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Coordination Chemistry Reviews 226 (2002) 137–141

COORDINATION
CHEMISTRY REVIEWS

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Anions of low Lewis basicity for ionic solid state electrolytes

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Received 16 April 2001; accepted 20 July 2001

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Abstract

Methods for the estimation of Lewis basicity of anions, especially of those showing low and very low donor properties are reported. These properties are of importance for technical applications, for example, when applying them as conducting salts for batteries or in catalytic systems both of which are shortly reviewed.

Keywords: Lewis basicity; Ionic solid state electrolytes; Donor number

1. Introduction

Anions are, at least in aqueous solutions, conjugated bases of acids, characterised by their Brønsted basicity and acidity, respectively. It is today trivial to remember that strong acids are associated with weak anionic bases and vice versa. In non-aqueous, especially non-protogenic solutions (including the 'immobile solvents' that constitute solvating macromolecules like poly(ethylene oxide)) the transposition is, however, somewhat more difficult. The two most relevant properties of a non-aqueous solvent are its Lewis basicity and Lewis acidity (i.e. donor and acceptor properties). Using similar parameters to describe ionic solute–solvent interactions appears therefore of marked interest.

Anions of low basicity are very important in all domains of chemistry and sought after, as they have weak interactions with (Lewis-acidic) cations, thus less prone to form ion pairs. In electrochemistry, this leads to higher conductivities. This is an increasingly important field of application with for instance the extraordinary development of energy-related systems, namely lithium batteries.

2. Weakly coordinating anions in batteries

Fig. 1 represents a typical electrochemical cell or battery with a metallic salt MX as electrolyte.

The ionic conductor can be: (i) a solution of the electrolyte or (ii) a non-protic polymer solvent (new generation of electrolytes). The 'sink' and the 'source' are the electrode materials (e.g. 'source' = metallic lithium, lithium intercalated in graphite; 'sink' = mixed oxides lithium/transition metal in high oxidation state).

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PII: S0010-8545(01)00416-7

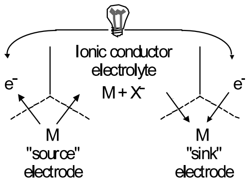

Fig. 1. Typical electrochemical cell with a M^+X^- salt as electrolyte.

It is now widely accepted that the same species (M = Li) must transit between the two electrodes to keep the composition of the electrolyte constant and thus maximise the conductivity (power) and the weight (specific energy). The dissociation ability and the mobility of the ionic species in the electrolyte are some major factors for the design of such batteries (free ions, contact ion pairs): the more dissociated, the more free ions in the electrolyte, the higher the conductivity. In non-protonic polymers as solvent, the salt MX is dissolved and the cations are solvated by the ether oxygens wrapping around the positive charge, forming transient cages or tunnels where the ions can move.

There, in addition to high conductivity, a wide voltage stability range is required for the organic-based polar solvent (or polymer) and salt. Up to now, the paucity of available anions (ClO_4^-, BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $AlCl_4^-$) reflects the relative lack of guidelines for their choice and for the design of alternative species. All the above-mentioned anions have several drawbacks: besides the explosive nature of perchlorates, all the others derive from the complexation of halide anions by electron-deficient Lewis acid, resulting in a dissociation equilibrium (i.e. $PF_6^- + :S \leftrightarrow PF_5{:}S_+ F^-$)—S = solvent—, shifted to the right when the lattice energy of the halide (LiF) or the donicity of the solvent (or one of its component) is high. In the latter case, often encountered when a high solvation of the cation is needed—again for conductivity—(ethers, esters, amides), a cascade of reactions related to the formation of carbocations derived from the Lewis acid complex results in fast degradation of the solvent. As seen below, the reference for non-coordinating anions is tetraphenyl borate $B\Phi_4^-$. This species does not contain electron pairs susceptible to interact with cations, thus its very low tendency to ion pairing. This also applies to $B(CH_3)_4^-$; however, the oxidative stability is too low for most applications, though the electron withdrawing effect of the phenyl rings brings the oxidation potential close to 3.2 V versus Li^+/Li^0, yet insufficient. Starting from the very stable electron-deficient $B_{12}H_{12}^{2}$-icosahedron, the replacement of one boron by carbon leaves a single negative charge, the resulting anion $B_{11}CX_{12}^-$ (X = H, Cl, Br, CF_3...) [1] being devoid of electron pairs (X = H), or tightly attached to an electronegative element (X = Cl, CF_3). The difficulty in the preparative chemistry of these species confines them presently to a laboratory tour de force.

Mostly driven by the needs of electrochemists seeking replacement for the unsatisfying properties of conventional salts, new anions were designed. Two principles were followed:

1. extensive delocalisation of the negative charge on highly electronegative centres;
2. participation of a ‘soft’ centre, either N or C to the charge-bearing moieties [2,3].

The first rule is easily understandable and justified, as it provides the possibility for the negative charge to be mostly insensitive to solvation, and especially H-bonding found in water, leaving a dipolar type interaction (see Fig. 2). The second criterion, having recourse to N or C centres appears at first view illogical; $=N^-$ and $\equiv C^-$ species are far better donors than the more electronegative O^- or F^- derivatives. In fact, the possibility to attach several electron-withdrawing groups due to the higher valence of N or C largely offsets this tendency, as these centres become weak donors, or in extreme cases, positively charged. Besides, lithium, the most widely used cation for electrochemistry in batteries has an especially strong interaction with ‘hard’ donors, like O and F, much less with softer N and C. This strategy has led to the study of the new lithium salts: $[R_fSO_2NSO_2R_f]^-$ [4] and $[(R_fSO_2)_3C]^-$ [5] where R_f is a perfluoro alkyl.

TFSI (bis(trifluoromethanesulfonyl)imide) [6–10], TFSM (bis(trifluoromethanesulfonyl)methanide) [7] and TriTFSM (and tris(trifluoromethanesulfonyl)methanide, respectively) complexed with poly(ethylene oxyde) (POE) have been studied. These give conductivities much higher than that obtained with conventional salts. Conductivity of POE–Li salt of low-coordinating anions is improved thanks to the higher dissociation of the ion pairs (dipolar solvation of the bulky anion).

With TFSI, the lithium salt $Li^+[(CF_3SO_2)N]^-$ is widely used in the polymer electrolytes [4], and is progressively replacing the unstable $LiPF_6$ in liquid electrolyte battery application. In a general study on the energy of ionisation of acids in vacuum, either the nitrogen or carbon-based corresponding protonated species were shown to be the strongest known [11]. The possibility to characterise the Lewis basicities of this type of anions by quantitative means (their donor number) therefore might provide a useful tool for solution chemists as well as to people searching for techno-

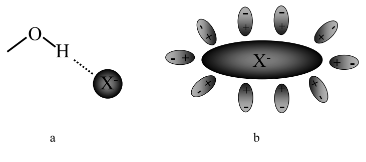

Fig. 2. (a) Small anions with localised charge: solvation by hydrogen bonds almost exclusively. (b) Anions with delocalised charge: strong dipolar solvation.

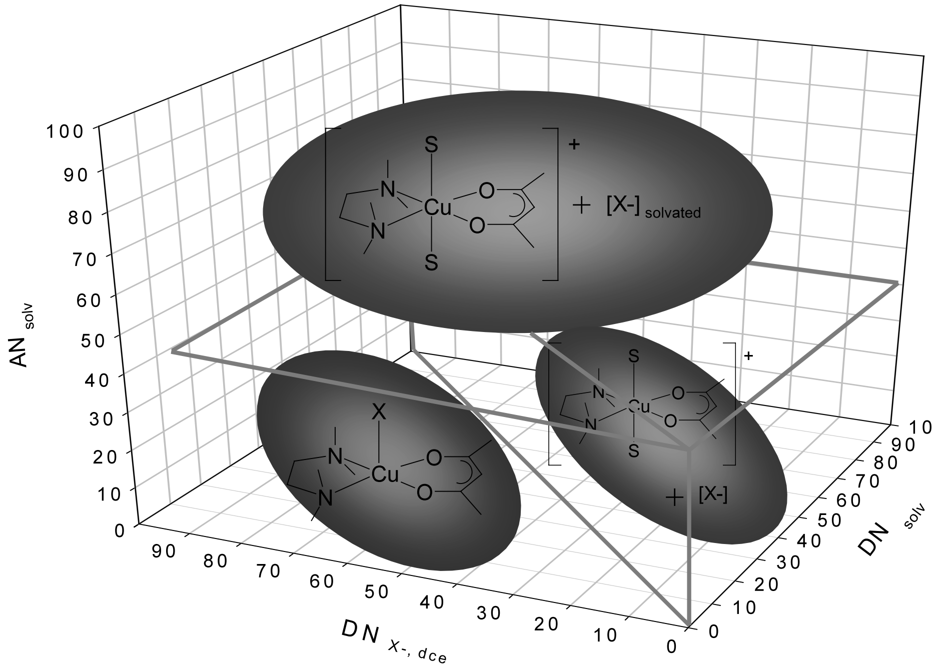

Fig. 3. Competition between solvent and anion in solution.

logical applications of ionic species involving anions. The role of the respective solvent (or molecular environment), its properties, especially from the point of view of its Lewis acid/base strength must be specially taken into account.

3. Relationship between conductivity and donor number

The solvatochromic technique to determine the donor number of anions in solution using the solvatochromic dye $[Cu(acac)(tmen)]BPh_4$ has been described in detail in the literature [12]. However, it is shortly explained here to underline the complexity of the empirical method. The ability of an anion to coordinate to a metal centre is determined in part by the competition it receives from the solvent (and other bases present in solution). When the donor strength of the solvent is higher than that of the anion the solvent preferably coordinates to the copper complex, but, on the other hand, a solvent exhibiting strong acceptor properties will compete with the copper complex for solvation of the anion. Fig. 3 summarises the phenomenon.

The shift of the visible d–d absorption bands of $[Cu(acac)(tmen)]BPh_4$ (acac: acetylacetonate; tmen: *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in various solvents at 25 °C resulting from the coordination of solvent molecules S and anionic species X^- has been investigated. Due to the competition between solvent and anion two distinct parts are found: a solvent- and a cation-dependent part. A multiple regression analysis leads to Eq. (1):

$$\mathrm{DN}_{\mathrm{X,\,Solv}} = 129.6 - 0.546\mathrm{AN}_{\mathrm{Solv}} - 0.00602\upsilon_{\mathrm{max,dce}} \qquad (1)$$

$[Cu(hfac)(tmen)]BPh_4$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetone) is a stronger Lewis acid due to the presence of electron-withdrawing fluorine substituents on the β-diketonate moiety. The magnitude of the in-plane ligand field strength is increased; the interactions with weak Lewis bases (especially low-coordinating anions) are therefore enhanced. A similar study of its solvatochromic properties leads to Eq. (2) [13]:

$$\mathrm{DN}_{\mathrm{X,Solv}} = 128.66 - 0.546.\mathrm{AN}_{\mathrm{Solv}} - 0.0135\upsilon'_{\mathrm{max,dce}} \qquad (2)$$

Due to its negligible donor properties, DCE does not in general dissolve lithium or other alkali metal salts, unless the organic moieties are predominant in the anion (e.g. $LiB[C_6H_3(3,5\text{-}CF_3)_2]_4$). For the measurement of donor numbers of such species, the tetrabutylammonium salts were systematically used. Due to the hydrophobic nature of both ions, the metathesis is done in water from the purified alkali (generally lithium) metal salt and either tetrabutylammonium (TBA) bromide or hydrogen sulfate (Table 1).

As seen from the results above, the new families of anion have DNs which are comparable (TriTFSM) or only slightly higher than those of the weakest known. To have a better comparison, the triflate anion $CF_3SO_3^-$, up to now widely accepted as derived from an acid as strong as ClO_4^- (and recommended as a substitute) has been included. Its donor number now compares with that of conventional non-protic solvents such as PC (15,1), acetonitrile (14,1) or γ-butyrolactone (18). In other words, their solutions of lithium triflate

Table 1
Stokes radii, conductivity and spectroscopic data

	Anion Stokes radius (nm)	Conductivity (PEO) 80 °C (Ω^{-1} cm^{-1}) (oxygen/Li ratio)	$DN_{X,dce}$ counter cation: TBA^+
PF_6^-	0.254 [a]	Decomposition	2.50
AsF_6^-	0.260 [a]	5×10^{-4} (12:1)	2.50
SbF_6^-	0.220 [b]	4×10^{-4} (12:1)	2.50
BF_4^-	0.229 [a]	2×10^{-4} (8:1)	6.03
ClO_4^-	0.234 [a]	10^{-4} (12:1)	8.44
$(CF_3SO_2)_3\ C^-$, triTFSM	0.375 [a]	10^{-3} (12:1)	2.50
$(CF_3\ SO_2)_2\ CH^-$, TFSM	0.260 [c]	8×10^{-4} (12:1)	7.80
$(CF_3\ SO_2)_2\ N^-$, TFSI	0.325 [a]	2×10^{-3} (12:1)	5.40
$CF_3SO_3^-$	0.270 [a]	2×10^{-5} (10:1)	16.90

[a] In propylene carbonate (PC) at 25 °C [14].

[b] In methylene chloride [15].

[c] From molecular simulation.

as electrolyte contain an appreciable fraction of ion pairs, as verified by spectroscopy [16,17] or crystallography [18].

In contrast, the solutions of LiTFSI in PEO (DN $\approx$ 20) were shown to be devoid of ion pairs, even at high concentrations, as shown by various spectroscopic techniques ranging from NMR to Raman [19]. This compares well with recent X-ray data showing the complete separation of Li^+ and AsF_6^- in the complex $P(OE)_6LiAsF_6$ in its crystalline form [20]. The conductivity values were selected in PEO and measured at 80 °C, at a concentration close to the eutectic point between pure PEO (m.p. 65 °C) and the closest $P(OE)_n$–LiX complex, ($n = 3$ for BF_4^-, $CF_3SO_3^-$, $n = 6$ for all the others). The use of polymer electrolytes has an amplifying effect, reflecting both the dissociation of the salt and the mobility of the polymer segments allowing the motion of the ions. This is determined by the phase diagram salt–solvent, and in turn, depends largely upon the lattice energy of the salt. Thus, TFSI, highly delocalised and flexible gives practically the best conductivities (4 × that of AsF_6^-, despite a higher DN). This is a marked advantage in terms of utilisation, as the power delivered by a cell is approximately proportional to the conductivity of its electrolyte. Another advantage of these new anions is their purely covalent character, synonymous of chemical stability. Conversely, it is noteworthy that PF_6^-, prone to liberate PF_5, destroys the polymer through ether cleavage.

4. Weakly coordinating anions in catalysis

Another domain of application of weakly coordinating anions is in catalysis, as the cation, freed from ion pairs and in solvents of low donicity sees its activity enhanced (‘naked cation’), leading to improved kinetics and yields in organic chemistry; this applies to H^+, transition metals and rare earth ions. Conversely, weakly basic anions should be less solvated by Lewis-acidic solvents, and thus appreciably less dependant on this parameter for dissociation. In the solid-state, the interactions between charges of opposite species are small, for the same reasons, and thus the salt lattice energy is easily compensated by solvation, resulting in high solubility almost irrespective of the cations involved [21–25].

5. Conclusions

We tried here to stress the importance of preparing weakly coordinating anions and pointed out one of the most efficient and simple methods for characterising their donor properties. These materials and the corresponding research both for the design and use of optimised materials will inevitably grow in importance in the forthcoming years, spanning many domains in chemical science. It is hoped that this review will encourage those willing to enter this field.

Acknowledgements

Thanks for financial support are due to the ‘Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich’ (Project 15048-CHE) to the Training and Mobility of Researchers Network (TMR) project ‘Thermal and Optical Spin State Switching’ (TOSS) supported by the European Community under the Contract number ERB-FMRX-CT98-0199.

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