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OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0639

R&T Code 4133013...2

Technical Report No. 3

Kinetics of Complexation of Lithium Perchlorate with 18-Crown-6 in Propylene Carbonate

by

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Prepared for Publication

in the

Journal of Physical Chemistry

University of Utah
Department of Chemistry
Salt Lake City, UT 84112

June 30, 1988

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. 3	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 2217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO

11. TITLE (*Include Security Classification*)
(U) Kinetics of Complexation of Lithium Perchlorate with 18-crown-6 in Propylene Carbonate

12. PERSONAL AUTHOR(S)
D.P. Cobranchi, G.R. Phillips, D.E. Johnson, R.M. Barton, D.J. Rose, E.M. Eyring,* L.J. Rodriguez, and S. Petrucci

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (*Year, Month, Day*)	15. PAGE COUNT
Technical	FROM 9/87 TO 6/88	1988, June 30	15

16. SUPPLEMENTARY NOTATION
Prepared for publication in the Journal of Physical Chemistry

17 COSATI CODES			18. SUBJECT TERMS (*Continue on reverse if necessary and identify by block number*)
FIELD	GROUP	SUB-GROUP	Lithium ion, complexation, crown ether, ultrasonic absorption, dry propylene carbonate, aprotic solvents.

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

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (*Include Area Code*) / 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

Kinetics of Complexation of Lithium Perchlorate with 18-crown-6 in Propylene Carbonate

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ABSTRACT

The kinetics of complexation of $LiClO_4$ with the macrocycle 18-crown-6 have been studied in propylene carbonate using ultrasonic relaxation techniques. Two concentration-independent relaxations are observed and explained in terms of the Eigen-Winkler mechanism. The influence of propylene carbonate on the complexation of lithium with crowns is compared with the influence of other aprotic solvents.

INTRODUCTION

Kaplan et al.[1] recently reported that crown ethers added to poly(vinylene carbonate) containing a lithium salt enhance charge transport in this solid electrolyte. Thus possible applications in lithium batteries are a justification for studying the kinetics of decomplexation and complexation of lithium ions by crown ethers in nonaqueous, aprotic media. A more fundamental reason for such a kinetic study is the aim of understanding the relative importance of several competing factors that can all play a significant role in the reaction kinetics of nonaqueous solutions of alkali metal cations and crown ethers. These factors include the Gutmann donor number of the solvent, the flexibility of the macrocyclic ligand, the basicity of the ether oxygens of the macrocycle, and the reorganization of the solvent cage around the cation.[2] Whereas in aqueous solution the kinetics of lithium ion complexation are dominated by the rate limiting loss of a solvent water molecule from the first coordination sphere of the cation, in nonaqueous media the crown ether, cation, associated anion, and solvent form a "complex supramolecular assembly"[3] in which each participant plays a significant role in the reorganization accompanying the cation complexation or decomplexation.

The present kinetic study of lithium ion and 18-crown-6 (18C6) has been carried out in dry propylene carbonate(PC). This is an aprotic, nonassociated solvent with no hydrogen bond donating capacity. At 25°C this solvent has a higher relative permittivity (ε=64.4) and higher coefficient

of viscosity (η=2.53 cP) than most other solvents used in lithium batteries.[4]

The choice of the perchlorate anion for these kinetic studies was dictated by the availability[5] of stability constants for lithium perchlorate complexes fromed with 12C4, 15C5, and 18C6 in several solvents.

EXPERIMENTAL SECTION

Instrumentation. Ultrasonic absorption measurements were made using the laser Debye-Sears, resonator, and pulse techniques. The Debye-Sears apparatus differs from a previous description[6] in two major aspects: (1) the stepping motors in the present work were manually controlled and (2) an argon-ion laser previously used was replaced by a 5 mW HeNe laser. The lower power of the HeNe laser did not reduce the accessible (3 MHz to 240 MHz) frequency range. The Debye-Sears apparatus was housed in a glove box of local construction to exclude water vapor that was purged continuously with dry nitrogen gas. The resonator and pulse apparatus have been previously described.[7] Data from these three ultrasonic techniques were combined and analyzed using a Levenburg-Marquardt nonlinear least squares algorithm.[8]

Reagents. Propylene carbonate (Aldrich) was stored over activated (baked under vacuum) 3A molecular sieves for at least one week, and then distilled under reduced pressure. Anhydrous lithium perchlorate (G. F. Smith Chemicals) was heated under vacuum at 170°C until there was no further

decrease in pressure. 18-crown-6 (Parish) was recrystallized from acetonitrile and dried at room temperature in vacuo. All chemicals were stored in a Vacuum Atmospheres glove box until just prior to use. Solutions of $LiClO_4$ and 18C6 (in a 1:1 molar ratio) were prepared in the glove box and transferred under argon to the ultrasonic apparatus. The water content of all solutions was determined to be less than 20 ppm using the lead tetraacetate method.[9]

RESULTS

A solution of lithium perchlorate in dry propylene carbonate does not produce a detectable excess ultrasonic absorption. However, excess absorption is observed for solutions of $LiClO_4$ combined with 18-crown-6 in PC. The ultrasonic relaxation spectrum of a PC solution that is 0.125 M in $LiClO_4$ and 0.125 M in 18-crown-6 at 25°C is shown in Fig. 1. Only one-third of the experimental points are shown for clarity. The solid line in Fig. 1 corresponds to the sum of two relaxation processes, as given by the function:

$$\frac{\alpha}{f^2} = \frac{A_I}{1 + (f/f_I)^2} + \frac{A_{II}}{1 + (f/f_{II})^2} + B \qquad (1)$$

where A_I and A_{II} are the amplitudes of the two processes centered at the relaxation frequencies f_I and f_{II}, and B is the value of α/f^2, i.e. the amplitude of the background, at frequencies much greater than f_I and f_{II}.

Values of the relaxation frequencies are reported in Table I. The two relaxation frequencies are independent of concentration, with average values of 1.0 ± 0.1 MHz and 23.1 ± 0.6 MHz. These results can be explained in terms of pseudo first-order processes using the Eigen-Winkler mechanism:[10]

$$M^+ + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^+...C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MC^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (MC)^+ \qquad (2)$$

In this mechanism M^+ is the solvated metal cation, C is the crown ether, $M^+...C$ denotes the solvent-separated metal-crown ligand pair, MC^+ is a contact pair, and (MC^+) is the final complex with the metal cation imbedded in the crown cavity. Recent ultrasonic studies[11] have demonstrated consistently that this mechanism works well in describing reactions of metal cations with crown ethers.

Using the value of $\log_{10} K_\Sigma = 2.69 \pm 0.11$ reported by Smetana and Popov,[5] the general Eigen-Winkler mechanism reduces to

$$M^+ \ldots C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MC^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (MC)^+ \qquad (3)$$

The reduced mechanism is interpreted according to the relations

$$\tau_I^{-1} = 2\pi f_I = k_{-2} + k_2 \simeq k_2 \qquad (4)$$

for $k_2/k_{-2} >> 1$, and

$$\tau_{II}^{-1} = 2\pi f_{II} = k_{-3}\left(1 + K_3 \frac{K_2}{1 + K_2}\right) \simeq k_3 \qquad (5)$$

for K_3 and $K_2 >> 1$. Using a weighted mean of the relaxation frequencies in Table I, the calculated rate constants are $k_2 = 1.45 \pm 0.1 \times 10^8$ sec^{-1} and $k_3 = 6.3 \pm 0.6 \times 10^6$ sec^{-1}.

DISCUSSION

In a fairly thorough survey of the literature through 1984, Izatt et al.[12] found only twenty-four kinetic studies of lithium ion complexation by macrocycles. Only one of these studies involved a crown ether, in this case 18-crown-6 in aqueous solution.[13] (The other twenty-three studies involved the much slower formation of lithium cryptates.)

The above described results in PC are consistent with a general picture of lithium ion complexation kinetics in nonaqueous solvents that has emerged from studies made largely since 1984.

In the low permittivity solvent 1,2-dimethoxyethane (ε = 7.05 and η = 0.41 cP at 25°C) the solvent molecules, which resemble an acyclic fragment of a crown ether, compete successfully with 18C6 or 12C4 for coordination sites around the Li^+ ion.[14,15] Two well separated ultrasonic absorption maxima are observed (at roughly 90 MHz and 9 MHz) and their concentration dependence permits a calculation of $k_2 = 1.5 \times 10^8$ $dm^3 mol^{-1} s^{-1}$, $k_{-2} = 1.4 \times 10^7 s^{-1}$ and $K_2 = 10.7\ M^{-1}$ for 18C6 and $k_2 = 1.9 \times 10^7$ $dm^3\ mol^{-1} s^{-1}$, $k_{-2} = 5.5 \times 10^6 s^{-1}$ and $K_2 = 3.5\ M^{-1}$ for 12C4 in the equilibrium

$$LiS, X + C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} LiC, X + S \qquad (6)$$

where S denotes 1,2-DME, X denotes AsF_6^-, and C denotes the crown.[15] These rate constants are essentially the same when ClO_4^- is substituted for the AsF_6^- anion.[14] These two anions give rise to greater differences in the ultrasonic absorption spectra when Li^+ reacts with 18C6 in 1,3-dioxolane

(ε = 7.13 and η = 0.59 cP at 25°C), but the overall picture of what is happening[16,17] is much the same in 1,3-doxolane as in 1,2-DME.[14,15]

LiSCN plus 18C6 in the somewhat higher permittivity solvent dimethylformamide (ε = 36.71 and η = 0.80 cP at 25°C) shows no ultrasonic relaxation not already present when LiSCN alone is dissolved in DMF.[18] However, because ClO_4^- is a weakly coordinating anion the combination of $LiClO_4$ plus 18C6 in DMF does show a single ultrasonic relaxation process indicating an interaction between Li^+ and 18C6 in this solvent.[8] In ethanol (ε = 24.3 and $\eta \tilde{=}$ 1.1 cP at 25°C) the $LiClO_4$ plus 18C6 combination produces a double relaxation process.[8] These relaxations in DMF and in ethanol are concentration independent indicating that they arise from the second or third equilibrium in the Eigen-Winkler mechanism (3) as would be expected for larger values of the overall complex ion stability constant K_Σ than are found in 1,2-DME. Since the permittivities of DMF and EtOH are somewhat similar, some other factor or factors must be invoked to explain the difference in the number of relaxation processes observed in these two solvents.

The combination of $LiClO_4$ plus 18C6 in methanol (ε = 32.6 and η = 0.55 cP at 25°C) yields two observable relaxation frequencies at approximately 75 MHz and 7 MHz that both shift with concentration.[19] As in the cases of the same solutes in DMF, EtOH and now PC, the kinetic data may be interpreted in terms of the reduced mechanism (3).

When the lithium ion results are compared[19] with those for $NaClO_4$ and $KClO_4$ reacting with 18C6, dicyclohexano-18-crown-6, and dibenzo-18-crown-6 in DMF and MeOH it becomes clear that both steps in mechanism (3) depend on the metal, ligand and solvent with all of them participating in shaping the activation profile of the complexation process. Simplistic attributions of the faster relaxation process to partial cation desolvation and the slower relaxation process to a ligand conformational change are not borne out by the experimental data. Instead a concerted process occurs in which, depending on solutes and solvents, either the removal of solvent or ligand rearrangement may be rate determining.

Alkali metal cation nuclear magnetic resonance kinetic studies[2,20] of the dissociation of crown ether complexes of sodium-ion in nonaqueous solvents can provide additional insights regarding the relative importance of unimolecular and bimolecular contributions to the dissociation kinetics. Graves and Detellier[2] do not find a systematic relationship between Gutmann donor numbers and activation parameters in their rate study of sodium tetraphenylborate with 18C6 in PC, acetonitrile, pyridine and acetone. Thus they also reach the conclusion that "several factors, including conformational rearrangement of the ligand and reorganization of the solvent cage" contribute to the activation profile.[2]

Picosecond laser pulses and fluorescent probes[21,22] (in this case crown ethers) may eventually prove to be more effective tools than either nmr or ultrasonic absorption for unravelling the relative importance of these

various competing influences on the complexation-decomplexation activation profiles for lithium ion and crown ethers in nonaqueous solvents.

ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research.

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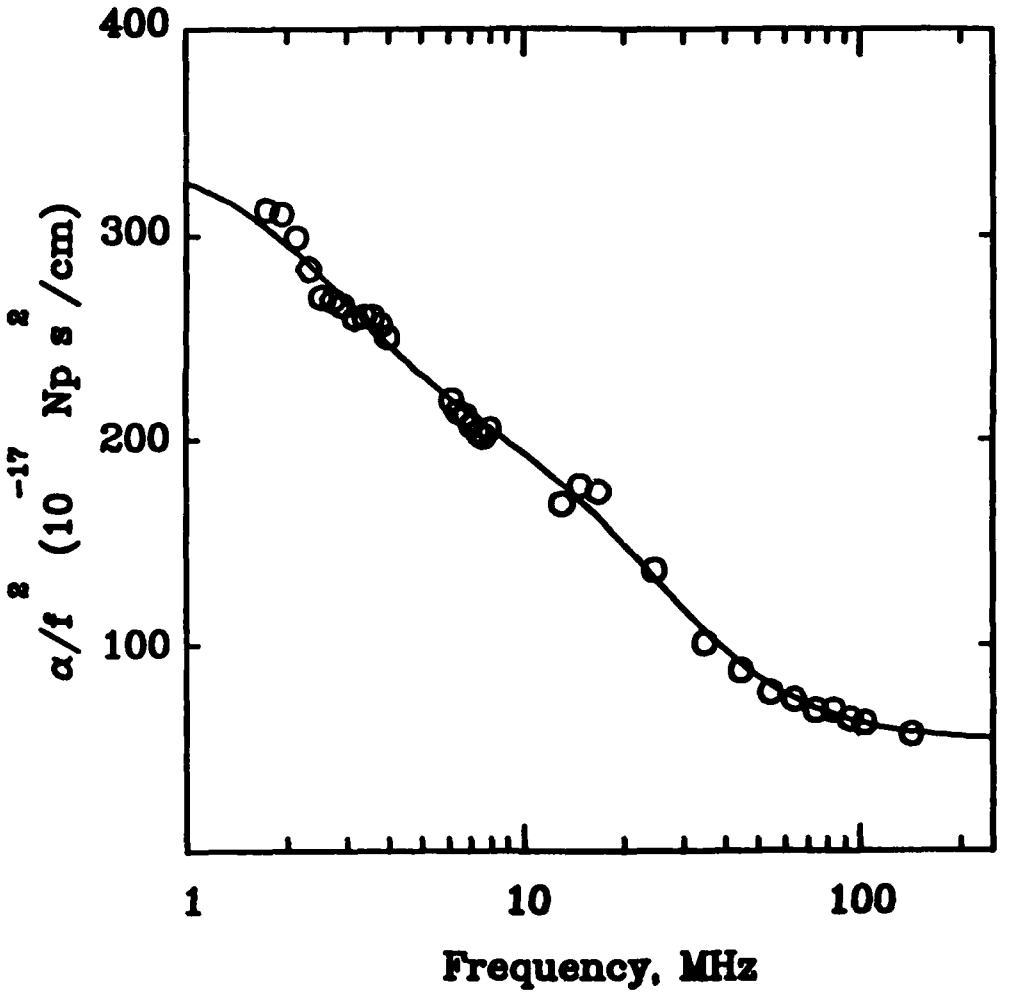
Table I. Ultrasonic Relaxation Frequencies for $LiClO_4$ and 18C6 in Propylene Carbonate at 25°C

C_{LiClO_4}, M	C_{18C6}, M	f_I, MHz[a]	f_{II}, MHz[a]
0.1	0.10	24.27 (2.26)	3.76 (0.16)
0.125	0.125	25.73 (1.27)	1.43 (0.54)
0.25	0.25	22.29 (0.82)	1.09 (0.66)
0.50	0.50	20.68 (1.31)	0.86 (0.16)
0.75	0.75	23.29 (4.58)	0.98 (0.18)
1.00	1.00	25.60 (1.87)	1.04 (0.22)

[a]Estimated standard errors are given in parentheses.

FIGURE CAPTIONS

Figure 1: Plot of α/f^2 as a function of ultrasonic frequency for a solution of 0.125 M $LiClO_4$ and 0.125 M 18C6 in propylene carbonate at 25°C. The solid line is the sum of two relaxations with relaxation frequencies at 1.4 MHz and 25.7 MHz.


400
300
200
100
α/f^2 (10^{-17} Np s^2/cm)
1
10
100
Frequency, MHz