AD-A237 168

②

OFFICE OF NAVAL RESEARCH

Role of the Solvent in the Kinetics of Heterogeneous Electron and Ion Transfer Reactions
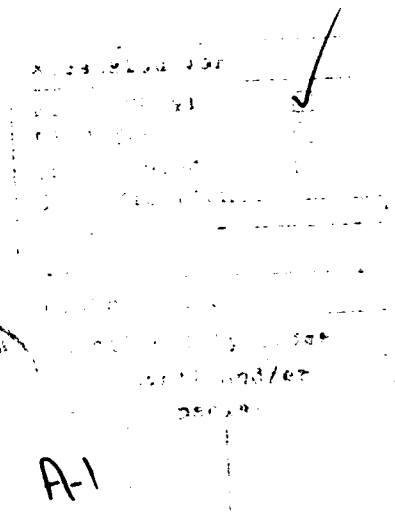
by

W. Ronald Fawcett and Colby A. Foss, Jr.

Prepared for Publication

in

Electrochimica Acta

Department of Chemistry
University of California
Davis, CA 95616

A-1

May 20, 1991

91-02545

91   18 145

REPORT DOCUMENTATION PAGE

	May 20, 1991	Technical

Role of the Solvent in the Kinetics of Heterogeneous
Electron and Ion Transfer Reactions

N00014-90-J-1235

W. Ronald Fawcett and Colby A. Foss, Jr.

Department of Chemistry
University of California
Davis, CA 95616

8. PERFORMING ORGANIZATION REPORT NUMBER

No. 12

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

Office of Naval Research
800 N. Quincy
Arlington, VA 22217-5000

10. SPONSORING MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT

Unclassified

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Solvent effects studied in simple heterogeneous redox reactions, and for amalgam formation reactions have been reviewed. It is emphasized that on the basis of a regression analysis of the data, solvent effects relating to the pre-exponential factor of the electron transfer rate constant can be separated from those for the exponential term. Analysis of data in non-Debye solvents such as the alcohols shows that the parameters relating to the second dielectric relaxation process are more important than those for the first in determining the magnitude of the rate constant. Examination of solvent effects for amalgam formation reactions reveals that they are quite different from those observed in electron transfer processes. As a result, it is concluded that the rate determining step in the amalgam formation reaction is ion transfer, not electron transfer, and that this rate limiting step is often located in the inner part of the double layer. Data recently obtained for the electroreduction of $Cu(I)$ in the nitrile solvents are presented and discussed with respect to solvent trends found for other systems.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Electron transfer, ion transfer, amalgam formation, solvent effects	11
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	unclassified

ROLE OF THE SOLVENT IN THE KINETICS OF HETEROGENEOUS ELECTRON AND ION TRANSFER REACTIONS

W. Ronald Fawcett and Colby A. Foss, Jr

Department of Chemistry, University of California, Davis, CA 95616, U.S.A.

Abstract—Solvent effects studied in simple heterogeneous redox reactions, and for amalgam formation reactions have been reviewed. It is emphasized that on the basis of a regression analysis of the data, solvent effects relating to the pre-exponential factor of the electron transfer rate constant can be separated from those for the exponential term. Analysis of data in non-Debye solvents such as the alcohols shows that the parameters relating to the second dielectric relaxation process are more important than those for the first in determining the magnitude of the rate constant. Examination of solvent effects for amalgam formation reactions reveals that they are quite different from those observed in electron transfer processes. As a result, it is concluded that the rate determining step in the amalgam formation reaction is ion transfer, not electron transfer, and that this rate limiting step is often located in the inner part of the double layer. Data recently obtained for the electroreduction of Cu(I) in the nitrile solvents are presented and discussed with respect to solvent trends found for other systems.

INTRODUCTION

During the last decade, considerable effort has been made to understand the role of the solvent in the thermodynamics and kinetics of relatively simple charge transfer reactions in liquid solutions[1, 2] and at electrodes[3, 4]. The simplest type of electrode reaction is the transfer of one electron to or from a reactant in which no bonds are formed or broken, and which remains in the solution near the electrode without interacting with it chemically. It is now generally recognized that the solvent affects the kinetics of such a reaction in two ways, namely through its effect on the magnitude of the Gibbs energy of activation, and its effects on the pre-exponential factor[4]. The role of the solvent in determining the activation barrier to electron transfer has been recognized for some time on the basis of the work of Marcus[5]. The observation that the solvent affects the kinetics of redox reactions in another way was first reported by Kapturkiewicz and Behr[6] who found that the variation in the heterogeneous rate constant for oxidation or reduction of transition metal salene complexes with solvent followed the variation in the reciprocal of the solvent's viscosity. At about the same time, it was predicted theoretically that the pre-exponential factor of the electron transfer rate constant should depend on the solvent's dynamical properties under certain circumstances[7–10]. Subsequently, solvent effects on simple heterogeneous electron transfer reactions have been examined in a number of experimental studies and the theoretical predictions examined in some detail[11–23].

Amalgam formation is an electrode reaction which is necessarily more complex than simple electron transfer but of fundamental interest when the ligands surrounding the metal ion being reduced are solvent molecules. In such a reaction, the reactant must pass through the double layer in order to become incorporated in the metallic electrode. These processes were traditionally regarded as electron transfer reactions in which the metal ion was reduced in the solution near the electrode, and the unstable metal atom then reacted with the mercury to form an amalgam[24]. On the basis of more recent discussion[25, 26], amalgam formation is considered to be a complex process involving a number of possible elementary steps including electron transfer, ion transfer, adsorption, metal ion incorporation in the electrode phase, and chemical steps. The elementary step of most interest on the basis of recent discussions[27, 28] is the ion transfer step in which the reactant moves from one position in the double layer to another and experiences a change in electrostatic potential. It is easily shown that the kinetics of such a step are potential dependent in the same way as those for simple heterogeneous electron transfer. It is obvious that the kinetic parameters for electron transfer and ion transfer steps should be quite different, more particularly they should be affected by the solvent in quite different ways. Considerable data now exist in the literature regarding solvent effects on the kinetics of reduction of the alkali metals[27–29], the alkaline earth metals[30], cadmium[31–33] and zinc[34, 35], so that a comparison with data for simple electron transfer reactions is possible.

In the present paper, we will review the present state of knowledge regarding solvent effects in electron transfer with special emphasis on methods for separating solvent dependence of the pre-exponential factor from that of the Gibbs energy barrier. Some consideration is also given to reactions in non-Debye solvents such as the straight chain alcohols, and the

interesting consequences of multiple relaxation processes in these solvents discussed. Finally, solvent effects for amalgam formation reactions are re-examined and compared with those for electron transfer processes.

SOLVENT EFFECTS IN SIMPLE ELECTRON TRANSFER REACTIONS

As a result of recent theoretical developments[7–10, 36, 37], the expression for the standard rate constant of a simple electron transfer reaction may be written as

$$k_s = A\tau_L^{-1}\exp(-\Delta G^* / RT),\qquad (1)$$

where A is the solvent independent part of the pre-exponential factor, x a fraction between 0 and 1, and ΔG^*, the Gibbs energy of reorganization. The last quantity is made up of inner and outer sphere contributions, ΔG_{is}^* and ΔG_{os}^*, respectively. The inner sphere contribution is normally solvent independent unless the ligands surrounding the redox center are solvent molecules. ΔG_{os}^* is always solvent dependent on the basis of Marcus theory, and can be written as

$$\Delta G_{os}^* = RTg\gamma,\qquad (2)$$

where g is a collection of constants together with the size–distance parameter which depends on the sizes of the reactants and, γ is the Pekar factor, namely,

$$\gamma = \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}.\qquad (3)$$

ϵ_{op} is the optical dielectric constant and ϵ_s its static value. The important parameter determining the solvent dependence of the pre-exponential factor is the longitudinal relaxation time τ_L. It is related to the Debye relaxation time, τ_D, the high frequency value of the dielectric constant in the near-infrared region,

ϵ_x, and the static value, ϵ_s as follows:

$$\tau_L = \frac{\tau_D \epsilon_x}{\epsilon_s}.\qquad (4)$$

These parameters are obtained by studying the frequency dependence of the solvent permittivity which, according to the Debye model, is given by

$$\epsilon(\omega) = \epsilon_x + \frac{\epsilon_s - \epsilon_x}{1 + j\omega\tau_D}.\qquad (5)$$

where ω is the angular frequency. The fraction x is a function of reaction adiabaticity and the relative contributions of the inner sphere and outer sphere reorganizational energies[37]. If the reaction is weakly adiabatic, and/or ΔG_{is}^* is large relative to ΔG_{os}^*, x approaches 0. On the other hand, if the reaction is strongly adiabatic and the contribution of ΔG_{is}^* is negligible, x approaches unity.

On the basis of the above, equation (1) may be rewritten as

$$k_s = A\tau_L^{-1}\exp(-\Delta G_{is}^*/RT)\exp(-g\gamma)\qquad (6)$$

or, after taking logarithms,

$$\ln k_s = \ln K - x\ln\tau_L - g\gamma,\qquad (7)$$

where $\ln K$ is the collection of terms remaining after removal of the terms in $\ln\tau_L$ and γ. One may assess the relative importance of solvent effects in the pre-exponential factor and the exponential term by fitting equation (7) to experimental data for $\ln k_s$ using values of τ_L and γ from the literature. Such an analysis ignores the possibility that other terms in the pre-exponential factor depend on the solvent, as will be discussed further below.

A collection of values of τ_L and γ for solvents whose dielectric relaxation behaviour is reasonably simple is given in Table 1. The longitudinal relaxation time for these systems varies by more than an order of magnitude, from a low value of 0.2 ps in aceto-

Table 1. Solvent parameters relevant to estimation of the electron transfer rate constant (Debye solvents)

Solvent	Longitudinal relaxation time* τ_L ps	Pekar factor† γ
Acetone (AC)	0.3	0.495
Acetonitrile (AN)	0.2	0.529
Benzonitrile (BN)	5.8	0.390
Chloroform (CF)	2.4	0.276
Dichloroethane (DCE)	1.6	0.384
Dichloromethane (DCM)	0.9	0.382
Dimethoxyethane (DMXE)	0.8	0.371
Dimethylacetamide (DMA)	1.5	0.459
Dimethylformamide (DMF)	1.1	0.463
Dimethylsulfoxide (DMSO)	2.1	0.437
Hexamethylphosphoramide (HMPA)	8.8	0.438
Nitrobenzene (NB)	5.3	0.387
Nitromethane (NM)	0.2	0.498
N-methylpyrrolidone (NMP)	2.5	0.435
Propionitrile (PN)	0.4	0.503
Pyridine (PYR)	1.3	0.359
Tetrahydrofuran (THF)	1.7	0.388
Tetramethylurea (TMU)	6.0	0.433

*Defined in equation (4).
†Defined in equation (3).

nitrile to a high of 8.3 ps in hexamethylphosphoramide, the corresponding variation in ln τ_L being close to a factor of four. On the other hand, the variation in the Pekar factor is somewhat less, and falls in the range from 0.28 to 0.53. It is easily shown that there is no correlation between ln τ_L and γ in general, so that, if one has data in a sufficient number of solvents, separation of the two main components of the solvent effect is possible on the basis of a regression analysis.

Literature data relating to solvent effects for simple heterogeneous electron transfer reactions were analyzed earlier on the basis of equation (7)[38]. An important component of that analysis was the presentation of partial regression coefficients which give the fraction of the explained variation in the ln k, due either to ln τ_L or to γ. Representative results including more recent data are summarized in Table 2. The relaxation coefficient x varies from 0.3 for the nitromesitylene system to 1.0 for tetrathiafulvalene. The partial regression coefficient x is usually high, indicating that most of the solvent dependence is associated with the pre-exponential factor in the rate constant. In assessing these data one should keep in mind that double layer effects were not considered. Although they are minimal for these systems, which involved singly charged reactants or products, they should be taken into account in a complete analysis of solvent effects[4]. On the basis of the results presented, most of the systems studied to date are only weakly adiabatic or involve relatively large contributions from ΔG_s^*. The one exception is the tetrathiafulvalene system discussed recently by Grampp et al.[22]. They showed that the kinetic data for homogeneous electron transfer could be described in some detail by the model for adiabatic systems[39] and that the size–distance parameter could be estimated rather precisely on the basis of an ellipsoidal representation of the reactant. Somewhat less success was obtained in the analysis of the heterogeneous data, probably because of double layer effects. Comparison of the parameters for the phenothiazene[16] and cobaltacenium systems[17] with those reported earlier[38] reveals some small differences. These are due to the fact that the datum for propylene carbonate was removed in the present analysis. According to dielectric relaxation data[40], propylene carbonate cannot be treated as a simple Debye solvent so that the parameters used in the earlier analysis[38] for this solvent were incorrect. It is interesting to note that the cobaltacenium system is only weakly adiabatic, a conclusion which is supported when data for non-Debye solvents are also considered[41].

Among the systems considered for the above analysis was the tris(hexafluoroacetylacetonato) ruthenium (III II) couple studied recently by Weaver et al.[23]. Heterogeneous rate constants were reported in six solvents, five of which could be considered simple on the basis of the criteria discussed above. However, statistical analysis of these data showed that the parameter ln τ_L was fortuitously correlated to the Pekar factor γ with a correlation coefficient of 0.997. Thus, the analysis presented here could not be applied to this set of data. Although we have no dispute with the conclusions reached by the authors of this study, it is very important that the choice of solvents be such that separation of the effects considered here can be made on a statistical basis with minimum reliance on detailed theoretical models.

Although a reasonable body of data is available in the Debye solvents considered above, the collection is considerably increased if one considers non-Debye solvents such as the alcohols. In a recent discussion of non-Debye solvents[41], it was shown that, if the relaxation time for the non-Debye system is assumed to follow the model proposed by Hynes[42], that kinetic data in non-Debye solvents fall in line with those obtained in Debye solvents. To a good approximation, the dielectric relaxation behavior of alcohols can be described by the equation

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_{mw}}{1 + j\omega\tau_1} + \frac{\epsilon_{mw} - \epsilon_\infty}{1 + j\omega\tau_2}, \qquad (8)$$

where ϵ_{mw} is the permittivity at the end of the first relaxation region (in the microwave region), τ_1, the relaxation time for the first process, and τ_2 that for the second process. The first process is associated with the breakup and formation of clusters in the alcohols, and the second with monomer rotation. In a more complete description of dielectric relaxation in the alcohols[43], a third process corresponding to rotation of the hydroxyl group around the C—O bond in the alcohol is recognized, but this process at very high frequencies is not distinguished from the second for present considerations which are limited to short chain alcohols. According to the treatment given by Hynes[42], the longitudinal relaxation time for a complex solvent with two relaxation processes is a function of frequency with a high frequency limit given by

$$\tau_{Lx} = \frac{\epsilon_\infty}{\epsilon_s}\left[\frac{f_1}{\tau_1} + \frac{f_2}{\tau_2}\right]^{-1}, \qquad (9)$$

where

$$f_1 = \frac{\epsilon_s - \epsilon_{mw}}{\epsilon_s - \epsilon_\infty} \qquad (10)$$

Table 2. Analysis of kinetic data for heterogeneous electron transfer for solvent effects on the basis of equation (7)

Reaction	Relaxation coefficient x	Normalized partial regression coefficients		Number of solvents n	Correlation coefficients r
		$\hat{x}$	$\hat{y}$		
1. Nitromesitylene(0/−)[10]	0.3 ± 0.1	0.67	0.33	5	0.992
2. Phenothiazene(0/+)[12]	0.8 ± 0.2	0.88	0.12	7	0.905
3. Cobaltacenium(+/0)[13]	0.9 ± 0.1	0.84	0.16	8	0.986
4. 1,4-Diaminobenzene(0/+)[14]	0.6 ± 0.1	0.95	0.05	6	0.961
5. Tetrathiafulvalene(0/+)[17]	1.0 ± 0.5	0.95	0.05	7	0.924

and

$$f_2 = \frac{\epsilon_{mw} - \epsilon_x}{\epsilon_s - \epsilon_x}. \qquad (11)$$

Hynes[42] demonstrated that in the case of weakly adiabatic reactions, a category which includes most systems considered here, the appropriate value of τ_L is that given by equation (9). It is interesting to note that values of τ_{Lx} are much smaller than values of τ_L estimated on the basis of equation (4). For example, in the case of methanol for which $\tau_1 = 49.8$ ps, the estimate of τ_L assuming $\epsilon_x = 2.00$ and $\epsilon_s = 32.65$ is 3.1 ps. On the other hand, on the basis of equation (9), the estimate of τ_{Lx} is 0.5 ps. It is clear that the high frequency limiting value of τ_L is greatly influenced by the faster relaxation process, the value of τ_{Lx} being close to that one would estimate in the alcohol under circumstances for which clusters did not exist[41, 44]. Another non-Debye solvent whose dielectric relaxation can be described on the basis of two processes is propylene carbonate[40]. Values of τ_{Lx} for the non-Debye solvents considered here are summarized in Table 3.

According to equation (7), $\ln k_s$ should be linear in $\ln \tau_L$ if solvent effects predominate in the pre-exponential factor. A plot of data for the reduction of cobaltacenium cation at a mercury electrode in 12 different solvents is shown in Fig. 1. It is clear that a good linear relationship exists between $\ln k$, and $\ln \tau_L$, the slope of the plot being -0.7. If there were no solvent dependence of the reorganizational barrier to electron transfer, the slope of such a plot would give the relaxation parameter x. However, one cannot rely on this result since the analysis ignores the term in γ. On the other hand, the data show clearly that when τ_{Lx} is used for the non-Debye solvents, the kinetic results in these solvents fall in line with those obtained in Debye solvents. If the estimate of τ_L for non-Debye solvents is based on ϵ_s, ϵ_x and τ_1, as was the case in earlier work[16–18], then the behavior of non-Debye solvents appears anomalous with respect to that in Debye solvents[41].

When the parameter x is known, the solvent dependence of the Gibbs energy of activation may be examined by correcting the logarithm of the rate constant for the solvent dependence of the pre-exponential factor. Thus, on the basis of equation (7), one may write

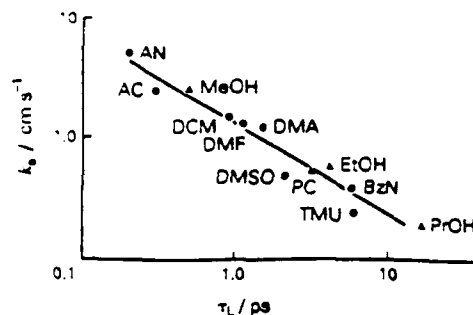$$\ln k_s + x \ln \tau_L = \ln K - g\gamma \qquad (12)$$

Fig. 1. Plot of the logarithm of the standard rate constant for the electroreduction of cobaltacenium cation at Hg in 12 solvents against the logarithm of the solvents' longitudinal relaxation time. Debye solvents are designated by (●) and non-Debye solvents by (▲). The abbreviations for the solvents are listed in Tables 1 and 3.

so that a plot of the function on the left-hand-side against the Pekar factor should yield an estimate of the size–distance parameter, g. In the case of heterogeneous reactions, this parameter is given by[5]

$$g = \frac{N_A e^2}{32\pi\epsilon_0}\left(\frac{1}{a} - \frac{1}{R_e}\right), \qquad (13)$$

where N_A is Avogadro's number, e the charge on the electron, a the radius of the reactant represented as a sphere. R_e its distance from its image in the conducting electrode, and ϵ_0, the permittivity of free space.

A plot of the kinetic data for heterogeneous electron transfer in the COB$^+$/COB system[17] according to equation (13) and assuming $x = 0.9$, is shown in Fig. 2. It is apparent that a reasonable fit to the experimental data is obtained for the Debye solvents alone. However, when the data for the alcohol solvents are added, the correlation between $\ln k_s + x \ln \tau_L$ and γ is lost, and one cannot make reasonable estimates of the kinetic parameters. On the other hand, it was shown recently[41] that if the Pekar factor for the non-Debye solvents is defined on the basis of the second relaxation process, that is, as

$$\gamma' = \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_{mw}} \qquad (14)$$

an excellent correlation between $\ln k_s + x \ln \tau_L$ and γ' is maintained (see Fig. 3). This arbitrary redefinition

Table 3. Solvent parameters relevant to estimation of the electron transfer rate constant (non-Debye solvents)

Solvent	Longitudinal relaxation time*		Pekar factor†	
	τ_{Lx} ps	τ_{Li} ps	γ	γ'
Methanol (MeOH)	0.5	3.1	0.538	0.387
Ethanol (EtOH)	4.1	14.8	0.500	0.315
1-propanol (PrOH)	16.9	44.7	0.474	0.248
1-butanol (BtOH)	25.6	66.1	0.454	0.221
Propylene carbonate (PC)	3.0	3.4	0.480	0.388

*τ_{Lx} is defined in equation (9); τ_{Li} is defined by equation (4) with the relaxation time τ_1 replacing τ_D.

†γ is the normal Pekar factor defined on the basis of the bulk dielectric constant ϵ_s [equation (3)]; γ' is the Pekar factor in the same solvent in the absence of the first relaxation process [equation (14)].
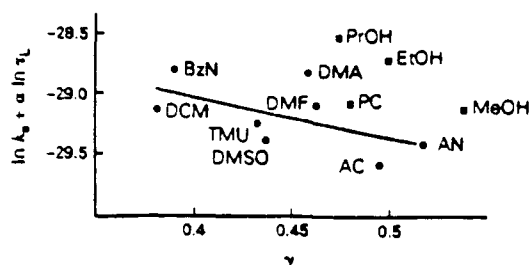
Fig. 2. Plot of the logarithm of the standard rate constant for reduction of COB^+ corrected for variation in the longitudinal relaxation time of the solvent, $\ln k_s - x \ln \tau_L$ against the permittivity parameter for the solvent, γ, with $x = 0.9$. Data for Debye solvents are designated (●) and those for non-Debye solvents (■). The dotted line shows the correlation based on Debye solvents only. The units of k_s are meters per second and of τ_L, seconds.

of the Pekar factor suggests that the reactant in the non-Debye solvent system is solvated mainly by monomers, and that the local dielectric constant is lower than the bulk value. It is obvious that the extent of dielectric saturation in the vicinity of the reactant would depend on the size of the reactant and its charge. For the systems tested to date, the correlation between $\ln k_s + x \ln \tau_L$ and the Pekar factor only holds when the latter quantity is estimated on the basis of equation (14) for non-Debye solvents. This result merits further investigation.

A problem with previous analyses of solvent effects on electron transfer kinetics is that the solvent dependence of the pre-exponential factor has been examined after correcting the observed rate constant for the solvent dependence of ΔG^*_{os} on the basis of the Marcus model in its simplest form [see equation (13)][16–18, 21]. It has been customary to assume that reasonable estimates of ΔG^*_{os} can be obtained assuming that the reactant can be represented as a sphere and that the imaging distance R_s is effectively infinity. As shown by Grampp et al.[22, 45], the estimate of ΔG^*_{os} is very sensitive to the geometrical model proposed for the reactant. Thus, serious errors in the estimation of the exponential part of the rate constant can result if one is not careful in estimating ΔG^*_{os}. In order to circumvent this problem, McManis et al.[46] proposed that better estimates of ΔG^*_{os} could be obtained for the metallocenes by measuring the

intervalence charge transfer energy, E_{op}, for biferrocene cations as a function of solvent nature. Although they had difficulty rationalizing their results on the basis of a simple model in which the cation was represented as two spheres between which an electron is transferred, the value of E_{op} was linear in the Pekar factor to a good approximation in Debye solvents[46]. As far as the present analysis is concerned, the assumption that ΔG^*_{os} is proportional to the Pekar factor is supported experimentally provided one does not include non-Debye solvents.

An important question remaining is whether or not other terms in the pre-exponential factor are solvent dependent. We pointed out earlier[47] that the electronic transmission coefficient κ is expected to be solvent dependent in a heterogeneous electron transfer process because the distance of closest approach of the reactant to the electrode depends on solvent size. Present treatments of double layer effects do not give any easy way of dealing with the discrete nature of the solvent. Another aspect of this problem has been addressed by McManis et al.[48], especially for the case of homogeneous electron transfer. They pointed out that the degree of overlap between orbitals on the components of a redox reaction affects the shape of the Gibbs energy barrier for electron transfer, and hence the value of κ. These considerations are critical in the interpretation of the x and g coefficients in the analysis discussed above [equation (7)], and in the choice of the appropriate relaxation time function, particularly in non-Debye solvents. Another aspect of this problem is related to the manner in which the non-reacting counter ion affects the local concentration of the reactant through local ion pairing or by changing the average distance to which a reacting species may approach the electrode. In this regard, Peterson and Evans[49] showed that the enthalpy of activation for the electroreduction of nitroethane in acetonitrile solution is essentially independent of the nature of the tetra-alkylammonium cation whereas the pre-exponential factor decreases markedly in going from 0.1 M tetraethylammonium perchlorate to 0.1 M tetraheptylammonium perchlorate as inert electrolyte. These authors attributed the observed differences to changes in κ[49]. The questions raised by these studies would be more easily addressed for heterogeneous reactions from the point of view of a molecular description of the interface, and it is encouraging that significant progress has been made in this direction[50].

SOLVENT EFFECTS IN AMALGAM FORMATION REACTIONS

The role of the solvent in amalgam formation reactions is clearly different on the basis of existing experimental evidence[4]. In the case of reduction of metal ions under conditions that the solvent is also incorporated around the ion as a ligand, the Gibbs energy of activation is found to increase with the Gibbs energy of metal ion solvation[4]. This result is taken to be evidence that the rate controlling step is ion transfer under circumstances for which some of the primary ligands around the reactant are changed. In an ion transfer step, as the reactant moves closer
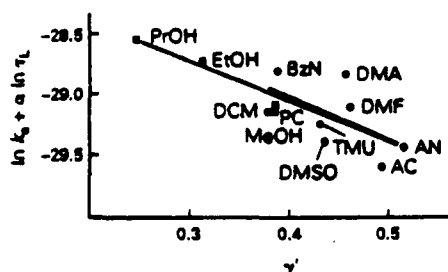

Fig. 3. The same plot as in Fig. 2 but using the revised permittivity parameter γ' [equation 14)] for non-Debye solvents. The full line shows the correlation based on all the solvents, and the dotted line, on the Debye solvents only. The units of k_s are meters per second and of τ_L, seconds.

to the interface. it can no longer maintain its original solvation sheath. and eventually must share the solvation sheath of the electrode. Finally. the reactant reaches the interface where it is solvated partially by solvent molecules and partially by mercury atoms. This step has been called an adsorption step but it can also be regarded as a special type of ion transfer step in which the environment of the reactant changes in a pronounced manner. In any case. partial desolvation is a likely component of ion transfer, so that the molecular aspects of ion–solvent interaction are critical in determining the kinetics of the reaction. On the other hand. a simple electron transfer reaction involves a fixed inner sphere environment, and the solvent is a continuum one. *[effect]*

Examination of kinetic data for the reduction of Li^+ ions in a variety of non-aqueous solutions[4, 27–29] led to the conclusion that the logarithm of the standard rate constant is linearly related to the Gibbs energy of reactant solvation, ΔG^0_{solv}. The resulting relationship is

$$\ln k_s = \text{constant} + 0.37\,\Delta G^0_{solv}. \qquad (15)$$

This may be regarded as a Bronsted relationship between the Gibbs energy of activation and the Gibbs energy of solvation. In the case of the reduction of Na^+ ion. the corresponding relationship is

$$\ln k_s = \text{constant} + 0.18\,\Delta G^0_{solv}. \qquad (16)$$

The Bronsted coefficient for the sodium reaction is considerably smaller than that for Li^+. This is attributed to the fact that solvation of the Na^+ ion is weaker. Correlations such as those given by equations (15) and (16) are often presented in terms of the donor number, DN, an empirical parameter which evaluates a solvent's ability to act as a Lewis base[51]. It has been shown that the donor number correlates well with the Gibbs energy of solvation of simple monatomic cations[52] as one would expect. Since values of ΔG^0_{solv} are often not available in non-aqueous systems for all cations that one would like to consider. it is simply more convenient to use the donor number and assume that a linear relationship exists between the two quantities.

On the basis of the data obtained for the alkali metal ions[27–29] and alkaline earth metal ions[30], it is clear that double layer effects are very important in these reactions. Large variations in the standard rate constant and experimental transfer coefficient were observed when the nature of the cation in the background electrolyte was changed. The experimental evidence indicated that the rate controlling step was located in the inner layer, and that it involved ion transfer. When the kinetic data in a given system were obtained over a wide potential range, evidence was obtained supporting the conclusion that the nature of the rate determining step (r.d.s.) changes with potential. Since the experimental transfer coefficient decreases with change in the potential in the negative direction, this was taken as evidence that the location of the r.d.s. is moving further from the interface under the same conditions. Since the rate of change of electrostatic potential with distance becomes smaller as one moves from the interface to the solution, one may make the general statement that an ion transfer reaction becomes more potential dependent the closer it occurs to the interface. If two or more steps are involved in the mechanism. steps occurring closer to the interface change their rates faster than those occurring further away. As a result. if the step occurring closest to the interface is slowest at the most positive potential. it is probably the fastest at the most negative potential. ~~Evidence for change in the r.d.s. with potential. it is probably the fastest at the most negative potential~~. Evidence for change in the r.d.s. with potential has also been obtained in studies of the reduction of Cd^{2+} and Zn^{2+} ions both from aqueous[53–55] and non-aqueous solutions[32–35]. These data also suggest that the r.d.s. involves an inner layer reaction at more positive potentials. and that the r.d.s. moves further away to the vicinity of the outer Helmholtz plane at more negative potentials. *[(o.H.p.)]*

More recently, we have investigated the reduction of Cu(I) at mercury from the nitrile solvents in which it is stable. This reaction was chosen because it involves only one electron and occurs close to the potential of zero charge (*pzc*) on mercury, whereas the reduction of the alkali metal ions occurs at very *[occurs]* negative potentials. It also provides an interesting contrast to the alkali metals in that its interaction with the solvent is much stronger. Otherwise, as is well known from the chemistry of transition metal ions. Cu(I) would be unstable to dismutation. If electron transfer is the rate determining step, the resulting Cu atom formed in the double layer would interact very weakly with the solvent so that one would expect the Gibbs energy barrier for this step to be very asymmetrical. the potential energy surface defining the reactant in the direction of the reaction coordinate being much steeper than that for the product[56]. Another possible rate determining step is adsorption in which some of the solvent molecules surrounding the Cu(I) reactant are replaced by mercury atoms. The Gibbs energy barrier for this step is undoubtedly asymmetrical as well because of the fact that Cu interacts rather weakly with mercury[57].

A summary of kinetic parameters for the reduction of Cu(I) obtained in four nitrile solvents with 0.1 M tetraethylammonium perchlorate as background electrolyte is given in Table 4. The donor number range in these solvents is small. from a low value of 12.0 for benzonitrile to a high of 16.6 for butyronitrile. With the tetraethylammonium perchlorate as electrolyte, a correlation between $\ln k_s$ and DN is apparent for the alkylnitriles, but not for benzonitrile. However, the viscosity of benzonitrile is almost four times that of acetonitrile, and it is entirely possible that this might affect an ion transfer step, particularly if the displacement of solvent molecules at the reaction site is involved.

The second feature of these data is the anomalously high values of the apparent transfer coefficient. It should be noted that the data reported in Table 4 have been corrected for the double layer effect in the usual way, that is. assuming that the reaction plane is coincident with the o.H.p.[26, 58]. The fact that values of α_a greater than unity were observed is attributed to the reaction site being located in the inner part of the double layer. Under these circumstances the apparent transfer coefficient is higher than the true or intrinsic value because the actual potential

alpha
α_a $\Delta H_r^{\ddagger}$ ← _activation symbol_

Heterogeneous electron and ion transfer reactions

Table 4. Kinetic parameters for Cu[I] reduction in the nitriles*

Solvent†	Standard Rate constant k, cm s^{-1}	Transfer coefficient α_r	Real enthalpy of activation $\Delta H_r^{\ddagger}$ kJ mol^{-1}
Acetonitrile	0.142	1.05	26.7
Propionitrile	0.134	1.05	23.1
Butyronitrile	0.080	1.02	16.4
Benzonitrile	0.128	0.90	24.6

*All kinetic parameters corrected for double layer effect.
†Electrolyte = 0.1 M TEAP; temperature = 25°C.

at the reaction site is more negative than that on the o.H.p. In addition, it is highly likely that the true value of the transfer coefficient is significantly greater than 0.5 as a result of marked asymmetry in the Gibbs energy barrier of the r.d.s.[56].

Finally, the values of the real enthalpies of activation for this reaction fall in the range from 16 to 27 kJ mol^{-1}. These can be compared with values for the reduction of cobaltacenium cation and other organometallic redox systems[59] which fall in the range from 15 to 20 kJ mol^{-1}. Since the present results are similar to those reported earlier, and since the corresponding $\Delta G_a^{\ddagger}$ for Cu$^+$ reduction would almost certainly be very large compared with the organometallic systems for which there is little structural change, it would seem unlikely that the rate determining step for the Cu$^+$ reaction is electron transfer. Unfortunately, too few data are available for the enthalpy of activation for electrode reactions in the two categories considered here to make a proper distinction at this time.

In summary, experimental evidence strongly indicates that the r.d.s. in amalgam formation reactions for the conditions considered here is ion transfer. It should be pointed out that these reactions have been studied for a number of years under a wide variety of circumstances. When an anion is present in solution which coordinates with the reduction cation, the mechanism of the reaction can change dramatically. This follows from the fact that the charge on the species arriving in the double layer is different from the valence of the cation being reduced. Moreover, the anions which are ligands for the cations are often also specifically adsorbed at the electrode/solution interface. Thus, analysis of kinetic data for these systems is considerably more complicated.

CONCLUSION

The study of solvent effects in electrode reactions during the last decade has led to a significant improvement of our understanding of these processes at a microscopic level. This is especially true in the case of electron transfer reactions, an area in which theoretical interest has been strong[7–10, 36, 37]. However, a problem which still exists in the interpretation of experimental data is that double layer effects have been ignored or are poorly understood. In order to reduce this problem to a minimum, studies have been restricted to reactions in which only one electron is transferred, so that the maximum charge on either reactant or product is +1 or −1. Nevertheless, double layer effects cannot be avoided, and can only

be easily treated on the basis of the simple Frumkin correction. This correction ignores the fact that the reaction site may not be located on the o.H.p. and, more importantly, that the actual potential at the reaction site may be quite different from the average value. The latter circumstance is especially true when non-reacting ions are specifically absorbed at the interface. The double layer effect can lead to significant changes in the Gibbs energy barrier involved in the reaction with solvent nature. If this change is ignored, solvent effects in heterogeneous reactions can easily be misinterpreted.

The most promising developments in the theory of the double layer are those based on a non-primitive description of the solution at the interface[50]. Using these methods, and recognizing the size of the various ionic and molecular components in the system, it should be possible to estimate more carefully the contribution to the Gibbs energy of a reactant due to its electrostatic environment. Then, a more molecular description of reactions in liquids and at interfaces will be possible.

REFERENCES

1. J. T. Hynes, in _Theory of Chemical Reaction Dynamics_, (Edited by M. Baer). Vol. 4, Ch. 4, CRC Press, Boca Raton (1985).
2. J. B. Hubbard and P. G. Wolynes, in _Chemical Physics of Solvation_, (Edited by R. R. Dogodnadze, E. Kalman, A. A. Kornyshev and J. Ulstrup), Part C, Ch. 1. Elsevier, Amsterdam (1988).
3. A. M. Kuznetsov, J. Ulstrup and M. A. Vorotyntsev, in _Chemical Physics of Solvation_, (Edited by R. R. Dogodnadze, E. Kalman, A. A. Kornyshev and J. Ulstrup), Part C, Ch. 3. Elsevier, Amsterdam (1988).
4. W. R. Fawcett, _Langmuir_ 5, 661 (1989).
5. R. A. Marcus, _J. chem. Phys._ 43, 679 (1965).
6. A. Kapturkiewicz and B. Behr, _Inorg. Chim. Acta_ 69, 247 (1983).
7. L. D. Zusman, _Chem. Phys._ 49, 295 (1980).
8. I. V. Alexandrov, _Chem. Phys._ 51, 449 (1980).
9. G. van der Zwan and J. T. Hynes, _J. chem. Phys._ 76, 2293 (1982).
10. D. F. Calef and P. G. Wolynes, _J. phys. Chem._ 87, 3387 (1983).
11. W. R. Fawcett and J. S. Jaworski, _J. phys. Chem._ 87, 2972 (1983).
12. A. Kapturkiewicz and B. Behr, _J. electroanal. Chem._ 179, 157 (1984).

13. C. Russel and W. Jaenicke. Z. phys. Chem. N.F. 139, 97 (1984); J. electroanal. Chem. 180, 205 (1984).

14. A. Kapturkiewicz and M. Opallo. J. electroanal. Chem. 185, 15 (1985).

15. T. Gennett, D. F. Milner and M. J. Weaver. J. phys. Chem. 89, 2787 (1985).

16. M. Opallo and A. Kapturkiewicz. Electrochim. Acta 30, 1301 (1985).

17. G. E. McManis, M. N. Golovin and M. J. Weaver. J. phys. Chem. 90, 6563 (1986).

18. M. Opallo. J. chem. Soc. Faraday Trans. 1 82, 339 (1986).

19. A. Kapturkiewicz and W. Jaenicke. J. chem Soc. Faraday Trans. 1 83, 2727 (1987).

20. D. A. Corrigan and D. H. Evans. J. electroanal. Chem. 233, 161 (1987).

21. R. M. Nielson and M. J. Weaver. J. electroanal. Chem. 260, 15 (1989).

22. G. Grampp, A. Kapturkiewicz and W. Jaenicke. Ber. Bunsenges. phys. Chem. 94, 439 (1990).

23. M. J. Weaver, D. K. Phelps, R. M. Nielson, M. N. Golovin and G. E. McManis. J. phys. Chem. 94, 2949 (1990).

24. T. Erdey-Gruz, in Kinetics of Electrode Reactions, p. 262. Wiley-Interscience, New York (1972).

25. C. P. M. Bongenaar, A. G. Remijnse, J. Sluyters-Rehbach and J. H. Sluyters. J. electroanal. Chem. 111, 139 (1980).

26. W. R. Fawcett. J. phys. Chem. 93, 2675 (1989).

27. A. S. Baranski and W. R. Fawcett, J. chem. Soc. Faraday Trans. 1 76, 1962 (1980).

28. A. S. Baranski and W. R. Fawcett. J. chem. Soc. Faraday Trans. 1 78, 1279 (1982).

29. A. S. Baranski, M. A. Drogowska and W. R. Fawcett. J. electroanal. Chem. 215, 237 (1986).

30. W. R. Fawcett and J. S. Jaworski. J. chem. Soc. Faraday Trans. 1 78, 1971 (1982).

31. W. R. Fawcett and A. Lasia. J. phys. Chem. 89, 5695 (1985).

32. G. M. Brisard and A. Lasia. J. electroanal. Chem. 221, 129 (1987).

33. A. Lasia and G. M. Brisard. J. electroanal. Chem. 266, 69 (1989).

34. W. R. Fawcett and A. Lasia. J. electroanal. Chem. 279, 243 (1990).

35. A. Lasia and M. Bouderbala. J. electroanal. Chem. 288, 153 (1990).

36. H. Sumi and R. A. Marcus. J. electroanal. Chem. 204, 59 (1986).

37. A. Nadler and R. A. Marcus. J. chem. Phys. 86, 3906 (1987).

38. W. R. Fawcett and C. A. Foss Jr. J. electroanal. Chem. 270, 103 (1989).

39. W. Harrer, G. Grampp and W. Jaenicke. J. electroanal. Chem. 209, 223 (1986).

40. J. Barthel and F. Feuerlein. J. solution Chem. 13, 393 (1984).

41. W. R. Fawcett and C. A. Foss Jr. J. electroanal. Chem., in press. 306, 71 (1991).

42. J. T. Hynes. J. phys. Chem. 90, 3701 (1986).

43. S. K. Garg and C. P. Smyth. J. phys. Chem. 69, 1294 (1965).

44. W. R. Fawcett. Chem. Phys. Lett. 174, 167 (1990).

45. G. Grampp and W. Jaenicke. Ber. Bunsenges. phys. Chem. 88, 325 (1984).

46. G. E. McManis, A. Gochev, R. M. Nielson and M. J. Weaver. J. phys. Chem. 93, 7733 (1989).

47. W. R. Fawcett and Colby A. Foss Jr. J. electroanal. Chem. 252, 221 (1988).

48. G. E. McManis, R. M. Nielson, A. Gochev and M. J. Weaver. J. Am. chem. Soc. 111, 5533 (1989).

49. R. A. Peterson and D. H. Evans. J. electroanal. Chem. 222, 129 (1987).

50. W. Schmickler and D. Henderson. Prog. Surf. Sci. 22, 323 (1986).

51. V. Gutmann and R. Schmid. Coord. chem. Rev. 12, 263 (1974).

52. T. M. Krygowski and W. R. Fawcett. J. Am. chem. Soc. 97, 2143 (1975).

53. R. Andreu, M. Sluyters-Rehbach, A. G. Remijnse and J. H. Sluyters. J. electroanal. Chem. 134, 101 (1982).

54. J. Struijs, M. Sluyters-Rehbach and J. J. Sluyters. J. electroanal. Chem. 171, 177 (1984).

55. M. Saakes, M. Sluyters-Rehbach and J. H. Sluyters. J. electroanal. Chem. 259, 265 (1989).

56. W. R. Fawcett and C. A. Foss Jr. J. electroanal. Chem. 250, 225 (1988).

57. L. F. Kozin, R. Sh. Nigmetova and M. B. Dergacheva. Thermodynamics of Binary Amalgam Systems. Nauka, Alma-Alta (1977).

58. W. R. Fawcett. Can. J. Chem. 59, 1844 (1981).

59. W. R. Fawcett and Z. Kovačova. J. electroanal. Chem. 292, 9 (1990).