

# Electrolyte solutions for technology—new aspects and approaches\*

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*Abstract:* The use of chemical models is shown for the calculation of thermodynamic and transport properties of concentrated electrolyte solutions. Comparison is made with empirical approaches.

Molecular ions with delocalized charges abolishing the concept of ionic point charges for the calculation of short range interactions are considered in the framework of chemical models.

Novel lithium salts for technical applications are presented and the influence of electron withdrawing substituents at the anions on ion-pair formation, conductivity and anodic stability limit is studied to illustrate the role of molecular ions with delocalized charges.

## INTRODUCTION

Electrochemical technologies search for electrolyte solutions with optimized properties for the special tasks which they must fulfil in devices and processes. Chemical models of the electrolyte solution which take into account the long range forces and short range forces stemming from the non-coulombic interactions in the solution often permit the construction of suitable solutions and the representation of wanted properties over large ranges of electrolyte concentration, solvent composition and temperature [1–3].

Lithium battery electrolytes are chosen as an example of technological interest. Following the theoretical guidelines recently synthesized lithium salts are based on large molecular anions with delocalized charges which offer small ion-ion interaction and hence sufficient solubility and electric conductivity. A new but similar approach utilizes the solubilization of salts by the solvation of anions with strong electron-withdrawing ligands.

## CHEMICAL MODELS

A chemical model of the electrolyte solution takes into account all types of interaction in the solution to calculate the mean activity coefficient of the free ions  $y_{\pm}'$  (FI) and that of the ion pairs  $y'$  (IP) which are appropriately joint to yield the mean activity coefficient of the electrolyte compound. Ion-pair formation of a cation  $C^+$  and an anion  $A^-$  is introduced by the use of equilibrium constants  $K_A$



In Eqn 1b  $\alpha$  is the degree of ion-pair dissociation. Limitation is made in this paper to a quantitative study of 1:1-electrolytes with ion-pair formation. Higher aggregates such as triple ions and unsymmetrical electrolytes are not quantitatively studied.

Depending on the concentration range the activity coefficients for practical applications are obtained from the Debye–Hückel theory (infinite dilution), the low-concentration ( $c < 0.15 \text{ mol/dm}^3$ ) or the

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extended ( $c < 0.8 \text{ mol/dm}^3$ ) chemical model overlapping with the concentration range of the integral equation methods, MSA and HNC, or from empirical equations such as the Pitzer equation.

The determination of association constants  $K_A$ , Eqn 1b, may be based on the precedingly mentioned theories, or  $K_A$  is taken from the adaptation of experimental data of arbitrary solution properties to chemical model equations. The preferred experimental methods for their determination are conductivity and heat of dilution measurements which both can be executed down to highly diluted solutions.

Spectroscopic methods permit the simultaneous determination of free ion and associate concentrations, even when more than only one type of associates is formed [4]. Figure 1 shows the relative concentrations of free ions, solvent separated ion pairs and contact ion pairs as obtained from a combination of IR and DRS (dielectric relaxation spectroscopy) measurements permitting the separate calculation of the partial equilibrium constants of the two ion-pair formation processes.

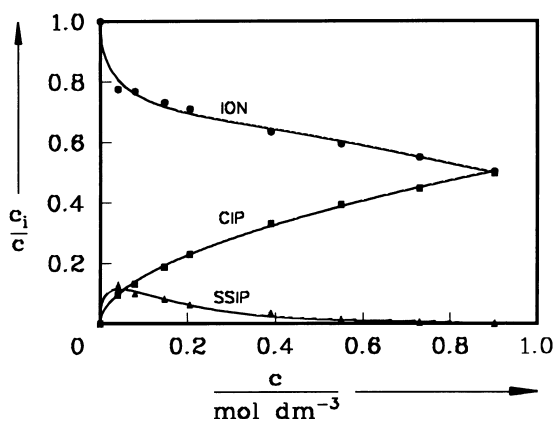


Fig. 1 Relative concentrations  $c_i/c$  of free ions, solvent shared and contact ion pairs in  $\text{LiClO}_4/\text{AN}$  ( $25^\circ\text{C}$ ).

## TRANSPORT PROPERTIES

Transport equations on the level of the low-concentration chemical model (lcCM) of electrolyte solutions are successfully used for the determination of limiting electrolyte and ion conductivities, association constants and ion distance parameters, diffusion coefficients, triple-ion constants, etc. [1].

Recently transport equations were established in the framework of the MSA for completely dissociated and associated electrolytes at moderate to high concentrations [5–9]. In the present paper a simplified version of the conductivity equation as described in [8] is applied to 1:1-electrolytes. The complete ionic conductivity expression  $\lambda_i$  is given in [7]. Here we use the expression to calculate the molar conductivity

$$\Lambda = \Sigma \lambda_i; \quad \lambda_i = \lambda_i^\infty \left( 1 + \frac{\delta u_i^{el}}{u_i^\infty} \left( 1 + \frac{\delta E}{E} \right) + \frac{\delta E}{E} \left( 1 + \frac{3}{2} \frac{\delta E}{E} \right) \right) \quad (2a, b)$$

which is good both for associated and nonassociated electrolytes [8].

The first order electrophoretic effect

$$\frac{\delta u_i^{el}}{u_i^\infty} = -\frac{kT}{3\pi\eta D_i^\infty} \frac{\Gamma}{1 + \Gamma\sigma}; \quad D_i^\infty = \frac{RT}{F^2} \lambda_i^\infty \quad (3a, b)$$

can be calculated from the electrophoretic velocity correction  $\delta u_i^{el}$  [5], where  $\Gamma$  is Blum's screening parameter in the approximation of the average diameter,  $\sigma = (\sigma_+ + \sigma_-)/2$ ;  $\sigma_+$  and  $\sigma_-$  are the ionic diameters and  $\kappa_D$  is the screening parameter of the Debye–Hückel theory

$$2\Gamma = \frac{\kappa_D}{1 + \Gamma\sigma}; \quad \kappa_D^2 = \frac{2e^2 N_A c}{\epsilon_0 \epsilon kT} \quad (4a, b)$$

The ionic limiting diffusion coefficients  $D_i^\infty$  are related to the corresponding ionic limiting conductivities  $\lambda_i^\infty$  by Eqn 3b.

The first order relaxation effect is obtained from the solution of the continuity equation at the MSA level [7].

$$\frac{\delta E}{E} = -\frac{1}{4\pi\epsilon_0\epsilon} \frac{\kappa_D^2 e}{6kT\sigma(1+\Gamma\sigma)^2} \frac{1 - \exp(-2\kappa_D\sigma)}{\kappa_D + 2\Gamma\kappa_D + 2\Gamma^2[1 - \exp(-\kappa_D\sigma)]} \quad (5)$$

Electrolyte association of 1:1-electrolytes to ion pairs can be included in the theory by the use of the association constant  $K_A$ , Eqn 1b. An iteration process is used for the calculation of the proportion of ion pairs  $(1-\alpha)$  [10]. The mean activity coefficient  $y_{\pm}'$  of the free ions is related to the single ion activity coefficient  $y_i'$  by Eqn 6a. At the MSA level the single ion and the ion-pair activity coefficients are made up by an electrostatic part and a hard sphere contribution, Eqn 6b.

$$y_{\pm}' = y_+ y_-'; \quad \ln y_i' = \ln y_i^{el} + \ln y_i^{hs} \quad (i = +, - \text{ or } IP) \quad (6a, b)$$

The electrostatic parts  $\ln y_i^{el}$  are given by the expressions [11,12]:

$$\ln y_i^{el} = -\frac{1}{4\pi\epsilon_0\epsilon} \frac{e^2}{kT} \frac{\Gamma}{1+\Gamma\sigma} \quad (i = +, -); \quad \ln y_{IP} = 0 \quad (7a, b)$$

For the hard sphere contribution only the ratio [13]

$$\frac{(y_{\pm}^{hs})^2}{y_{IP}^{hs}} = \frac{1 - 0.5\xi_o}{(1 - \xi_o)^3}; \quad \xi_o = \frac{\pi\sigma^3 N_A c}{3} \quad (8)$$

is needed for the calculation of the association constant.

Data analysis uses for the calculation of  $D_i^\infty$ , Eqn 3b, the data for the single ion conductivities  $\lambda_+^\infty$  and  $\lambda_-^\infty$  obtained from measurements at dilute solutions.

It is important for applied research that MSA permits the reproduction of conductivity data up to high electrolyte concentrations by the use of an analytical expression which contains meaningful physical parameters.

The reproduction of specific conductivities  $\kappa$  of concentrated electrolyte solutions which currently is done with empirical equations such as the Casteel–Amis equation [14] needing four empirical parameters

$$\frac{\kappa}{\kappa_{\max}} = \frac{m}{\mu} \exp \left[ b(m - \mu)^2 - a \frac{m - \mu}{\mu} \right] \quad (9)$$

can be advantageously taken over by the analytical MSA equation which is based on only two physically meaningful parameters,  $K_A$  and  $\sigma$ .

The four-parameter Casteel–Amis equation is based on the fact that specific conductivity goes through a maximum of height  $\kappa_{\max}$  (not reached at insufficient electrolyte solubility) situated at molality  $\mu$ , cf. [2]; the parameters  $a$  and  $b$  are matching parameters.

Figure 2 shows the conductivity of  $\text{LiClO}_4/\text{PC}$  at 25 °C up to 1 M solutions based on MSA calculation yielding  $K_A = 4.2 \text{ dm}^3/\text{mol}$ . Data analysis with the help of the lcCM yields the same curve up to 0.05 mol and  $K_A = 5.2 \text{ dm}^3/\text{mol}$ . Figure 3 compares the conductivity curves obtained by the use of MSA and the empirical Casteel–Amis equation.

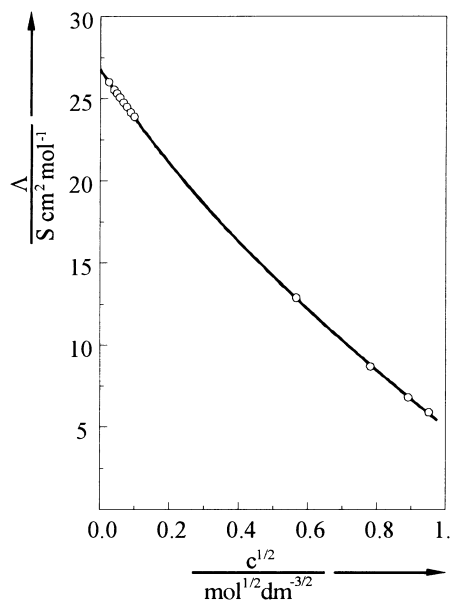
The maximum of conductivity  $\kappa_{\max}$  is the consequence of two competing effects [15]

$$\kappa = \Lambda c; \quad d\kappa = (\Lambda dc + c d\Lambda)_{\max} = 0 \quad (10a, b)$$

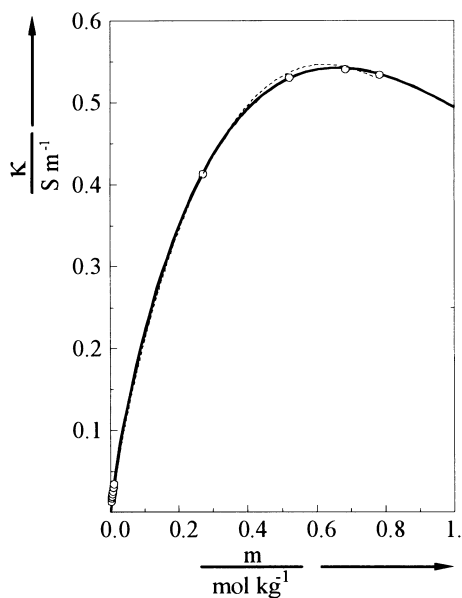
Increasing electrolyte concentration increases the charge density and lowers the ionic mobilities, see decreasing  $\Lambda$  in Fig. 2. Equations 10a,b are valid for associating and nonassociating electrolytes. The position  $\mu$  and the height  $\kappa_{\max}$  of the maximum play an important role for the usability of an electrolyte solution in applied research.

## ELECTROLYTES WITH MOLECULAR IONS

The theoretical approaches given in the preceding sections treat ions as hard spheres bearing isolated charges. This model is not suited to predict solution properties when molecular ions are involved [3], especially not for particles bearing electron withdrawing substituents such as fluorine or trifluorocarbon or at very low solvent permittivities. When in molecular anions or cations atoms are substituted by more electronegative ones, even without change of their size parameters, the association constants decrease by



**Fig. 2** Molar conductivity of  $\text{LiClO}_4/\text{PC}$  (25 °C) lc CM ( $c < 0.03 \text{ mol/dm}^3$ )  $K_A = 5.2 / \text{mol} \cdot \text{dm}^3$ ; MSA ( $0 < c/\text{mol/dm}^3 < 1$ )  $K_A = 4.2 / \text{mol} \cdot \text{dm}^3$ .



**Fig. 3** Specific conductivity of  $\text{LiClO}_4/\text{PC}$  (25 °C) (O) experiment; (—) Casteel-Amis equation; (---) MSA.

orders of magnitude. Very large association constants are obtained, in contrast to the predictions of the classical theories, when specific ion-ion interaction takes place with steric predisposition enhancing the stability of the resulting ion pair. Very small amounts of additives, able to act as ligands, which do not change the solution permittivity, may cause significant change of the association constants due to selective solvation. These effects are reflected in the short range part of the ionic pair-correlation functions and may be taken into account in chemical models by appropriately calculated association constants.

### NOVEL TYPES OF LITHIUM SALTS WITH MOLECULAR IONS

The first electrolytes used for primary lithium cells [16,17] were based on lithium salts with coordinatively

saturated molecular anions, such as  $\text{ClO}_4^-$  and anions based on Lewis acids  $\text{XF}_n$  as well as the corresponding Lewis base  $\text{F}^-$ , e.g.  $\text{BF}_4^-$ ,  $\text{AsF}_6^-$  and  $\text{PF}_6^-$ . More recently considered anions are large molecular anions with delocalized anionic charges, which offer low lattice energies, relatively small ion-ion interaction, and hence sufficient solubility and relatively large conductivity. Delocalization of the charge is achieved by electron-withdrawing substituents such as  $-\text{F}$  or  $-\text{CF}_3$ ,  $-\text{COOR}$ ,  $-\text{SO}_2\text{OR}$  or by substituting carbon by nitrogen, which has a higher value of electronegativity. These anions generally show in contrast to Lewis acid based salts better chemical stability in various solvents and often also excellent thermal stability.

The latest developments in this field include lithium imides such as the well known lithium bis(trifluoromethylsulfonyl)imide,  $\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$ , Fig. 4A, the cyclic imides such as  $\text{Li}[\text{N}(\text{SO}_2)(\text{CF}_2)_4(\text{SO}_2)]$  [18] and  $\text{Li}[\text{N}(\text{SO}_2)(\text{CF}_2)_n(\text{SO}_2)]$ ,  $n = 1-3$ , by Sartori *et al.* [19,20] (Fig. 4B for  $n = 3$ ) the methides, such as lithium tris(trifluoromethylsulfonyl) methanide  $\text{Li}[\text{C}(\text{SO}_2\text{CF}_3)_3]$ , Fig. 4C and  $\text{Li}[\text{C}(\text{SO}_2\text{CF}_3)_2(\text{SO}_2\text{C}_4\text{F}_9)]$ , Fig. 4D, the new bismethanide  $\text{Li}_2[\text{C}_2(\text{SO}_2\text{CF}_3)_4(\text{S}_2\text{O}_4\text{C}_3\text{F}_6)]$ , Fig. 4E [19], the tetrakis[4-(trifluoromethyl)phenyl]borate and the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate synthesized by Kita *et al.* [35], the family of chelatoborates with the general formula  $\text{Li}[\text{BR}_2]$ , R = bidentate ligand, developed in our laboratory, [21–26], and the similar lithium phosphates of general formula  $\text{Li}[\text{PR}_3]$ , recently developed by Handa *et al.* [27].

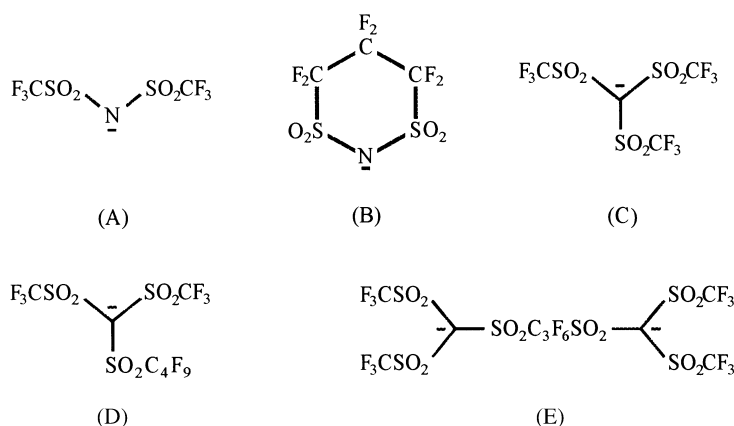


Fig. 4 Selection of imides and methides.

The chelatoborates include derivatives of pyrocatechol and fluorinated analoga,  $\text{Li}[\text{B}(\text{C}_6\text{H}_{4-x}\text{F}_x\text{O}_2)_2]$  ( $x = 0, 1, 4$ ), i.e. lithium bis[1,2-benzenediolato(2-)-O,O']borate, [23], lithium bis[3-fluoro-1,2-benzenediolato(2-)-O,O']borate [21], and lithium bis[tetrafluoro-1,2-benzenediolato(2-)-O,O']borate [25], for ligands see Fig. 5A–C, derivatives of other aromatic diols, lithium bis[2,3-naphthalenediolato(2-)-O,O']borate, lithium bis[2,2'-biphenyldiolato(2-)-O,O'] borate [24], derivatives of aromatic hydroxyacids, lithium bis[salicylato(2-)-O,O']borate, Fig. 5D [24], lithium bis[2-olato-1-benzenesulfonato(2-)-O,O']borate, Fig. 5E, the fluorinated sulfoborate lithium bis[5-fluoro-2-olato-1-benzenesulfonato(2-)-O,O']borate, Fig. 5F [22], a borate based on a heterocyclic diol, lithium bis[2,3-pyridinediolato(2-)-O,O']borate, Fig. 5G [26], and a borate which has not been published so far, lithium bis[4-(trifluoromethyl)-salicylato(2-)-O,O']borate, Fig. 5H. Only two chelatophosphates were synthesized and electrochemically investigated so far including lithium tris[1,2-benzenediolato(2-)-O,O']phosphate [27] and lithium tris[3-fluoro-1,2-benzenediolato(2-)-O,O']phosphate [28].

## CHARGE DELOCALIZATION AND ASSOCIATION

The description of electrolytes with molecular ions requires the replacement of isolated ion charges in chemical models by charge distributions. Charge delocalization in a molecular anion caused by electron withdrawing substituents entails a charge decrease at the atoms bearing negative charge which can be estimated by quantum mechanical calculations.

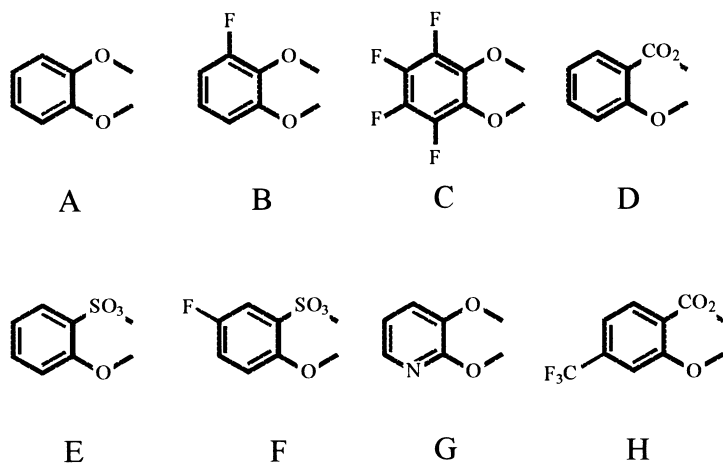


Fig. 5 Bidentate ligands R for borates and phosphates.

As an example a family of lithium acetates,  $\text{LiO}_2\text{CCH}_x\text{F}_y$  with  $(x + y = 3)$ , is considered at increasing substitution of hydrogen by fluorine. It follows from MNDO calculations that the mean oxygen partial charge  $q(\text{O})$  at the oxygen atoms decreases by about 0.1 charge unit upon increasing substitution [29].

Figure 6 and Table 1a show the stepwise decrease of the association constant on stepwise substitution of these compounds in DMSO solutions. The linear decrease of  $\ln K_A$  vs.  $q(\text{O})$  indicates that the decrease of association is governed by decreasing electrostatic interaction. Evaluation of the temperature dependence of the association constants by lCCM calculations shows that the noncoulombic part of the association entropy decreases at increasing fluorination indicating that the acetate anions are increasingly less able to compete in the first solvation shell with the strong ligand DMSO ( $\epsilon = 47.0$ ) of donor number  $\text{DN} = 29.8$ .

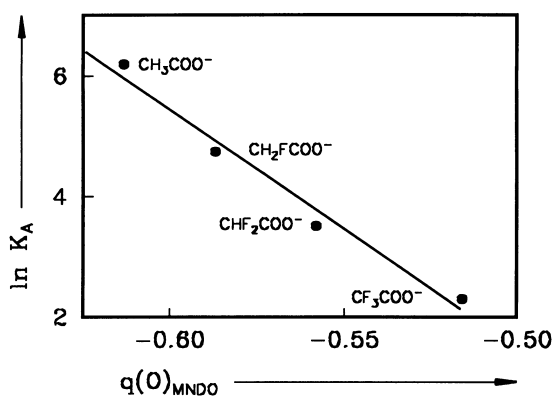


Fig. 6 Linear correlation of  $\ln K_A$  vs. mean charge density of the oxygen atoms  $q(\text{O})$   $\text{LiO}_2\text{CCH}_x\text{F}_y$  ( $x + y = 3$ ) / DMSO.

Propylene carbonate with a much lower donor number of  $\text{DN} = 15.1$ , despite its significantly higher permittivity ( $\epsilon = 64.95$ ) yields for  $\text{LiO}_2\text{CCF}_2\text{H}$  and  $\text{LiO}_2\text{CCF}_3$  association constants in the range of  $10^4 \text{ dm}^3/\text{mol}$ , Table 1b, for comparison  $K_A(\text{LiClO}_4/\text{PC}) < 10 \text{ dm}^3/\text{mol}$  [30] showing that PC, in contrast to DMSO, cannot substitute the acetate ions, which are bidentate ligands, in the first solvation shell of the lithium ion [29]. In addition, triple-ion formation is observed in the PC solutions.

Salts with large anions and small cations are particularly suited for the study of charge delocalization effects on ion-pair formation. Table 1 contains some more examples from conductivity studies in various pure solvents and some binary solvent mixtures showing the role of charge delocalization by electron

**Table 1** Association constants  $K_A$  and limiting conductivities  $\Lambda^\infty$  of salts with fluorinated anions

|   | Solution  | $K_A/(\text{dm}^3/\text{mol})$ | $\Lambda^\infty/(\text{S cm}^2/\text{mol})$ | Ref. |
|---|---|--------------------------------|---|------|
| a | LiO <sub>2</sub> CCH <sub>3</sub> /DMSO                                 | 488                            | 33.7  | 29   |
| a | LiO <sub>2</sub> CCFH <sub>2</sub> /DMSO                                | 115.0                          | 33.7  | 29   |
| a | LiO <sub>2</sub> CCF <sub>2</sub> H/DMSO                                | 37.4                           | 33.4  | 29   |
| a | LiO <sub>2</sub> CCF <sub>3</sub> /DMSO                                 | 10.0                           | 33.3  | 29   |
| b | LiO <sub>2</sub> CCF <sub>2</sub> H/PC                                  | $2.97 \times 10^4$             | –   | 32   |
| b | LiO <sub>2</sub> CCF <sub>3</sub> /PC                                   | $0.62 \times 10^4$             | –   | 32   |
| c | Li[B(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ]/DME  | 423.3                          | 108.4                                       | 21   |
| c | Li[B(C <sub>6</sub> FH <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]/DME | 77.0                           | 108.4                                       | 21   |
| d | Li[B(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ]/PC   | 14.2                           | 19.3  | 21   |
| d | Li[(C <sub>6</sub> FH <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]/PC   | 4.1                            | 19.1  | 21   |

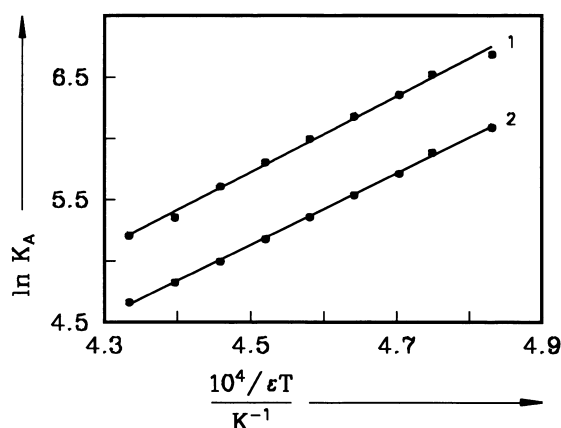
  

|   | DMC/EC mole fraction  | $x_{\text{DMC}} = 0.66$ | $x_{\text{DMC}} = 0.5$ | $x_{\text{DMC}} = 0.66$ | $x_{\text{DMC}} = 0.5$ | –  |
|---|---|-------------------------|------------------------|-------------------------|------------------------|----|
| e | Li[B(C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ]  | 170.4                   | 32.4                   | 46.9                    | 38.7                   | 33 |
| e | Li[B(C <sub>6</sub> FH <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ] | 60.6                    | 6.4                    | 46.9                    | 38.4                   | 33 |
| e | Li[B(C <sub>6</sub> F <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ]  | 7.7                     | 2.9                    | 47.1                    | 38.1                   | 33 |

DMSO = Dimethyl sulfoxide; PC = propylene carbonate, DME = dimethoxyethane, DMC = dimethyl carbonate.

withdrawing substituents at large anions of lithium salts. The expected decrease of the association constant  $K_A$  is a net effect because the almost unchanged limiting conductivity  $\Lambda^\infty$  indicates that neither the radius of the anion nor its solvation is changed to a remarkable extent.

The lithium chelatoborates Li[B(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub>] and Li[B(C<sub>6</sub>FH<sub>3</sub>O<sub>2</sub>)<sub>2</sub>] in DME and PC (Tables 1c and d) show a behaviour similar to that of the acetates. The parallel plots in Fig. 7 of  $\ln K_A$  vs.  $(\epsilon T)^{-1}$  show that the ion-pair distance parameters are approximately equal. The association constants in DME solutions ( $\epsilon = 7.08$ ) are extremely small in comparison to those of lithium salts with small anions where the charge can not be delocalized, e.g.  $K_A[\text{LiBF}_4/\text{DME}] = 2.4 \times 10^7 \text{ dm}^3/\text{mol}$ , and where additionally triple-ion formation is observed [31]. The behaviour of chelatoborates in solvent mixtures DMC/EC fits into the precedingly sketched framework (Table 1e).



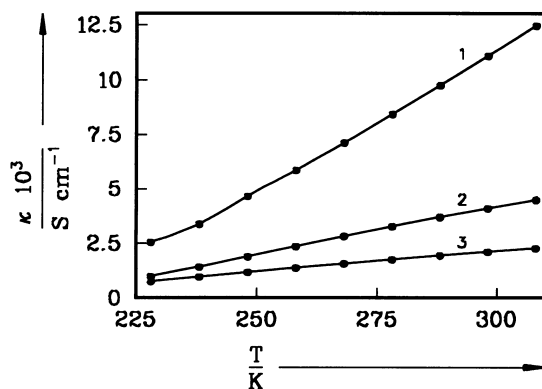
**Fig. 7**  $\ln K_A$  vs.  $(\epsilon T)^{-1}$  for DME solutions of (1) Li[B(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)<sub>2</sub>]; (2) Li[B(C<sub>6</sub>H<sub>3</sub>FO<sub>2</sub>)<sub>2</sub>].

## CHARGE DELOCALIZATION AND CONDUCTIVITY

The boundary conditions of transport equations may be chosen in a way that they take into account the region of the short range interactions around the moving particles [1] and then permit the use of chemical model equations also for molecular ions with delocalized charges. Generally the effect of ion association

is hardly separable from that of other conductivity determining effects (ionic radii, solvent viscosity, cation and anion solvation). From a recent approach by Ue & Mori [34] based on a multiple linear regression,  $\Lambda_c = C_A \Lambda^\infty + C_K K_A$  ( $C_A$  and  $C_K$ : regression coefficients), the authors conclude that ion association has a stronger influence than ion-mobility effects on the conductivity of highly concentrated solutions and showed this for seven lithium salts in PC,  $\gamma$ -butyrolactone and equimolar mixtures of PC/DMC and PC/EMC ( $K_A > 300 \text{ dm}^3/\text{mol}$ ).

The fluorinated lithium salts with ionic radii which are independent of the degree of fluorination offer the direct possibility to study the influence of ion association on conductivity. Figure 8 shows the conductivities of chelatoborates in DME at concentrations of about  $1 \text{ mol}/\text{dm}^3$  with an increase of 440% at  $25^\circ\text{C}$  and 240% at  $-45^\circ\text{C}$  due to decreased ion-pair formation.



**Fig. 8** Conductivities of chelatoborates ( $\approx 1 \text{ mol}/\text{dm}^3$ ) in DME  $\text{Li}[\text{B}(\text{C}_6\text{O}_2\text{H}_x\text{F}_y)_2]$ ;  $x + y = 4$  (1)  $y = 4$ ; (2)  $y = 1$ ; (3)  $y = 0$ .

The increase of the characteristic conductivity maximum  $\kappa_{\text{max}}$  of some electrolyte solutions due to electron withdrawing substituents at the anion is shown in Table 2.

**Table 2** Increase (%) of maximum conductivity  $\kappa_{\text{max}}$  upon anion fluorination with reference to the unsubstituted compound

| Solution   | Increase of $\kappa_{\text{max}}$<br>(in %) |
|--|---|
| PC/Li[B(C <sub>6</sub> FH <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]                             | 30  |
| Li[B(C <sub>6</sub> FH <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]/DME                            | 80  |
| Li[B(C <sub>6</sub> F <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ]/DME                             | $\approx 1000$                              |
| Li[B(C <sub>6</sub> FH <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]/DMC/EC $x_{\text{DMC}} = 0.5$  | 60  |
| Li[B(C <sub>6</sub> F <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ]/DMC/EC $x_{\text{DMC}} = 0.5$   | 150   |
| Li[B(C <sub>6</sub> FH <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ]/DMC/EC $x_{\text{DMC}} = 0.75$ | 110   |
| Li[B(C <sub>6</sub> F <sub>4</sub> O <sub>2</sub> ) <sub>2</sub> ]/DMC/EC $x_{\text{DMC}} = 0.5$   | 260   |

## CHARGE DELOCALIZATION AND ELECTROCHEMICAL WINDOW

A most desired consequence of charge delocalization is the shift of the anodic decomposition limit to higher positive values increasing the electrochemical window of the electrolyte so long as the solvent is stable. The voltammogram at gold electrodes, Fig. 9, shows that the anodic stability limits of  $\text{Li}[\text{B}(\text{C}_6\text{H}_x\text{F}_y\text{O}_2)_2]$  in PC increases the oxidation limit by 0.5 V upon complete fluorination [25].

Two linear correlations of HOMO energies vs. anodic oxidation limits for various borates, Fig. 10, obtained for sets of compounds with different decomposition mechanisms confirm this result [22]. The anodic decomposition of lithium benzenediolatoborates (**1**, **2**, **4**) and that of the lithium



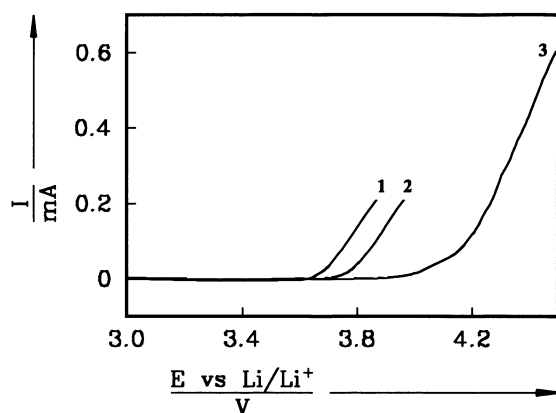


Fig. 9 Anodic stability limits at Au-electrodes  $\text{Li}[\text{B}(\text{C}_6\text{H}_x\text{F}_y\text{O}_2)_2]$ ;  $x + y = 4$ ; (1)  $y = 0$ ; (2)  $y = 1$ ; (3)  $y = 4$ .

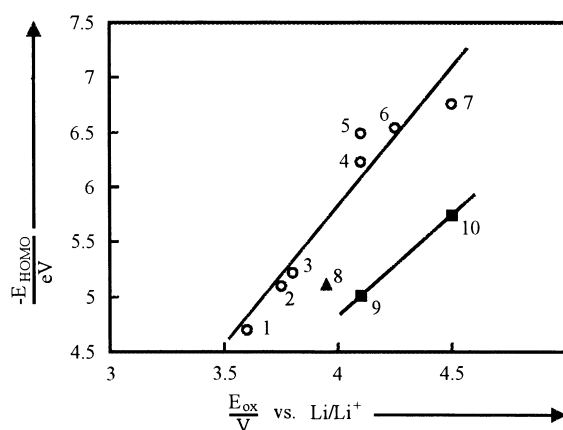


Fig. 10 Homo energies vs. anodic oxidation limit of various lithium borates (explanation in the text).

bis[2,3-naphthalenediolato(2-)-O,O'] (3), bis[4-(trifluoromethyl)-salicylato(2-)-O,O'] (5), bis[2-olato-1-benzenesulfonato(2-)-O,O'] (6) and bis[5-fluoro-2-olato-1-benzenesulfonato(2-)-O,O'] (7) borates results in the formation of soluble products whereas the lithium bis[2,2'-biphenyldiolato(2-)-O,O'] (9) and bis[salicylato(2-)-O,O'] (10) borates entail the formation of thin electrochemically insulating, lithium ion-conducting polymer films preventing further anion decomposition as well as anodic decomposition of oxidation-sensitive solvents [3,24]. Lithium bis[2,3-pyridinediolato(2-)-O,O'] borate (8) and  $\text{Li}[\text{B}(\text{C}_6\text{H}_3\text{FO}_2)_2]$  show different oxidation limits but equal values  $E_{\text{HOMO}} = -5.1$  eV due to the different decomposition mechanisms. Film formation without preventing lithium from being cycled is a common feature of these compounds.

### EFFECTS OF SELECTIVE SOLVATION AND COMPETITION BETWEEN SOLVATION AND ION ASSOCIATION

It is well known that addition of strong ligands to electrolytes can decrease the association constants of electrolytes, due to the displacement of the anion in the vicinity of a cation by ligands which selectively solvate cations. This effect which increases the conductivity of electrolytes can be utilized for technical electrolytes [3,36–40]. A similar example is given by Whitney *et al.* [41] who have shown that addition of 1,1,4,7,7-pentamethyldiethylenetriamine (PMDT) even produces sufficiently conductive solutions of lithium salts in toluene, where the lithium salts are scarcely soluble.

A new approach is based on ligands which, instead of solvating cations, displace cations in ion pairs by anion solvation. This is made possible by the strong interaction of the anions with aza-ether compounds

[42]. Electron withdrawing substituents such as  $-\text{SO}_2\text{CF}_3$  make the local charge at the nitrogen positive so that these compounds become effective ligands for anions. Anion complexation has been proven by conductivity and NEXAFS measurements. For example, a 0.2 M LiCl/THF solution possesses only a very low conductivity of  $1.6 \times 10^{-6}$  S/cm. Addition of  $\text{N}[\text{CH}_2\text{CH}_2\text{NR}_2]_3$ ,  $\text{R} = \text{SO}_2\text{CF}_3$ , yields an increase by three orders of magnitude of conductivity to  $1.7 \times 10^{-3}$  S/cm. This approach is especially useful for battery electrolytes because, in contrast to lithium ion solvation, the transference number of the lithium ion is increased. The results for the solubilization of the scarcely soluble LiF which is electrochemically very stable towards oxidation is even more impressing [43]. Addition of tris(pentafluorophenyl)borane to DME allows to obtain 1 M solutions of LiF, where the anion is complexed by this electrochemically stable ligand. By this approach, a conductivity of 6.8 mS/cm is obtained. Conceptually this approach is similar to the use of lithium salts with large anions or the immobilization of anions at polymer backbones and identical with the use of Lewis acid (borane) Lewis base ( $\text{F}^-$ ) salts as mentioned above.

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