ELECTROLYTE SOLVATION IN APROTIC SOLVENTS

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Summary

The nature of specific ion–solvent, ion–ion and solvent–solvent inter-actions is reviewed in the context of their relation to the development of lithium batteries. For aprotic solvents of permittivities $> \approx 15$, the "medium effect" has been found to offer insights into basic problems (*e.g.*, solubilities and relative rates of electrochemical reactions) as well as offering predictive capabilities. For aprotic solvents of permittivities $< \approx 15$, the use of high and audiofrequency conductivity data are commonly used in elucidating the nature of electrolyte solutions since thermodynamic data are often lacking.

Introduction

It has long been realized that selection of a solvent and electrolyte are key problems involved in the development of both primary and secondary lithium cells and batteries. The problems relating the structure of non-aqueous electrolyte solutions to lithium cell performance are complex, particularly for concentrated solutions where classical thermodynamic theory is inapplicable. Even in dilute solutions, *e.g.*, for $c \ll 0.01$ mol dm^{-3}, interpretations of the nature of ion solvation are difficult owing to the existence of ion–ion and solvent–solvent interactions as well as numerous complex species in solution. In the present review, the nature of the struc-ture of electrolyte solutions is reviewed using data from both reversible and irreversible thermodynamic studies, and selected examples of practical applications of basic research results are cited where appropriate. Table 1 lists the physical properties of a number of solvents which are important from the viewpoint of lithium cell development. The abbreviations used in this Table are:

THF	= tetrahydrofuran	EC	= ethylene carbonate
2 MeTHF	= 2-methyltetrahydrofuran	PC	= propylene carbonate
2-ClMeTHF	= 2-chloromethylTHF	DMC	= dimethyl carbonate
AN	= acetonitrile	DEC	= diethyl carbonate
DMF	= dimethylformamide	DMSO	= dimethyl sulfoxide
SDMF	= thiodimethylformamide	DMS	= dimethyl sulfite
MF	= methyl formate	DME	= dimethoxyethane
MA	= methyl acetate		

TABLE 1

Properties of selected solvents at 25 °C[a]

Solvent	ϵ	η (cP)	d_0 (g cm^{-3})	$10^8 \kappa$ (S cm^{-1})	q (nm)
THF	7.39	0.46	0.880	—	3.79
2-MeTHF	6.20	0.457	0.848	—	4.52
2-ClMeTHF	12.84	1.383	1.1031	4.4	2.18
DME	7.15	0.402	0.8612	0.3	3.99
DMC	3.12	0.585	1.063	—	8.98
MF	8.90	0.328	0.9663	1.6	3.15
MA	6.67	0.368	0.9279	0.74	4.19
SO$_2$ (0 °C)	15.35	0.403	—	~3	1.99
DMS	20.80	0.8732	1.2054	4.2	1.35
DMSO	46.68	2.016	1.1044	~0.3	0.60
AN	35.95	0.341	0.7768	1	0.78
PC	64.92	2.53	1.1995	2	0.43
H$_2$O	78.40	0.8903	0.9971	10	0.36

[a]ϵ is the relative permittivity, η the viscosity, d_0 the density, κ the electrolytic conductance of the pure solvent, and q is the Bjerrum distance. See text for solvent abbreviations.

Key problem areas encountered in lithium cell development are those relating to electrolyte reactivity with anode and cathode, and ability of the electrolyte solution to sustain high rates of charge and discharge over a wide temperature range. Basic research has played an important role in solving a number of these problems, and the interrelation of basic and applied research is explored below with emphasis given to those studies from the author's laboratory.

Solvents of relatively high permittivities ($\epsilon > \approx 15$)

For solvents of permittivity $> \approx 15$, classical thermodynamic methods (*e.g.*, e.m.f., solubilities, calorimetry) appear to yield important information on the structure of electrolyte solutions. For solvents of very low permittivity, the use of these classical thermodynamic techniques is difficult to interpret due to extensive ion association and the formation of complex species such as triple ions, quadrupoles, and probably higher aggregates at practical concentrations of around 1 - 2 mol dm^{-3}. For these solvents of very low permittivity, conductivity studies have played an important role in determining the nature of the structure of electrolyte solutions, as discussed below.

In solvents of relatively high permittivity, early researches explored the use of metal halide cathode materials; the major problem encountered was that of the solubility of the cathode in the presence of excess anion. For example, the solubility of Ag halides (AgX) is governed mainly by the two equilibria

$$AgX(s) \longleftrightarrow Ag^+(sln) + X^-(sln) \qquad K_{s0} \qquad (1)$$

and

$$AgX(s) + X^-(sln) \longleftrightarrow AgX_2^-(sln) \qquad K_{s2} \qquad (2)$$

Qualitatively it follows that selection of a solvent which will strongly co-ordinate X^- will reduce K_{s2}, but will simultaneously increase K_{s0}. However, since K_{s0} values for metal halides are often very small (*e.g.*, 10^{-20} for Ag halides [1, 2]), solvents which specifically solvate X^- will significantly reduce K_{s2} and have a minor effect on K_{s0}: the net result is an overall lowering of the solubility [3]. Considerable success in understanding the nature of simple and complex ion solvation is found in the concept of the "medium effect" [2, 4 - 7]. The importance of the medium effect is simply that, based on the energetics of transfer of individual ions from a reference solvent (*e.g.*, water) to an aprotic solvent, the relative stabilities of individual ions can be determined. For Gibbs energies of transfer of single ions, $\Delta G_t^0(ion)$, it is also possible to predict equilibrium constants for those instances where experimental data are not available. For solvents of permittivity > 15, fairly complete tabulations of $\Delta G_t^0(ion)$ values are available [2, 4 - 7]. Considering the ions K^+, Ag^+ and Cl^-, these tabulations reveal that the order of increasing $\Delta G_t^0(ion)$ values is, respectively,

$$DMSO, DMD > H_2O, PC > AN > SDMF \qquad (3)$$

$$SDMF \geqslant DMSO, SO_2 > AN > PC, DMS \qquad (4)$$

and

$$H_2O, SO_2 > DMS > PC, AN, DMSO, DMF \qquad (5)$$

This order of relative stabilities closely follows the Pearson classification of hard–soft acids and bases [8, 9]. Based on the order of $\Delta G_t^0(Cl^-)$ in eqn. (5), it was proposed that the Cl^- ion can interact with the sulfur in specific solvents containing S–O groups by $d\pi$-bonding [3, 5]. The conclusion was that in addition to being positively charged, the sulfur must have low-lying, vacant d-orbitals available for π-bonding with Cl, and that the availability of low-lying d-orbitals is associated with the electronegativity of the groups/atoms surrounding the sulfur. For example, DMS has three equilibrium structures in which the hybridization of sulfur is either sp^3d or sp^3d^2:
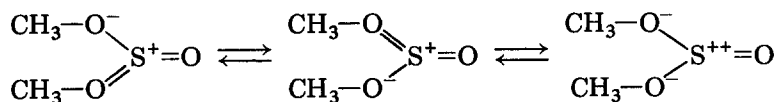
On the other hand, DMSO has two equilibrium structures $(CH_3)_2$–S=O and $(CH_3)_2$–S^+–O^- in which the sulfur is sp^3d and sp^3, respectively. Since the structure in which the sulfur is positively charged has no low-lying d-orbitals, anions such as Cl^- do not strongly coordinate with DMSO. Another solvent having low-lying d-orbitals due to coordination with highly electronegative oxygen is SO_2, and the recent successes in demonstrating the

feasibility of a rechargeable $Li/CuCl_2$ cell in $SO_2-LiAlCl_4$ electrolytes is due, in large part, to the reduced solubility of $CuCl_2$ in sulfur dioxide solutions [10, 11]. Although research and development on rechargeable Li cells utilizing metal halide cathodes has been largely abandoned in favor of insoluble lithium-intercalating cathodes, it is clear that there are considerable opportunities for metal halide cells provided that suitable solvents can be found. The possibility of using fluorine substitution to contract the d-orbitals on sulfur with the object of reducing metal halide solubilities has received little attention (but see ref. 12).

The effect of solvent on reaction rates can also be treated in terms of the medium effect [13, 14]. For example, the rate of the simple electrochemical "neutralization" reaction

$$Li^+(sln) + e^-(in\ solid\ Li) \longrightarrow Li(s) \tag{6}$$

can be treated in terms of absolute rate theory using tabulated values for $\Delta G_t^0(Li^+)$. In general, it is found for both Li^+ and Na^+ that the electrochemical neutralization rate follows the order $H_2O > PC > AN > DMF > DSMO$, which is the same order of decreasing (*i.e.*, more negative) $\Delta G_t^0(M^+)$ values (see ref. 14 for details and references).

Solvents of low permittivity ($\epsilon < \approx 15$)

Impetus on lithium cells utilizing solvents having very low permittivities can probably be attributed to the initial work of Koch *et al.* [15, 16] which reported very high lithium cycling efficiencies (>95%) using the electrolyte $LiAsF_6$ in 2-MeTHF. The increased stability of Li in 2-MeTHF, compared with the reactive parent ether THF, was attributed to raising of the LUMO on THF by α-substitution of the methyl group. In addition to perturbation of LUMO by α-substitution, it is also likely that both the compactness and the solubility of the passivating film on Li contributes to this increase in cycling efficiency. While the use of ether-based electrolyte solutions has found successful application in low voltage cells such as those employing TiS_2 intercalating cathodes, these electrolytic solutions perform poorly with high voltage intercalating cathodes such as V_2O_5, ns-V_6O_{13} and Li_xCoO_2 [17, 18]. The reason for the poor performance of ether-based electrolytic solutions in Li/metal oxide cells was attributed to a combination of solvent co-intercalation and oxidation at high potentials (>3 V) during charge. The use of ester-based solutions has received little attention in the past, but they are highly conductive over a wide temperature range, and they are much more stable towards oxidation than are ethers [17 - 21]. Figure 1 compares the electrolytic conductivities of $LiAsF_6$ in MF, MA, PC and 2-MeTHF, demonstrating the superior conductances of esters over PC and 2-MeTHF solutions. While $LiAsF_6$ solutions in MF and MA do not cycle lithium as efficiently as does 2-MeTHF solutions, the use of additives such as DMC, DEC and CO_2 significantly increases the lithium cycling
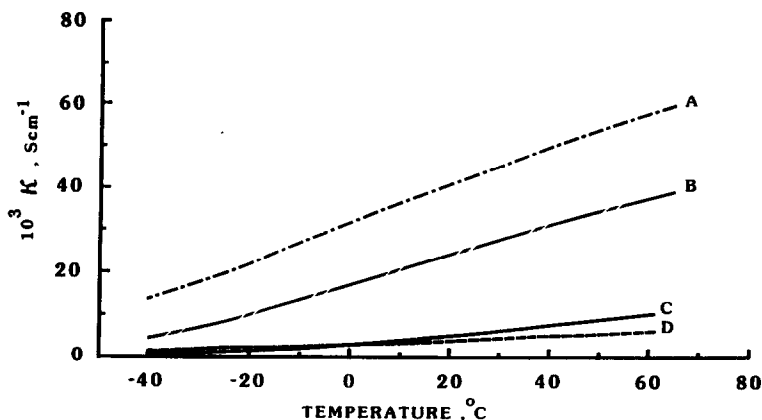
Fig. 1. Electrolytic conductivities as a function of temperature. A, 2.0 M LiAsF$_6$ + 0.4 M LiBF$_4$ in MF; B, 2.0 M LiAsF$_6$ in MA; C, 1.0 M LiClO$_4$ in PC; D, 1.5 M LiAsF$_6$ in 2-MeTHF.

TABLE 2

Properties of ester-based solutions at 25 °C

Electrolyte	Solvent	Electrolytic conductance (10 S cm^{-1})	Li cycling efficiency (%)
2.0 M LiAsF$_6$	MA	2.6	29
2.1 M LiAsF$_6$	MF	4.7	71
1.9 M LiAsF$_6$	DMC	1.1	80
1.5 M LiAsF$_6$	DEC	0.5	0
1.9 M LiAsF$_6$	MF/DMC[a]	2.6	84
1.9 M LiAsF$_6$	MF/DEC[b]	2.1	83
0.5 M LiAsF$_6$ + 0.1 M LiBF$_4$	MF/CO$_2$[c]	∼1.7	96.3
1.0 M LiAsF$_6$ + 0.2 M LiBF$_4$	MF/CO$_2$[c]	∼3.4	98.3

[a]47 mass % MF.
[b]50 mass % MF.
[c] Carbon dioxide pressure ∼50 psi.

efficiency to practical levels as shown in Table 2 [20, 21]. It is interesting to note that in pure DEC, the lithium cycling efficiency is 0%, but in MF/DEC mixtures the efficiency is increased to around 83%. The nature of this phenomenon is not known, but it is almost certainly associated with the formation of a highly insoluble passive film on Li, probably lithium ethyl carbonate [22].

There is little doubt that cations, particularly Li$^+$, are highly coordinated in ethers and esters. The high solubilities of Li salts in ethers such as DMM, DME, THF and 2-MeTHF are due, in part, to the strong coordination with the oxygen, particularly with DMM and DME which act as bidentate ligands with Li$^+$ [23, 24]. In esters, Li$^+$ is strongly coordinated to the

TABLE 3

Single anion mobilities at 25 °C[a]

Solvent	$\lambda^{\infty}(ion)$ (S cm^2 mol^{-1})			
	Cl$^-$	ClO$_4^-$	AsF$_6^-$	BPh$_4^-$
THF	—	—	61.8	40.4
2-ClMeTHF	—	22.6	20.5	17.6
MF	—	92.8	104.2	56.7
AN	98.7	103.7	103.2	58.3
SO$_2$	160	137	—	66
DMS	43.8	47.5	42.0	23.6
DMSO	24.0	24.1	—	10.2
H$_2$O	76.4	67.4	56.2	~ 20

[a]Data taken from refs. 24 - 29.

carboxyl group [25]. For electrolyte solutions in pure ethers or esters, the ionic mobilities of alkali metal cations generally increase as the ionic radius increases, but at the same time the Stokes radius decreases, thereby indicating a higher degree of coordination for the smaller cations. This phenomenon is also generally observed for other aprotic solvents such as DMF, AN and DMSO [26]. In 2-ClMeTHF, $\lambda^{\infty}(Li^+) = 13.6$ S cm^2 mol^{-1} (Pauling radius = 0.06 nm) compared with $\lambda^{\infty}(Bu_4N^+) = 13.8$ S cm^2 mol^{-1} (Pauling radius $\approx$ 0.44 nm) [26]. In MF solutions, the limiting mobilities for Li$^+$, Na$^+$, and Bu$_4$N$^+$ are, respectively, 64.2, 65.5 and 64.0 S cm^2 mol^{-1} [27]. Anion solvation details are also revealed by trends in their mobilities at infinite dilution, as seen in Table 3. The data in this Table suggest higher degrees of solvation for the smaller anions Cl$^-$ and ClO$_4^-$ in MF and DMS, which was described as arising from specific ion–solvent interactions of Cl$^-$ with the sulfinal sulfur of DMS [28] (see structures above) or via H-bonding of ClO$_4^-$ with the formal proton of MF [25]. An important consequence of strong ion–solvent interactions is the observation that ion association constants (K_a) for lithium salts are often orders of magnitude smaller than expected based on the Bjerrum equation. The departure of K_a from the Bjerrum equation can be attributed to the formation of solvent separated ion pairs and to a non-coulombic contribution to the energy of formation of the ion pair, W_{+-} (e.g., π-bonding and H-bonding). This contribution can be estimated using Barthel's modification of the Bjerrum equation [30 - 32]:

$$K_a = 4\pi N_A \times 10^{-3} \int_a^q R^2 \exp[(ze)^2/\epsilon k T R - W_{+-}/kT] \, dR \qquad (7)$$

In eqn. (7), the integration is carried out for R values from the distance of closest approach, a, to the Bjerrum distance q (see Table 1). Fitting experimental K_a data for various salts in MF [25] and DMS [27] to eqn. (7) yielded the W_{+-} values given in Table 4. It is well known that LiAsF$_6$ is a

TABLE 4

Non-coulombic energy contributions to ion pair formation[a]

Salt	$r_\pm$	Methyl formate		Dimethyl sulfite	
		a	W_{+-}	a	W_{+-}
$LiClO_4$	0.260	0.441	−4.49	0.473	−0.56
$LiAsF_6$	0.444	0.544	2.06	0.619	0.52
$NaClO_4$	0.296	0.476	−6.00	0.505	−1.59
$NaBPh_4$	0.516	0.562	5.04	0.857	−0.80
Bu_4NClO_4	0.637	0.714	−5.40	0.637	−1.11

[a]$r_\pm$ is the Pauling radius and a is the distance of closest approach in nm. W_{+-} units are kJ mol^{-1}.

unique salt in that it has one of the highest conductivities of any lithium salt in aprotic solvents, and this is reflected in the positive W_{+-} values in Table 4. Positive values of W_{+-} are interpreted in terms of structure breaking effects which destabilize the ion pair, whereas negative W_{+-} values indicate structure making effects which tend to stabilize the ion pair [14, 25, 28, 30 - 32].

Complex equilibria

The unique properties of $LiAsF_6$ in aprotic solvents referred to above are dramatically presented in Fig. 2 where the molar conductances of this salt are compared with $LiBF_4$ in 2-MeTHF [33]. In this Figure the dashed lines represent the classical Ostwald law for dissociation of simple ion pairs, and in both cases significant positive departures are observed with conductance minima around 0.03 - 0.04 mol dm^{-3}. These positive deviations and the appearance of a minimum were originally postulated by Fuoss and Kraus [34]
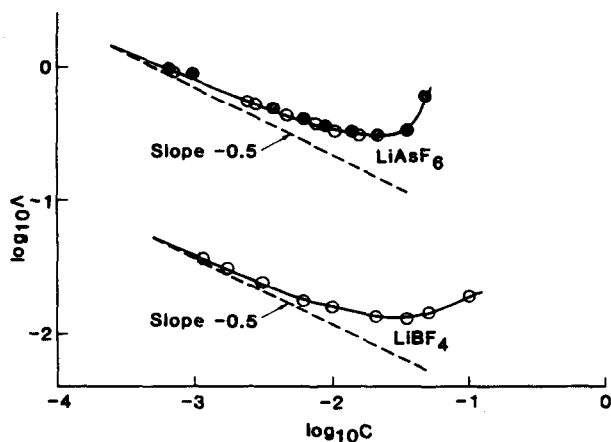

Fig. 2. Log Λ vs. log c for $LiAsF_6$ and $LiBF_4$ in 2-MeTHF at 25 °C. Data from ref. 33.

TABLE 5

Ion association and triple ion constants at 25 °C[a]

Solvent	LiBF$_4$		LiClO$_4$		LiAsF$_6$	
	K_a	K_t	K_a	K_t	K_a	K_t
2-MeTHF[b]	9.5×10^9	39	1.8×10^8	33	3.3×10^7	23
DME[c]	1.2×10^7	50	4.1×10^6	20	1.0×10^4	28
2-ClMeTHF[d]	—	—	5.3×10^4	0	3.7×10^3	0
MF[e]	—	—	6.5×10^5	22	4.3×10^4	69
MA[f]	—	—	7.8×10^7	38	9.4×10^5	71

[a]K_a and K_t in units of $mol^{-1}\ dm^3$. References are: b = 33; c = 37 - 39; d = 27; e = 25; f = 35.

to be due to the formation of triple ions (Table 5). At these low concentrations, the major equilibria thus appear to be:

$$M^+(sln) + X^-(sln) \longleftrightarrow MX(sln) \qquad K_a \qquad (8)$$

$$MX(sln) + M^+(sln) \longleftrightarrow M_2X^+(sln) \qquad K_{t+} \qquad (9a)$$

and

$$MX(sln) + X^-(sln) \longleftrightarrow MX_2^-(sln) \qquad K_{t-} \qquad (9b)$$

In concentrated solutions ($c > 0.1$ mol dm^{-3}), higher aggregates form in significant concentrations, particularly quadrupoles (*i.e.*, dimers):

$$2MX(sln) \longleftrightarrow (MX)_2(sln) \qquad K_d \qquad (10)$$

For most electrolyte solutions for $c <$ around 0.03 mol dm^{-3}, the molar conductivities, Λ, can be fitted to the Fuoss–Hsia equation [36] considering only free ions, ion pairs and triple ions

$$\Lambda = \alpha \Lambda_f + \alpha_3 \Lambda_{f3} \qquad (11)$$

where Λ_f and Λ_{f3} are, respectively, the molar conductivities of free ions and triple ions at respective concentrations αc and $\alpha_3 c$. For symmetric triple ion formation ($K_{t+} = K_{t-}$), the equilibrium constants are defined by

$$K_a = [1 - \alpha - 3\alpha_3] y_{ne}/\alpha_2 y_\pm{}^2 c \qquad (12)$$

$$K_t = \alpha_3/[(1 - \alpha - 3\alpha_3)\alpha c y_{ne}] \qquad (13)$$

where $y_\pm$ is the mean molar activity coefficient for ions, and y_{ne} is the activity coefficient for the ion pair (*i.e.*, the non-electrolyte). While y_{ne} is generally assumed to be unity, there are cases where y_{ne} may be less than unity (see below).

To account for the positive deviations in observed molar conductivities from the simple ion pair model, it is clear that an additional, variable parameter must be added to the theory. According to Fuoss and Kraus [34], this variable is the triple ion term in eqn. (11). As an alternative to triple ion

formation, several recent approaches assume that only simple ions and ion pairs exist in solution and, accordingly, new variable parameters must be introduced into the simplified conductivity relation

$$\Lambda = \alpha \Lambda_f \tag{14}$$

In ref. 40 Grigo used the mean spherical approximation [41, 42] in which the new variable parameter is a distance R similar to the distance of closest approach. Using Beronius' data for NaI in 1-butanol [43], an improved fit was obtained using eqn. (14), but in ref. 44 we have obtained a slightly better fit using eqn. (11). Another approach suggested by Cavell and Knight in 1968 [45] interprets the increase in conductance and appearance of a minimum in Λ as the result of increasing solution permittivity as the total concentration, c, increases. It has been known for some time that in aprotic solvents of low permittivity where ion association is extensive, the solution permittivity increases due to the increasing presence of polar ion pairs which, in turn, increase the polarization of the medium. Ions and neutral species can also decrease the solution permittivity, a fact which led Hückel to modify the Debye–Hückel equation as early as 1925 [46]:

$$\ln y_\pm = -Az^2 I^{1/2}/[1 + BaI^{1/2}] + CI \tag{15}$$

In eqn. (15), I is the ion strength, and C is an empirical constant accounting for the dependence of the solution permittivity, ϵ, on concentration. In ref. 35 we have used experimental solution permittivities in the original Debye–Hückel equation (*i.e.*, eqn. (16) taking $C = 0$) as discussed below. In a series of recent papers, Songstad *et al.* [47, 48] suggest that triple ions can be neglected, and that the observed increase in Λ is due to decreasing ion association, which results from a decreasing K_a as the solution permittivity increases. These authors suggest that the increase in K_a over the infinite dilution value $K_a{}^0$ can be calculated from the Born equation

$$\ln K_a = \ln K_a{}^0 + [e^2/r_\pm kT][1/\epsilon_0 - 1/\epsilon] \tag{16}$$

If eqn. (16) is to be used to derive the conductivity parameters from eqn. (14), then it is necessary to use $r_\pm$ as a variable parameter [35].

Salts influence solution permittivities due to interactions of the solvent with ions, ion pairs, and higher aggregates, if present. The dependence of ϵ on concentration is often linear over a small range and can be represented by:

$$\epsilon = \epsilon_0(1 - \beta c_{ne} - \delta c_\pm) \tag{17}$$

In eqn. (17), β is the dielectric increment (salting-in) or decrement (salting-out) due to the non-electrolyte (*i.e.*, the ion pair), and δ is the corresponding increment/decrement due to ions. In aprotic solvents of low permittivity where ion association is extensive, the concentration of free ions is negligible compared with c_{ne}, and in which case eqn. (17) reduces to
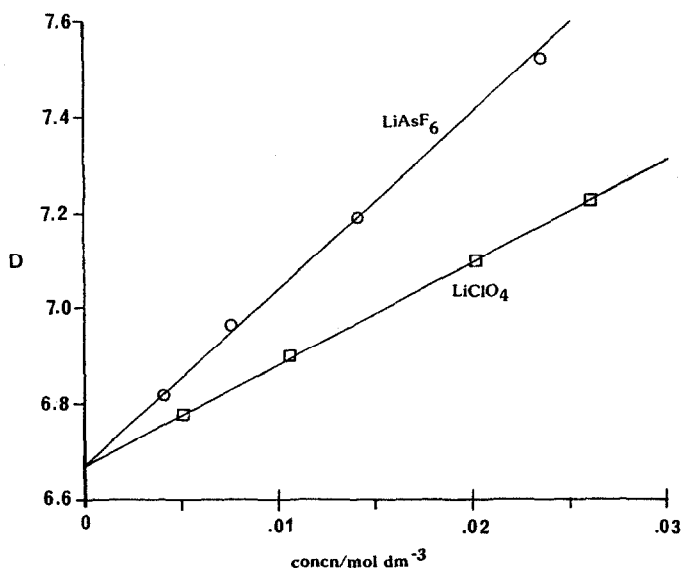
$$\epsilon = \epsilon_0 + \Delta c \tag{18}$$

Fig. 3. Solution permittivity as a function of concentration (25 °C). Data from ref. 35 for LiAsF$_6$ and LiClO$_4$ in MA.

where Δ is the overall dielectric increment. Figure 3 shows that eqn. (18) is followed for LiClO$_4$ and LiAsF$_6$ in MA [35] as it is for many salts [33, 38, 39, 47, 48] over a concentration range not exceeding around 0.03 mol dm^{-3}. In this context, triple ion formation now takes on striking similarity to salting-in phenomena which occurs when the relative attraction of an ion for a non-electrolyte is comparable to the ion–solvent attraction. The relationship for the non-electrolyte activity coefficient to the solution permittivity is such that $y_{ne} < 1$, implying that the solvent activity increases as the concentration of the non-electrolyte (ion pair) increases. Based on eqn. (17) and the Born treatment for Gibbs energies of solvation, Debye and MacAulay [49] derived the following equation for the non-electrolyte activity coefficient:

$$\ln y_{ne} = (ze)^2 \beta c_{\pm} / 2\epsilon_0 r_{\pm} kT \tag{19}$$

We have examined the effect of changing solution permittivities on the conductivity parameters in eqns. (11) and (14) for LiAsF$_6$ and LiClO$_4$ in MA [35], and the results of our studies are summarized in Table 6. In this Table, Λ_3^{∞} values were fixed at $2\Lambda^{\infty}/3$ for all calculations. For LiAsF$_6$ in MA using the triple ion model (eqn. (11)), we were able to simultaneously adjust Λ^{∞}, K_a and K_t to obtain a minimum in the standard error σ_{Λ}, and the neglect or inclusion of changing solution permittivities gives essentially identical results: i.e., in dilute solutions ($c < 0.01$ mole dm^{-3}), the fact that the solution permittivity is dependent upon total salt concentration has insignificant effect on the derived conductivity parameters. The model which

TABLE 6

Conductivity parameters in MA solutions at 25 °C[a]

	Equation	Λ^∞	$10^{-6} K_a$	K_t	σ_Λ
LiAsF$_6$	(11)[b]	155.7	0.943	70.8	0.0079
	(11)[c]	156.2	0.950	74.4	0.0083
	(14)[c,d]	128.5	0.642	—	0.016
LiClO$_4$	(11)[b]	186.3	77.8	38.0	0.011
	(11)[c]	186.3	77.9	39.6	0.012
	(14)[c,e]	186.3	77.3	—	0.010

[a]Λ^∞ units are S cm^2 mol^{-1}, K_a and K_t units are mol^{-1} dm^3. For all calculations, Λ_3^∞ was fixed at $2\Lambda^\infty/3$.
[b]Permittivity of the pure solvent used, and $y_{ne} = 1$.
[c]Eqns. (18) and (19) used in these calculations.
[d]Distance of closest approach = 0.518 nm ($r_\pm$ in eqn. (16)).
[e]Distance of closest approach = 0.579 nm.

assumes that triple ions do not form, *i.e.*, eqns. (14) - (19), is seen from Table 6 to yield poorer conductivity parameters.

For LiClO$_4$ in MA, it was not possible to include Λ^∞ as a variable parameter because of the extremely long extrapolation involved: experimental Λ values are around 0.3% of Λ^∞, and it is not possible to accurately measure conductivities below 10^{-4} mol dm^{-3} since they are close to the conductance of the pure solvent. We therefore used Walden's rule and our previous conductance data for LiClO$_4$ in PC and γ-butyrolactone solutions [50] to determine Λ^∞ in MA at 25 °C = 186.3 S cm^2 mol^{-1}. The derived conductivity parameters for LiClO$_4$ in MA based on the triple ion model or the ion pair model are, within experimental error, essentially indistinguishable.

There is no doubt that electrolytes greatly alter the structure of aprotic solvents at high concentrations, as indicated by the large increases in solution permittivities for increasing concentrations. While this phenomenon has obvious practical advantages, detailed descriptions of the complexes and nature of the solution structures have yet to be elucidated.

Acknowledgements

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