Journal of Solution Chemistry, Vol. 22, No. 8, 1993

Conductance of Solutions of Lithium Bis(trifluoromethanesulfone)imide in Water, Propylene Carbonate, Acetonitrile and Methyl Formate at 25°C

Mark Salomon[1]

Received May 9, 1991; Revised July 7, 1992

Conductance data for lithium bis(trifluoromethanesulfone)imide, $LiN(CF_3SO_2)_2$, are reported for the solvents water, propylene carbonate, acetonitrile and methyl formate at 25°C. Limiting molar conductivities Λ_0, association constants K_A, and triple ion formation constants K_t are reported where applicable. These data are compared with literature data for the commonly studied lithium salts $LiClO_4$ and $LiAsF_6$. Non-coulombic energy contributions to ion pair formation are evaluated and discussed in terms of ion-ion and ion-solvent interactions.

KEY WORDS: Electrolyte conductance; ionic conductance; ion-pair formation; triple ion formation; non-coulombic interactions; lithium salts; bis(trifluoromethanesulfone)imide anion; water; propylene carbonate; acetonitrile; methyl formate.

1. Introduction

Historically, $LiClO_4$ and $LiAsF_6$ have played key roles in the development of lithium batteries both in liquid electrolytes(1) and in immobilized polymer electrolytes.(2) Problems with the low conductivity and explosive tendency of $LiClO_4$(3) and the stability and toxic byproducts of $LiAsF_6$(4) when used in lithium cells have been the impetus for continuing development of new electrolytes. The development of the imide salt $LiN(CF_3SO_2)_2$ (LiTFSI) by Armand(5) has created considerable interest in the use of this salt in both polymer electrolytes(5,6) and liquid electrolytes.(7) This imide salt exhibits remarkable stability towards lithium over a wide temperature range. It has a low lattice energy and is therefore highly soluble. The $N(CF_3SO_2)_2^-$ anion is highly

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[1] U. S. Army Electronics Technology and Devices Laboratory (LABCOM) Power Sources Division, Ft. Monmouth, NJ 07703-5601.

0095-9782/93/0800-0715$07.00/0

delocalized resulting in relatively weak cation-anion coulombic interactions which results in a tendency to undergo less ion association in solvents of low permittivity. To supplement the practical studies of $LiN(CF_3SO_2)_2$ in polymer and liquid electrolytes,(5-7) the present study focuses upon its more fundamental conductance behavior in a series of solvents ranging from water (relative permittivity = 78.40) to methyl formate (relative permittivity = 8.90).

2. Experimental

2.1. Chemicals

Conductivity water was prepared by passing tap water through two ion exchange columns followed by distillation in an all quartz still. Prior to use, ultra high purity argon was bubbled through the water for around 15 h. Burdick and Jackson "Distilled in Glass" grade propylene carbonate (PC) was stored for at least 24 h over type 4A molecular sieves, vacuum distilled (head temperatures 85 to 95°C) and the middle fractions stored over activated neutral alumina in an Ar-filled dry box. Fisher HPLC grade acetonitrile (AN) was distilled in a stream of high purity Ar, and middle fractions collected and stored in a dry box over type 4A molecular sieves. Methyl formate, Alpha Inorganics, 99+ % pure, was dried with 4A sieves for 24 h and fractionated in a stream of ultra high purity Ar. This solvent was stored in the dry box and treated with activated neutral alumina for 24 h prior to use. The experimental conductances of these pure solvents at 25°C are given in Table I. Water contents of the aprotic solvents were not measured, but based on our previous work and on the conductances of these solvents (see Table I), it is estimated that water impurity levels are in the 10 to 50 ppm range: *e.g.*, identical treatment of methyl formate reported in several of our earlier publications was found to result in water contents of 40 ppm(9) to less than 20 ppm.(26) Also included in Table I are literature values for densities d; relative permittivities ε; viscosities η; and the Bjerrum distances q, calculated from the relative permittivities. The data for water, PC, and AN were taken from Ref. 8 and those for MF were taken from Ref. 9.

The imide salt $LiN(CF_3SO_2)_2$ (kindly supplied by M. Gauthier of Hydro-Québec Research Institute) was heated to 80-130°C under vacuum for at least 15 hours and not treated any further. A similar treatment of this imide salt by Weber (heating to 110°C under vacuum) resulted in a water impurity of less than 70 ppm.(7)

Table I. Properties of Pure Solvents at 25°C[a]

Solvent	d	ε	η	q	κ
H_2O	0.9971	78.40	0.8903	0.357	1.2×10^{-6}
PC	1.1995	64.97	2.53	0.431	7.3×10^{-8}
AN	0.7768	35.96	0.3426	0.779	5.9×10^{-7}
MF	0.9663	8.90	0.3280	3.148	2.5×10^{-8}

[a] Density d, units are g-cm^{-3}; ε, the relative permittivity; η, the viscosity in cP; q, the Bjerrum distance in nm; κ, the experimental electrolytic conductance in S-cm^{-1}.

2.2. Conductivity Measurements

Stock solutions of around 0.05 mol-kg^{-1} in the aprotic solvents were prepared in a dry room (dew point varied from -35 to -50°C) and their densities determined with a Parr DMS 45 digital density meter. Around 20 g of pure solvent were placed in a Kraus-type conductivity cell (cell constant 0.12139 cm^{-1} for aqueous and AN solutions, and 0.06299 cm^{-1} for PC and MF solutions), and the cells removed to the laboratory and placed in a water thermostat at 25.00±0.02°C (NBS traceable calibration). Incremental additions of the stock solutions to the Kraus cells were made with air-tight plastic syringes which were weighed before and after each addition. Conversion of concentrations to volume units utilized calculated solution densities from the relations

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

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 data, c is the concentration in mol-dm^{-3} units, and m and $\tilde{m}$ are the concentrations in molality and mol-kg^{-1} of solution units. Solution resistivities were measured with a Wayne Kerr model 6425 Precision Component Analyzer.

3. Results and Calculations

Molar conductivies Λ (S-cm^2-mol^{-1}) were calculated from the electrolytic conductances κ after correcting for the pure solvent conductance, and are given in Table II. In fitting the conductivity data to a conductance equation, the molar conductivities in Table II were analyzed using Fernández-Prini's expansion(10) of the Fuoss-Hsia equation(11) in combination with the following equilibria

Table II. Experimental Data from Conductance Measurements at 25°C[a]

$10^3 c$	Λ	$10^3 c$	Λ
Water		Propylene Carbonate	
0.7473	67.894^b	0.6436	22.003
1.7444	67.668	1.4380	21.666
2.8297	67.010	2.1288	21.410
4.0409	66.352	2.4692	21.316
4.7797	66.017	3.1296	21.178
5.5864	65.676	3.7691	21.044
6.2910	65.403	4.5901	20.889
7.0795	65.082	5.1895	20.786
8.0992	64.637	5.9601	20.661
8.8935	64.438	6.8553	20.530
10.086	64.070	7.9442	20.369
11.079	63.745	10.341	20.064
12.790	63.274	11.804	19.890
14.141	62.868	13.662	19.696
		15.681	19.491
Acetonitrile		Methylformate	
1.8348	138.934^b	0.5584	37.890^b
2.3384	137.783	1.4148	27.230
2.9463	136.098	2.4022	22.837
3.6811	134.423	3.1393	21.144
4.9496	131.761	4.1801	19.573
5.9450	129.859	4.9622	18.744
6.9928	128.002	6.2231	17.676
8.0621	126.264	7.4560	17.108
8.9425	124.905	8.8165	16.490
10.324	122.908	10.249	16.083
11.628	121.135	11.717	15.751
13.275	118.989	12.771	15.639
14.897	117.033	14.515	15.440
16.891	114.747	17.009	15.163
		19.404	14.990

[a] Units: concentration c, mol-dm^{-3} and molar conductivities, S-cm^2-mol^{-1}. [b] Data points not included in evaluating Λ_0 and equilibrium constants.

$$\mathrm{Li^+ + N(CF_3SO_2)_2^- \rightleftarrows LiN(CF_3SO_2)_2} \qquad K_A \qquad (1)$$

$$\mathrm{LiN(CF_3SO_2)_2 + Li^+ \rightleftarrows Li_2N(CF_3SO_2)_2^+} \qquad K_{t+} \qquad (2a)$$

$$\mathrm{LiN(CF_3SO_2)_2 + N(CF_3SO_2)_2^- \rightleftarrows Li(N(CF_3SO_2)_2)_2^-} \qquad K_{t-} \qquad (2b)$$

While all calculations for systems involving triple ions employed the common assumption that $K_{t+} = K_{t-} = K_t$, the possibility of asymmetric triple ion was explored, but the standard errors of calculated and observed molar conductivities were larger than those for symmetric triple ion formation. In evaluating equilibrium constants, mean molar activity coefficients $y_\pm$ were calculated from

$$\ln\gamma_\pm = \frac{-AI^{1/2}}{1 + BR_yI^{1/2}} \qquad (3)$$

where A and B are the Debye-Hückel constants and I is the total ionic strength. In all calculations, the distance parameter R_y was equated to the Bjerrum distance q. From mass and charge balance requirements, the concentrations of all species were obtained by solving the following basic equation by the Newton-Raphson method

$$f(x) = 3[\mathrm{X^-}]^3 y_\pm^2 K_a K_t + [\mathrm{X^-}]^2 y_\pm^2 K_a + [\mathrm{X^-}] - C_x = 0 \qquad (4)$$

In the above equation, X represents the anion, and C_x is the total salt concentration in mol-dm^{-3}. The total conductivity of the solutions can be represented by the general equation

$$\Lambda_{\text{total}} = \alpha\Lambda + \alpha_3\Lambda_3 \qquad (5)$$

where $\alpha C_x = [\mathrm{N(CF_3SO_2)_2^-}]$

and $\alpha_3 C_x = [\mathrm{Li(N(CF_3SO_2)_2)_2^-}]$ (6)

The total ionic strength is simply defined as $(\alpha + \alpha_3)C_x$, and the molar conductance terms Λ and Λ_3 were calculated from

$$\Lambda_n = \Lambda_n^o - S_n I^{1/2} + E_n I \ln(I) + J_{1,n}(R_1)I - J_{2,n}(R_2)I^{3/2} \qquad (7)$$

Equations (5-7) were solved by the grid-search method$^{(9,12)}$ where initial values are estimated for the variables Λ_o, K_A, K_t and R_2 and the concentrations and molar conductivities calculated from Eqs. (4 - 7). The variables were then adjusted in small increments until a minumum was found for the function s

$$s = \sigma(\Lambda_{\text{obsd}} - \Lambda_{\text{calcd}})^2 \tag{8}$$

The standard error in Λ and σ_Λ is computed from $[s/(k-1)]^{1/2}$ where k is the number of data points. In all calculations, R_1 was equated to the Bjerrum distance, R_2 treated as a variable parameter except in cases where R_2 approached zero and thus had to be fixed at the Bjerrum distance, and when triple ions were present, the assumption was made that $\Lambda_3^{\circ} = 2\Lambda_o/3$.(13) The results of these calculations are given in Table III, and included in this table are corresponding literature values for $LiClO_4$ and $LiAsF_6$. Data for $LiClO_4$ in water, PC, AN and MF were taken from Refs. 9, 14 to 16, respectively, and data for $LiAsF_6$ in water, PC, AN and MF were taken from Refs. 9, 17 to 19, respectively. The parameters for $LiClO_4$ in AN using the data from Ref. 16 were recalculated by the present author from Eqs. (5-7) for consistency: *i.e.*, Barthel *et al.*(16) equated R_2 to a or $a + s$ (a is the sum of crystal radii and s is the solvent diameter), and in the modified Bjerrum equation (see below), the upper integral limit was taken as either $a + s$ or $a + 2s$. In the present analyses, R_2 is used as a variable parameter or is fixed at the Bjerrum distance q, and in the modified Bjerrum equation the upper integral limit is also equated to the distance q. Table IV gives values of single ion limiting molar conductances based on $\lambda_o(Li^+)$ values obtained from Refs. 14 and 22 for water,(23) for PC,(16) for AN, and(9) for MF.

To compare solvent effects on ion pair formation in acetonitrile and methyl formate, the Bjerrum equation as modified by Barthel *et al.*(8,15,20) was used. This equation empirically accounts for noncoulombic energy contributions (W_{+-}) to the Gibbs energy of ion pair formation

$$K_a = \frac{4\pi N_a}{1000}\int_a^q r^2 \exp\left\{\frac{(ze)^2}{\varepsilon kTr} - \frac{W_{+-}}{kT}\right\} dr \tag{9}$$

In Eq. (9), integration is carried out from the distance of closest approach, a, to the Bjerrum distance q. For a contact ion pair, the distance of closest approach is simply equated to the sum of the anion and cation crystal radii, and for a solvent-separated ion pair, the distance of closest approach is taken as $a + s$ where s is the diameter of the solvent molecule. As pointed out in previous publications(8,15,20) for general discussion and(9) for 1:1 salts in MF, the distance of closest approach may indeed be smaller than $a + s$, and the problems in assigning values for these limits are discussed below. Using literature data,(21) the length of the methyl formate molecule is estimated to be 0.51 nm, and Barthel *et*

Table III. Derived Parameters at 25°C[a]

Salt	Solvent	Λ_o	K_A	Λ_3^o	K_t	R_2	σ_Λ
$LiClO_4$	H_2O	105.9					0.04
	PC	26.75	1.3			0.55	0.004
	AN	173.604	16.15			0.743	0.009
	MF	157.0	6.54×10^5	104.7	22.0	3.148^b	0.013
$LiAsF_6$	H_2O	95.07				0.357^b	0.24
	PC	22.53				0.432	0.19
	AN^c	172.8				0.68	~0.4
	MF	168.4	4.38×10^4	112.3	69.1	3.148^b	0.14
LiTFSI	H_2O	70.89				0.422	0.057
		(0.059)					
	PC	22.76				0.553	0.016
		(0.016)					
	AN	153.71	4.73			0.861	0.090
		(0.11)	(0.23)				
	MF	131.50	2.34×10^4	87.67	20.12	23.08	0.041
		(1.02)	(120)	(0.84)	(1.13)		

[a] Units: Λ, S-cm^2-mol^{-1}; K_A and K_t, mol^{-1}-dm^3; and R_2, nm. For the present studies, standard deviations for the derived parameters are given in parenthesis below the adjusted parameter. Source of derived parameters for $LiClO_4$ and $LiAsF_6$ discussed in the text. [b] R_2 held constant at the Bjerrum distance in these calculations. [c] Parameters recalculated by present author using data from Ref. (19).

al.⁽¹⁶⁾ give the length of the acetonitrile molecule as 0.58 nm. Using molecular models, L. Dominey of Covalent Associates has estimated the length of the $N(CF_3SO_2)_2^-$ anion to be 1.45 nm and the width to be 0.45 nm: in calculating the contact distance for $LiN(CF_3SO_2)_2$, the values of 0.078 nm (for Li^+) and 0.45 nm (for the anion) were used. The crystal radius used for Li^{+}(8) was 0.078 nm and for ClO_4^- was 0.240 nm and that for AsF_6^- was 0.384 nm(17) The results of these analyses are given in Table V.

4. Discussion

In fitting the conductivity data to the conductance equations, ion association was found, as expected, to be significant only in AN and MF solutions. Where comparative data exist, the imide salt generally exhibits smaller ion association than does $LiClO_4$ and $LiAsF_6$. The singular exception appears to be $LiAsF_6$ in AN for which no ion associa-

Table IV. Limiting Ionic Conductances at 25°C[a]

Ion	H_2O[b]	PC[c]	AN[d]	MF[e]
Li^+	38.7	7.86	69.97	64.2
ClO_4^-	67.2	18.89	103.62	92.8
AsF_6^-	56.4	14.67	108.2	104.2
$N(CF_3SO_2)_2^-$	32.2	14.90	83.72	67.3
$Li_2N(CF_3SO_2{}_2^+$			32.49	23.5

[a] Values of λ_o (S-cm^2-mol^{-1}) based on $\lambda_o(Li^+)$. [b] Refs. 14 and 22. [c] Ref. 23. [d] Ref. 16. [e] Ref. 9.

Table V. Non-Coulombic Energy Contributions to Ion Pair Formation[a]

		Acetonitrile		Methylformate	
Salt	$r_+ + r_-$	a	W_{+-}	a	W_{+-}
$LiClO_4$	0.318	0.318	0.70	0.828	-13.13
$LiAsF_6$	0.462	0.462	-	0.972	-7.33
$LiN(CF_3SO_2)_2$	0.528	0.528	1.58	1.038	-6.09

[a] Units: distances in nm and W_{+-} in kJ-mol^{-1}. r_+ and r_- is the sum of the ionic crystal radii, and a is the distance of closest approach used in Eq. (9).

tion could be detected using the data of Hopkins *et al.*,$^{(19)}$ but it is noted that these data were difficult to fit to the conductance equation, and that the precision of these data is significantly poorer than those for other data (see the σ_A values in Table III). In fitting selected data to the triple ion model, both the possibility of asymmetric triple ion and quadrupole formation were explored, the latter being defined by $Li_2X^+ + X^- \rightleftarrows Li_2X_2$. In all cases, the simple model of symmetric triple ion formation resulted in smaller σ_A values.

The above differences in complex formation of $LiClO_4$ and $LiAsF_6$ compared with $LiN(CF_3SO_2)_2$ can be attributed mainly to the unique properties of the $N(CF_3SO_2)_2^-$ anion: having a highly delocalized charge density and having a relatively large ionic radius results in smaller ion association, and in formation of triple ions in acetonitrile. These properties are also reflected in the limiting ion conductivities, λ_i in Table IV where it is seen that if there is a strong electropositive center on the solvent molecule, there appears to be abnormally strong interaction between the solvent and the anion. For example, the acetonitrile molecule is considerably delocalized resulting in a weak positive center (on the nitrile carbon and/or on the methyl hydrogens) which results in relatively weak interactions with anions(24) whereas methyl formate has a relatively strong positive center (the formyl proton) which will strongly interact with anions(9) These properties are revealed in Table III which shows that the λ_i values for anions in methyl formate are smaller than those in acetonitrile when, based on Stoke's Law, the opposite behavior would be expected. The large difference between $\lambda(N(CF_3SO_2)_2^-)$ in acetonitrile and methyl formate is suggestive of an unusually large methyl formate - $N(CF_3SO_2)_2^-$ interaction. The significance of strong ion-solvent interactions which results in disruption of bulk solvent properties and weak ion-solvent interactions which results in enhancement of bulk solvent structure is discussed below.

Equation (9) was used to estimate the non-coulombic interaction energies of the three lithium salts in acetonitrile and in methyl formate. Assigning values to the integration limits is subject to uncertainties, particularly with respect to the distance a when the ion pair is a solvent separated species. Barthel *et al.*(8,15,20) pointed out that this distance may not necessarily be represented as the sum $r_+ + r_- + s$, but is often associated with the center-to-center distance of the ions coordinated to a solvent molecule based on the shortest possible distance arising from the known geometry of the system. This approach often leads to values of a less than $r_+ + r_- + s$, and was in fact the method used previously by Plichta *et al.*(9) Deciding which species form solvent separated ion pairs can also be difficult since departures from the simple Bjerrum equation can be attributed to short range forces rather than, or in addition to, insertion of a solvent molecule between the gegen ions. These short range forces, related to the sign and magnitude of W_{+-}, vary as a function of solvent depending upon competing effects for ion-ion and ion-solvent interactions,(16,25) and this model of the overall association process can be represented by

$$Li^+(s)_n + X^-(s)_m \rightleftarrows Li^+(s)\, X^-(s)_{m+n-1} \rightleftarrows Li^+X^-(s)_{m+n-1} + s$$

Thus while Li^+ is certainly highly solvated in acetonitrile(16,25) the present analysis will consider that the predominate complex in this solvent is the contact ion pair: *i.e.*, the last complex in the above equation which may still be a solvated species. This model therefore assumes that upon association, the anion displaces a solvent molecule from the solvation sphere of the cation. This appears to be the mechanism for

Na^+ association in $NaClO_4$-AN solutions as determined by Greenberg and Popov(27) from IR spectra. However, with very strong electron donors such as THF, $NaClO_4$ ion pairs are mainly solvent separated species.(27) For lithium salts in methyl formate, the present analyses assumes that all complexes are solvent separated species, and the bases of this assumption are the abnormally low values of λ_i for Li^+, the anions, and for the triple ion complexes (see Table IV). Based on these assumptions, Table V was constructed as described above. Negative values of W_{+-} can be attributed to the enhancement of solvent structure by highly solvated ions which tends to decrease ion pairing whereas positive values of W_{+-} can be attributed to a disruptive effect of the ions on solvent structure thereby tending to assist ion pair formation(15,20,9) While the magnitude of W_{+-} clearly depends upon the values selected for the integration limits in Eq. (11), the trends are quite significant: for anion effects on ion association in the individual solvents acetonitrile and methyl formate: *i.e.*, W_{+-} becomes more positive according to $ClO_4^- < AsF_6^- < N(CF_3SO_2)_2^-$, and in comparing ion association in both solvents, W_{+-} is generally more negative in methyl formate.

ACKNOWLEDGMENT

The author is grateful for help received from C. W. Walker (ETDL) for purification of the acetonitrile, to M. Gauthier (Hydro-Québec) for his generous gift of purified $LiN(CF_3SO_2)_2$, to L. Dominey (Covalent Associates) for helpful discussions and for calculating the dimensions of the $N(CF_3SO_2)_2^-$ anion, and to A. Weber (Eveready) for providing a copy of his paper(7) prior to publication.

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