(2)

OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract N00014-86-K-0639

R&T 4133013...02

LASER TEMPERATURE-JUMP KINETIC STUDIES OF FAST REACTIONS IN NONAQUEOUS SOLUTIONS

Edward M. Eyring, Principal Investigator

Department of Chemistry

University of Utah

Salt Lake City, Utah 84112

February 28, 1990

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) Final Report	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION University of Utah 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry, 2428 HEB University of Utah, Salt Lake City, UT 84112	7b ADDRESS (City, State, and ZIP Code)
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b OFFICE SYMBOL (If applicable)	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) Laser Temperature-Jump Kinetic Studies of Fast Reactions in Nonaqueous Solutions

12 PERSONAL AUTHOR(S)
Edward M. Eyring

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Final Technical	FROM 9/87 TO 2/90	1990 February 28	4

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	ultrasonic absorption; crown ethers; lithium ion complexation; poly(ethylene oxide); nonaqueous solutions; sequential simplex.

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Ultrasonic absorption methods have elucidated the kinetics of complexation of lithium ions by cyclic and acyclic polyethers in nonaqueous solvents. The interaction between the cation and polyether chain is localized and does not depend on chain length. Stability constants for lithium-ion-crown-ether complexes in a room temperature molten salt have been determined by lithium-7 nmr. Error estimation using the sequential simplex method in nonlinear curve-fitting has been demonstrated on small computers.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21 ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL Edward M. Eyring	22b TELEPHONE (Include Area Code) (801) 581-8658 / 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

☆ U.S. Government Printing Office: 1986—607-044

Laser Temperature-Jump Kinetic Studies of Fast Reactions in Nonaqueous Solutions

(Final Report)

Model systems for two different types of lithium battery electrolytes have been examined with ultrasonic absorption and nuclear magnetic resonance techniques. The rate of complexation of lithium ion by the macrocyclic polyether 18-crown-6 in dry propylene carbonate was successfully analyzed[1] in terms of two high frequency relaxation processes involving the stepwise desolvation of the lithium ion. Comparisons were made between 18-crown-6 and several nitrogen heterocyclic ligands in a subsequent paper.[2] Ethylene oxide oligomers were explored kinetically as ligands for Li^+ in dry acetonitrile in what one referee said "is a massive paper which adds significantly to our understanding of the dynamics of poly(ether) coordination." The most interesting generalization to emerge from this work is that the cation-polyether interaction is a localized one that is independent of the length of the poly(ethylene oxide) chain at least up to an average molar mass of 15,000.

A parallel study[4] of lithium ion complexation by crown ethers in a room temperature molten salt (the binary $AlCl_3$-1-methyl-3-ethylimidazolium chloride melt) has been carried out by lithium-7 nmr. The objective was the determination of stability constants between Li^+ and four crown ethers. In order of increasing complex ion stability the ligands are 18-crown-6 < 12-crown-4 < benzo-15-crown-5 < 15-crown-5. Stability constant data for the Li^+-15-crown-5 complex were obtained over a range of temperatures thus permitting a determination also of ΔH and ΔS for the formation of this complex.

An investigation[5] of error estimation using the sequential simplex method was carried out. An expert in the field subsequently made the following assessment[6] of this paper: "The simplex method is used extensively in nonlinear curve-fitting applications. The present study [Phillips and Eyring, 1988] reports an advance that will be extremely useful in this context. Incorporation of this approach into nonlinear curve-fitting routines would be quite a step forward in the production of realistic values for fitted parameters along with the estimates of their errors. The major implication of this work is that there is now no reason to settle for parameter estimates without accompanying error estimates, even from statistical programs running on very small machines. There is essentially no penalty for evaluating the error along with the parameters themselves."

References

1. D. P. Cobranchi, G. R. Phillips, D. E. Johnson, R. M. Barton, D. J. Rose, E. M. Eyring, L. J. Rodriguez, and S. Petrucci, J. Phys. Chem. 93, 1396 (1989).

2. L. J. Rodriguez, M. Xu, E. M. Eyring and S. Petrucci, Pure & Appl. Chem. 61, 1593 (1989).

3. J. Eschmann, J. Strasser, M. Xu, Y. Okamoto, E. M. Eyring and S. Petrucci, J. Phys. Chem., in press.

4. B. A. Garland, D. P. Cobranchi, A. Gerhard, E. M. Eyring and J. S. Wilkes, in preparation.

5. G. R. Phillips and E. M. Eyring, Anal. Chem. 60, 738 (1988).

6. P. C. Jurs, Chemtracts: Anal. & Phys. Chem. 1, 39 (1989).

Contract Publications

1. G. R. Phillips and E. M. Eyring, "Error Estimation Using the Sequential Simplex Method in Nonlinear Least Squares Data Analyses," Anal. Chem. 60, 738 (1988).

2. D. P. Cobranchi, G. R. Phillips, D. E. Johnson, R. M. Barton, D. J. Rose, E. M. Eyring, L. J. Rodriguez, and S. Petrucci, "Kinetics of Complexation of Lithium Perchlorate with 18-Crown-6 in Propylene Carbonate," J. Phys. Chem. 93, 1396 (1989).

3. G. R. Phillips and E. M. Eyring, "Exchange of Comments on the Simplex Algorithm Culminating in Quadratic Convergence and Error Estimation," Anal. Chem. 61, 1786 (1989).

4. L. J. Rodriguez, M. Xu, E. M. Eyring and S. Petrucci, "Molecular Dynamics of Macrocycle-metal Ion Complexes Involving Heteronuclear Binding Atoms," Pure & Appl. Chem. 61, 1593 (1989).

5. J. Eschmann, J. Strasser, M. Xu, Y. Okamoto, E. M. Eyring and S. Petrucci, "Nanosecond Molecular Dynamics and Vibrational Spectra of Li^+-Chain-Polyethers in Acetonitrile," J. Phys. Chem., in press.

6. E. M. Eyring and S. Petrucci, "Rates and Mechanism of Complexation Reactions of Cations with Crown Ethers and Related Macrocycles," in Cation Binding by Macrocycles, Y. Inoue and G. W. Gokel, Eds., Marcel Dekker, New York, NY, in press.

Contract Technical Reports

1. G. R. Phillips and E. M. Eyring, "Error Estimation Using the Simplex Method in Nonlinear Least Squares Data Analyses," (June 17, 1987).

2. G. R. Phillips and E. M. Eyring "Optimization in Analytical Chemistry Using Robust Estimation," (July 30, 1987).

3. D. P. Cobranchi, G. R. Phillips, D. E. Johnson, R. M. Barton, D. J. Rose, E. M. Eyring, L. J. Rodriguez, and S. Petrucci, "Kinetics of Complexation of Lithium Perchlorate with 18-Crown-6 in Propylene Carbonate," (June 30, 1988).

4. G. R. Phillips, C. N. Merrow, J. K. Mitchell, R. M. Barton and E. M. Eyring, "Low Frequency Laser Debye-Sears Ultrasonic Measurements," (June 30, 1988).

5. S. Petrucci and E. M. Eyring "Ultrasonic Absorption Rate Studies of Crown Ether and 222 Cryptate Complexes of Alkali Metal Cations in Nonaqueous Solutions," (June 30, 1988).

6. L. J. Rodriguez, M. Xu, E. M. Eyring and S. Petrucci, "Molecular Dynamics of Macrocycle-metal Ion Complexes Involving Heteronuclear Binding Atoms," (January 23, 1989).

7. E. M. Eyring and S. Petrucci, "Rates and Mechanisms of Complexation Reactions of Cations with Crown Ethers and Related Macrocycles," (January 23, 1989).

8. G. R. Phillips and E. M. Eyring, "Comments on the Simplex Algorithm Culminating in Quadratic Convergence and Error Estimation," (June 27, 1989).

9. J. Eschmann, J. Strasser, M. Xu, Y. Okamoto, E. M. Eyring and S. Petrucci, "Nanosecond Molecular Dynamics and Vibrational Spectra of Li^+-Chain-Polyethers in Acetonitrile," (June 27, 1989).