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Technical Report No. 5

Ultrasonic Absorption Rate Studies of Crown Ether and
222 Cryptate Complexes of Alkali Metal Cations in Nonaqueous Solutions

by

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Prepared for Poster Presentation

at the

Third Chemical Congress of North America
Toronto, Canada on June 8, 1988

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June 30, 1988

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Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release and sale. Distribution unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 5		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION University of Utah	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Resident Representative	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Utah Salt Lake City, UT 84112		7b. ADDRESS (City, State, and ZIP Code) University of New Mexico Bandelier Hall West Albuquerque, NM 87131	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable) ONR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0639	
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) (U) ULTRASONIC ABSORPTION RATE STUDIES OF CROWN ETHER AND 222 CRYPTATE COMPLEXES OF ALKALI METAL CATIONS IN NONAQUEOUS SOLUTIONS			
12. PERSONAL AUTHOR(S) Sergio Petrucci and Edward M. Eyring			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 9/87 TO 6/88	14. DATE OF REPORT (Year, Month, Day) 1988, June 30	15. PAGE COUNT 6
16. SUPPLEMENTARY NOTATION Poster paper presented at the Third Chemical Congress of North America, Division of Physical Chemistry, Paper #174, June 8, 1988, Toronto, Ontario, Canada			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		→ Ultrasonic absorption, aprotic solvents, infrared spectra, metal cation complexation, cryptates, <i>JSJ</i> ←	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Sound absorption in liquids in the 0.5 MHz to 400 MHz frequency range can be measured by partially overlapping resonance, laser Debye-Sears, and pulse relaxation techniques. With appropriate precautions ultrasonic relaxation frequencies can be reliably determined in nonaqueous solutions prepared with dry aprotic solvents such as propylene carbonate and 1,3-dioxolane. Mid infrared spectra of counteranions can furnish valuable insights to the reactions responsible for the ultrasonic absorptions. The Eigen-Winkler reaction mechanism, involving several successive stages of desolvation as the metal cation approaches and enters the macrocycle, appears to apply in all cases. In the case of the 222 cryptates the stability of the complex is so great that one does not observe the coming together of the reactants on the ultrasonic time scale but only two intramolecular rearrangements of the cryptates. <i>May 1988</i>			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

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[Poster Paper #174 in the program of the Division of Physical Chemistry at the Third Chemical Congress of North America, Toronto, Ontario, Canada, June 5-10, 1988]

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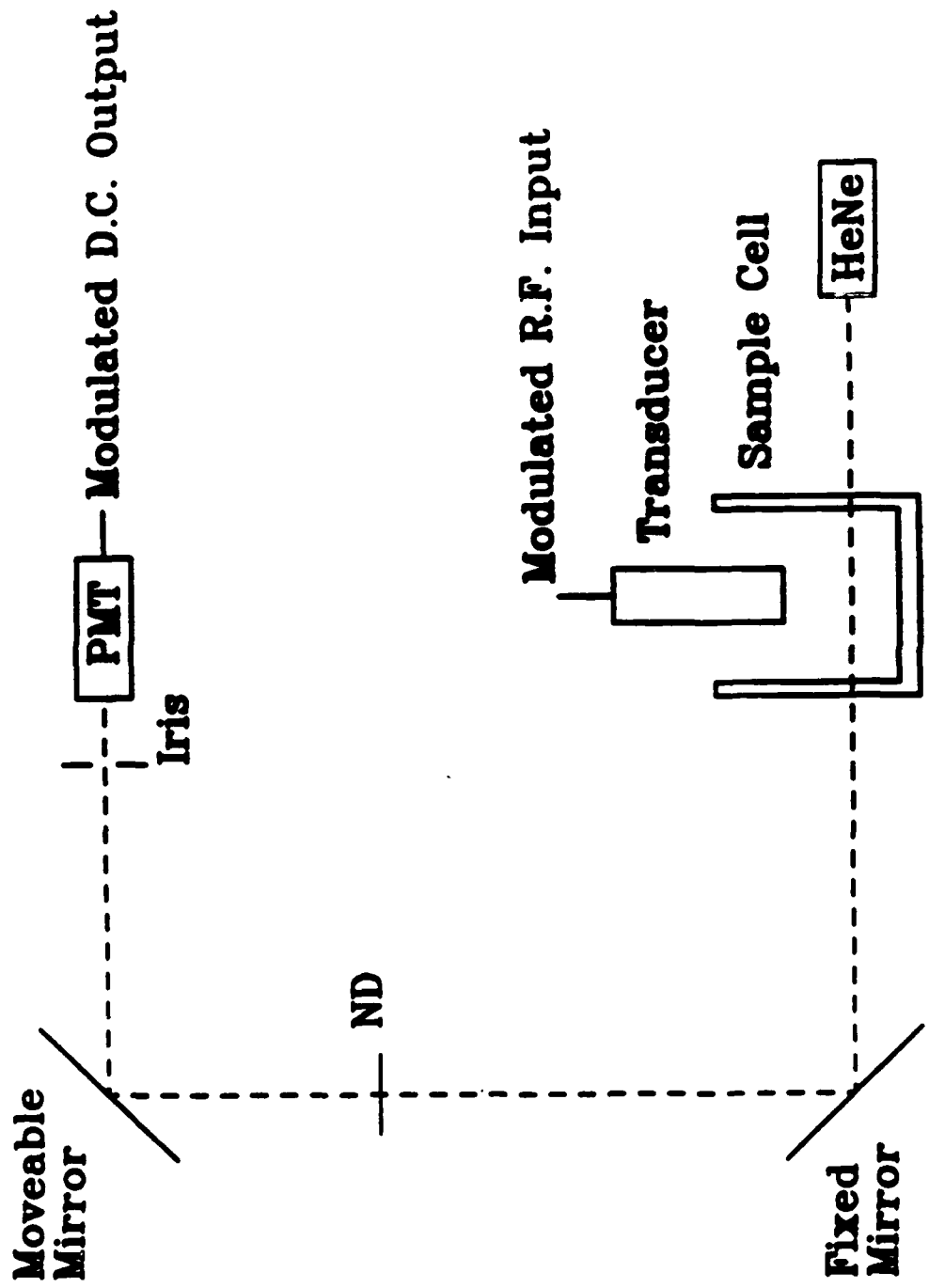
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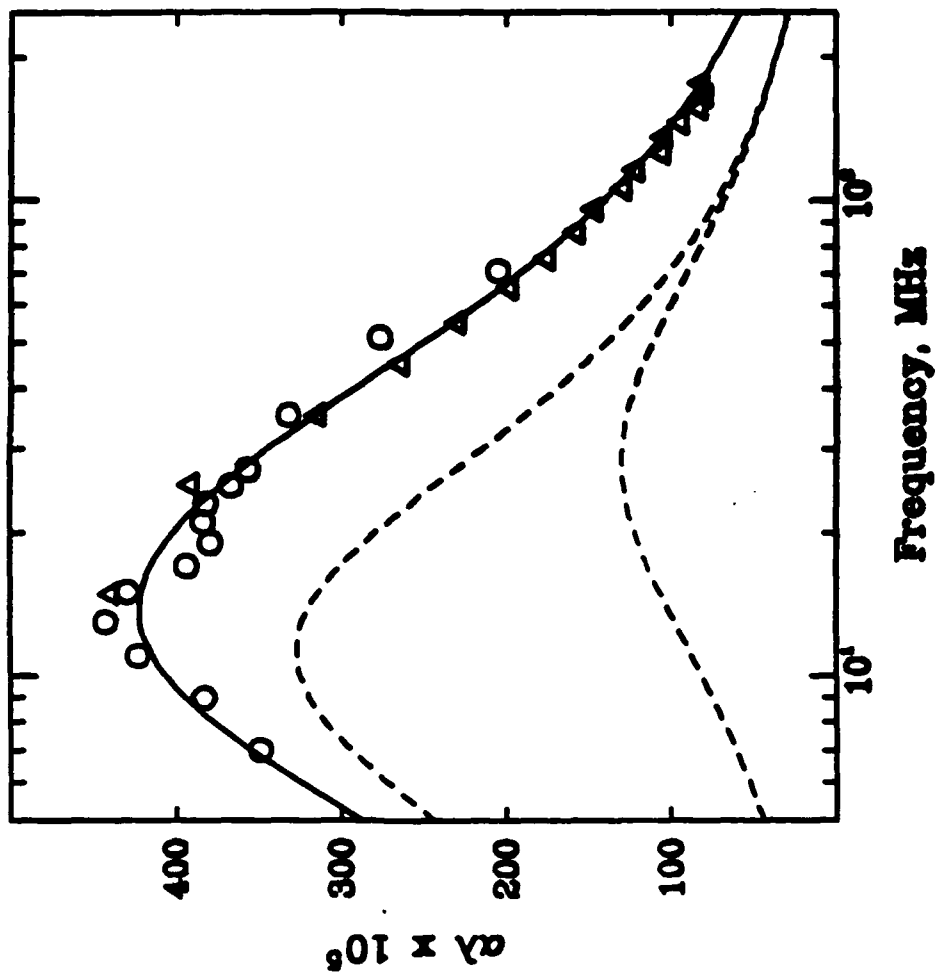
WHY ARE ULTRASONIC ABSORPTION REACTION RATE STUDIES IN LIQUIDS SELDOM REPORTED?

Several different experimental set ups (resonator, laser Debye-Sears and pulse) are needed to cover the full 0.5 MHz to 500 MHz ultrasonic absorption frequency range of interest. Even when extensively automated with laboratory computers these ultrasonic absorption experiments may require a day to yield the same amount of information as in an exponential decay curve of concentration versus time obtained in a single stopped flow or Joule heating temperature-jump experiment. The laser Debye-Sears experimental set-up is shown schematically at right. ND stands for a neutral density filter. The HeNe laser is operated at 5 mW.



The full curve at right is a fit of experimental points (circles obtained with a 1 MHz quartz transducer and triangles with a 5 MHz transducer) for a 0.3 M NaCl plus 0.096 M 18-crown-6 aqueous solution at 25°C. The dashed lines are for relaxation frequencies of 11.2 MHz and 28 MHz. The acoustic absorption coefficient is α , and λ is the ultrasonic wavelength.





If the sample liquid of interest is colorless at visible and near ultraviolet wavelengths and the chemical relaxation times characteristic of the sample lie between about 0.8 microseconds and 300 picoseconds, ultrasonic absorption with all its faults is still the method of choice for such a kinetic study.

WHY STUDY ALKALI METAL CATION COMPLEXATION KINETICS IN NONAQUEOUS MEDIA?

Lithium batteries have found many domestic and military applications. The electrolyte for these batteries is an aprotic medium prepared from a variety of nonaqueous liquids or polymeric solids. M. L. Kaplan *et al.*, *Solid State Ionics* 25, 37 (1987) have reported that crown ethers added to poly(vinylene carbonate) containing dissolved lithium salt facilitate ionic charge transport in this solid electrolyte. Specifically, 12-crown-4 added to the polymeric electrolyte increases conductivity by three orders of magnitude.

BY WHAT MECHANISM DOES A CROWN ETHER COMPLEX AN ALKALI METAL CATION IN A DRY APROTIC SOLVENT?

In the many cases we have examined so far the Eigen-Winkler reaction mechanism



adequately describes the ultrasonic absorption kinetic data. In the first step an outer-sphere complex is formed involving some rearrangement of the macrocyclic ligand and partial cation desolvation. The third step may be rate limited either by desolvation (as in aqueous solution) or ligand rearrangement (as in dimethylformamide). When the more rigid dibenzo-18-crown-6 ligand is substituted for 18-crown-6 with K^+ in DMF rate limiting ligand rearrangement becomes particularly apparent [J. Phys. Chem. 89, 1357 (1985).]

HOW DO THE KINETIC PROPERTIES OF THE 222 CRYPTATES OF ALKALI METAL CATIONS DIFFER FROM THOSE OF THE CORRESPONDING CROWN COMPLEXES?

The 222 cryptand experiences isomeric relaxations on the ultrasonic time scale in solvents such as methanol, methylcellosolve and propylene carbonate [J. Phys. Chem. 91, 1961 (1987).] Cryptand 222 is also well known to form cryptates with alkali metal cations on a stopped-flow [millisecond] time scale. When the 222-cryptates of Na⁺, K⁺, Rb⁺ and Cs⁺ are examined ultrasonically in dry propylene carbonate two very fast relaxation processes are detected. Neither relaxation has a significant concentration dependence indicating first order or pseudo first order character for the chemistry responsible for these relaxations. The higher frequency relaxation is detected at around 130 MHz at 25°C. The lower frequency relaxation (2 MHz to 25 MHz at 25°C) decreases in frequency in the order Na⁺ > K⁺ > Rb⁺ >> Cs⁺. The relaxations are interpreted by a scheme of the form



probably involving a rotation of the two nitrogen atoms of the cryptand which coordinate the metal cation (with the cation always bound to the cryptand). When the cation diameter exceeds the ligand cavity size in the case of Cs⁺ the rotational process becomes more difficult and the lower relaxation frequency declines steeply.

TO WHAT EXTENT DOES MODERN THEORY OVERLAP EXPERIMENTAL STUDIES OF Li⁺ COMPLEXATION KINETICS?

Ajit Banerjee, Jack Simons and coworkers [J. Chem. Phys. 68, 415 (1979); JACS 103, 2180 (1981); JACS 101, 1038 (1987)] have probed the equilibrium properties of ions and ion-pair hydration using quantum electronic structure and Monte-Carlo methods. They examined (a) the structure of hydration shells of the individual ions NO₂⁺(H₂O)_n and Li⁺(H₂O)_n as well as the complex NO₂⁻:Li⁺(H₂O)_n, (b) the changes in hydration shells during complex formation, and (c) changes in potential energy and mapping of potential barriers for chemically important pathways toward complex formation.

They found the first hydration shell of NO₂⁻(H₂O)_n to be highly anisotropic with the second and third hydration shells forming even before the first shell is completely closed. Thus inner hydration shells may have "weak spots" susceptible to attack by an approaching reactant.

Water molecules between the ions in the solvent separated ion-pair $\text{NO}_2^- \text{Li}^+(\text{H}_2\text{O})_n$ [$R \sim 5\text{\AA}$] achieve orientations favorable to both ions whereas for the intimate ion-pair [$R \sim 3\text{\AA}$] the hydration shells are very anisotropic. The second and third shells form before the first is completely closed. The solvent separated and intimate ion pairs both have a potential minimum. The solvent separated ion-pair is more stable than the intimate ion-pair by $\sim 20 \text{ kcal/mol}^{-1}$ with a $\sim 25 \text{ kcal/mol}^{-1}$ potential energy barrier above the solvent separated ion-pair cluster. This potential barrier may slow the rearrangement of the solvent separated ion-pair to an intimate ion-pair.

There are no experimental stability constants in the literature for the complexation of aqueous lithium ion by nitrite ion nor are there any reports of kinetic studies of the complexation reaction



The trend in condensed phase chemical kinetics seems to be in the direction of studying larger and larger reactant molecules and ions. Experimentalists should consider investigating systems such as aqueous lithium nitrite having comparatively few total electrons that are thus more propitious for concurrent theoretical investigation.

ACKNOWLEDGEMENTS

Financial support was provided by the NSF and ONR. Recent coworkers include H. Schneider, K. H. Richmann, T. Funck, P. Firman, F. Eggers, L. J. Rodriguez, G. R. Phillips, C. N. Merrow, R. M. Barton, D. P. Cobranchi and D. E. Johnson.