,TiO_2,ZrO_2,PbO were added.

Leaching tests were performed on all glasses and then pH and electrical conductivity measurements made on the solutions thus resulted.

Electrical conductivity measurements were also made in some glass melts whose compositions were so chosen as to be placed within the metastable glass domain on the phase diagram of SiO_2-K_2O-PbO system.

The equations expressing the temperature variation of the melt conductivity may be used to compute the limiting values corresponding to highly stable glasses.

A direct correlation could be established between the electrical conductivity of the melts and the weight losses registered on leaching, which allows for some adjustments of the glass composition during the melting process.

8.32 STRUCTURE AND PROPERTIES OF HYPEREUTECTIC Al - Si ALLOYS OBTAINED BY LIQUID STATE QUENCHING AND SOLID STATE QUENCHING

Maria Petrescu*, Mirela Britchi**, N.Petrescu*, Mihaela Danescu**,
Elena Maria Anghel**, I.Pencea*

* Polytechnic University of Bucharest, Materials Science and Engineering Faculty,
Spl.Independentei 313,Bucharest,Romania
** Institute of Physical Chemistry,Romanian Academy,Spl.Independentei 202,
Bucharest,Romania

Rapid solidification or liquid state quenching is known to be a powerful mean to produce metastable structures in aluminum alloys, showing increased solid solubility, grain refinement or even or even amorphous structures. Rapid solidification of Al-Si alloys increased the solid solubilities up to hundred of times out of the equilibrium value and led to a micronic and even submicronic dispersion of the brittle secondary phases. Also it is known the fact that solidification rate achieved during the process has strong influence on the degree of metastability of the obtained structures. In order to have an insight on how strongly is this influence acting on the microstructure, experimental studies have been conducted in binary aluminium cast alloys (hypereutectic Al-Si alloys having silicon content 30% at.). The solidification rate was continuously increased from values specific to equilibrium conditions up to values approaching the high rate solidification range, by using a specially designed V shaped copper mold.

The aluminium-silicon alloy, with composition of 30% Si ,.was quickly quenched from the melt at cooling rate of 10^5 K s^{-1}, using melt -spinning technique. The ribbons were irregular, varying in thickness from about 10 μm to 100 μm. The obtained ribbons were investigate by optical microscopy, microhardness measurements, differential scanning calorimetry (DSC) and X-ray diffraction methods. Solid-quenching (SQ) material was obtained by annealing melt-spun ribbons of the composition 30% Si, in vacuum during 5 minutes at following temperatures: 423, 623, 673, 723, 773, 823 K, followed by quenching in ice water. All SQ ribbons were investigated by optical microscopy and microhardness measurements. The termic treatment increases the grain size and progresses the precipitation/coarsening of the second phase contributed to a drastic decrease in hardness. For liquid quenching ribbons (LQ) of compositions 30% Si we obtained values of microhardness of $HV_{(10gf)}$=270-202 Kgf/mm^2 and for SQ ribbons of this composition, the values obtained were:$HV_{(10gf)}$=121-95 Kgf/mm^2.

8.33 THE INFLUENCE OF SOME FACTORS ON THE ORIENTED CRYSTALLISATION PROCESS OF SOME LOW SOLUBILITY ELECTROLYTES

Gabriel Balea, Ludovic Sayti, Andrea Balea
Romanian Academy, Institute of Chemistry Timişoara, Bdv. Mihai Viteazu, nr. 24

The researches made by the authors were to clarify the mechanism of interference of some factors in crystallisation process (electrostatic potentials on the crystal faces, structure of surfaceactive agents) and so they can influence the crystalline habitus of some calcium and magnesium low solubility compounds.

The experiments concerning the preparation of undermicronic size calcium carbonates, used in PVC compounds for special use, lead to the idea that there is a dependence between the structure of surfaceactive agents and his way of action .

The way of action of surfaceactive agents could be explained by two kind of parameters: the geometrical parameter and the atomic charge for "key" atoms, which are essential in the process of binding and forming crystal, and steric parameter of molecule respectively, gets from the atomic coordinates of optimised molecule by MM+.

On the basis of experimental data and the value of ellipsoidal parameter which were calculated for the surfaceactive agents molecules (lauric acid, palmitic acid, stearic acid) it was possible to get a calitative dependence between the size of axe on hyhrocarbonate radicals direction and the forming capacity of a hydrofob layer on the crystal surface.

Using as a parameter the electrostatic potential on the crystal faces, it was possible to establish the area in which the binding of surfaceactive agents was mainly made in this way offering an explanation for the forming of some crystal with regulate habitus and dimensions about 75 - 100 nm, and crystal habitus in the shape of needles respectively.

8.34 EXPERIMENTS OF COPPER LEACHING FROM ORES

Varga Camelia - *University of Baia Mare*

The purpose of present work is to find out the optimal work conditions, as well the leaching agent, for the hydrometallurgical treatment of complex ores from zone, with the view of copper extraction.

For this purpose, there was maked attempts to solubilization for two types of ores, more exactly, ore from Cavnic mine and ore from Baia Sprie mine. There was maked the chemical and mineralogical analysis of ores.

It was haved in view the influence of particle size concerning copper solubilization. Also, it was haved in view the influence of temperature and the effect of mechanic agitation concerning copper solubilization. It was, also, used leaching agents of variated concentrations.

8.35 ION-EXCHANGE INTERDIFFUSION COEFFICIENTS

Ana-Maria Oancea, Eugen Pincovschi, Cristina Barbulea, Nora Spiru
Faculty of Industrial Chemistry, University "Politehnica" Bucharest
1, Polizu Street, OP 12, Bucharest

The knowledge of ion-exchange rates are very important in ion exchange chromatography, elimination and/or recovery of ions from waste waters, and even in using monofunctional organic exchangers as prototypes of ion-exchange processes occuring in natural systems as proteins, cell membranes, nerve fibres etc.

It has been established that the rate-determining step in ion exchange is the interdiffusion of counter-ions, except systems using resins with chelating groups, in which the chemical reaction is the slower process. When ion exchange is considered only a diffusion phenomenon the rate of exchange is controlled by interdiffusion of counterions either in the resin particle ("particle diffusion control") or in an adherent liquid diffusion layer ("film-diffusion control"), which is not affected by stirring.

The systems investigated were: a) strong-acid cation exchangers (copolymers styrene-divinylbenzene (8%), sulfonic functional groups, in hydrogen form) type gel (Vionit CS-3, Purolite C-100) or macroporous (Vionit CS-32, Duolite CS-101) and Na^+, Cu^{2+}, Zn^{2+}; b) strong-base anion exchanger resin type I in hydroxide form (Vionit AT-1) and Cl^-, Br^-, NO_3^-, SO_4^{2-}.

The kinetics of ion exchange was investigated by using a potentiometric method, following the pH variation in time, with a pH-meter Mettler-Toledo, instead of a radiochemical method as usually.

In concentrated solutions (1N) the rate determining step is the interdiffusion of counter ions within the ion exchanger itself. The interdiffusion coefficients of the Nernst-Planck model were obtained for H^+/Na^+, H^+/Cu^{2+}, H^+/Zn^{2+}, HO^-/Cl^-, HO^-/Br^-, HO^-/NO_3^-, HO^-/SO_4^{2-}. The experimental results are in agreement with the literature data and support a particle diffusion control mechanism. The influence of the nature of the ion, the resin matrix (gel or macroporous) and the particle size on the interdiffusion coefficient is revealed. The pontentiometric method proposed is discussed and compared with the radiometric methods. The experimental curves were fitted using spline functions. Linear regressions with good correlation coefficients were employed in order to obtain the interdiffusion coefficients.

8.36 VISCOSITY AND EXCESS VISCOSITY OF MIXTURES CONTAINING 1,4-DIOXANE

O. IULIAN, C. MATEESCU, O. LANDAUER, L.HAMPLEA
Dept. of Physical Chemistry, POLITEHNICA University BUCHAREST
Spl.Independentei, 313

Viscosities and excess viscosities for some binary and ternary mixtures containing 1,4-dioxane, sulfolane, tetrahydrofurane, methanol and water are presented at 303.15 and 313.15 K over the whole range of mixture composition.

Some of the models suggested in the literature for correlating and representing the viscosity of the binary and ternary systems of liquids are reviewed. A new model and some of the models in the literature are applied to the above systems. The correlation both for evaluating the quality of experimental data (by means of statistical parameters) and for introducing the results in computer data bases is made.

Experimental data were correlated and compared with McAllister, Redlich-Kister, NRTL/ν models. The excess viscosities were also correlated by the Redlich-Kister type equation. The results of the testing of the viscosity models are presented. The best correlation for every system was established.

9.1 Recent developements in the Minimal Steric Difference (MTD)-method

Z.Simon
Department of Biophysics, University of Medicine and Pharmacy, P-ţa E. Murgu nr. 2,
1900-Timişoara, Romania

Recent developement in the MTD-method are reviewed, together with description of QSAR-results and of predictive value, as indicated by a cross-validation-like method. These developments refer to use of docking methods for the construction of hypermolecules, inclusion of multiple low energy conformations of ligand molecules and of their calculated conformational energies. The series for QSAR include gestagenic steroids, protein-kinase activating cyclonucleotide derivatives, polyhalogenated arylic derivatives with dioxin-type activity, oligopeptide binding to HLA-protein. These series contain up to 75 molecules with large variations in stereochemistry.

As compared with CoMFA, MTD-results are more related to ligand molecule structure, MTD is less computer time consuming, but CoMFA benefits of a very friendly computer program, and hypermolecule construction is difficult for molecules with complicated condensed cycles. Predictive **r^2** (CV) values of MTD are similar to those of CoMFA, suggesting that the the two methods represent similar quality of approximation for the force field implied in ligand-receptor interactions. 3D-QSAR-methods and structural parameters used for QSAR are compared with partial dehidration effects and force fields which are expected to determine the ligand-receptor affinity.

9.2 A Multiconformational Approach to Biological Activity. MTD-ADJ: Multiconformational Minimal Topologic Difference for Determining Bioactive Conformers.

Ludovic Kurunczi, Tudor I. Oprea, Traian Sulea

University of Medicine and Pharmacy Timisoara, P-ta Eftimie Murgu 2,
1900-Timisoara

A typical pharmacological assay (100 μL probe: 10^7 cells/mL, each with 10^4 receptors/cell and 10^{-9} M ligand concentrations) means that at equilibrium the measured biological activity value is averaged over 10^{10} ligand-receptor pairs, over a long period of time, typically 10 - 20 minutes.[1] Also recently have been demonstrated[2] that differences exist between single-biological molecule activities. Thus experimental biological activity (Y_{exp}) is a function of substance, statistically averaged over large numbers of ligand-receptor pairs and long period of time. If this property is also the result of a single conformer's interaction with the binding site (only) we should adjust the biological activity (Y_{adj}) using a correction factor (e.g. the Boltzmann partition function) for the relevant conformers.

$$Y_{\exp} = -\lg c_T \qquad c_F = \alpha_F \cdot c_T \qquad \alpha_F = \frac{g_F \cdot e^{-U_F/RT}}{\sum g_i e^{-U_i/RT}} \qquad \Rightarrow \quad Y_{adj} = Y_{\exp} - \lg \alpha_F$$

These was incorporated in the flow of the multiconformational MTD 3D-QSAR and the method tested on the acetylcholinesterase hydrolysis rates for a series of 25 acetic esters.[3] The summary of the results are in the next table and equations.

Statistic index	3D-QSAR model	MTD-MC	MTD-MC-ADJ
r^2	MTD+σ^*	0.948	0.966
q^2 (CV2)	MTD+σ^*	0.806	0.810
q^2 (LOO)	MTD+σ^*	0.834	0.777

[r^2 - conventional regression coefficient, q^2 - predictive regression coefficient obtained by the leave half out (CV2) and leave one out (LOO) cross validation method, respectively]

$$Y_{exp} = 2.45\ (\pm 0.28)\sigma^* - 0.76\ (\pm 0.04)\mathrm{MTD} + 8.47\ (\pm 0.26)$$

$$Y_{adj} = 2.95\ (\pm 0.28)\sigma^* - 0.88\ (\pm 0.04)\mathrm{MTD} + 12.94\ (\pm 0.38)$$

The crude (unadjusted) and the adjusted multiconformational models being comparable and statistically significant one could select the active conformations for the studied series. The optimized conformational map of neutral ligands thus obtained was graphically overlapped in the active site of crystallised acetylcholinesterase from *Torpedo californica*.

1. T.I. Oprea, Speech at the Gordon Conference, QSAR, August 1995, Tilton, USA

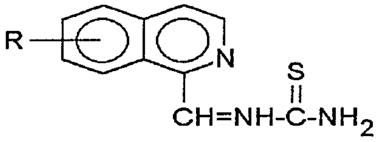
2. Q. Xue, E.S. Yeung, *Nature*, 373, 681 (1995)

3. J. Jarv, T. Kesvatera, A. Aakvisaar, *Eur. J. Biochem.*, 67, 315 (1976

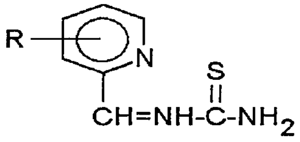
9.3 INVESTIGATION OF THE RELATIONSHIP BETWEEN ANTITUMOR ACTIVITY AND CHEMICAL STRUCTURE OF THE THIOSEMICARBAZONE DERIVATIVES

Dimoglo A.S*., Chumakov Yu.M**., Dobrova B.N.*
(*) Institute of Chemistry, Academy of Science, Kishinev.
(**) Institute of Applied Physics, Academy of Science,
Kishinev.

In the frameworks of the electron - topological approach (ETA) the `structure-antitumor activity` relationship was investigated for a series (70 compounds) of thiosemicarbazone derivatives (1,2)



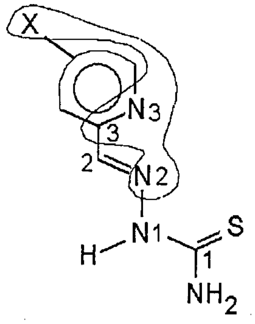
(1)



(2)

Following the scheme of ETA, conformational analysis and quantum - chemical calculations were carried out for all compounds. The revealed activity feature showed a satisfactory description of the class of active compounds according to two different parameters α_a and P_a estimating the probabilities of the feature realization in the class of active compounds.

The fragment of activity is presented by a group of atoms entering in the heteroaromatic ring and thiosemicarbazone.



X	N3(N2)	C3(C2)	N2(S)
-0.21 ± d1	5.00 ± d3	5.10 ± d3	7.09 ± d3
	-0.15 ± d1	1.43 ± d2	2.90 ± d3
		0.11 ± d1	2.34 ± d3
			-0.10 ± d1

The data resulting from the electronic structure calculations for the series of compounds under investigation were used for constructing the quantitative model of SAR (QSAR). Biological activities are evaluated as pC 50 . The multistep regressional analysis is used to provide an empirical link among the observed values of pC 50 and the parameters presently calculated. HOMO energies (E homo), the difference in the HOMO\LUMO energies (Δ E) and the charge on the atom of nitrogen N3 (Q^N) were taken as independent parameters.

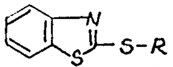
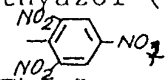
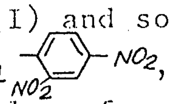
$$pC50 = 37.34(\pm 4.17) + 2.87(\pm 0.42)E(homo) + 0.46(\pm 0.28)\Delta E - 20.23(\pm 3.48)Q^N$$

The results obtained enable us to apply the rules stated above to the purposeful search of new compounds capable of demonstrating antitumor activity.

9.4

LIPOPHILICITY STUDIES OF SOME 2-MECAPTOBENZTHYAZOL DERIVATIVES USING PARTITION DATA

V.E.Sahini[a], Gabriela Ioniţă[b], P.Ioniţă[c], Cristina Popa[a]
a.University of Bucharest; b. University of Piteşti;
c. Institute of Physical Chemistry, Bucharest

In QSAR studies which involve as molecular parameters the apparent lipophilicity (R_M) and the specific hydrophobic surface area (b), thin layer chromatography and reverse phase thin layer chromatography has been applies in the case of 2-mercaptobenzthyazol (I) and some of its derivatives  where R is:  , $-CH_2COOH$, $-CH_3$, $-COCH_3$, $-COC_6H_5$, $-CO(CH_2)_{11}CH_3$. The R_M value of each compound was determined according to the equation: $R_M = \log(1/R_F-1)$ and $R_M = R_M + bc$, b value being obtained from linear correlation between R_M^o of the compound and the concentration (c) of organic solvent in the eluent. As stationary phases were used silanisiert silica gel, silica gel impregnated with paraffin oil, cellulose impregnated with paraffin oil, and polyamide. The mobile phase was water-acetone mixtures. The obtained results show the lipophilicity dependence of both stationary phase and compound structure. In the case of the first three derivatives, R_M value are higher probably because their very polar groups are^{o}able to strength the interaction with the stationary phase. MO-CNDO calculations of atomic charges for some of studied molecules are used in order to support several proposed mechanisms of their interaction with biomolecules. (I) and some of its derivatives are physiological active, used to control some moulds and insect population.

9.5 STRUCTURE-ACTIVITY STUDY OF A SERIES OF ANTIFUNGAL N-PHENYLSUCCINIMIDES

Maria Mracec[a], M. Mracec[b], Z. Simon[c] and G. Náray-Szabó[d]

[a] Romanian Academy, Timisoara Branch, Inorganic Chemistry Laboratory, Bv. Mihai Viteazu 24, R-1900 Timisoara
[b] Western University of Timisoara, Faculty of Chemistry, Department of Physical Chemistry, Str. Pestalozzi 16, R-1900 Timisoara
[c] Medicine and Pharmacy University of Timisoara, Department of Biophysics, Spl. T. Vladimirescu 14, R-1900 Timisoara
[d] Eötvös University of Budapest, Department of Theoretical Chemistry, Pázmány Péter sétány 2, H-1117 Budapest

N-Phenylsuccinimides with different substituents on the benzene ring possess antifungal activity against *Botrytis cinerea* [1]. To understand how the substituents affect biological activity, quantitative structure-activity relationships (QSARs) of 61 compounds were analysed using simple or multiple linear regressions. The descriptors used in correlation with pI_{50} (log of the reciprocal of the molar concentrations for 50% inhibition of mycelial growth of *B. cinerea*) were of steric, electronic and lipophylicity nature. As electronic descriptors (calculated by AM1 method) were used different local (net charges on phenyl ring atoms) or global properties (energy of HOMO and LUMO, absolute hardness (defined as semi-difference of HOMO and LUMO energies), electronic chemical potential (defined as semi-sum of HOMO and LUMO energies)). There were tried two types of lipophilicity calculated either as logP according to Suzuki, or as average electrostatic potential, AEP. Both descriptors had been calculated for the whole molecule or for the groups bonded at 3- and/or 5-positions of the phenyl ring. Minimum Topological Differences, MTD, was used as steric descriptor. All obtained correlations were tested statistically by a cross-validation-like method. The correlation coefficients, r^2, had values between 0.773 and 0.876 and cross-validated correlation coefficients, r^2_{cv}, between 0.647 and 0.814. The QSAR models suggested that the steric effects are important for the antifungal activity of the N-phenylsuccinimdes, especially the presence of the substituents at 3- and/or 5- positions of the phenyl ring. MTD descriptor explains almost 80% from variance data. The correlations with HOMO and LUMO energies have low correlation coefficients. However, the correlations are statistically significant and they support the idea of a charge transfer mechanism between the ligand and the receptor site. The lipophilicity descriptors correlate only marginally with biologic activity. For some related compounds the antifungal activity was calculated with QSAR models obtained in this work.

References

[1] K. Kamoshita, C. Takayama, J. Takahashi, and A. Fujinami, **Rational Approaches to Structure, Activity, and Ecotoxicology of Agrochemicals**, Eds. W. Draber and T. Fujita, CRC Press, Boca Raton, 1992, p. 430

9.6 THE BINDING OF VIOLAMYCIN BI TO POLY C

Tatiana Oncescu, Mihaela Ştefan, L. De Maeyer*
Department of Physical Chemistry, Faculty of Chemistry,
University of Bucharest, R-70346 Bucharest, Bd. Carol 1 nr. 13
*Max-Planck-Institut für Biophysikalische Chemie,
POB 2842, D-37018 Göttingen,Germany

Our results on the binding of VBI to poly C at small and medium values of the concentration ratio p (0-12) were obtained spectrophotometrically in a phosphate-EDTA buffer, pH 7 and ionic strength I=0.02 M,using the procedure of Schwartz.One determined firstly the dimerization constant $K_d=732\ M^{-1}$ of the free VBI and then the binding constant $K_{st} = 3.3 \times 10^4\ M^{-1}$ characteristic to the formation of a stacked complex (VBI-poly C). One determined also the number of binding sites per monomeric segment of polymer and the cooperativity parameter q=13 which measures the extent of cooperativ interaction between nearest neigbours, $q=K_{st}/K$, K being the equilibrium constant of nucleation process, 2500 M^{-1}. Theoretically such binding is favored at very high concentration of poly C when one binds izolated monomeric VBI on the chain.

In our case at large p values up to 300 we evidenced the formation of bound dimers, by the increase of the molar absorption coefficient ε, until a value which remain constant between 90-300, not far from that of the free dimers in solution in the absence of poly C. These bound dimers are the most stable arrangement of two neighbouring ligands, which is different from the stacked structure at low p. The circular dichroism spectra confirmes our supposition. It was not possible to determine experimentally the equilibrium constant for dimeric binding K_{db} but we estimated the lower bound value :

$$K_{db} = K_{st}^2 \ /\ qK_d = 1.1 \times 10^5\ M^{-1}$$

as well as the upper bound one : $K_{db} = K^2 = 6.3 \times 10^6\ M^{-1}$.

Our results permitted some structural considerations.

9.7 SPECTRAL MONITORING OF THE INTERACTION OF EPIRUBICIN AND DOXORUBICIN WITH DNA

E.Volanschi, M.Hillebrand, L.Vijan
Department of Physical Chemistry, Faculty of Chemistry, Bucharest University
Bucharest, B-dul Republicii 13, RO-70034, Romania

Purpose: Epirubicin and doxorubicin are anthracyclin antibiotics which induce better responses in leukemia and have lower toxicity than daunomicyn. They are believed to act by direct interaction with DNA. The present paper investigates comparatively the binding properties of epirubicin and doxorubicin to calf-thymus DNA using spectrophotometric titration methods.

Methods: The analysis of the absorption spectra was made using deconvolution techniques. The equilibrium binding data were analysed in the frame of the Mc Ghee and Von Hippel modell, taking into account complicating effects due to ligand dimerization as developed by Schwartz and Watanabe (J. Mol. Biol. 1983, 163, 467-484).

Results: The cooperative binding constant, the degree of cooperativity and the number of binding sites per polymer segment are determined for both epirubicin and doxorubicin at three different ionic strngths (NaCl added). The influence of the ionic strength is outlined. From the dependence of the binding constant on the concentration of the Na^+ ions the contribution of the electrostatic interaction of the drug with DNA is evaluated.

Conclusion: Comparison of the results obtained for epurubicin and doxorubicin with those on model cationic dyes points out a smaller contribution of the electrostatic external binding as against that due to intercalation.

9.8 DNA-PSORALEN INTERACTION

Rodica Repanovici, Oswald Horer
"Stefan S. Nicolau" Institute of Virology

The psoralens or furocoumarins are suitable photoprobes for the study of different cell constituents structure and function. Their photoreactivity has found application in practical purposes as biology or medicine. Owing to their chemical structure and properties, psoralens interact especially with the 5,6-double bond of thymine residue.

Not all the reactions involved have been fully elucidated as therapeutic mechanisms or thermodynamic parameters.

The use of psoralens in the treatment of psoriasis - a skin disorder in humans, and the side-effects of this therapy focused the interest on the influence of these drugs which interact with DNA in B conformation (a prerequisite condition), in aqueous solution, by a three-step-reaction. The first step consists in the planar drug intercalation between the base pairs, the so-called dark reaction. The second step of this reaction involves the addition of the drug molecule to the pyrimidine moiety, forming a monoadduct under UV-A light (λ=365 nm) action. In the third step, a diadduct is formed, and as a result crosslinks between the two DNA strands appear.

From different biological experiments on the influence of UV-A dose on the transformation capacity of the pH2.3 DNA plasmid complexed with 8-methoxypsoralen (8-MOP) at different ratios, some thermodynamic parameters have been calculated.

9.9 STERIC AND ELECTRONIC EFFECTS IN DYE-CELLULOSE BINDING

[φ] *Simona Timofei*[a], *Ludovic Kurunczi*[a], *Walter Schmidt*[a] *and Zeno Simon*[b]
[a] *Institute of Chemistry, Romanian Academy, Bul. Mihai Viteazul 24,*
1900 Timisoara Romania
[b] *Departmant of Biophysics, Department of Physiology, University of Medicine*
and Pharmacy, P-ţa. E. Murgu 2, 1900 Timisoara, Romania

The present review includes results of many recent published papers. Molecular mechanics, quantum chemical and statistical methods used in the QSAR methodology are applied to dye-cellulose fibre binding. Dye-fibre interactions are considered similar to ligand-biological receptor ones. Electrostatic interactions are dominant in comparison to the steric effects. Hydrogen bonding and dipole interactions are noticed as polar effects. Increasing positive charges in the dye molecules yield increased dye affinities for fibre. Sterical effects are dominant in molecules with extended aromatic area.

9.1o COOPERATIVE EFFECTS IN ENZYMIC OXIDATION IN MIXED SOLVENTS

D.Oancea, Adina Raducan,
Department of Physical Chemistry,Faculty of Chemistry,
University of Bucharest, bd.Republicii no. 13, Bucharest

The oxidation of hidroquinone in the presence of bacterial tyrosinase obtained from a strain of Streptomycetes was studied in several mixed solvents:MeOH,EtOH,nPrOH,2 PrOH or nBuOH and water in different quantities.

In all these solvents the enzyme exhibited an allosteric behaviour.

The curves [S]=f(t) were fitted on polynomials of 4-th degree and the rates of enzymic reaction were obtained by the differentiation of these polynomials.

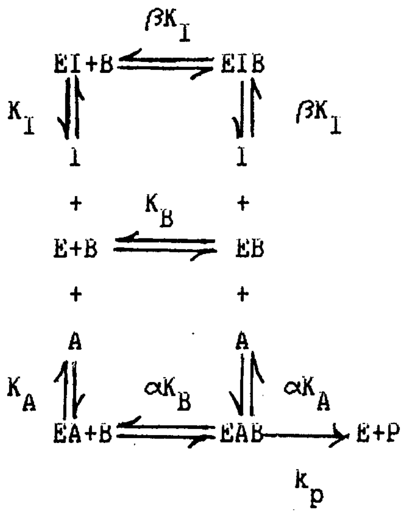
The curves V=f([S]) were processed by nonlinear regression, on the Hill equation, using for the initial estimates of parameters the values obtained from a linear regression assuming different values for cooperativity factor.

The results obtained show the high activity of this enzyme in mixed solvents as compared to water solution.

9.11 INHIBITOR EFFECT ON GLUTATHIONE-S-TRANSFERASE ACTIVITY

Tatiana Oncescu, Laura Chirică, Marinela Borca, S. Cincă*
Department of Physical Chemistry, Faculty of Chemistry,
University of Bucharest, Bd. Carol I, nr. 13, Bucharest, R-70346
*Institute of Oncology, Bd. Fundeni, nr.252, Bucharest, R-72425

In the presence of inhibitors (I) the reaction between gluthatione (GSH) and an electrophylic agent catalyzed by glutathione-S-transferase (GST) takes place according to the following scheme:



A = 1-Cl-2,4 Dinitrobenzene
B = Gluthatione (GSH)
I = inhibitors : Benzochinone (BQ)
and Hydrochinone (HQ)
P = reaction product, thioether

The kinetic treatment permitted the evaluation of the factor β and the dissociation constant K_I of the enzyme-inhibitor complex EI. The other parameters α, K_A, K_B and k_p, are known from the study of the same reaction in the absence of inhibitor.

We determined from our experimental data the factor β = 7.5 and the dissociation constant $K_I = 1 \times 10^{-10}$ mM when the inhibitor is benzochinone and in the case of hydrochinone β = 2.5 , $K_I = 4 \times 10^{-9}$ mM.These values show that both complexes EI are very stable but one notices a much more effect of benzochinone. This result is confirmed also by the value ID_{50} which represents the inhibitor concentration for which GST activity is reduced to 50 per cent. Such results are important to find suitable inhibitors in the treatment of chemotherapeutic drug resistance tumors.

9.12 A COMPARATIVE KINETIC STUDY FOR THE HYDROLYSIS OF TWO ARYL PHOSPHATE MONOESTERS BY ACID PHOSPHATASE

Carmen Postolache*, C. Postolache**, V. Em. Sahini*
*University of Bucharest, ** Atomic Physic Institute

The aim of this study was to make a comparison between the hydrolysis catalysed by acid phosphatase of two aryl phosphate monoesters, differing only in the structure of the phenolic leaving groups. Information about the nature of the transition - state structure in the phosphorylation step maybe obtained from correlation of kinetic parameters of the two substrates with their electronic structure.

Acid phosphatase was separated by Sephadex G-200 filtration from cock seminal plasma.

Optimum parameters for enzyme action were determined: pH = 5, t = 50°C, substrate concentration of 6 μM for p-nitrophenyl phosphate (pNPP) and 0.8 μM for o-carboxyphenyl phosphate (oCPP). K_M and k_{cat} values for phosphatase catalysed hydrolysis of pNPP and oCPP were measured at pH = 5 in the temperature range 25 - 55°C. At 323 K, the values obtained for K_M are 1.67×10^{-3} M for pNPP and 6.9×10^{-4} M for oCPP and for k_{cat} : 19.1×10^{-4} s^{-1} for pNPP and 5.89×10^{-4} s^{-1} for oCPP. The ratio k_{cat}/K_M expresses a higher catalytic efficiency of the enzyme for pNPP hydrolysis as compared to oCPP hydrolysis.

The values of rate constants k_{cat} at various worked temperatures permitted the calculation of the activation energy ΔE^* and the preexponential coefficient A, by plotting Arrhenius equations for both substrates. With the values obtained, the activation enthalpies ΔH^*, the activation entropies ΔS^* and the activation free energies ΔG^* were calculated. The activation enthalpy at 323 K is about 3 times higher in the case of oCPP (20.76 kcal/mol) as compared to pNPP (6.64 kcal/mol), indicating a lower reactivity of the complex enzyme-substrate (ES) for oCPP. The activation entropy ΔS^* is more negative in the case of pNPP (-48.37 cal/mol · K), which suggests a more ordered structure of the transition state with a greater possibility of charge separation and formation of products as compared to oCPP substrate ($\Delta S^* = -6.88$ cal/mol · K).

These data correlate with the values obtained for ΔG of the ES complex formation in both cases, the slightly more negative value for oCPP (-4.65 kcal/mol compared with - 4.09 kcal/mol for pNPP) suggesting a higher affinity of the enzyme for this substrate and a higher stability of the ES complex in this case (with a lower reactivity).

The kinetic and thermodynamic data are supported by data obtained as a result of quantum mechanical treatment applied to both substrate structures.

13

CROSS-LINKED AMYLOSE AS MATRIX FOR DRUG CONTROLLED RELEASE. PHYSICAL AND CHEMICAL PROPERTIES

P. Szabo [1], *Y. Dumoulin* [2], *L. Cartilier* [2], *V. Lenaerts* [3] *and M. A. Mateescu* [1]

[1] Department of Chemistry, Université du Québec Montréal, CP 8888, Succ.
Centre-Ville, Montréal (Qué), H3C 3P8 Canada
[2] Faculté de Pharmacie, Université de Montréal, CP 6128-A, Montréal (Qué),
H3C 3J7 Canada
[3] Labopharm, Ste-Thérese (Qué), J7E 1M5 Canada

Cross-linked Amylose (CLA) - obtained by cross-linking of amylose with epichlorohydrin, was recently introduced as a matrix for drug controlled release. For CLA (Contramidtm) tablets prepared by direct compression, it was found that a linear increase in the cross-linking degree (cld, expressed as the amount of epichlorohydrin used to cross-link 100g of amylose) generates a non-monotonous variation of drug release time. Optimal release kinetics were obtained for CLA in the range CLA-1 to CLA-8. The decrease of release time with increasing cld is a particular characteristic of CLA matrix and differs from other matrices for which higher clds lead to longer release times.

The hypothesis was that the release mechaism can be controlled by the network, stabilised by hydrogen association as result of molecular rearrangement of CLA matrix. Hydrogen interchain associations could insure a better cohesion of the polymer, preventing thus water excess penetration and further polymer disintegration. FT-IR and X-ray diffraction data, correlated with swelling and thermodynamic analysis for CLA powders and tablets with various clds, supported this hypothesis. The hydration state of the CLA may be followed by direct monitoring of the intensity and frequency position of bending mode d(OH) of water located at ca. $1640 cm^{-1}$. The plot of IH2O as a function of cld shows that the polymer looses water for clds ranging from non-linked (CLA-0) to CLA-8 and then regains water for higher clds. This is consistent with the hypothesis that for low clds amylose chains are closely located, allowing only a limited amount of water to penetrate the polymer. X-Ray patterns of powders and tablets, in function of clds indicated peaks at 6.95 - 7.24 Å for CLA powders (ascribed to the glycerine cross-linking bridge: calculated length 8 - 8.7 Å). After compression, the unique diffused peak at 4.5-5 Å (possibly ascribed to H-bonding) signifies that this distance becomes predominant in the tablet and that the compression leads to physical re-arrangements (possibly extended hydrogen association).

For drugs with low solubility the CLA matrix can be used in association with a-amylase within the tablet (enzymatically controlled drug release system - ECDR).

9.14 SPECTRAL STUDY REGARDING SILICA-TETRANDRINE AND ALUMINUM LACTATE INTERACTIONS

Cristina Mandravel [1], Rodica Dumitru-Stanescu [2], Cristiana Bercu [3], Emil Fagarasan [4]
[1] Faculty of Chemistry, University of Bucharest, Romania
[2] Institute of Hygiene, Public Health, Health Services and Management, Bucharest, Romania
[3] Institute of Chemical Research, Bucharest, Romania
[4] University of Medicine and Pharmacy, Cluj-Napoca, Romania

Experimental research demonstrates that biological activity of the silica must be related to its surface activity.

In this work , we studied the presence of interactions of silica with two compounds that are used to prevent experimental silicosis: aluminum lactate and tetrandrine. We also studied the influence of chemical pretreatment of silica in relation with its surface activity.

We used Dorentrup α -quartz without and with chemical pretreatment (by using a HCl solution) which was treated with aluminum lactate and tetrandrine in phosphate buffer at pH 7.4 and 37° C.

The presence of the interactions between silica with lactate and tetrandrine has been studied using Fourier transform (FT-IR) spectrometry (Nicolet 205 instrument) and wide-line nuclear magnetic resonance spectrometry (NMR-^{1}H) (Specord 75 instrument).

Regarding *aluminum lactate*, from FT-IR spectra, we have found low, physical silica-lactate interactions. In these interactions lactate CO, COO and Al-O groups and silica Si-O group were involved. Al-O-O-Si bonds are occur.

Regarding *tetrandrine* , chemical interactions with silica were observed. In silica-tetrandrine interactions, tetrandrine OCH_3, C-N and ether groups and silica Si-O group were involved.

Chemical pretreatment of silica altered the interaction capacity of its Si-O groups.

The line width and intensity variations in NMR spectra agree with FT-IR results.

9.15 THE STUDY OF THERMAL STABILITY OF THE IMMUNOMODULATOR CANTASTIM

Ion Salageanu[1], Aurora Salageanu[2], Geza Szegli[2] and Eugen Segal[1]

[1]Department of Physical Chemistry, University of Bucharest
[2]Cantacuzino Institute, Bucharest

CANTASTIM is a partially purified bacterial extract of *Pseudomonas aeruginosa* with immunomodulating properties. It comprises proteins, sugars and other components of bacterial wall. The lipid moiety plays an essential biological role due to its interaction with target cells membranes.

By X-ray diffraction we established that this extract has a crystalline structure.

In an attempt to better correlate the chemical composition with biological activity, the thermal behavior of CANTASTIM was studied by thermogravimetry. The freeze-dried extract was analyzed by using different heating rates. The decomposition takes place in two main stages. The first thermal decomposition stage is exothermal and it is attributed to the decomposition of lipids containing amino groups. The second stage which is endothermal is attributed to the decomposition of the phospholipids.

The ratio between the two decomposition steps is well correlated with the biological properties of the extract.

10.1 PHYSIC-CHEMICAL STUDY CONCERNING DEFERRISATION AND DEMANGANISATION OF THE GROUND WATERS

C. Mandravel*, V. Chiosa*, M. Stănciulescu**

* *University of Bucharest, Phys. Chem. Dept., Bd. Carol I, 13, cod 70034, Bucharest, ROMANIA*
** *Institute of Research and Engineering of Environment, Spl. Independenței 294, cod 77703, Bucharest, ROMANIA*

For the improvement of water treatment methods, which is still an actual problem, is necessary first of all, the praising of physical-chemical decisive factors in the oxidation process. An oxidation process is always at the base of pollutants removal and this process can be achieved by a chemical and biological way.

In this paper are praised decisive physic-chemical factors in oxidation processes which are the basis of Fe(II) and Mn(II) removal from waters. For the ferruginous ground waters case have been analyzed the efficiency of oxidation process as function of the source temperature in different conditions of concentration and pH. For Mn(II) is improved a theoretical examination of the corresponding oxidation processes.

In this paper we reproduce the results of the Fe^{2+} oxidation from synthetic ground waters, using as oxidant the compressed air and performing the oxidation in standardized conditions concerning the concentration, water temperature and pH. Also are comparatively analyzed the characteristics of Mn^{2+} oxidation processes.

All the data concerning $|c| = f(t)$ at different temperatures (5-20°C) and pH (6,5-9) were fitted by of third or fourth degree polynomials, using a regression program of n degree. From the derivatives of these polynomials have been calculated the speed of reaction, v_R. Using a linear regression program have been calculated the values of the activation energy, E_a, preexponential factor's, A, and correlation coefficient, r, by the smaller squares method. We supposed the validity of Arrhenius type equation for the temperature interval between 5-20°C.

1o.2 ENZYMATIC PURIFICATION OF THE PHENOLIC WATERS

Maria Olea. Liviu Oniciu, Sebastian Nechita
Universitatea "Babes-Bolyai" Cluj
Facultatea de Chimie si Inginerie Chimică
Catedra de Chimie-fizică

The paper deals with the determination of the optimum conditions for a phenolic waters purification plant. The purification is carry out with the horseradish peroxidase, in the presence of H_2O_2.

For this, first, we studied the reaction kinetics in the laboratory. We used, as reactants, phenolic solutions of different concentrations as well as pyrogallol, o-dianisidine and ascorbic acid. We repeated the experiments for a lot of solutions of substrate (H_2O_2) and enzyme and for many temperatures.

Because all products are coloured, we pursued the reaction by recording the UV-VIS spectra.

The Lineweaver-Burk graphic method was used to setup the experimental data and to determine the value of Michaelis constant and of maximum rate of reaction.

The experimental data: product concentrations - time have represented graphically as a sigmoid curve in two parts: one for the reaction initiation and one for the reaction, in fact.

The Michaelis constant is appropiate to the which is found in literature, even thouch we used our peroxidase from indigenous horseradish.

The rate of enzymatic reaction increase with the increasing of the substrate concentration and temperature.

Such, we could to determine the optimum conditions for the phenolic waters purification.(We have had the phenolic waters from S.A. Sinteza Oradea).

We used a computer programme too, to find the best equation: concentration (C/C_0) = f(time). This equation was:

$$C_A/C_{A_0}=a+bt+c\sqrt{t}+de^{-t}$$

where: $a = 1.0999$;
$b = 4.91519*10^{-5}$;
$c = -0.0394971$;
$d = -0.0999873$;

and, we have, in this way, a possibility to calculate the reaction rate in the other conditions.

In conclusion, we can say that this method of enzymatic purification of phenolic waters is well-chosen.

1o.3 SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF NICKEL AND COPPER WITH DIMETYLGLYOXIME - TETRACIANOETHYLENE-COMPLEX

D.Chuguryanu,Gh.Zaiaţ,V.Rusu,V.Meryanu
Institute of Chemistry, Academy of Sciences of
Moldova, Kishinev, Moldova

A new spectrophotometric method for simultaneous determination of Nickel and Copper in aqueous solutions has been developed. As an chromogenic Reactive was used Dimethylglyoxime-Tetracianoethylene-molecular complex(L). The colour complexes NiL_2 and CuL have absorption maxima at 440nm($\varepsilon = 1.25 \cdot 10^4 l \cdot mol^{-1} \cdot cm^{-1}$) and 290nm ($\varepsilon = 1.37 \cdot 10^4 l \cdot mol^{-1} \cdot cm^{-1}$). The absorbance maximum of the Reactive alone being at 226nm($\varepsilon = 3.75 \cdot 10^4 l \cdot mol^{-1} \cdot cm^{-1}$). The difference of maxima $\Delta\lambda = \lambda_{NiL_2} - \lambda_{CuL} = 150nm$ makes possible simultaneous determination of Nickel and Copper in aqueous solutions (at pH 9-11) without preseparation to one another. Reactive is highly selective and sensitive to Ni(III) and Cu(II). Relative to Reactive solution the UV-vis spectrum obtained by the procedure showed two well-defined maxima at 440nm (NiL_2) and 290nm (CuL). Complexes obeyed Beer's Law in the ranges of concentrations $8 \cdot 10^{-7} \div 8 \cdot 10^{-5}$ $mol \cdot l^{-1}$(NiL_2) and $7.3 \cdot 10^{-7} \div 7.3 \cdot 10^{-5}$ $mol \cdot l^{-1}$(CuL) with correlation factor R=0.99. Identification limits of Nickel and Copper were found to be 0.047$\mu g \cdot ml^{-1}$ and 0.046$\mu g \cdot ml^{-1}$ respectively. Reproductibility tests fo eight results at the 2.35μg Ni and 2.3μg Cu levels showed a relative standard deviation of ±2%.

1o.4 THE SPECTROGRAFIC DOSAGE OF IRON,NICKEL AND COPPER IN LOW CONCENTRATIONS FROM LEAD ALLOYS

Manuela Munteanu
Institute of Phisical Chemistry,Splaiul Independenţei 202,
77208 Bucharest

The method has as foundament the next relation between the analitical line's intensity of the element studied in the sample and it's concentration:

$$\log I = k \log c$$

By the aid of the darkness curve representing the variation analytical line's darkness of an element in a standard as dependence of the transmission logaritm filter's with variable transmission degrees in steps anexated to the entrance slit of the spectrograf and of dosage curve representing the intensity's analytical line logaritm variation of the element studied in standards as dependence of the concentration logaritm of the same element in standards is determined the concentration of the element analysed in the sample.

The lead alloys studied had in composition 4,5% Sn and 0,5% Sb. For to be spectrografiated the samples analysed were transformed in sulfates,these being dried and therafter calcinated to 600 C during 30 minutes.

The standards had been prepared such a way as to contain the same quantity of Pb,Sn and Sb like the samples.Four standards were obtained.

In the standard one the analysed elements had the concentrations: Fe=12,5 ppm,Cu=100 ppm,Ni=5 ppm.The concentrations of these elements in the other standards are obtained by the succesive multiplication of the first with four.

The standards were dried and calcinated in the same conditions like the samples.

For the analysed samples resulted concentrations contained in the concentration range of standards,not overpassing it's first half.

1o.5

THE I.R. SPECTROSCOPY USE FOR THE STUDY OF THE COMPOUNDS FORMED ON THE SURFACE OF CERUSSITE TREATED WITH 8-HYDROXYCHINOLINE

Oprea Gabriela - The University of Baia Mare

ABSTRACT

The paper presents the results obtained by an infrared spectroscopic investigation on compounds formed at the surface of cerussite in the course of flotation with 8-hydroxychinoline (oxyne).

In solution, 8-hydroxychinoline forms insoluble, stable chelate compounds with many metal ions, lead included. This chelating action reagent performs important lead recoveries in the flotation of cerussite ($PbCO_3$) and it proves to be a good collector.

In optimal conditions of pH and the reagentts concetration, that is of the 8-hydroxychinoline, the lead oxinate (II) was prepared. The mineral (cerussite) wa ground in the agate mortar up to a granulation of approximately 2 microns.

Using the potassium bromide pelleting technique, we recorded the infrared spectra in the 400-1700 cm^{-1} region, for: pure natural cerussite, 8-hydroxychinoline, lead oxynate (II) and cerussite treated with acetone solution of oxine.

By comparing the spectra obtained, we observed the presence of lead (II) oxynate strips in the infrared spectrum of cerussite treated with oxyne solution, that demonstrates the formation of the lead oxynate (II) on the surface of cerussite during the flotation process in which 8-hydroxychinoline is used as a collector.

10.6 METODE DE DETERMINARE A IMPURITĂȚIILOR ŞI A FACTORULUI DE CALITATE PENTRU CUARȚUL MONOCRISTALIN UTILIZÎND SPECTROFOTOMETRIA ÎN INFRAROŞU

ing. Stan Gheorghe
ing. Mitrea Cristina
ROM-QUARTZ S.A

ABSTRACT : This work presents some aspects related to characterization methods of the synthetic quartz and the way to estimate it is quality through infrared absorbation bands.

Among the impurities , the one that influences acoustic losses of quartz resonators is banded hydrogen as-OH . We determined the absorption, coefficient , according to Beer's law , using the absorption line occuring from O-H streteking vibration , independent of alcali impurities presents in the crystals (Na^+ ,K^+, Li^+).

Quality factor (Q) is to be determined from a $Q=Q(\alpha)$ standard curve, correlated with the electrical measurements upon quartz resonators.

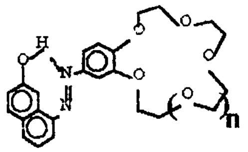
The mathematical dependence between Q and is obtained for many types of infrared spectrometers. Finally we discurs some aspects related to the concretion between estimated Q factor and the location of the blanK into the "as grown crystal ".

10.7
GAS CHROMATOGRAPHIC STUDIES USING GLASS CAPILLARY COLUMNS WITH NAPHTYL AZOCROWN ETHERS AND RELATED COMPOUNDS AS STATIONARY PHASES. 2. PHASE TRANSITIONS AND DISTRIBUTION MECHANISMS.

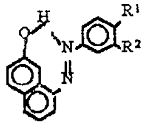
Florica Spafiu*, T.Constantinescu*, Ecaterina Tudor*, V.Popa* and C. Luca.**

** Institute of Physical Chemistry, Splaiul Independentei 202, 77208 Bucharest.*
*** Polytechnic University Bucharest, Department of Analytical Chemistry, str.Polizu 1.*

The GC investigation of **pure, well defined crown ethers** (CE^{-s}) as stationary phases, though not very promising from the analytical point of view because of some difficulties connected with thermal stability and separation efficiency, is still very interesting for physico-chemical characterization of these new materials. In a previous paper[1], synthesis and some properties of the crystalline CE^{-s} **1a,b** and related non-CE^{-s} **2a-c** were reported.



1a:n=1
1b:n=2



2a:R^1=R^2=H
2b:R^1=OCH^3;R^2=H
2c:R^1=R^2=OCH^3

Glass capillary columns with these pure compounds and some mixtures with silicones OV-101 and OV-17 were prepared using barium carbonate procedure and static coating. Chromatographic behavior during phase transitions by heating and cooling was tested, with several aliphatic homologous series, groups of isomers and other compounds as solutes.

The results were fully compatible with DSC thermograms.

The **lg k versus 1/T** diagrams (k- capacity ratio, T-colum temperature, ° K) for **1a,b;2a-c** in the **heating mode**, reveals a rather normal for ordinary organic crystal behavior, with two linear sections for G/S adsorbtion and G/L repartition mechanisms and an intermediate premelting range ended by a curve maximum, which stands for the melting point. The GC -determined melting points :160° for **1a**, 130-140° for the **1b,2a-c**, are the same with DSC-results. In the G/S adsorbtion range, the points for the two **1a and b** CE^{-s} lies on the same straight line.

In the **cooling mode**, some interesting peculiarities connected with supercooling and recristallization which differentiate between the studied stationary phases are observed, sustained also by DSC data. So, i **)** **2a, 2c** ,after a 30-40° supercooling interval congelates with a net retention drop, until almost initial state is reached; ii)**1b** and **2b**, after the same 40° interval, presents only an inflexion of the lgk-1/T curve, probably with transition to a high disordered quasi-solid state; iii) **1a**, containing the 15C6 moiety is an exception, behaving like a plastic crystal with thermal memory; after succesive heatings/coolings, the solid seems to become more and more stabilized with progressive retention decrease, while the retention in the G/L repartition mode is reproductible showing that no bleeding or chemical transformation of the stationary phase arose.

[1] *C.Luca, F.Spafiu, M.T.Caproiu, E.Tudor, P.Ionita, T.Constantinescu, M.Danescu and A.Stanciuc*, **Rev. Roumaine Chim.**, in press.

10.8

STRUCTURAL EFFECTS ON THE TEMPERATURE DEPENDENCE OF THE RETENTION INDEX. 1. C8- AND C12-RING SIZE HYDROCARBONS ON SE-30, UCON LB-550X AND CARBOWAX-20M GLASS CAPILLARY COLUMNS.

Ecaterina Tudor

Institute of Physical Chemistry "I.G.Murgulescu", Splaiul Independentei 202, 77208 Bucharest.

The retention index I and his temperature dependence as (t-°C, T-°K):

$$I = a + b\,t \quad ; \quad I = a' + bT \qquad (1\,a;\ 1b)$$

was measured for cyclooctane, cyclooctene, 1,3-and 1,5-cyclooctadienes, cyclooctatetraene, cyclododecane, *ttt-*, *ttc-*, *tcc-* 1,5,9-cyclododecatrienes, as well as for 1-octene, vinyl-cyclohexane, on nonpolar SE-30, medium polar Ucon and polar Carbowax-20M glass capillary columns.

The thermodynamic meaning of the coefficients on a given stationary phase is:

$$b = dI/dt = ct_1(\Delta S_i - \Delta S_z) + ct_2(\Delta H_i - \Delta Hz) \approx ct_1(\Delta S_i - \Delta S_z) \qquad (2)$$

$$a' - 100\,z \approx ct_3(\Delta H_i - \Delta H_z) \qquad (3)$$

The thermodynamic functions stand for the solution process of the solute i and reference n-alkane with z carbon atoms, from the mobile to stationary phase. The constants ct_1-ct_3 contain ΔH, ΔS, ΔG-increments for the methylene group, so they depend on the stationary phase polarity.

Having in view **the entropic meaning of dI/dt**, topological, geometrical, shape, flexibility or rigidity and other order effects that differentiate the solute i from the reference n-alkane, must be important. **ΔH-ΔS compensation** is however possible, making difficult the total separation of this features from the energetic effects; indeed, an **(a' - 100z) versus dI/dt** graph for all the solutes, is a straight line.

The representations of **dI/dt versus** $\Delta I^{CW-SE30}$, a global polarity descriptor and **dI/dt versus** $\Delta\chi$, a simple electrotopological index, both responding to the presence of double bonds in molecule, indicate a linear decrease of the temperature dependence of the retention index with unsaturation in each of C8 -and C12-ring size series. The reason seems to be a reduction of cycle flexibility. On the other side, dI/dt has an accentuate increase with the cyclization and ring size.

The nine C8-, C12- ring size hydrocarbons, but not 1-octene and vinyl-cyclohexane, obey a rather good linear correlation($r > 0.95$ for all the columns) of **dI/dt with** $^1\chi^v$, the first order valence molecular connectivity index.

The above regularities are general for the tested stationary phases, with some quantitative differences; dI/dt increase with the stationary phase polarity.

1o.9 STRUCTURAL EFFECTS ON THE TEMPERATURE DEPENDENCE OF THE RETENTION INDEX. 2. TERPENES AND SESQUITERPENES ON SE-30 GLASS CAPILLARY COLUMN.

Ecaterina Tudor

Institute of Physical Chemistry "I.G.Murgulescu", Splaiul Independentei 202, 77208 Bucharest.

The aim of present study is to point-out other regularities in the dependence of the temperature coefficient of the retention index, I, on molecular structure. The parameters of the equations 1 and 2 have been established for 23 terpenes and sesquiterpenes (t- °C, T- °K).These two groups consist from isomers differing by combinations of the number of cycles and double bonds; three of terpenes are acyclic.

$$I = a + b\,t \quad ; \qquad I = a' + b\,T \qquad (1a;\ 1b)$$

$$I = A + B\,/\,T \qquad (2)$$

The meaning of the coefficients of interest is:

$$b = dI/dt \approx ct_1\,(\Delta S_i - \Delta S^z) \qquad (3)$$

$$a' \approx ct_2\,(\Delta H_i - \Delta h_z) \quad ; \quad B \approx ct_3\,(\Delta H_i - \Delta H_z) \qquad (4;\ 5)$$

ΔH, ΔS- solution molar partial enthalpy and entropy of the solute i and reference n-alkane with z carbon atoms used in I definition, from the mobile to stationary phase.

Graphical representations **B versus b** and **(a' - 100) versus b** are straight lines (essentially ΔH- ΔS compensation lines), on which the terpenes and sesquiterpenes lays in well-organised clusters, according to their molecular structure.

The plots **dI/dt versus** $\Delta I^{Cw\text{-}SE30}$(a global polarity measure) and **dI/dt versus** $\Delta\chi = {}^1\chi - {}^1\chi^v$ (first order differential molecular connectivity index reflecting the presence of π electrons in the molecule's topological environment), reveals: 1) a clear tendency of decrease of dI/dt with the number of double bonds in each group of terpenes and sesquiterpenes, somehow obscured by the influence of context; so, the terpenes are: acyclic 3 double bonds (db^{-s}), monocyclic 2 db^{-s}, bicyclic 1 db and the sesquiterpenes are: monocyclic 3 db^{-s}, bicyclic 2 db^{-s}, tricyclic 1 db, tetracyclic saturated. 2) a very clear increase of dI/dt with the number and magnitude of cycles.

A linear correlation exists between **dI/dt and** ${}^1\chi^v$, the first order valence molecular connectivity index :

$$dI/dt = o.2321\,{}^1\chi^v - 0.6942 \qquad n = 23 \qquad r = 0.9425 \qquad r^2 = 0.8883$$

and excluding the outlier ledene with a peculiar structure,

$$dI/dt = 0.2443\,{}^1\chi^v - 0.7440 \qquad n = 22 \qquad r = 0.9551 \qquad r^2 = 0.9197$$

1o.1o THE STUDY OF MALEIC ANHYDRIDE-VINIL ACETATE COPOLYMER BY ELECTROCHEMICAL METHODS

GH. NEMŢOI, C. BELDIE, *I. POPA, ** S. NEMŢOI
DEPARTMENT OF PHYSICAL CHEMISTRY, AL.I.CUZA UNIVERSITY, 71, JASSY, 6600
* INSTITUTE OF MACROMOLECULAR CHEMISTRY, JASSY, 6600
** NATIONAL INVENTICS INSTITUTE, JASSY, 6600

The copolymer was synthesized from vinylacetate and maleic anhydride by polimerization in benzene - methylethylketone solution at 80°C using benzoyl peroxide as initiator.

The solution of copolymer free of electrolyte or in the presence of electrolyte was studied by potentiometric titration and conductometry.

The data obtained for this copolymer were compared with those obtained for other polyelectrolytes.