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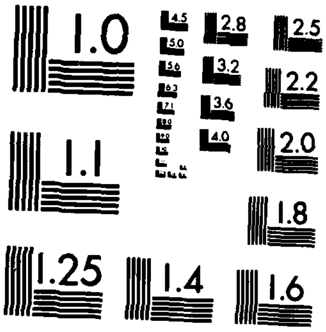

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

During the past three years, we have investigated the structure and dynamics of lithium electrolytes dissolved in solvents of low permittivity as ethers and dimethylcarbonate. These systems are highly relevant for the construction of batteries using lithium anodes.

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It appeared necessary to offer the electrochemist a detailed knowledge of the electrolyte species present in the electrolyte solutions and the lifetime and structure of these species. This information is essential for an optimum choice of the electrolyte solution to be used for battery planning and construction. To the above end we have used Raman spectra (occasionally), electrical conductance, microwave dielectric relaxation and radio frequency ultrasonic relaxation. [The first two techniques (Raman and conductivity) give information on the species present in a very *different concentration* range of electrolyte. Microwave dielectric relaxation gives information on the rotation relaxation time of dipolar species in solutions. From calculated parameters as microscopic relaxation time and static permittivity, one can get information on the charge separation and apparent dipole moment of the dipolar species. Ultrasonic relaxation studies the kinetics of formation and dissociation of complex species in solutions in the half time range 10^{-6} to $\sim 10^{-9}$ seconds. Within these limits the lifetime of the complex species can be estimated.] As shown below, many systems show a significant amount of quadrupoles or dimers present in the solution. Theoretical expression for the formation constant K_q of dimers and of ΔH_o, ΔS_o, ΔV_T and ΔV_s^o (namely the enthalpy, entropy, isothermal and adiabatic volume changes) have been calculated from statistical thermodynamic arguments. In particular, a Bjerrum-type theory for association of electrolytes (AB) to dimers $(AB)_2$ has been developed.

The following systems have been investigated:

A) Molecular Relaxation of $LiAsF_6$ in 1,2-Dimethoxyethane.
B) Molecular Relaxation of Lithium Salts in 2-Methyltetrahydrofuran at 25°C.
C) Thermodynamics of Dimerization of Lithium Salts in 1,2-Dimethoxyethane.
D) Kinetics of Complexation of the Macrocycles 18C6 & 12C4 Ethers with $LiAsF_6$ in 1,2-Diomethoxyethane at 25°C.
E) Ionic Conductivity & Microwave Dielectric Relaxation of $LiAsF_6$ and $LiC\ell O_4$ in Dimethylcarbonate.
F) Molecular Dynamics & Ionic Associations of $LiAsF_6$ in 4-Butyrolactone Mixtures with 2-Methyl Tetrahydrofuran.

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FINAL REPORT

to

The U.S. Army Research Office
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Research Triangle Park, NC 27709-2211
Attn: Dr. Bernard Spielvogel

Title: "Investigation of the Structure and Dynamics of Electrolytes in Solvents Used for Primary and Secondary Li-Batteries"

Date: February 1985

US ARO GRANT NO.: DAAG/29/82/K0048

Principal Investigator: S. Petrucci
Department of Chemistry
Polytechnic Institute of New York
Long Island Center, Route 110
Farmingdale, NY 11735

FORWARD

During the past three years, we have investigated the structure and dynamics of lithium electrolytes dissolved in solvents of low permittivity as ethers and dimethylcarbonate. These systems are highly relevant for the construction of batteries using lithium anodes.

It appeared necessary to offer the electrochemist a detailed knowledge of the electrolyte species present in the electrolyte solutions and the lifetime and structure of these species. This information is essential for an optimum choice of the electrolyte solution to be used for battery planning and construction. To the above end we have used Raman spectra (occasionally), electrical conductance, microwave dielectric relaxation and radio frequency ultrasonic relaxation. [The first two techniques (Raman and conductivity) give information on the species present in a very different concentration range of electrolyte. Microwave dielectric relaxation gives information on the rotation relaxation time of dipolar species in solutions. From calculated parameters as microscopic relaxation time and static permittivity, one can get information on the charge separation and apparent dipole moment of the dipolar species. Ultrasonic relaxation studies the kinetics of formation and dissociation of complex species in solutions in the half time range 10^{-6} to $\sim 10^{-9}$ seconds. Within these limits the lifetime of the complex species can be estimated.] As shown below, many systems show a significant amount of quadrupoles or dimers present in the solution. Theoretical expression for the formation constant K_q sub q of dimers and of ΔH_0, ΔS_0, ΔV_T and ΔV_S^0 (namely the enthalpy, entropy, isothermal and adiabatic volume changes) have been calculated from statistical thermodynamic arguments. In particular, a Bjerrum-type theory for association of electrolytes (AB) to dimers $(AB)_2^{\mp}$ has been developed. Additional keywords: lithium (ethers); Theory (research statistics); lithium salts.

STATEMENTS OF PROBLEMS STUDIED AND SUMMARY OF RESULTS

As stated above, we have tried to give a molecular structural and dynamic description of selected systems potentially relevant to battery construction. The choice of the systems has been discussed with the Fort Monmouth Army Laboratory Staff dedicated to lithium batteries. To date, the systems investigated, and briefly reviewed here, are as follows:

A) Molecular Relaxation of $LiAsF_6$ in 1,2-Dimethoxyethane.

Audiofrequency electrical conductivity, Raman spectra, radiofrequency ultrasonic absorption, and microwave dielectric permittivity of $LiAsF_6$ in the solvent 1,2-dimethoxyethane (DME) are reported. An analysis of the electrical conductivity data reveals the electrolyte to be associated to ion pairs ($K_A = 1 \times 10^5 M^{-1}$). Raman spectra of the symmetrical stretching mode of AsF_6^- suggest the ion to be "spectroscopically free", namely, either unpaired or solvent separated from the cation. Ultrasonic relaxation data are interpreted in terms of the equilibrium $Li^+, S, AsF_6^- \rightleftarrows LiAsF_6$, (S being a solvent molecule). The equilibrium appears to be heavily shifted toward solvent-separated ion pairs in accord with the information obtained from Raman spectra. In other words, the majority of the electrolyte is associated in the form of a solvent-separated ion pair symbolized by Li^+, S, AsF_6^-. Microwave dielectric relaxation data can be interpreted as due to the diffusion rotation relaxation of ion pairs. The estimate of the charge-to-charge distance in the ion pairs reinforces the model that the solvent resides between the cation and the anion in the majority of the pairs. The equilibrium is shifted to increase contact pairs, by increasing the electrolyte concentration, in accordance with the law of mass action.

B) Molecular Relaxation of Lithium Salts in 2-Methyltetrahydrofuran at 25°C

Ultrasonic absorption data are reported in the frequency range 1-7 MHz and 10-500 MHz for the electrolytes $LiAsF_6$ and $LiBF_4$ and described by a single Debye relaxation for $LiAsF_6$ and by two Debye relaxation processes for $LiBF_4$. The observed processes are interpreted by a multistep Eigen type dimerization process leading to contact quadrupoles. In the case of $LiAsF_6$ the products are solvent-separated quadrupoles and contact dimers, whereas for $LiBF_4$ contact species predominate. Literature data for $LiClO_4$ suggest that the dimers are the major species present. Hence, the extent of dimerization process for the three electrolytes seems to follow the order: $LiAsF_6 \simeq LiBF_4 < LiClO_4$. Electrical conductance data at $t = 25.00$°C for $LiAsF_6$ and $LiBF_4$ in 2-methyltetrahydrofuran (2MTHF) are reported. The data in the concentration range $6 \times 10^{-4} - 1.50 \times 10^{-2}$M are interpreted by the Fuoss-Kraus theory of triple-ion formation yielding estimates of the ion-pair formation constant K_p and triple ion formation constant K_T. Microwave dielectric complex permittivities in the frequency range 0.6-90 GHz and concentration range 0.02-0.1 M for $LiAsF_6$ and $LiBF_4$ in 2 MTHF at 25°C are reported. Two Debye relaxation processes, one related to the solute and one to the solvent, are able to describe the data. The solute relaxation is interpreted as due to the rotational relaxation of ion pairs. From the calculated apparent dipole moments it is surmised that on the average $LiBF_4$ pairs exist more as contact species with respect to $LiAsF_6$ pairs.

C) Thermodynamics of Dimerization of Lithium Salts in 1,2-Dimethoxyethane

Electrical conductance data in the concentration range 10^{-4} to 10^{-2} for

$LiBF_4$ in 1,2-DME are interpreted by the Fuoss-Kraus theory yielding values for the ion-pair and triple-ion formation constants. Complex dielectric permittivities for $LiBF_4$ in 1,2-DME at 25°C in the frequency range 0.9-81 GHz are reported. The data are interpreted by two Debye relaxation processes, one for the solvent and one for the solute. The latter is interpreted as due to the diffusional rotation of the ion pairs. Ultrasonic absorption data for $LiBF_4$ in 1,2-DME at 25°C in the concentration range 0.28-0.55 M and frequency range 10-550 MHz are reported. The data are described by a single Debye relaxatioin process and are interpreted as due to an ion-pair dimerization equilibrium leading to formation of quadrupoles. Theoretical expression (similar to the ones of Fuoss and Bjerrum for ion pairs) are developed for the dimerization of ion pairs to quadrupoles. To this end, a point dipole-point dipole potential has been used including the mutual dipole orientation. The dependence of K_F and K_{Bj} on the dipole-dipole separation distance is illustrated. Further, the thermodynamic increments ΔV_T, ΔS_0, ΔH_0, and ΔV_S have been calculated. The Fuoss-Kraus expressions for the quadrupole formation constants based on ellipsoidal and two-sphere models for the dipoles have been also used to calculate the parameters ΔV_T, ΔS_0, ΔH_0, and ΔV_S. The latter quantity ΔV_S is compared to the corresponding parameter found during the present and previous ultrasonic research.

D) Kinetics of Complexation of the Macrocycles 18C6 and 12C4 Ethers with $LiAsF_6$ in 1,2-Diomethoxyethane at 25°C

Ultrasonic relaxation spectra of the systems $LiAsF_6$ added to the macrocycles 18C6 or 12C4 ethers, in molar ratio $R \approx 1$, in the solvent 1,2-Dimethoxyethane (DME) at t = 25°C are reported. The concentration range covered was 0.05 to 0.25M for 18C6 and 0.1 to 0.3M for 12C4. Ancillary electrical conductance data for the same systems in the concentration range

10^{-4} to ~0.05M at 25.00°C reveal that the lithium-macrocycle interaction is weak, the conductance data being the same up to ~10^{-2}M, within experimental error of the one for the electrolyte in DME. Based on a previous work revealing the presence of an outer sphere-inner sphere equilibrium $LiSAsF_6 \rightleftharpoons LiAsF_6$, the present data are interpreted by a mechanism envisaging competition between the above reaction and the complexation scheme $LiSAsF_6 + C \rightleftharpoons LiC, AsF_6 + S$ where C is the crown ether. The results for $LiAsF_6$ + 18C6 are compared with previous ones for the system $LiClO_4$ + 18C6 in DME.

E) Ionic Conductivity and Microwave Dielectric Relaxation of $LiAsF_6$ and $LiClO_4$ in Dimethylcarbonate

Audiofrequency electrical conductivity data are reported in the solvent dimethylcarbonate (DMC) at 25°C in the concentration range 10^{-4} to 1M for $LiAsF_6$ and 10^{-4} to 0.3M for $LiClO_4$. From 10^{-4} to ≈10^{-2}M the data are interpreted by the Fuoss-Kraus triple-ions theory leading to the values of the ion pair formation constant K_p and triple ion formation constant K_T. For the data at higher concentration, it is shown that the change of static permittivity of the solution (due to the presence of solute ion-pairs and other polar species, which increase the polarization of the solution) can account qualitatively for the behavior of the conductance data and their deviation from the Fuoss-Kraus theory. In other words, these deviations are mostly due to changes in permittivity, not accounted for in the conventional treatment of the data, rather than by the failure of the theory, which is better than recognized so far. Introduction of the quadrupole formation constant is necessary, however, for $LiAsF_6$ for a more quantitative treatment of the conductance data. Microwave complex permittivities in the concentration range 0.05M to 0.3M, frequency range ≈ 1 to 90 GHz are intepreted by two Debye relaxation processes, one due to the solute and one to the solvent. For $LiAsF_6$ the Böttcher plot, (expressing a quantity related to the change of the relaxation strength $(\epsilon_0 - \epsilon_{\infty_1})$ with the concentration of electrolyte), is nonlinear with the concentration. Correction of the concentration, by postulating the presence of dielectrically apolar dimers linearizes the plot with a quadrupole formation constant of the order of $K_q \approx 50 M^{-1}$, although this figure is very tentative. For $LiAsF_6$ both rotational relaxation time and the distance separation of the charges as calculated from the apparent dipole moment suggest distances of the order of contact ion pairs. For $LiClO_4$ no curvature in the Böttcher plot is visible, suggesting that presence of quadrupoles is not significant for this electrolyte in DMC, a notion already reported in the literature. This is somewhat surprising in view of the ionic association constant to pairs K_p, being an order of magnitude larger for $LiClO_4$ with respect to $LiAsF_6$. The distance separation of the charges, as calculated from the apparent dipole moment of $LiClO_4$ suggests presence of contact species.

F) Molecular Dynamics and Ionic Associations of $LiAsF_6$ in 4-Butyrolactone Mixtures with 2-Methyl Tetrahydrofuran

Solutions of $LiAsF_6$ at 298.2 K were studied by audiofrequency conductance in the concentrations range 10^{-4}-10^{-2} mol dm^{-3}, and by radiofrequency ultrasonic absorption in the concentration range 0.05 - 0.5 mol dm^{-3}. The solvents employed were mixtures of 4-butyrolactone with 2-methyl tetrahydrofuran varying in compositions from mole fractions $X_{BL} = 0.10$ to $X_{BL} = 0.75$. In dilute solutions the audiofrequency conductivity data yield ion association constants which appear to represent both contact and solvent-separated ion pairs for mixtures up to $X_{BL} = 0.36$. At higher $LiAsF_6$ concentrations and in solvent mixtures of composition $X_{BL} = 0.75$, and $X_{BL} = 0.35$, the ultrasonic spectrum shows a single relaxation process which again is attributed to the formation of both contact and solvent separated ion pairs. For $X_{BL} = 0.10$, the ultrasonic spectrum is the sum of two Debye relaxation processes identified with the equilibria $2LiAsF_6 \rightleftharpoons LiAsF_6...LiAsF_6 \rightleftharpoons (LiAsF_6)_2$. Section F will be fully described in the next report of June, 1985 of the second Army Grant.

CONCLUSIONS AND PROJECTIONS

The above studies have revealed that for lithium salts, in media of permittivity $\epsilon \leq 10$ the following association scheme seems to occur

$$Li^+ + B \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} Li...B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} LiB \tag{1}$$

$$2LiB \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} LiB...LiB \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (LiB)_2 \tag{2}$$

where B is the ligand (anion), Li...B and LiB...LiB the solvent separated ion-pair and solvent separated dimer and LiB and $(LiB)_2$ the contact pair and contact dimer respectively. The extent of the reaction to the far right depends on the competing "ligand", namely, the solvent for the same anion, and on the donor ability of the ligand.

So, for instance, in 1,2 DME only reaction (1) above can be studied by ultrasonic relaxation through equilibrium $Li...B \rightleftharpoons LiB$, (no evidence of dimers existing). The same electrolyte in 2MTHF, an almost isodielectric solvent to DME, shows evidence of reaction (2) at least up to the formation of LiB...LiB species. $LiClO_4$ is so heavily associated in 2MTHF that only the last step of reaction (2) $LiB...LiB \rightleftharpoons (LiB)_2$ appears to be present.

Further work will be necessary to possibly arrive at meaningful correlations of the association constants with parameters as permittivity and solvent donor number for a given electrolyte. Work at various temperatures and in solvent mixtures is also planned in the next project.

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3. "Thermodynamics of Dimerization of Lithium Salts in 1,2-Dimethoxyethane," by H.E. Maaser, M. Delsignore, M. Newstein and S. Petrucci, J. Phys. Chem., *88*, 5100 (1984).
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1. Technical Report #1 (June 1982), "Molecular Relaxation of $LiAsF_6$ in 1,2 Dimethoxyethane," by H. Farber, D. Irish and S. Petrucci.
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LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL (in alphabetical order)

1. Delsignore, Marta, Post-doctoral, June 1982-June 1983 and August-September 1984, presently at Colgate-Palmolive, Piscataway, NJ.
2. Farber, Herman, Dept. of Electrical Engineering, Polytechnic Institute of New York, Brooklyn Campus, 333 Jay Street, Brooklyn, NY.
3. Harada, Yoshifumi, Post-doctoral, September 1983-September 1984, presently at The Dept. of Applied Physics, University of Fukui, Fukui, Japan.
4. Irish. D.E., University of Waterloo, Ontario, Canada.
5. Maaser, [illegible]drun, Post-doctoral, June 1982-June 1983, presently at Colgate-Palmolive, Piscataway, NJ.
6. Newstein, Maurice, Dept. of Electrical Engineering, Polytechnic Institute of New York, Long Island Center, Route 110, Farmingdale, NY.
7. Petrucci, Sergio, Dept. of Chemistry, Polytechnic Institute of New York, Long Island Center, Route 110, Farmingdale, NY.

8. Richman, Helmut, Research Associate, October-December 1983, presently at the Max-Planck Institute of Biophysical Chemistry, am Fassberg, Goettingen-Nikolausberg, West Germany.
9. Salomon, Mark, U.S. Army ET and DL, Ft. Monmouth, NJ.

Note: Profs. Farber, Irish, Newstein, and Dr. Salomon have contributed to the research program and are co-authors of the published papers. They have not received any financial reward from the contract funds.