Ion–solvent effects and high energy batteries

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Abstract – A brief review on the practical advances in rechargeable
lithium cells is presented, and particular emphasis is placed on the
relation of solvent/solute properties. A number of problem areas are
identified, and details on how these problems relate to specific ion-
solvent interactions are discussed. The problem areas identified are
(1) chemical and kinetic properties of the lithium anode, (2)
chemical and kinetic properties of various cathode materials, and (3)
general solvent–solute properties as they relate to (1) and (2)
above.

INTRODUCTION

For the last 25 years, the almost universal choice for the negative electrode in a high
energy cell or battery has been lithium. The required use of aprotic solvents for this
cell has introduced numerous problems. Although lithium is thermodynamically unstable
in most aprotic organic and inorganic solvents, the stabilizing phenomena of passivation
due to corrosion followed by film formation is, as expected, highly dependent on the
choice of solvent and electrolyte.

Cathode selection has also proved to be solvent dependent, and it is not uncommon that a
specific solvent/electrolyte which is stable in the presence of solid lithium is
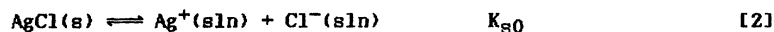reactive with the cathode.

The problem of solvent/electrolyte selection must also be considered with regard to
stability, conductivity, and safety.

The essential requirements of a practical rechargeable lithium cell are energy and power
densities comparable to primary systems, and sufficient cycle life to overcome the higher
costs of rechargeable systems compared to primary batteries. A major objective of
rechargeable lithium batteries has traditionally been directed towards traction and load
leveling applications which require cycle lifetimes of hundreds to thousands. However
there are numerous applications for portable electronic devices in which a rechargeable
cell of limited cycle life (30–100 cycles) would prove economically advantageous.
Relaxation of the high cycle life requirement has interesting consequences since, as
shown below, it permits the use of more aggressive solvents which would otherwise be
excluded in a high cycle life cell.

A number of rechargeable configurations have been investigated, and up until around 1980
the cells receiving most attention were those utilizing a metal fluoride or chloride
cathode. The cell reaction for the Li/MX cell is:

$$Li(s) + MX(s) \rightleftharpoons Li^+(sln) + X^-(sln) + M(s) \qquad [1]$$
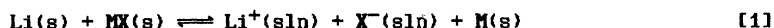
The major problem with metal halide cathodes such as $CuCl_2$ and $AgCl$ is their high
solubilities leading to rapid cell self–discharge (1). For example, the solubility of
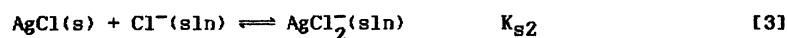$AgCl$ is governed by the two equilibria

$$AgCl(s) \rightleftharpoons Ag^+(sln) + Cl^-(sln) \qquad K_{s0} \qquad [2]$$

and

$$AgCl(s) + Cl^-(sln) \rightleftharpoons AgCl_2^-(sln) \qquad K_{s2} \qquad [3]$$

Table 1. Properties of selected intercalating cathodes

cathode (MX) discharge product	range of x per mole of MX[a]	open circuit cell voltage	average cell voltage at 2 mA cm^{-2} discharge
Li_xMoS_2	0.2 < x < 0.9	2.5	1.6
Li_xMoS_3	0 < x < 3	3.0	1.8
Li_xTiS_2	0 < x < 1	2.8	2.0
$Li_xV_2O_5$	0 < x < 1	3.5	3.3
$Li_xV_6O_{13}$[b]	0 < x < 6	3.4	2.3
Li_xCoO_2	0.2 < x < 0.9+	4.3[c]	3.9

[a] determined from experimental cells.   [b] Non-stoichiometric V_6O_{13} $(VO_{2.19})$
[c] Cathode prepared in discharged state $(Li_{0.9+}CoO_2)$, OCV ≈ 3.0 V

Clearly, both the solubility product K_{s0} and the complex formation constant K_{s2} can be reduced by selecting an aprotic solvent which increases the chloride-solvent interaction and decreases the Ag^+-solvent interaction. Although this approach resulted in partial success (1), research on metal halide cathodes has largely been abandoned in favor of insoluble intercalating cathodes, and liquid SO_2 as a rechargeable depolarizer.

The general cathodic reaction for an intercalating cathode is

$$xLi^+(sln) + xe^-_{MX} + MX(s) \rightleftharpoons Li_xMX(s) \qquad [4]$$
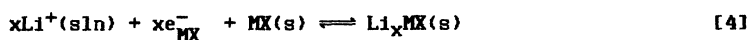
Table 1 lists a number of important intercalating cathodes (oxides and sulfides), and the maximum and minimum values of x determined chemically (n-butyl lithium method) and electrochemically (charge/discharge method). Since Li^+ is produced at the anode and reduced at the cathode, the e.m.f. of the Li/Li_xMX cell is independent of electrolyte concentration, but is dependent upon the lithium content in the solid phase. For a given solid phase, the e.m.f. of this cell is given by (2,3)

$$E = E^0 - RT/F \; ln\left\{ x/(x_{max} - x)\right\} + x\Delta U/F \qquad [5]$$

In eq. [5], E^0 is the standard potential associated with the energetics of inserting an electron into the conduction band of the intercalating solid, ΔU is a composition dependent energetic term associated with the electrostatic interaction between intercalated lithium ions, and the ln term represents configurational entropy of mixing. It is this entropy of mixing term which is important when $x \rightarrow x_{max}$ (cell discharge) or $x \rightarrow 0$ (cell charge) since under these conditions, the cell potentials change rapidly which can result in solvent/electrolyte reduction or oxidation, respectively.

Table 2 lists the physical properties of a number of solvents presently being considered for use in rechargeable lithium cells, and the abbreviations used are:

THF	= tetrahydrofuran	DMC	= dimethyl carbonate
2Me-THF	= 2-methyl tetrahydrofuran	MF	= methyl formate
DME	= dimethoxyethane	MA	= methyl acetate
1,3-DIOX	= 1,3-dioxolane	DMSI	= dimethyl sulfite
γ-BL	= γ-butyrolactone	TMSO	= sulfolane
EC	= ethylene carbonate	DMSO	= dimethyl sulfoxide
PC	= propylene carbonate		

A recent advance in electrolyte development is based on SO_2-$LiAlCl_4$ complexes first reported in a Doctoral Dissertation in 1980 (4). Koslowski found that SO_2 forms stable complexes with $LiAlCl_4$ which are super-cooled liquids at room temperature, and which have relatively low vapor pressures. The dissertation reveals that the stable $3SO_2$ complex has a low vapor pressure of 517 mm Hg (68928 Pa) at 298 K, and a more recent study (5) shows that at 298 K the electrolytic conductivity of $LiAlCl_4 \cdot 3SO_2$ is 0.09 S cm^{-1}, and the

Table 2. Properties of important solvents at 298 K[a]

solvent	ϵ	η/cP	$d_0/g\ cm^{-3}$	$10^8\kappa/S\ cm^{-1}$	q/nm
2Me-THF	6.20	0.457	0.848	——	4.52
THF	7.39	0.46	0.880	——	3.79
DME	7.15	0.402	0.8612	0.3	3.99
γ-BL	41.77	1.727	1.1234	2	0.67
EC[b]	89.6	1.85	1.321	——	——
PC	64.92	2.53	1.9995	2	0.43
DMC	3.12	0.585	1.063	——	8.98
MF	8.90	0.328	0.9663	1.6	3.15
MA	6.68	0.364	0.9279	0.74	4.19
1,3-DIOX	6.86	0.5969	1.0580	0.5	4.08
SO_2[c]	15.35	0.403	——	$\approx$ 3	1.99
DMSI	20.80	0.8732	1.2054	4.2	1.35
TMSO[d]	43.3	10.29	1.262	——	0.59

[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.
[b] 338 K.   [c] 273 K.   [d] 328 K.

$LiAlCl_4 \cdot 6SO_2$ complex has an electrolytic conductivity of 0.11 S cm^{-1}. Initial applications of this unique solvent were concerned with rechargeable $Li/CuCl_2$ cells (5), but more recent applications involve the direct use of SO_2 as the cathode depolarizing material (5,6). Although some (insoluble) LiCl is found as a discharge product in the rechargeable Li/SO_2 cell, the major cell reaction may involve the formation of lithium dithionate:

$$2SO_2(sln) + 2Li^+(sln) + 2e^- \rightleftharpoons Li_2S_2O_4(s) \qquad [6]$$

LITHIUM ELECTRODE

The stability of lithium in aprotic solvents is generally attributed to passivation, and the type of passive film formed directly influences performance and cycling efficiency (7- 12). Passivation is a kinetic (corrosion) phenomena. Radiationless electron transfer occurs when the energy of the electron in the metal equals the energy of the lowest unoccupied molecular (electronic) orbital (LUMO) of the solvent (ion). Perturbation of the LUMO of the solvent can be accomplished by chemical modification such as the introduction of an α-CH_3 group in THF to yield 2Me-THF (12, 13), or by selection of an electrolyte which specifically coordinates with the active moiety of the solvent molecule. Although lithium stability is greatly enhanced, 2Me-THF solutions have very low conductivities and poor low temperature properties. To increase conductivities and enable low temperature operation, Abraham et al. have developed a number of binary and ternary mixed solvents based primarily on THF/2Me-THF mixtures (14). In fact the use of mixed solvents where one solvent is aggressive and the other passive towards lithium is receiving increased attention, and probably represents the practical approach in compromising cycle life for increased performance (1, 14-17). In studies involving ethers (10) and esters (18), $LiAsF_6$ has emerged as a superior electrolyte both for high conductivities and increased lithium stability. It appears that the AsF_6^- ion is reduced at lithium producing LiF and a passive polymeric film with the structure $[>As-O-As<]_n$ (13). While the effect of passivation on lithium dissolution and deposition has only been treated qualitatively, a more quantitative treatment in terms of ion-solvent effects at non-passivated electrodes (e.g. amalgams and solid lithium where films do not form) is given below.

For the simple electrochemical "neutralization" reaction

$$Li^+(sln) + e^-(in\ solid\ Li) \rightleftharpoons X^{\neq} \longrightarrow Li(s) \qquad [7]$$
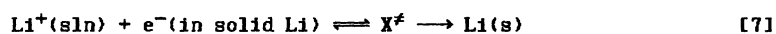
where $X^{\neq}$ is the activated complex, it expected that the solvation of Li^+ and $X^{\neq}$ will
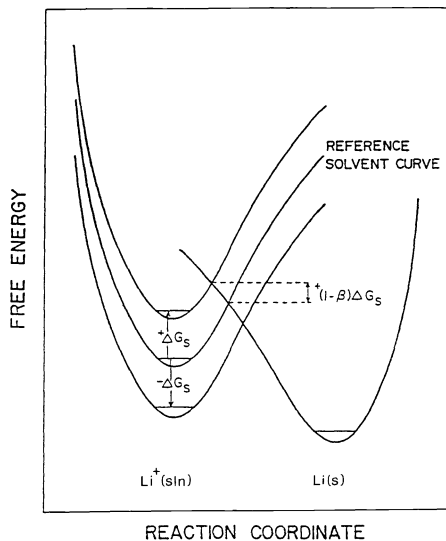
Fig. 1. Schematic representation of the solvent effect for the electrode reaction [7].

effect the rate of reaction. The effect is shown schematically in Fig. 1 where the overall changes in Gibbs energies of solvation (ΔG_s) based on an arbitrarily selected reference solvent is plotted along a reaction coordinate. The effect of changing the solvent is regarded as changing only the initial state by ΔG_s and the activated state by some fraction β of ΔG_s, the final state remaining independent of solvent changes. The Gibbs energy term ΔG_s is complex, containing both "chemical" and "electrochemical" contributions as discussed below. For a decrease in solvation energy ($+\Delta G_s$) there is a net reduction of the free energy of activation of $-\beta \Delta G_s$ resulting in an increase in the rate of dissolution of lithium. Solvation effects for electrochemical redox reactions are different from the simple atom-ion transfer reaction of eq. [7] as they also involve solvent reorganization which is treated elsewhere (19, 20). For the simple atom-ion transfer reaction, the rate expressed in units of A cm^{-2} (i) is simply $i = zFv$, and expressing the velocity v in terms of absolute rate theory (20-24)

$$i = (\tau kTzF/h)c_1 exp\left\{ \left(-\Delta G^{\neq} - \beta\phi F - (1 - \beta)\psi F \right) /RT\right\} \qquad [8]$$

In eq. [8], τ is the transmission coefficient taken as unity, c_1 the Li^+ concentration in mol cm^{-2} at the outer Helmholz plane at potential ψ, $\Delta G^{\neq}$ is the Gibbs energy of activation, ϕ the absolute metal-solution potential difference, β the symmetry factor, and all other terms have their usual significance (e.g. see 21-23). While absolute values of ϕ cannot be measured, differences between some solvent s and some reference solvent r, $\phi_s - \phi_r$, can be calculated. It is therefore easier to treat *relative* rates of reaction, i_r/i_s, and by comparing these rates at the standard reversible potential ϕ^0, i.e. for $\phi = \phi^0$ where $i = i^0$ (the standard exchange current density). The relative rate of standard exchange current densities is thus given by (23)

$$i_r^0/i_s^0 = exp\left\{ \left(\Delta G_t^0(\neq) - \Delta G_t^0(Li^+) + (1 - \beta)(\psi_s - \psi_r)F + \beta(\phi_s^0 - \phi_r^0)F \right) /RT\right\} \qquad [9]$$

Note that in eq. [9], Gibbs energy terms are now expressed in terms of Gibbs energies of transfer of one mole of activated complex ($\Delta G_t^0(\neq)$) and lithium ions ($\Delta G_t^0(Li^+)$) (see (23) for details). The $\phi_s^0 - \phi_r^0$ term can be evaluated from (23, 24)

$$(\phi_r^0 - \phi_s^0)F = \Delta G_t^0(Li^+) + (\chi_s - \chi_r)F = \Delta \alpha_t^0(Li^+) \qquad [10]$$

where χ is the surface potential (i.e. the p.d. across the gas/liquid interface), and $\Delta \alpha_t^0$ is the *real* Gibbs energy of transfer. There are a number of instances in which χ and $\Delta \alpha_t^0$ data are known from experiment or from calculation (23), and in which case eq. [9] follows the expected trend depending upon $\Delta G_t^0(M^+)$ values. For Li^+ and Na^+ reduction at amalgam electrodes, and using water as the reference solvent, i_r^0/i_s^0 is greater than unity and follows the order $H_2O > PC > AN > DMF > DMSO$ (23, 25-27). This is the same order of decreasing (more negative) $\Delta G_t^0(M^+)$ values (28). Providing sufficient data exist for $\Delta G_t^0(M^+)$ and $\Delta \alpha_t^0(M^+)$, the above treatment can have important predictive applications to selection of solvents for use in high energy batteries.
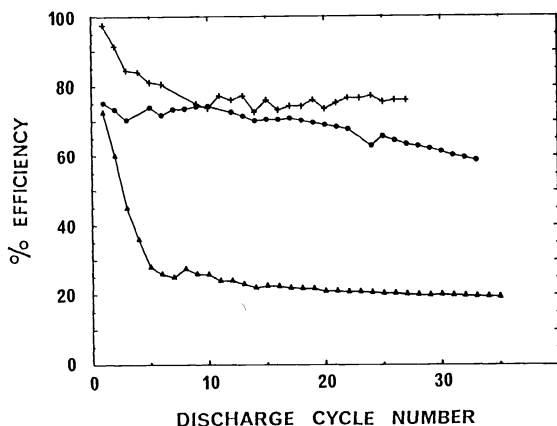
Fig. 2. Efficiency of TiS_2 in various solvents at 298.2 K (discharge and charge currents are 1.0 and 0.5 mA cm^{-2}, respectively).
+ 1.7 mol dm^{-3} $LiAsF_6$ in 2Me-THF
● 0.8 mol dm^{-3} $LiAsF_6$ in 24 mass % γ-BL/DME
▲ 2 mol dm^{-3} $LiAsF_6$ in MF
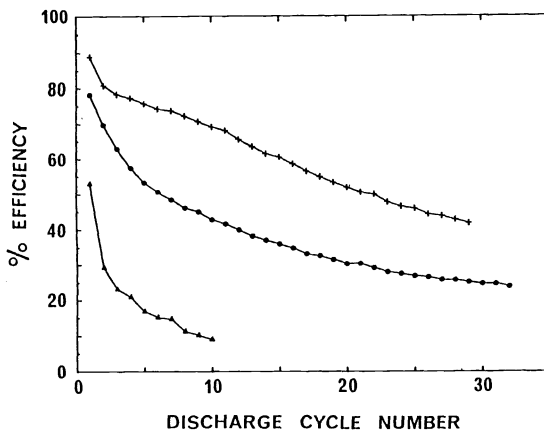
Fig. 3. Efficiency of ns-V_6O_{13} in various solvents at 298.2 K (discharge and charge currents are 1.0 and 0.5 mA cm^{-2}, respectively).
+ 2.0 mol dm^{-3} $LiAsF_6$ in MF
● 1.3 mol dm^{-3} $LiAsF_6$ in 2Me-THF
▲ 1.3 mol dm^{-3} $LiAsF_6$ in 24 mass % γ-BL/DME

RECHARGEABLE CATHODES

The kinetics of reduction processes for cell [1] (e.g. $AgCl + e^- \rightleftharpoons Ag + Cl^-$) or cell [4] (e.g. $xLi^+ + xe^- + TiS_2 \rightleftharpoons Li_xTiS_2$) can be treated analogously to that given above, but the rate capabilities of rechargeable cathodes are generally limited by complex phenomena other than electrodically kinetic limitations. Solid state diffusion, catalytic and electrochemical oxidation/reduction of solvent and/or electrolyte, and complex solubilities all contribute to cathode limitations. The problem of complex solubilities of metal halides (e.g. AgCl and $CuCl_2$) was discussed above and in (1), and below the roles of the the solvent and electrolyte are addressed.

Not unexpectedly, we have found that there is specificity of intercalating cathodes towards the solvent (29). Figures 2 and 3 above show the cycling efficiencies of cathode limited Li/TiS_2 and Li/ns-V_6O_{13} cells in the same solvents, and it is seen that there is a reversal in cycling efficiencies for these two cathodes in the same solvents. It was concluded (29) that for Li/TiS_2 cells, MF co-intercalates with Li^+ followed by solvent reaction in the layered structure of TiS_2. Unlike TiS_2, ns-V_6O_{13} is a channeled structure, and much more specific toward Li^+ (30) which sterically inhibits solvent co-intercalation. This phenomena was recently confirmed by Matsuda et al. (31) who reported that both capacity and cycle life of TiS_2 cells are increased by addition of crown ethers to PC-based electrolytes. The crown ether forms a strong 1:1 complex with Li^+ thereby de-intercalating Li^+as the Li^+-solvate complex upon cell charging. It is well known that TiS_2 cycles very efficiently in ethers (10, 11) which can also be attributed to the fact that ethers such as THF and DME strongly coordinate Li^+ (1).
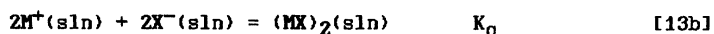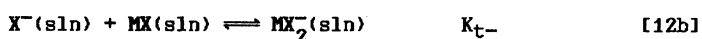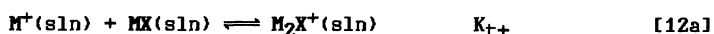
ELECTROLYTE SOLUTIONS

The above discussions demonstrate the relations between ion–solvent effects and lithium rechargeable batteries, and how these concepts can have important impact upon technological innovation in developing practical systems. For these reasons, studies directed towards elucidation of solvent-solvent and ion-solvent interactions continue to play an important role in our studies. Although considerable information can be extracted from solubility and e.m.f. measurements (24, 28), these methods are difficult to use with electrolytes of interest to high energy batteries. The reasons are that the electrolytes of interest are generally extremely soluble (e.g. > 2 mol dm^{-3}), and e.m.f. data are

difficult to apply (an anion reversible electrode is required) and difficult to interpret in view of the existence of ion pairs, triple ions, quadrupoles (dimers) and higher aggregates. Some useful experimental techniques include calorimetry, spectroscopy, and audio and high frequency conductance measurements, the latter being the focus of the present author's studies.

Audiofrequency conductance measurements yield information on the extent of association, and ultrasonic or dielectric relaxation measurements yield information on relaxation times which can be used to determine the sizes and dipole moments of rotating species.
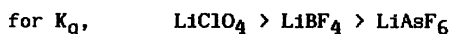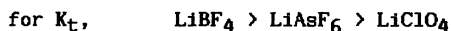
In solvents of low relative permittivity ($\approx$ 10 or less), the complex behavior of electrolytes can generally be described in terms of free ions, triple ions, and quadrupoles (or dimers) according to

$$M^+(sln) + X^-(sln) \rightleftharpoons MX(sln) \qquad K_a \qquad [11]$$

$$M^+(sln) + MX(sln) \rightleftharpoons M_2X^+(sln) \qquad K_{t+} \qquad [12a]$$

$$X^-(sln) + MX(sln) \rightleftharpoons MX_2^-(sln) \qquad K_{t-} \qquad [12b]$$

$$2MX(sln) \rightleftharpoons (MX)_2(sln) \qquad K_d \qquad [13a]$$

$$2M^+(sln) + 2X^-(sln) = (MX)_2(sln) \qquad K_q \qquad [13b]$$
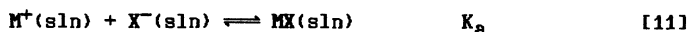
For dilute solutions ($c < 0.01$ mol dm^{-3}), the equilibria in [11]-[13] can be accurately analyzed in terms of Onsager-Fuoss-Hsia treatments for the molar conductivities Λ (32-36):

$$\Lambda = \alpha\Lambda_f + \alpha_3\Lambda_{f3} \qquad [14]$$

In eq. [14], Λ_f and Λ_{f3} are, respectively, the molar conductivities of free ions and triple ions at respective concentrations of αc and $\alpha_3 c$. For concentrations greater than around 0.05 mol dm^{-3}, the equilibrium constants derived from the audiofrequency measurements may be used in conjunction with relaxation time data to estimate rates of formation of triple ions and quadrupoles, and to determine whether these species are inner or outer sphere complexes (37-41). From the studies cited in (34-43), the following behavior was found for the electrolytes $LiBF_4$, $LiClO_4$, and $LiAsF_6$ in DME, 2Me-THF and MF:

$$\text{for } K_a, \qquad LiBF_4 \gg LiClO_4 \gg LiAsF_6$$

$$\text{for } K_t, \qquad LiBF_4 > LiAsF_6 > LiClO_4$$

$$\text{for } K_q, \qquad LiClO_4 > LiBF_4 > LiAsF_6$$

The comparative magnitude of these equilibria can be understood by consideration of inner and outer sphere complexation, and the effect of these complexes on solvent structure (in terms of the Frank and Wen concept of structure making and structure breaking effects). To accomplish this, we recently fitted experimental K_a and K_t data to theoretical expressions for K_a and K_t (43, 44). For ion association, Barthel's modification (33, 34, 45) of the Bjerrum equation was used:

$$K_a = 4\pi N_A \times 10^{-3}\int_a^q R^2\exp\left((ze)^2/\varepsilon kTR - W_{+-}/kT\right)dR \qquad [15]$$

where the integration is carried out for values of R from the distance of closest approach, a, to the Bjerrum distance, q, and W_{+-} is the non-coulombic contribution to the ion pair equilibrium in eq. [11]. For triple ion formation, we used the DFP equation (41) derived for the interaction of an ion with a dipole of dipole moment μ:

$$K_t = 2\pi N_A \times 10^{-3} a_3^3 Q b^{3-2} \qquad [16]$$

Table 3. Association data for salts in methyl formate (MF) at 298.15 K[a]

salt	r_{cryst}	a_3	$10^{-4}K_a$	K_t	W_{+-}
$LiClO_4$	0.260	0.441	65.41	22.0	-4.49
$LiAlCl_4$	0.28	0.451	8.85	27.4	1.44
$LiAsF_6$	0.444	0.544	4.38	69.1	2.06
$NaClO_4$	0.296	0.476	60.42	24.5	-6.00
$NaBPh_4$	0.516	0.562	0.37	162.2	5.04
Bu_4NClO_4	0.637	0.714	7.28	65.8	-5.40

[a] Crystal (Pauling) radii and a_3 in units of nm, K_a and K_t in units of mol^{-1} dm^3, and W_{+-} is in kJ mol^{-1}.

In eq. [16], Q is an integral solved by expansion to n = 15 in

$$Q = \sum Y^{(n-5/2)}/[(n-5/2)n!] \Big|_2^b \qquad [17]$$

where

$$b = e\mu/a_3^2\epsilon kT \quad \text{and} \quad Y = e\mu/\epsilon kTR^2 \qquad [18]$$

In eqs. [16] – [18], a_3 is the distance of closest approach between the dipole and the ion. If one assumes that the dipole is always a contact ion pair and that the dipole-ion distance a_3 is either a contact or solvent separated distance, then it follows that a = a_3. Thus experimental K_t values used in eq. [16] yield a_3 values which can now be used in eq. [15] to calculate the W_{+-} terms. Table 3 lists the results of this type of analyses for several salts in MF at 298.15 K (43). The results in Table 3 are similar to those in other solvents (e.g. in DMSI (44) where W_{+-} for perchlorates are negative and positive for $LiAsF_6$). These results, supported by relaxation time data (37–41) are strong evidence for specific cation–solvent interactions, and surprisingly for specific anion–solvent interactions with the perchlorate ion. For example, in MF the perchlorate anion appears to coordinate at the formyl proton, and in DMSI coordination takes place at the sulfinyl sulfur. Larger anions such as AsF_6^- and BPh_4^- appear to be relatively slightly solvated. As discussed previously (34, 43–45), negative values of W_{+-} suggest structure making effects which tend to stabilize the ion pair, and positive W_{+-} values indicate structure breaking effects which destabilizes the ion pair. Thus K_a values are comparatively very large for perchlorates while K_t values are small which is consistent with the interpretation that perchlorates form solvent separated triplets in solvents such as MF and DMSI.

Of all the electrolytes studied to date, $LiAsF_6$ appears to be unique since it tends to exhibit the least association, the least dimerization, and intermediate triple ion formation. We have attributed these properties to both specific ion–solvent interactions (solvent separated complexes) and the structure breaking effect of the AsF_6^- anion. The state of solvation of Li^+ was also seen to be of equal importance, and subject to practical variation by proper selection of solvent. This also relates to the use of mixed solvents which will probably play a major role in the development of practical rechargeable lithium batteries. Components can be selected to enhance cycle life and conductivities over a wide temperature range. The objective is, of course, to be able to predict the properties of electrolytes in mixed solvents, but this ability will require extensive knowledge of the properties of electrolytes in pure solvents. Only a few of the solvents listed in Table 2 have been subjected to exhaustive investigation, but work with these and new solvents are presently being pursued.

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