

ARMY RESEARCH LABORATORY



Conductivities of Lithium Tris(trifluoromethanesulfonyl)
Methide in Aqueous and Nonaqueous Solutions at 25°C

Charles W. Walker, Jr. and Mark Salomon

ARL-TR-928

February 1996

19960313 084

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official Government endorsement or approval of commercial products or services referenced herein.

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE February 1996	3. REPORT TYPE AND DATES COVERED Technical Report: Jun 95 to Feb 96	
4. TITLE AND SUBTITLE CONDUCTIVITIES OF LITHIUM TRIS(TRIFLUOROMETHANESULFONYL) METHIDE IN AQUEOUS AND NONAQUEOUS SOLUTIONS AT 25°C		5. FUNDING NUMBERS	
6. AUTHOR(S) Charles W. Walker, Jr. and Mark Salomon		8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-928	
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) US Army Research Laboratory (ARL) Physical Sciences Directorate (PSD) ATTN: AMSRL-PS-CC Fort Monmouth, NJ 07703-5601		10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)		11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.		12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>In order to determine the solution properties of lithium tris(trifluoromethanesulfonyl) methide (LiMe) in water and the aprotic solvents acetonitrile (AN), propylene carbonate (PC), N,N-dimethylformamide (DMF), and nitromethane (MeNO₂), conductance measurements have been carried out at 25°C. Molar conductivities at infinite dilution and ion pair association constants were obtained analyzing the experimental data with the Fuoss-Hsia conductance equation using the expansion of Fernández-Prini and Justice with and without inclusion of the Chen effect. The results show that according to the ability of the solvents to solvate lithium ion, ion pair formation is small or non-existent in solvents with high donor number (water, PC, DMF and AN) but fairly moderate, in nitromethane. Single ion molar conductivities at infinite dilution for perchlorate, hexafluoroarsenate, hexafluorophosphate, triflate, imide and methide anions, obtained by combining our results with literature data, decrease as expected as the ionic radius increases, and with one exception are always greater than that of the lithium ion. This general trend does not however apply in water where the limiting ionic conductance of the lithium cation is greater than that of the methide anion. This anomalous behavior is attributed to significant solvation of the methide ion in water. Voltammetric measurements indicate high electrochemical stability of methide anion. Such anodic stability and the increase in the transference number of lithium ion in LiMe solutions strongly support the use of this electrolyte in high energy, high voltage lithium batteries.</p>			
14. SUBJECT TERMS lithium tris(trifluoromethanesulfonyl) methide, molar conductivities, ionic conductivities, transport numbers, ion association, cyclic voltammetry, propylene carbonate, dimethylformamide, nitromethane, acetonitrile, water		15. NUMBER OF PAGES 18	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

Contents

	Page
Introduction.....	1
Experimental.....	1
Results and Calculations.....	3
Discussion and Additional Calculations.....	8
Conclusion.....	10
References.....	11

Tables

Table I.	Physical properties of solvents at 25°C.....	2
Table II.	Molar conductivities of LiC(CF ₃ SO ₂) ₃ in various solvents and LiAsF ₆ in DMF at 25°C.....	3
Table III.	Derived parameters at 25°C.....	5
Table IV.	Anodic limits of DmpiX ionic liquids on Pt at 80°C.....	7
Table V.	Comparison of present and literature conductivity parameters at 25°C.....	8
Table VI.	Single ion molar conductivities, λ° , in various solvents at 25°C.....	9
Table VII.	Cation transport numbers, t_+° , at 25°C.....	10

Figures

Figure 1.	Plot of the variance in molar conductivities (U from (eq. [5]) and K_a as a function of the distance parameter R_2 for LiC(CF ₃ SO ₂) ₃ in MeNO ₂ . Solid lines fitted empirically by a cubic spline, and the solid circle represents the point for $R_2 = q$	6
Figure 2.	Plot of the variance in molar conductivities (U from (eq. [5]) and K_a as a function of the distance parameter R_2 for LiAsF ₆ in DMF. Solid lines fitted empirically by a cubic spline, and the solid circle represents the point for $R_2 = q$	6
Figure 3.	Linear sweep voltammograms for LiX in DmpiX at 80°C. X = AsF ₆ , PF ₆ , N(SO ₂ CF ₃) ₂ and C(SO ₂ CF ₃) ₃	7

INTRODUCTION

The search for highly stable and highly conductive lithium salts for use in both primary and rechargeable lithium batteries has been a major objective in numerous recent investigations. For safety considerations LiClO_4 is no longer considered for commercial use, and to avoid possible toxic byproducts of LiAsF_6 (e.g., see ref. 1), industry is focusing upon LiPF_6 as the prime candidate for use in a commercial rechargeable system utilizing liquid electrolytes. Our experience is that LiPF_6 is not as conductive as LiClO_4 or LiAsF_6 , and, as shown below, the PF_6^- anion is more readily oxidized than most other anions. The stable salt lithium triflate, LiCF_3SO_3 , also suffers from low conductivities (2, 3), and in seeking new electrolytes, an important advance was made by Armand et al. (4) with the introduction of the imide salt $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ [lithium bis(trifluoromethanesulfonyl) imide], or LiIm . This imide salt is attractive since it appears to be quite stable at high anodic potentials, and the conductivities of its solutions are comparable to those based on LiAsF_6 (e.g. see 3, 5). A more recent development involves the synthesis of a new lithium salt based on a new organic anion, $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ [lithium tris(trifluoromethanesulfonyl) methide], or LiMe (6), and the basis of the present study is to determine the solution properties of this methide salt in several aprotic solvents and in water. This new salt also appears to have superior plasticizing properties when used as the electrolyte in gelled polymer systems based on polyacrylonitrile and poly(vinylidene) difluoride polymers (7). It should also be noted that the methide salt, LiMe , is highly soluble in aprotic solvents, and its electrolytic conductances are comparable with LiIm solutions. For example, in 1.0 mol dm^{-3} THF solutions, electrolytic conductances of $6.0 \cdot 10^{-4}$, $1.0 \cdot 10^{-2}$ and $1.2 \cdot 10^{-2} \text{ S cm}^{-1}$ were determined, respectively, for LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ (6).

EXPERIMENTAL

Solvents: All solvents used were high purity commercial products dried with activated $\text{N}^\circ. 3$ molecular sieves before use. PC and AN were Burdick and Jackson "Distilled in Glass" grade products, DMF was "Analytical Reagent Grade" from Baker Chemicals, and MeNO_2 was "puriss" grade from Fluka. Another sample of acetonitrile (UV spectroscopic grade) was further purified by refluxing over molecular sieves and P_2O_5 and then fractionally distilled. The water content of these "dried" solvents as determined by coulombic Karl Fischer titration was in the range of 20 to 50 ppm. For the aqueous experiments, conductivity water was used and was prepared by passing tap water through two ion exchange columns followed by distillation in an all quartz still. The physical constants and electrolytic conductivities of the pure solvents are given in Table I.

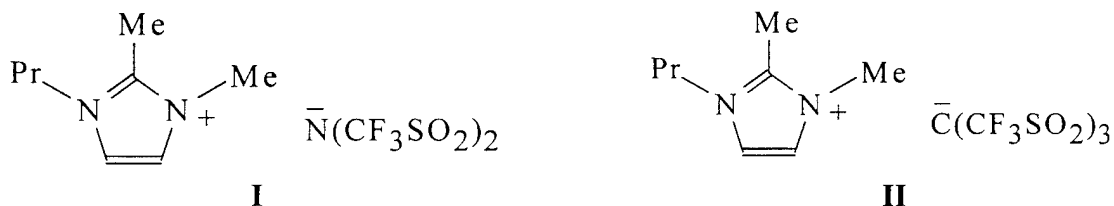
Salts: The preparation of $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ is fully described in Ref. (6) and was 99.9+% pure as determined by ^{19}F NMR spectroscopy. The salt has a sharp melting point of $272 - 273^\circ\text{C}$, is very hygroscopic and contained 46 ppm water; it was further dried in vacuum at 100°C before use. LiAsF_6 (US Agri Chemicals, Electrochemical grade) was dried in vacuum at $60-70^\circ\text{C}$ and not treated further.

Table I. Physical properties of solvents at 25°C

solvent	ϵ	η/cP	$d_0/g\text{ cm}^{-3}$	$\kappa_0/S\text{ cm}^{-1}$	q/nm	DN^a
H ₂ O	78.40	0.8903	0.99707	$1.4 \cdot 10^{-6}$	0.357	33
PC	64.97	2.53	1.1995	$1.4 \cdot 10^{-6}$	0.431	15.1
AN	35.96	0.3426	0.7765	$7.7 \cdot 10^{-6}$	0.779	14.1
DMF	36.71	0.7939	0.9439	$1.4 \cdot 10^{-6}$	0.763	26.6
MeNO ₂	35.99	0.6162	1.1304	$9.0 \cdot 10^{-7}$	0.779	2.7

^a Gutmann Donor Number (29)

For anion stability comparison tests using linear sweep voltammetry, salts based on the organic cation 1,2-dimethyl-3-propylimidazolium (Dmpi) were synthesized. The salts Dmpilm (I) and DmpiMe (II)



were prepared and purified as described previously (8). The arsenate, phosphate and imide salts, DmpipF₆, DmpiasF₆ and Dmpilm were prepared as described in (8) using as received LiAsF₆ (FMC), LiPF₆ (Hashimoto), and LiN(CF₃SO₂)₂ (3M Company, St. Paul, MN).

Conductivity measurements: Density measurements and conductivity measurements were determined, respectively, with a Parr DMS model 45 digital meter and a Wayne Kerr model 6425 Precision Component Analyzer which has an accuracy of $\pm 0.05\%$. Several measurements were carried out in Kraus-type conductivity cells in an oil bath thermostated to $\pm 0.005\text{ K}$, and others in Kraus-type cells in a water bath thermostated to better than $\pm 0.02\text{ K}$. In all cases except one run in AN as described below, conductivity measurements were begun by initially placing pure solvent in the Kraus cell, measuring the conductance, and then adding small aliquots of salt stock solutions with air-tight plastic syringes which were weighed before and after each addition. For run number 2 in acetonitrile, weighed amounts of salt were directly added to the solvent in the cell and resistances were determined after each addition. Conversion of molality to concentration units utilized solution densities calculated from the relations

$$d = d_0 + Am \quad \text{and} \quad c = \tilde{m}d$$

In the above equations, d and d_0 are, respectively, the densities of the electrolyte solution and pure solvent in g cm^{-3} , the constant A being evaluated from the stock solution concentration data, c is in mol dm^{-3} , and m and \tilde{m} are, respectively, in units of mol kg^{-1} of solvent and mol kg^{-1} of solution.

Voltammetry studies: Linear sweep voltammetry was accomplished via a PARC 273 potentiostat/galvanostat under computer control in a Brinkmann three-electrode cell (Model EA 875-1/6), and for all studies a sweep rate of 20 mV sec⁻¹ was used. The working electrode was a 0.07 cm² Pt disk while Li foil (Foote) served as the reference and counter electrodes. To assure a stable reference potential, LiAsF₆, LiPF₆, LiIm and LiMe were added to their respective Dmp⁺X⁻ ionic liquids to form a 0.020 mol dm⁻³ solution. We arbitrarily selected a current density of 1 mA cm⁻² to define the “anodic limit” of each ionic liquid. Because Dmp⁺PF₆⁻ and Dmp⁺AsF₆⁻ are solids at room temperature (8), for direct comparisons all linear sweep voltammograms were conducted at 80 ± 1°C.

RESULTS AND CALCULATIONS

Conductivity studies: Molar conductivities, Λ/S cm² mol⁻¹, were calculated from the electrolytic conductances, κ , after correcting for the conductance of the pure solvent, κ_0 , and the results are given in Table II.

Table II. Molar conductivities of LiC(CF₃SO₂)₃ in various solvents and LiAsF₆ in DMF at 25°C^a

Λ	$10^3 c$	Λ	$10^3 c$	Λ	$10^3 c$	Λ	$10^3 c$
water		acetonitrile (run 1)		acetonitrile (run 2)		dimethylformamide	
63.771	1.4169	135.53	0.82718	127.35	3.9722	52.479	2.4957
63.569	1.6677	133.02	1.4603	126.36	4.7324	51.646	3.5557
63.241	1.9170	130.70	2.3499	125.17	5.6296	50.303	5.8560
62.976	2.2498	128.15	3.3941	123.83	6.5914	49.754	7.0556
62.742	2.6572	126.29	4.4786	122.70	7.6775	49.004	8.9400
62.518	3.0871	124.30	5.7313	121.29	9.1991	48.199	11.3631
62.227	3.6151	122.79	6.8925	119.62	11.1382	47.565	13.5819
61.284	5.6552	121.61	7.8866	118.42	12.7664	46.906	16.2260
60.249	9.1217						

Λ	$10^3 c$	Λ	$10^3 c$	Λ	$10^3 c$
nitromethane		propylene carbonate		LiAsF ₆ in DMF	
77.381	3.3188	19.164	1.6041	67.177	2.5354
75.053	4.4119	18.981	2.0520	66.434	3.2669
71.707	6.4296	18.778	2.7189	64.565	5.6670
69.763	7.7843	18.613	3.4288	63.609	7.3619
67.794	9.2378	18.498	4.0877	62.599	9.6182
65.976	10.7922	18.493	4.7240	61.492	12.3980
64.237	12.4059	18.289	5.4276	60.749	14.6914
62.375	14.1506	18.186	6.2050	59.970	17.5047
59.739	16.9656	18.057	7.1874	59.248	20.3707
57.539	19.7307	17.937	8.2698	58.291	24.3886
		17.783	9.6825	57.723	27.2395
		17.405	13.7599		

^a Units: Λ/S cm² mol⁻¹ and $c/\text{mol dm}^{-3}$

These data were fitted to the Fuoss-Hsia (FH) equation (9) using the expansion of Fernández-Prini (FH-FP) (10) which has the form:

$$\Lambda = \alpha \left\{ \Lambda^\circ - S\sqrt{I} + EI \ln(I) + J_1(R_1)I - J_2(R_2)I^{3/2} \right\} \quad [1]$$

In eq. [1], α is the degree of dissociation defined by equations [2] and [3], I is the ionic strength ($I = \alpha c$), and all other terms have their usual significance. For the ion association process



the thermodynamic equilibrium constant is defined in the usual manner by

$$K_a = \frac{[\text{LiX}]}{[\text{Li}^+][\text{X}^-]y_{\pm}^2} = \frac{1-\alpha}{\alpha^2 cy_{\pm}^2} \quad [3]$$

The mean molar activity coefficients in eq. [3] were calculated from the Debye-Hückel relation

$$\ln y_{\pm} = \frac{-A\sqrt{I}}{1 + BR_y\sqrt{I}} \quad [4]$$

where the distance parameter R_y is fixed at the Bjerrum distance q (see Table I). Eqs. [1] - [4] were solved by a grid search method (11, 12) where the distance parameter R_1 is fixed at the Bjerrum distance, and R_2 is treated as a variable distance parameter. The variables Λ° , K_a and R_2 were initially selected arbitrarily and then adjusted in small increments until a minimum, U_o , was reached in the function U ; for n data points, U is defined by

$$U = \sum_1^n (\Lambda_{\text{obsd}} - \Lambda_{\text{calcd}})^2 \quad [5]$$

The final adjusted parameters for $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ in water, AN, PC, DMF and NM and for LiAsF_6 in DMF are given in Table III.

Included in Table III are values for the parameters derived by neglect of the Chen effect (13), and by inclusion of the Chen effect where $E = E_1 - 2E_2$ which accounts for spatial charge density in large organic anions with localized charges. All results reported in Table III were, as described above, derived using a three-parameter fit to the Fuoss-Hsia equation, i.e., $\Lambda = \Lambda(\Lambda^\circ, K_a, R_2)$. In most instances, the adjusted R_2 values are reasonably close to the Bjerrum distance q as expected (10, 16, 23) with the exception of R_2 for $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ in MeNO_2 . By including R_2 as a variable parameter, it is not unusual to find a strong correlation between K_a and R_2 (16, 34, 35), particularly when K_2 is small (36). Attempts to

Table III. Derived parameters at 25°C^a

salt/solvent	Λ°	K_a	R_2	σ_Λ	Chen effect
LiMe / H ₂ O	66.47 (0.087)	----	0.357 ^d	0.085	no
	66.30 (0.073) ^e	----	0.357 ^d	0.073	yes
LiMe / PC	20.22 (0.024)	----	0.337	0.024	no
	20.20 (0.026) ^e	1.24 (0.7 ₅)	0.431	0.025	yes
LiMe / AN ^b	144.94 (0.087)	----	0.747	0.077	no
	144.46 (0.086)	5.99 (0.19)	0.791	0.074	yes
LiMe / AN ^c	144.70 (0.076)	----	0.789	0.069	no
	144.46 (0.037)	5.05 (0.10)	0.875	0.032	yes
LiMe / DMF	58.61 (0.056)	----	0.696	0.050	no
	58.36 (0.021)	4.87 (0.10)	0.764	0.017	yes
LiMe / MeNO ₂ ^c	91.74 (0.07 ₅)	27.81 (0.20)	0.911	0.051	no
	91.79 (0.077)	34.15 (0.21)	0.971	0.051	yes
LiAsF ₆ / DMF	74.18 (0.033)	3.27 (0.09)	0.705	0.025	no
	74.19 (0.033)	8.90 (0.09)	0.724	0.024	yes

^a Units: $\Lambda^\circ / \text{S cm}^2 \text{ mol}^{-1}$; $K_a / \text{dm}^3 \text{ mol}^{-1}$; R_2 / nm . Values in parentheses are standard deviations, and the standard error in molar conductivities calculated from $\sigma_\Lambda = \{U_o/(n-1)\}^{1/2}$ where U is defined in eq. [5].

^b Run number 1. ^c Run number 2. ^d R_2 fixed at the Bjerrum distance q .

^e Fuoss-Onsager term E (see eq.[1]) is negative.

use a two parameter fit to the Fuoss-Hsia equation, i.e., $\Lambda = \Lambda(\Lambda^\circ, K_a)$, by fixing R_2 at the Bjerrum distance q invariably resulted in significantly larger standard deviations. Two representative examples are given in Figures 1 and 2.

Fig. 1 is a plot of the variance U (eq. [5]) and the association constant K_a as a function of R_2 for $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ in MeNO_2 , and Fig. 2 is a similar plot for LiAsF_6 in DMF . In the former case, setting $R_2 = q = 0.779 \text{ nm}$ results in $U = 0.8009$ compared to $U^\circ = 0.0234$ for the minimum at $R_2 = 0.911 \text{ nm}$. For the latter system, it is found that $U^\circ = 0.00636$ at $R_2 = 0.705 \text{ nm}$ compared to $U = 0.6468$ for $R_2 = q = 0.763 \text{ nm}$. While the values of K_a are obviously dependent upon R_2 , the dependency is not sufficiently large to change any conclusions (see below) based on use of the three parameter fitting method. In fact for the purpose of the present analyses, it is not necessary that a two parameter fit be employed, and since R_2 need not necessarily equal q or R_1 from J_1 of eq. [1] (23, 34) it is more realistic to use those parameters derived from the actual statistical best fit (e.g., see 36).

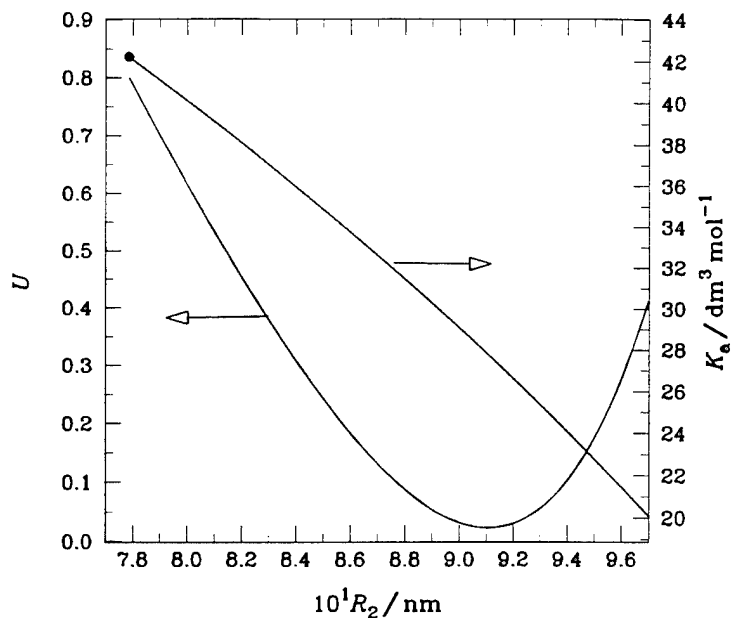


Figure 1. Plot of the variance in molar conductivities (U from (eq. [5]) and K_a as a function of the distance parameter R_2 for $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ in MeNO_2 . Solid lines fitted empirically by a cubic spline, and the solid circle represents the point for $R_2 = q$.

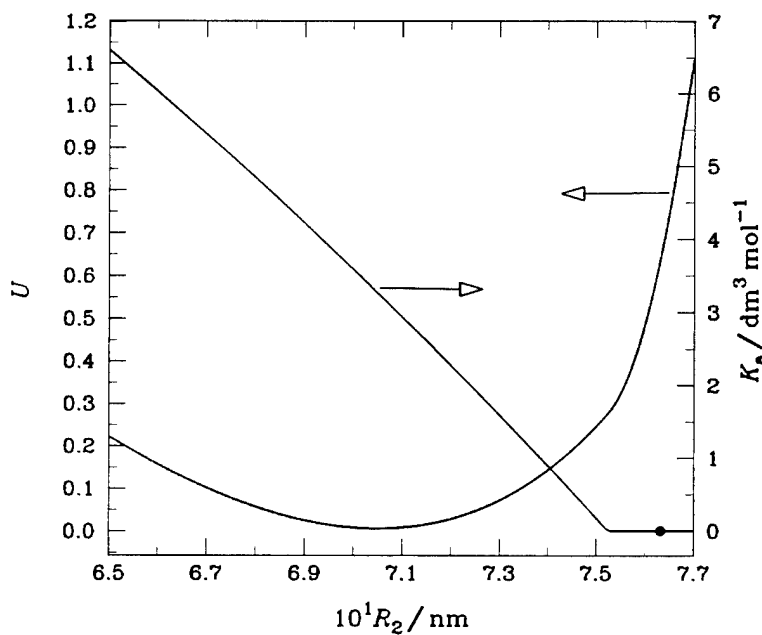


Figure 2. Plot of the variance in molar conductivities (U from (eq. [5]) and K_a as a function of the distance parameter R_2 for LiAsF_6 in DMF . Solid lines fitted empirically by a cubic spline, and the solid circle represents the point for $R_2 = q$.

Voltammetry studies: Figure 3 shows an overlay of linear sweep voltammograms obtained in each of the four ionic liquids obtained at a Pt working electrode at 80°C

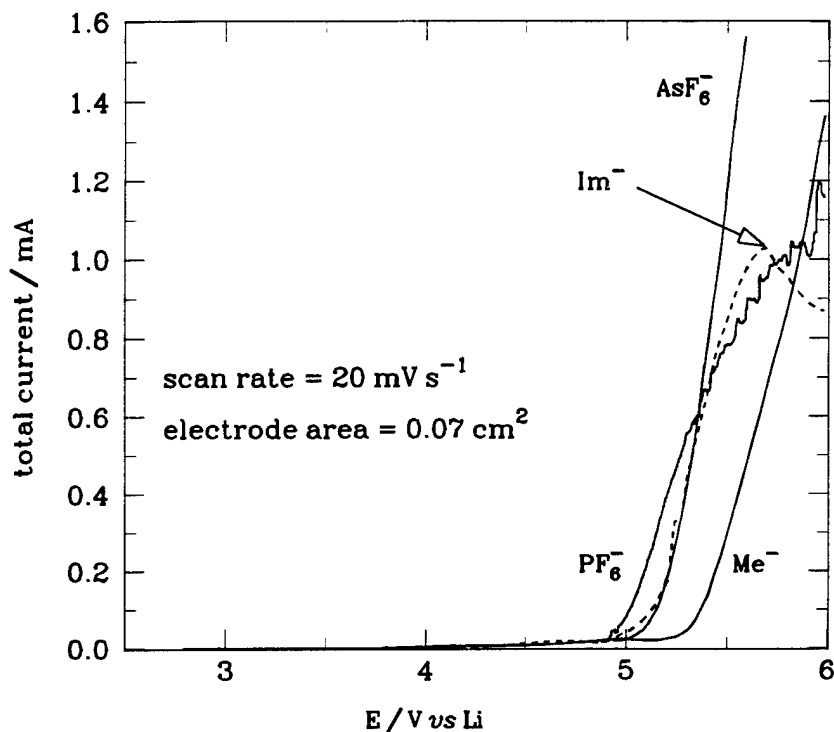


Figure 3. Linear sweep voltammograms for LiX in Dmpix at 80°C.
 X = AsF₆⁻, PF₆⁻, N(SO₂CF₃)₂ and C(SO₂CF₃)₃.

From the rest potential at 2.7 V no anodic current is observed until about 4.8 V where DmpipF₆ begins to oxidize. The experimental oxidation potentials obtained from these scans are reproducible to ± 20 mV, and the “anodic limits” for the four dimethylpropylimidazolium-based ionic liquids at 80°C are given in Table IV.

Table IV. Anodic limits of Dmpix ionic liquids on Pt at 80°C

anion	limit (E/V vs Li)
PF ₆ ⁻	5.00
AsF ₆ ⁻	5.10
Imide ⁻	5.13
methide ⁻	5.35

We believe that these data, free of the influence of solvent, reflect the intrinsic oxidative stability of the anion, at least in the case of PF₆⁻, AsF₆⁻ and Im⁻. Were the Dmpi⁺ cation *more* readily oxidizable than the anions, the four distinct linear sweep voltammograms shown in Fig. 1 would have collapsed to a single voltammogram at a potential negative of 4.8 V. Thus, while we are clearly measuring the intrinsic oxidation potentials of PF₆⁻, AsF₆⁻ and Im⁻, we do not unequivocally know whether the value of 5.35 V for DmpiMe reflects the oxidation of Dmpi⁺ or of Me⁻. The instability in the voltammogram for PF₆⁻ starting at about 5.2 V in Fig. 1 suggests complex reaction including, possibly, gas evolution. While DmpiAsF₆ and DmpiIm oxidize at the same potential within

experimental error, Dmp_iMe is clearly the most electrochemically stable ionic liquid surpassing the limit for Dmp_iPF₆ by some 350 mV. Such high anodic stability is desirable for electrolytes employed in high energy, high voltage lithium battery systems.

DISCUSSION AND ADDITIONAL CALCULATIONS

There are basically little surprises in the derived parameters given in Table III. Values of the molar conductivities at infinite dilution (Λ°) are, for the most part, independent on whether the Chen effect is included or neglected, similar to our findings for the alkali metal perchlorates in PC (28). Ion association in solvents with high Donor Numbers (e.g., water, PC and DMF, see Table 1 and Ref. 29) appears to be small or non-existent depending upon the model used (i.e., inclusion or neglect of the Chen effect), but K_a for the methide salt in MeNO₂ is quite high as calculated by either model. While AN, DMF and MeNO₂ can be considered to be "iso-dielectric" solvents, differences in K_a are directly related to the ability of the solvent to solvate cations (30), and to a lesser extent, anions as discussed below. Salts of a given anion in solvents which can strongly coordinate small cations such as water, PC and DMF are expected to undergo little or no ion association whereas solvents which weakly coordinate these cations generally exhibit increased association. For example, based on both the Gutmann Donor Number (DN) and assuming anion solvation effects are negligible, the order of increasing ion association would simply be H₂O < DMF < PC < AN < MeNO₂ which, for the most part, is what is observed when comparing the present results for LiIm with other salts as shown in Table V.

Table V. Comparison of present and literature conductivity parameters at 25°C^a

salt	H ₂ O		PC		AN		DMF		MeNO ₂	
	Λ°	K_a	Λ°	K_a	Λ°	K_a	Λ°	K_a	Λ°	K_a
LiClO ₄	105.9 ^b	----	26.75 ^e	1.3	173.26 ^h	16.47	73.40 ^j	6.6	110.60 ^k	182.2
LiPF ₆			26.1 ^f	2.1						
LiAsF ₆	95.07 ^c	----	22.53 ^g	----	170.06 ⁱ	9.1	74.18	3.3		
LiIm	70.89 ^d	----	22.76 ^d	----	153.71 ^d	4.7				
LiMe	66.47	----	20.22	----	144.7	----	58.61	----	91.74	27.8

^a Λ° /S cm² mol⁻¹ and K_a / dm³ mol⁻¹. All results based on common analysis using eq. [1] (Chen effect not included) as reported in the following references and, where required, reanalyzed by the present authors. ^b14; ^c15; ^d5; ^e16; ^f17; ^g18; ^h19; ⁱoriginal data from (20) which seems preferable to the earlier data from (21); ^joriginal data from (22) reanalyzed in (23); ^k30.

For those systems in which lithium imide salt appears to undergo small ion association, e.g. in AN (5), and possibly PC (17), but see the opposing opinion in (5), no evidence for association of lithium methide has been reported. We believe that these effects are, in part, related to solvation of the methide anion, and additional discussions in support of this conclusion are given below.

One of the features leading to small K_a values for LiIm probably lies in significant charge delocalization of the imide anion as discussed by Weber (3), but the situation for LiMe appears to be slightly different. The negative charge on the central carbon of the methide anion appears to be more strongly delocalized due to the combination of the strong electronegative groups surrounding the central carbon (31). The CS_3 skeleton of the anion is planar and the orientation of the CF_3 groups is unsymmetrical, two groups lying above and one group lying below the CS_3 plane, and the increased delocalization facilitates polarization by either large polarizable cations and/or by neutral and highly polarizable solvent molecules: i.e., the anion appears to act as a "soft" base (in the Pearson sense (32)). For example, in (31), $HC(SO_2CF_3)_3$ is reported to be a very strong acid in aqueous solution, and the solubility of alkali metal salts decreases in the order of $Ag^+ > K^+ > Rb^+ > Cs^+$, and the silver salt can be used to prepare the halogen derivatives $X C(SO_2CF_3)_2$ where $X = Cl$ or Br (31).

Table VI lists single ion molar conductivities at infinite dilution calculated by combining the present results with literature data as indicated in the footnotes to Table VI.

Table VI. Single ion molar conductivities, λ° , in various solvents at 25°C^a

ion	H ₂ O	PC	AN	DMF	MeNO ₂
Li ⁺	38.7 ^b	8.22 ^c	69.97 ^d	25.0 ^e	42.9
ClO ₄ ⁻	67.2 ^b	18.51 ^c	103.62 ^d	52.5	67.7 ^f
PF ₆ ⁻	59.2 ^h	17.9	102.8 ⁱ	-----	-----
AsF ₆ ⁻	56.4	14.3	100.1	49.2	-----
Imide ⁻	32.2 ^g	14.5 ^g	83.72 ^g	-----	-----
methide ⁻	27.8	12.0	74.7	33.6	48.8

^a $\lambda^\circ/S\text{ cm}^2\text{ mol}^{-1}$ derived from Λ° values in Tables III and IV and literature λ° values as indicated.
^b24; ^c28; ^d16; ^e22-23; ^f25; ^g5; ^hbased on data for KPF_6 from (26) reanalyzed using eq. [1]. Results are $\Lambda^\circ = 132.70$ and $K_a = 1.78$ which were combined with $\lambda^\circ(K^+) = 73.50$ from (24);
ⁱdetermined by present authors using data for Me_4NPF_6 and Bu_4NPF_6 from (27). Results for Me_4NPF_6 are $\Lambda^\circ = 196.92$ and $K_a = 11.8$. Results for Bu_4NPF_6 are $\Lambda^\circ = 164.76$ and $K_a = 3.14$, and average $\lambda^\circ(PF_6^-) = 102.8\text{ S cm}^2\text{ mol}^{-1}$.

An initial inspection of the data in this table appears to reveal the expected behavior, i.e., $\lambda^\circ(Li^+)$ is generally smaller than those of most anions due to the high solvation of Li^+ , and $\lambda^\circ(\text{anion})$ decreases as the ionic radius increases. However, it appears that an anomaly exists for the methide anion in water which we attribute to an increase in solvation of this anion (as discussed above) leading to a more pronounced decrease in its mobility. This interpretation is further supported by considering the lithium transference number, $t^\circ(Li^+)$ calculated as $\lambda^\circ(Li^+)/\Lambda^\circ$ from the data in Tables V and VI. Values for $t^\circ(Li^+)$ are given in Table VII.

Table VII. Cation transport numbers, t_+^0 , at 25°C

salt	H ₂ O	PC	AN	DMF	MeNO ₂
LiClO ₄	0.365	0.307	0.403	0.323	0.388
LiPF ₆	0.395	0.314	0.405	---	---
LiAsF ₆	0.407	0.36 ₅	0.414	0.337	---
LiIm	0.546	0.361	0.455	---	---
LiMe	0.582	0.407	0.484	0.427	0.468

From the results given in Table VII, it is seen that the increase in $t^0(\text{Li}^+)$ is surprisingly large for the methide salt compared to the perchlorate. In water, the increase in $t^0(\text{Li}^+)$ observed when changing the anion from perchlorate to methide is almost 60%. In PC, AN, DMF and MeNO₂ these increases are, respectively, 33%, 20%, 32% and 21%. Note that in PC, the increase in $t^0(\text{Li}^+)$ in changing the anion from perchlorate to imide while still large (18%) is significantly less than for the methide (33%).

CONCLUSION

Both conductometric and voltammetric data explored in this paper show that lithium tris(trifluoromethanesulfonyl) methide in the aprotic solvents (AN, PC, DMF, MeNO₂) and in water has better solution properties (i.e., electrolytic conductance and anion stability) than other lithium salts (LiClO₄, LiAsF₆, LiPF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂) commercially used in rechargeable systems. The non-existent or negligible ion pair formation and the increased transference number [$t_+^0(\text{LiMe})$] indicate LiMe as a most suitable electrolyte for both primary and rechargeable lithium batteries.

REFERENCES

1. V.R. Koch, *J. Electrochem. Soc.*, **126**, 181 (1979).
2. L.A. Dominey, J.L. Goldman, V.R. Koch and C. Nanjundiah in *Rechargeable Lithium Batteries*, S. Subbareao, V.R. Koch, B.B. Owens and W.H. Smyrl, eds., PV90-5, The Electrochemical Society Proceedings Series, Pennington, NJ (1990).
3. A. Weber, *J. Electrochem. Soc.*, **138**, 2586 (1991).
4. M. Armand, W. Gorecki and R. Andréani in *Second International Symposium on Polymer Electrolytes, Siena, 1989*. Elsevier, London, 1990, p. 91.
5. M. Salomon, *J. Solution Chem.*, **22**, 715 (1993).
6. L.A. Dominey, U.S. Patent 5,273,840 (1993).
7. G.B. Appetecchi, F. Croce, S. Slane, C.W. Walker, M. Salomon, *MRS Meeting, Boston, Nov. 1995*, Submitted.
8. V.R. Koch, L.A. Dominey, C. Nanjundiah and M.J. Ondrechen, Submitted to *Journal of The Electrochemical Society*.
9. R.M. Fuoss and K.-L. Hsia, *Proc. Natl. Acad. Sci. USA*, **57**, 1550 (1967).
10. R. Fernández-Prini and J.-C. Justice, *Pure and Applied Chem.*, **56**, 541 (1984).
11. e.g., see M. Salomon and M. Uchiyama, *J. Solution Chem.*, **16**, 21 (1987) based on the program given in Ref. 12 below.
12. G. Beech, *Fortran IV in Chemistry*. Wiley, London, 1975, p. 41.
13. M.S. Chen, *Ph.D. Dissertation*, Yale University, 1969.
14. A. D'Aprano, *J. Phys. Chem.*, **75**, 3290 (1971).
15. G. Atkinson and C.J. Hallada, *J. Phys. Chem.*, **64**, 1487 (1960).
16. J. Barthel, L. Iberl, R. Rossmairer, H.-J. Gores and B. Kaukal, *J. Solution Chem.*, **19**, 321 (1990).
17. M. Ue, *J. Electrochem. Soc.*, **141**, 3336 (1994).
18. M. Salomon and E.J. Plichta, *Electrochim. Acta* **28**, 1681 (1983).

19. A. D'Aprano, *J. Phys. Chem.*, 76, 2920 (1972).
20. A. Balkowska, A. Kowalska, M. Góral and L. Werblan, *J. Electroanalyt. Chem.*, 354, 11 (1993).
21. H.P. Hopkins, D.V. Jahogirder and A.B. Norman, *J. Solution Chem.*, 8, 147 (1979).
22. J.E. Prue and P.J. Sherrington, *Trans. Faraday Soc.*, 57, 1795 (1961).
23. J.-C. Justice, *Electrochim. Acta* 16, 701 (1971).
24. R.A. Robinson and R.H. Stokes in *Electrolyte Solutions*, Butterworths, London, 1955.
25. T. Fujinaga and I. Sakamoto, *J. Electroanalyt. Chem.*, 85, 185 (1977).
26. R.A. Robinson and R.H. Stokes, *J. Phys. Chem.*, 65, 542 (1961).
27. J. Eliassaf, R.M. Fuoss and J.E. Lind, *J. Phys. Chem.*, 67, 1941 (1963).
28. A. D'Aprano, M. Salomon and M. Iammarino, *J. Electroanalyt. Chem.* (submitted).
29. V. Gutmann and E. Vychera, *Inorg. Nucl. Chem. Lett.*, 2, 257 (1966).
30. A. D'Aprano, B. Sesta, A. Princi, C. Filippi and M. Iammarino, *J. Electroanalyt. Chem.*, 365, 119 (1994)
31. L. Turowsky and K. Seppelt, *Inorg. Chem.*, 27, 2135 (1988).
32. R.G. Pearson, *J. Am. Chem. Soc.*, 85, 3533 (1963): see also Ref. 33 below.
33. S. Ahrland, J. Chatt and N.B. Davies, *Quart. Rev. Chem. Soc.*, 12, 265 (1958)
34. J. Barthel, R. Wachter and H.-J. Gores, in *Modern Aspects of Electrochemistry*, Vol. 13. B.E. Conway and J. O'M. Bockris, eds., Plenum Press, New York, 1979.
35. A.D. Pethybridge and D.J. Spiers, *J. Chem. Soc. Faraday Trans. I*, 73, 768 (1977).
36. G.T. Hefter and M. Salomon, *J. Solution Chem.*, 23, 579 (1994).

ARMY RESEARCH LABORATORY
PHYSICAL SCIENCES DIRECTORATE
MANDATORY DISTRIBUTION LIST

August 1995
Page 1 of 2

Defense Technical Information Center*
ATTN: DTIC-OCC
8725 John J. Kingman Rd, STE 0944
Fort Belvoir, VA 22060-6218
(*Note: Two DTIC copies will be sent
from STINFO office, Ft Monmouth, NJ)

Advisory Group on Electron Devices
ATTN: Documents
Crystal Square 4
1745 Jefferson Davis Highway, Suite 500
(2) Arlington, VA 22202

Director
US Army Material Systems Analysis Actv
ATTN: DRXSY-MP
(1) Aberdeen Proving Ground, MD 21005

Commander, CECOM
R&D Technical Library
Fort Monmouth, NJ 07703-5703
(1) AMSEL-IM-BM-I-L-R (Tech Library)
(3) AMSEL-IM-BM-I-L-R (STINFO Ofc)

Commander, AMC
ATTN: AMCDE-SC
5001 Eisenhower Ave.
(1) Alexandria, VA 22333-0001

Director
Army Research Laboratory
ATTN: AMSRL-D (John W. Lyons)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

Director
Army Research Laboratory
ATTN: AMSRL-DD (COL Thomas A. Dunn)
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197

Director
Army Research Laboratory
2800 Powder Mill Road
Adelphi, MD 20783-1197
(1) AMSRL-OP-SD-TA (ARL Records Mgt)
(1) AMSRL-OP-SD-TL (ARL Tech Library)
(1) AMSRL-OP-SD-TP (ARL Tech Publ Br)

Directorate Executive
Army Research Laboratory
Physical Sciences Directorate
Fort Monmouth, NJ 07703-5601
(1) AMSRL-PS
(1) AMSRL-PS-T (M. Hayes)
(1) AMSRL-OP-FM-RM
(22) Originating Office

ARMY RESEARCH LABORATORY
PHYSICAL SCIENCES DIRECTORATE
SUPPLEMENTAL DISTRIBUTION LIST
(ELECTIVE)

August 1995
Page 2 of 2

- Deputy for Science & Technology
Office, Asst Sec Army (R&D)
(1) Washington, DC 20310
- Cdr, Marine Corps Liaison Office
ATTN: AMSEL-LN-MC
(1) Fort Monmouth, NJ 07703-5033
- HQDA (DAMA-ARZ-D/
Dr. F.D. Verderame)
(1) Washington, DC 20310
- Director
Naval Research Laboratory
ATTN: Code 2627
(1) Washington, DC 20375-5000
- USAF Rome Laboratory
Technical Library, FL2810
ATTN: Documents Library
Corridor W, STE 262, RL/SUL
26 Electronics Parkway, Bldg 106
Griffiss Air Force Base
(1) NY 13441-4514
- Dir, ARL Battlefield
Environment Directorate
ATTN: AMSRL-BE
White Sands Missile Range
(1) NM 88002-5501
- Dir, ARL Sensors, Signatures,
Signal & Information Processing
Directorate (S3I)
ATTN: AMSRL-SS
2800 Powder Mill Road
(1) Adelphi, MD 20783-1197
- Dir, CECOM Night Vision/
Electronic Sensors Directorate
ATTN: AMSEL-RD-NV-D
(1) Fort Belvoir, VA 22060-5806
- Dir, CECOM Intelligence and
Electronic Warfare Directorate
ATTN: AMSEL-RD-IEW-D
Vint Hill Farms Station
(1) Warrenton, VA 22186-5100