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M. Xu, E. M. Eyring, S. Petrucci      DAAH04-93-G-0014

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  
Polytechnic University  
Route 110, Farmingdale, NY 11735  
University of Utah  
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A study has been performed on the association and molecular dynamics of alkali-ion salts, especially lithium salts dissolved in acyclic polyethers. The purpose of the study was to investigate the status of the electrolyte in these media, the lifetime of the species in solution and their molecular dynamics. Several techniques such as electrical conductance, infrared spectra, ultrasonic relaxation kinetics, microwave and infrared dielectric relaxation and molar refractometry have been used for the above research. The subject of this study is highly relevant for the construction of lithium batteries using polymer electrolyte media. Four published papers, and three more in preparation, have resulted from this project.

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Statement of the Problem Studied

It was of interest to study the structure and molecular dynamics of alkali metal-ion salts, especially lithium salts dissolved in acyclic polyethers in order to investigate the status of electrolytes in these media, the lifetime of the species in solution and their molecular dynamics. To this end several techniques (such as electrical conductance, infrared spectra, ultrasonic relaxation kinetics, microwave and infrared dielectric relaxation and molar refractometry) were employed. The above systems are highly relevant as electrolyte-polymer media for the construction of lithium batteries.

The research program has sponsored Dr. Meizhen Xu, a research associate in addition to Edward M. Eyring and Sergio Petrucci the two PI's of the present research and a graduate student at the University of Utah.

The particular subjects and results of this study can be summarized as follows:

1) Molecular Relaxation Dynamics of LiClO<sub>4</sub> in Acyclic Polyether Solvents

Ultrasonic relaxation spectra are reported for LiClO<sub>4</sub> dissolved in acyclic polyethers of increasing chain length including 1,2-dimethoxyethane (1,2-DME), CH<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OCH<sub>3</sub> with  $n = 1$ ; diglyme with  $n = 2$ ; and tetraglyme with  $n = 4$ . Spectra were measured at 25°C at various concentrations in the frequency range ~1 to ~500 MHz. The data are analyzed in terms of the dimerization equilibrium  $2\text{LiClO}_4 \rightleftharpoons (\text{LiClO}_4)_2$ , determining rate constants, equilibrium constants of dimerization,  $K_{\text{d}}$ , and isoentropic volume changes for the process,  $\Delta V_s$ . Infrared spectra for the  $\bar{\nu}_4$  mode of ClO<sub>4</sub><sup>-</sup> at approximately 623 cm<sup>-1</sup> reveal a satellite band at wavenumbers ranging from 633 to 638 cm<sup>-1</sup> that is attributed to contact ion pairs. Microwave dielectric relaxation spectra of LiClO<sub>4</sub> in the above polyethers reveal a relaxation process involving the solute (that is absent in the pure solvent) which is attributed to the rotational relaxation of LiClO<sub>4</sub> ion pairs. The relaxation process shifts in frequency from around 2 GHz for LiClO<sub>4</sub> in 1,2-DME to 0.21 GHz for LiClO<sub>4</sub> in tetraglyme at 25°C. This behavior correlates well with the change in the viscosity of the solvents which has been determined separately. The apparent dipole diameter is about  $a_0 = 4 \times 10^{-8}$  cm. Comparable values have been calculated from the Böttcher function determining the apparent dipole moment of the ion pairs in solution. The molar refraction of lithium perchlorate,  $R_{\text{LiClO}_4}$ , has been calculated from measured refractive indices and densities of solutions of LiClO<sub>4</sub> in polyethers at various electrolyte concentrations. The values of  $R_{\text{LiClO}_4}$  vary with the solvent and can be correlated with the gas-phase value of the dipole moment of the solvent. This is interpreted as reflecting electrostatic interactions of the solvent dipoles with ClO<sub>4</sub><sup>-</sup>, the more polarizable ion (compared to Li<sup>+</sup>).

This project has been published under the above title by the Journal of Physical Chemistry 1993, 97, 3606 by P. Firman, M. Xu, E.M. Eyring, S. Petrucci.

A discussion of the results of this paper when compared to a parallel work by Schültz and Stockhausen has been published in Ber Bunsenges Phys. Chem. 1994, 98, 872 by P. Firman, M. Xu, E.M. Eyring, S. Petrucci.

Radio frequency and microwave frequency complex dielectric permittivity  $\epsilon^* = \epsilon' - i\epsilon''$  data for  $\text{LiClO}_4$  in tetraglyme as well as similar previously published data for  $\text{LiNO}_3$  in liquid polyethylene oxides are reviewed. The reliability of the dielectric loss coefficient  $\epsilon''_d$  at concentrations  $C \gg 0.1$  M (obtained as the difference between the total loss  $\epsilon''$  and the conductance loss  $\epsilon''_x = 1.8 \times 10^{12} X/f$ ) is questioned for frequencies  $f \leq 0.1$  GHz. The interpretation of the dielectric spectra of  $\text{LiClO}_4$  (and of  $\text{LiNO}_3$ ) in polyethers is critically analyzed.

2) Molecular Structure and Dynamics of  $\text{LiClO}_4$ -Polyethylene Oxide-400 (Dimethylether and Diglycol Systems) at 25°C

Infrared spectra of the  $\bar{\nu}_4$  mode of the  $\text{ClO}_4^-$  ion, for the systems  $\text{LiClO}_4$ -polyethylene oxide dimethyl ether of average molar mass 400 (PEO-400) and  $\text{LiClO}_4$ -polyethylene oxide glycol of average molar mass 400 (PEG-400), at 25°C, have been determined and quantitatively described by the sum of two Gaussian-Lorentzian product functions centered at  $\sim 623$  and  $\sim 635$   $\text{cm}^{-1}$ , respectively. Bands are assigned to spectroscopically free  $\text{ClO}_4^-$  (at  $\sim 623$   $\text{cm}^{-1}$ ) and to bound  $\text{ClO}_4^-$  (at  $\sim 635$   $\text{cm}^{-1}$ ). From the relative amplitudes of the two bands, it is concluded that the majority of the  $\text{ClO}_4^-$  exists out of contact with  $\text{Li}^+$ , probably as solvent-separated ion pairs. This conclusion is based on a large ion-pair formation constant  $K_p = 4.5_2 \times 10^3$  for  $\text{LiClO}_4$  in PEO-400, as reported in the literature and reanalyzed in this work. Electrical conductance data for  $\text{LiClO}_4$  in PEG-400 are also reported and analyzed with current theories furnishing values of  $K_p$  for this system. Existence of dimer aggregates  $(\text{Li}^+ \text{S}_x \text{ClO}_4^-)_2$ , with S symbolizing an oxygen moiety of a polyether chain, is inferred from ultrasonic relaxation spectra of  $\text{LiClO}_4$ -PEO systems. The presence of some  $(\text{LiClO}_4)_2$  dimeric contact species is also inferred. The ultrasonic absorption spectra show two relaxation processes followed, at high frequency, by a solvent relaxation process. Matrix analysis has been applied to the two-step dimerization process  $2\text{LiClO}_4 \rightleftharpoons \text{LiClO}_4 \cdots \text{LiClO}_4 \rightleftharpoons (\text{LiClO}_4)_2$  (which is used to interpret the electrolyte ultrasonic relaxation processes) The analysis yields all the rate and equilibrium constants for the above steps. In addition, from the amplitude of the ultrasonic spectra, the isoentropic volume changes of the two normal modes, associated with the above equilibria, are calculated. The larger shear viscosity of the PEG solvent precludes the measurement of the solute ultrasonic relaxation in this medium. The molecular dynamics of the above systems have also been explored through microwave and far-infrared dielectric spectra measured in the frequency range from 0.4 GHz to 15 THz (i.e.  $500\text{cm}^{-1}$ ). The spectra are quantitatively described by the sum of a Cole-Cole distribution, operative mainly in the UHF-microwave region, and of three Powles-Rocard component bands (recently discussed in the literature) that are operative mainly at IR frequencies. In the microwave region, the Cole-Cole distribution describes the ethereal chain segmentational rotation, influenced by  $\text{Li}^+$  cations that increase the intertangling of the ethereal chains. In the far-IR region the highest frequency Powles-Rocard band at  $\sim 300$   $\text{cm}^{-1}$  has been assigned, in accordance with the literature, to torsion of ethereal chains. The other two bands are probably due to librations, namely to hindered molecular rotations limited to small angles. Molar refractivities for  $\text{LiClO}_4$  in PEO-400 and in PEG-400 have been determined in a concentration range comparable to that used in the above work.

The above work under the same title has been published in J. Phys. Chem. 1994, 98, 8234 by M. Salomon,

M. Xu, E.M. Eyring, S. Petrucci.

3) Molecular Dynamics and Infrared Spectra of NaSCN dissolved in the Solvent Macrocycle 15C5 and Polyethylene Oxide Dimethyl Ether - 250

NaSCN dissolved in liquid 15-crown-5 (15C5) at 25°C has been studied by audio frequency electrical conductivity and by infrared spectroscopy ("CN stretch mode" or antisymmetrical stretch of the SCN<sup>-</sup> anion). Analysis of the conductance data by the Fuoss-Onsager theory (concentration range (6-80) x 10<sup>-4</sup> M) indicates that the electrolyte is *unassociated*. This conclusion is corroborated by infrared spectra described by a single Gaussian-Lorentzian band centered at ~2058 cm<sup>-1</sup> for electrolyte concentrations up to ~0.1 M. The molecular dynamics of the above systems have been studied by ultrasonic and UHF relaxation spectroscopy over the ~1 to 600 MHz frequency range. At 25°C the solute relaxation centered at ~10 MHz is that of a pseudo-first-order kinetic process. It is attributed to a Na<sup>+</sup>-15C5 interaction. The microwave dielectric spectrum of a 15C5-NaSCN solution in the frequency range 0.3-130 GHz is described by a Cole-Davidson distribution function, as was feasible for the microwave dielectric spectrum of the 15C5 solvent determined previously. The molar refraction *R* calculated from sodium doublet refractive indices has also been determined. The above experiments have been repeated with NaSCN dissolved in the acyclic polyethylene oxide dimethyl ether polymer of average molar mass 250 g mol<sup>-1</sup> (PEO-250). The electrolyte appears to be heavily associated in the acyclic polymer in contrast to the case of 15C5 solvent. Thus, 15C5 may find use as a solvent in electrolyte-polymer batteries. Because of the practical importance of some Li<sup>+</sup> salts in batteries, some of the above investigation has been repeated for LiSCN in 15C5 and compared with the NaSCN in 15C5 results.

The above work under the same title has been published in J. Phys. Chem 1995, 99, 14589 by M. Xu, E.M. Eyring, S. Petrucci.

4) Molecular Relaxation Dynamics of Polypropylene-oxide-glycol-400 LiClO<sub>4</sub> systems

The dynamics of electrolytes dissolved in polypropylene glycols are addressed by a combination of audio frequency electrical conductivity measurements, infrared spectra of the  $\bar{\nu}_4$  mode of ClO<sub>4</sub><sup>-</sup>, microwave and far-infrared dielectric spectra, radiofrequency and UHF ultrasonic absorption spectra, and visible refractivities at the sodium doublet wavelength. The combination of infrared and conductivity results indicates that the majority of the electrolyte exists in these low relative permittivity media as a solvent separated ion-pair and not as free ions. The high viscosity of the medium causes an overlap of solvent and solute relaxations that requires a new analysis of the molecular dynamics. The dielectric and ultrasonic spectra correlate with a similar average relaxation time but with different distribution parameters. This is ascribed to a similar polymer chain response to the two perturbing functions although with different cooperative character of the response. The dielectric modulus approach is also analyzed revealing serious errors committed by previous users of this method of analysis. The calculated molar refractions suggest that the anion is solvated by the end protons of the polymer chains.

The above work is now being prepared to be submitted for publication.

5) Anion Solvation Effects in Polymer-Electrolytes: NaSCN and LiSCN in PEO-400 and PEG-400

Infrared spectra in the "CN-stretch region of the  $\text{SCN}^-$  anion for NaSCN and LiSCN dissolved in polyethylene oxide dimethyl ether of average molar mass 400, PEO-400, show dramatic differences from the infrared spectra of the same electrolyte dissolved in polyethylene oxide glycol (PEG-400) of average molar mass 400.

The differences are attributed to anion solvation by the -OH end of the PEG polymer. The different molecular status of the above electrolytes in the two solvents, should be considered, when planning their use as ion transport media in polymer-electrolyte batteries.

The above work is now being prepared to be submitted for publication.

6) Infrared Spectra and Molecular Relaxation Dynamics of LiSCN in Polyethers: Toward the Polymer Electrolyte

Infrared spectra of the antisymmetric stretching mode ("CN-stretch") of the  $\text{SCN}^-$  anion for LiSCN dissolved in the ethers 1,2-dimethoxyethane (1,2-DME); diglyme; triglyme and polyethylene oxide dimethylether of average molar mass 250 (PEO-250) at various concentrations at 25 °C reveal that the electrolyte LiSCN is heavily associated to contact ion-pairs  $\text{LiNCS}$ . A minor amount exists as solvent-separated and/or free ions ( $\text{Li}^+\text{S}$ ,  $^-\text{NCS}$  or  $^-\text{NCS}$ ), the so called "spectroscopically free" thiocyanate ions.

The molecular dynamics of the same electrolyte in the same ethers have been studied by ultrasonic (except for triglyme because of limited solubility of LiSCN) and microwave dielectric relaxation techniques. The ultrasonic relaxation spectra, in the frequency range 1-400 MHz, can be interpreted by the sum of two Debye relaxation processes, which are taken to reflect the multistep Eigen process;  $\text{Li}^+ + ^-\text{NCS} \rightleftharpoons \underset{1}{\text{Li}^+\text{S}_x}$ ,  $^-\text{NCS} \rightleftharpoons \underset{2}{\text{Li}^+\text{S}_{x-1}}$ ,  $^-\text{NCS} \rightleftharpoons \underset{3}{\text{LiNCS}}$ . The "fast" observed process attributed to step 2, is coupled to the faster step 1, through a pre-equilibration constant  $K_1$ .

The "slow" observed process is interpreted as due to step 3, coupled with the two faster processes 1 and 2. The interesting finding is that, whereas for 1,2-DME the data follow a separate trend, the data for the diglyme and for the PEO-250 appear to have the same concentration dependence of both the relaxation times  $\tau_1$  and  $\tau_{II}$ . Yet, the repetition unit  $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n$  number is 2 for diglyme and 4.6 for PEO-250. For  $\tau_{II} \text{ vs } c_{\text{LiSCN}}$  the common concentration dependencies extends to the data in PEO-400, namely  $n = 8.0$ . These results are interpreted as meaning that the observed processes, characterized by  $\tau_1$  and  $\tau_{II}$ , reflect the local relaxation dynamics of desolvation of ions by interchange of the  $-\text{CH}_2-\text{CH}_2-\text{O}-$  groups by  $^-\text{NCS}$ , independent of the increase of the chain length of the polyether, within the above range of n.

The UHF-microwave dielectric relaxation spectra of LiSCN, in the above solvent systems 1,2-DME, diglyme and PEO-250 at 25 °C, and concentration  $c=0.1 \text{ mol cm}^{-3}$ , when coupled with the results of the same spectra in triglyme, reveal a correlation between the solute dielectric relaxation time  $\tau_1(D)$  and the repetition number n of the  $(-\text{CH}_2-\text{CH}_2-\text{O}-)$  units of the polyether. This is taken to indicate that the rotational relaxation time of the solute  $\text{LiNCS}$  dipoles depends on the chain length of the polyether, namely  $\tau_1(D)$  reflects the long range dynamics of the solvent.

The above work is being prepared to be submitted for publication.

**List of the papers published so far**

- 1) Molecular Relaxation dynamics of  $\text{LiClO}_4$  in Acyclic Polyether Solvents, *J. Phys. Chem.* 1993, 97, 3606 by P. Firman, M. Xu, E.M. Eyring, S. Petrucci
- 2) Comment on "Relaxation Spectroscopy of Electrolyte Solutions:  $\text{LiClO}_4$  in Tetraethylene glycol Dimethylether" *Ber. Bunsenges Phys. Chem* 1994, 98, 872 by P. Firman, M. Xu, E.M. Eyring, S. Petrucci
- 3) Molecular Structure and Dynamics of  $\text{LiClO}_4$ -Polyethylene Oxide-400 (Dimethylether and Dimethylglycol systems) at 25°C *J. Phys. Chem.* 1994, 98, 8234 by M. Salomon M. Xu, E.M. Eyring, S. Petrucci
- 4) Molecular Dynamics and Infrared Spectra of  $\text{NaSCN}$  dissolved in the Solvent Macrocycle 15C5 and Polyethylene oxide Dimethyl Ether-250 *J. Phys. Chem.* 1995, 99, 14589 by M. Xu, E.M. Eyring, S. Petrucci

**Conclusions**

The above research should point out of the complexities of the studied systems in terms of the extent of association of the electrolytes, the lifetime of the complex species present and the molecular dynamics of the same.

Whereas this complex picture should discourage application of simple minded transport theories, at times proposed in the literature, it is hoped that the more detailed picture, at a molecular level, exposed in this research, will stimulate theories of transport based on realistic models. Eventually this deeper understanding will lead to the construction of more efficient batteries using lithium-polymer electrolytes.