

Highly concentrated “solutions” of metal cations in ionic liquids: current status and future challenges

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In this article we summarize a series of conditions that allow highly concentrated “solutions” of metal cations in ionic liquids to be obtained, evidencing structural features and some of the most important physico-chemical properties of these systems. We try to emphasize aspects and problems that are not conventionally discussed in detail in the literature. In particular, we provide a full length discussion on the topics of: (i) solvation of metal salts in ionic liquids, (ii) anion coordinating ability and homologous and heterogeneous complexes. A brief outlook into future perspectives of metal containing ILs is also provided.

Introduction

Ionic liquids (ILs) have attracted considerable interest during the past ten years due to their unique properties (low vapour pressure, wide liquid range, good conductivity, large electrochemical window) which make them promising new media with several possible applications.¹ They are typically composed by an organic cation (ammonium, phosphonium, pyridinium, imidazolium, guanidinium, pyrrolidinium and many other more exotic cations) with a variety of substituents (typically, linear alkyl chains) associated to an inorganic or organic anion. By choosing an appropriate anion-cation combination, the physical and chemical properties of the ILs can be modified to meet the requirements of a given application.^{2,3} Acidic, basic, neutral, coordinating and polymerizable ILs have been prepared selecting anion and cation or *via* functionalization of the alkyl chain(s) normally present on cation.⁴

Metal-containing ILs represent a promising area in the multi-faceted IL universe, since they combine the unique properties of ILs with the peculiar properties (magnetic, photophysical/optical or catalytic) of the incorporated metal. In the last ten years, several combinations of ILs and transition metals have been tested in catalysis,⁵ and, more recently, solutions of f-element compounds have been proposed as soft luminescent materials for use in photochemistry and spectroscopy, although their excellent Lewis acidity makes them promising also as catalysts in synthesis.⁶

Nevertheless, binary mixtures of IL-metal salts are considered promising systems for electrochemical applications; at the moment, it is well known that several metals can be electrodeposited from suitable ILs to obtain new materials having specific characteristics (thin films, nanostructures and so on).⁷

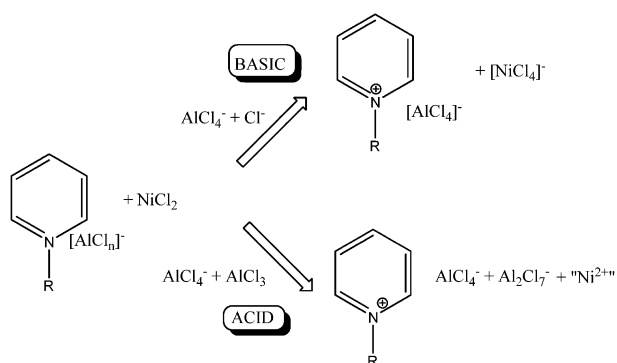
To better understand the importance of obtaining metal ions solubilized in ILs (or, more generally, non-aqueous solutions), it is sufficient to consider that some metals have limited or no applications in electrochemistry from aqueous solutions; a lithium ion battery would never have been possible in this medium.

The electrochemical window of ILs allows the reduction of many metals (*e.g.* aluminium, magnesium, tungsten) that cannot be treated in aqueous solutions. Environmentally harmful processes can be substituted with “greener” ones;⁸ it is possible, for instance, to obtain anticorrosive layers of Al by electrodeposition from ILs,⁹ thus avoiding the presence of harmful metals as Ni, Cr and Cd.

Nevertheless, in order to have efficient processes with an acceptable time and energy cost, it is important to have sufficiently high concentrations of the metal (>0.3 mol L);¹⁰ this is true for both electrodeposition and high energy batteries and for more specific applications where metal containing ILs are used as materials, for example in membranes for selective gas separations¹¹ or in new uses such as sensors with fast response times. On the other hand, a high metal concentration is not strictly necessary for the application in catalysts, unless metal containing ionic ILs are used as enzyme-like super-molecular host systems. The metal centre embedded in a liquid three-dimensional network should display a noticeable degree of organization and be able to catalyze selective reactions, exploiting synergistically all the possible pathways to enhance the rate of chemical reaction: the electronic coordinating ability of the metal centre could be in principle assisted by the selectivity of the ILs towards solubilization of (even very similar) different chemical species and by the chemical (acid/base) assistance of the liquid ions, giving a sort of “artificial enzymatic system”. In addition, since ILs can be considered dynamically active assemblies with a link between structure and dynamics, IL vibrations and motions might play a role in the fluctuation of the activation energy barrier as in natural organized systems (enzyme). But, at the moment this latter is only a fascinating hypothesis.

Unfortunately, contrary to the well-known statement of chemistry that “like dissolves like”, the solubility of common inorganic salts in the classical ILs is generally low. This is particularly true in the case of ionic liquids characterized by low coordinating anions, like tetrafluoroborate, hexafluorophosphate or bis(trifluoromethylsulfonyl)imide, reported also as bistriflimide, (BF₄)[−], [PF₆][−], or [Tf₂N][−]) and common unfunctionalized cations, such as dialkylimidazolium, alkylpyridinium and dialkylpyrrolidinium. The solubility of metal

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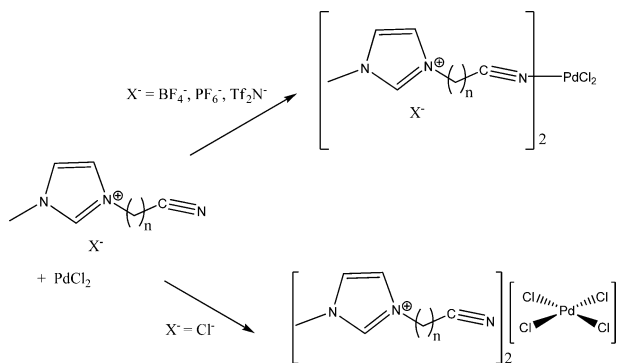
Scheme 1

salts in ILs based on unfunctionalized cations generally increases introducing stronger coordinating anionic components, such as chloride, thiocyanate or dicyanamide (Cl^- , SCN^- , or $[(\text{CN})_2\text{N}]^-$), which are able to bind the metallic cations giving new anionic species ($[\text{AlCl}_4]^-$, $[\text{ZnCl}_3]^-$, $[\text{NiCl}_4]^{2-}$ and so on), sometimes stabilizing unusual oxidation states. The incorporation of the metal in the IL as part of the anion gives however solutions of “strongly-coordinated” metals which can have a chemical behavior significantly different from that of “naked” or more probably “weakly-coordinated” metallic ions.

The reduction of Ni^{2+} is possible in acidic butylpyridinium chloroaluminate (*i.e.* containing an excess of AlCl_3) but not in basic chloroaluminate IL (containing an excess of organic salt, $[\text{BuPy}][\text{Cl}]$) where divalent Ni cations are likely to form a chlorocomplex ($[\text{NiCl}_4]^{2-}$) which cannot be reduced within the electrochemical potential window (Scheme 1).¹²

Analogously, although nitrile-functionalized ILs are able to facilitate solubilization of Pd^{2+} salts *via* coordination of the nitrile groups, when the IL anion is chloride, divalent Pd cations preferentially react with this anion forming the corresponding chlorocomplex, $[\text{PdCl}_4]^{2-}$, which is less catalytically active or, more probably, less prone to the transformation in the active species, palladium nanoparticles (Scheme 2).¹³

The approach to incorporate specific functional groups on the IL cation and, less frequently on anion, has been applied extensively in catalysis, where the complex formation ensures simultaneously a high metal activity and stability,¹⁴ and in metal extraction processes.¹⁵ Although generally functionalized ILs are characterized by an increased performance with respect to common ILs, often their synthetic procedures



Scheme 2

do not conform with the important goal of developing cheap and easily available cations and anions, through simple and sustainable procedures. Moreover, when the solubility of the metal salts is due to the presence of groups able to increase hydrophilicity ($-\text{OH}$, $-\text{COOH}$ and so on), one has to realize that these solvents also tend to retain relevant amounts of water after drying, and the possibility that the solubility of the metallic salt may be a consequence of the presence of water cannot be excluded. The presence of water as a cosolvent can help in solubilizing metal cations, through its coordination ability which is often higher than that of many ILs anions; anyway, the presence of water in non-aqueous electrochemical systems is usually not desirable for the reasons reported above.

In a search for “simpler and greener” procedures to synthesize ILs, we have recently reported on the possibility of solubilizing metal salts in hydrophobic or hydrophilic ILs by simply dissolving metal salts in ILs which contain the same anion.¹⁶ Ionic liquids with different unfunctionalized cations (based on imidazolium, pyridinium and pyrrolidinium) and common anions (triflate, bistriflimide, nitrate and acetate) gave concentrated solutions ($1\text{--}2\text{ mol L}^{-1}$) with homoanionic metal salts but not with heteroanionic salts.

Although the strategy surely provides new opportunities in the chemistry of ionic systems, to fully exploit the potentiality of these metal-containing ILs we consider it important to address two important questions: (i) why is the dissolution of homoanionic metal salts favored in all tested ILs? and (ii) what is the situation of the metal in ILs on going from strongly to weakly coordinating anions?

Molecular structures of metals in ILs

As starting point, it may be useful to consider the possible interactions of ILs with metal cations.

The nature of the ionic components of the ILs determines the solvation ability of these media towards uncharged or charged species. In the case of metallic salts, the interaction can be driven by Coulombic forces (in this case, we speak of “solvation”) or by overlap of d orbitals of the metal with the IL ions (“coordination”). While the first interaction is reserved to anions, coordination could in principle be given by both anions or specifically functionalized cations, such as those bringing electron-withdrawing moieties or having conjugated π -systems; for example, functionalization of alkyl chains on cations with groups such as carboxyl,¹⁷ urea, thiourea,¹⁸ or nitrile¹⁹ allows the metal to host the positively charged ions in their coordination shell.

Among the anions, typical ligands for metallic cations are halides and pseudohalides, but several “classic” ILs anions have been found to give coordination complexes with a wide range of metals. Lanthanide thiocyanate anionic complexes, of the type $[\text{Ln}(\text{NCS})_6]^{3-}$ ($\text{Ln} = \text{Sc}, \text{Y}, \text{La--Lu}$), combined with a $[\text{bmim}]^+$ cation have been recently prepared and characterized.²⁰ Most of these salts are liquids or supercooled liquids at room temperature and tend to give glasses rather than crystals upon cooling. Single crystal X-ray analyses show that the lanthanide(III) ions are coordinated by seven (for La and Pr) or six (for Y) isothiocyanate anions and one water molecule. Absorption spectra for the crystalline and the liquid show no significant

differences for the ratios of the integrated intensities of the f–f transitions supporting the hypothesis that the anionic complexes observed in the solid state persist in the liquid state.

But, a strong coordinating ability also characterizes dicyanamide anion based ILs, which are able to dissolve most of the metal chlorides practically insoluble in the $[\text{BF}_4]^-$, $[\text{PF}_6]^-$ and $[\text{Tf}_2\text{N}]^-$ based ILs.²¹ The structures of 3D anionic metal dicyanamide salts $(\text{MePh}_3\text{P})[\text{M}(\text{NCN}_2)_3]$ and $(\text{EtPh}_3\text{P})[\text{M}(\text{NCN}_2)_3]$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$) have been recently reported.²² Notably, both series of salts contain anionic $[\text{M}(\text{NCN}_2)_3]^-$ networks in which octahedral metal ions are bridged by bidentate $\mu_{1,5}$ dicyanamide anions, to generate three-dimensional five connective networks where cations seem to have a templating function and lie in pairs within cavities in the anionic networks. Amide nitrogens are not involved in the metal coordination. This peculiar behavior probably strongly affects the physico-chemical properties and the chemical behavior metal containing dicyanamide based ILs.

The ability to coordinate metals is not however a prerogative of N-donor ligands. The strong metal-complexing ability of the hexafluoroacetylacetonate anion ($[\text{hfac}]^-$) has been used to obtain highly coordinating ILs.²³ These hydrophobic salts (it is noteworthy that coordinating ILs are generally hydrophilic) are able to extract metal salts from water and, upon saturating the IL with metal salts, anhydrous anionic hexafluoroacetylacetonate complexes precipitate out of the solution. Crystal structures of $[\text{bmim}][\text{Na}(\text{hfac})_3]$, $[\text{bmim}][\text{Co}(\text{hfac})_3]$, $[\text{bmim}][\text{Cu}(\text{hfac})_3]$ and $[\text{bmim}][\text{Nd}(\text{hfac})_3]$ show that Na^+ , Cu^{2+} and Co^{2+} are octahedrally coordinated by three hexafluoroacetylacetonate ligands, whereas Nd^{3+} is surrounded by four bidentate coordinating β -diketonate anions in an antiprismatic geometry. On the other hand, ILs based on lanthanide nitrate complex anions ($[\text{cat}]^{3+}[\text{Ln}(\text{NO}_3)_6]^{3-}$) have been also synthesized.²⁴

But what is the situation in less coordinating ILs? Bis-(trifluoromethylsulfonyl)imide, $[\text{Tf}_2\text{N}]^-$, is surely the weakest complexant among the generally used IL anions. Structural X-ray crystallographic data indicate that, at least in the absence of any other stronger ligand (including water) in the solid state, this anion is able to coordinate a metal center.²⁵ Fig. 1 shows the coordination complex with Ni^{2+} as obtained by *ab initio* DFT calculations. The anion acts as a bidentate ligand, coordinating the metal with oxygen atoms bonded to different sulfur centers and retaining the same *trans*-configuration, which usually is mostly populated in the neat ILs formed by this anion.

X-Ray data reported²⁶ for an ytterbium $[\text{Tf}_2\text{N}]^-$ complex and, more recently, for a series of europium salts, synthesized from stoichiometric amounts of $\text{Eu}([\text{Tf}_2\text{N}])_3$ and imidazolium and pyrrolidinium $[\text{Tf}_2\text{N}]^-$ -based ILs²⁷ reveal ninefold oxygen coordination for the Eu^{3+} center and confirm that the oxygen donors come from four bidentate bistriflimide ligands and one monodentate ligand. It is however noteworthy that whereas Raman and IR spectroscopy confirm the complexation of the metal cation by the bistriflimide anion at the solid state, the excitation and emission spectra of the same samples at liquid and solid state show significant differences suggesting a change in the coordination number on going from solid to liquid state, in contrast with the behavior observed with lanthanide thiocyanate anion complexes.

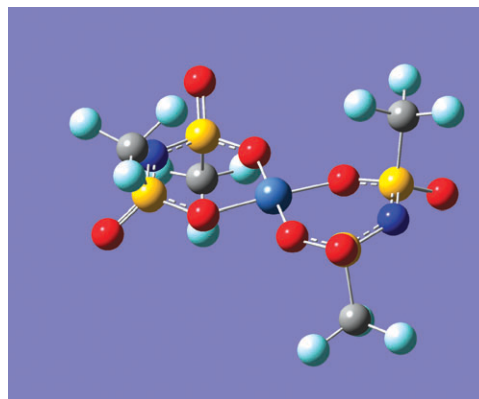


Fig. 1 Coordination complex of bis(trifluoromethylsulfonyl)imide with Ni^{2+} , as obtained by *ab initio* DFT calculation.

Solvation of metal salts in ILs

In molecular solvents (water or polar solvents), the solubilization of an electrolyte is the consequence of the ability of the molecules of the solvent to separate and “solvate” the single ions. Solutions of metal salts in molecular solvents consist of solvated ions, their combinations (ion pairs and solvent-separated ion pairs) and solvent molecules. In ILs, the solubility is again a consequence of the capability of the components of the IL to “solvate” anions and cations but the arising system is constituted exclusively by ions and it is free of any solvent molecule. The solubility of metal salts in ILs is governed by the coordination of the ionic species to the metal center; the anionic components of the IL and of the dissolved salt play a fundamental role during the dissolution process affecting both the thermodynamic and kinetics.²⁸ The nature of the first coordination sphere of the metal depends on the competition between the metal counteranion and IL anions; this competition affects also the complexation reaction with other eventually added anions.

In order to better rationalize the phenomenon, we sketch briefly the solvation process in ionic liquids and summarize step by step the elementary actions necessary to dissolve a metal salt in a IL (Fig. 2). To transfer chemical species from the gas phase to the liquid, the liquid modifies its structure in the following way:

- A suitable cavity is created in the solvent to accommodate the solute.
- The different (anionic and cationic) species redistribute around the solute; for charged solutes, the anions and cations will tend to get closer or farther from the solutes according to their charge and the subsequent positive (or negative) Coulomb interaction energy. For neutral species, the Coulombic interaction will be absent, and only the dispersion energy will contribute (translational redistribution).
- Due to their dipole moments and polarizabilities, solvent molecules will align and orient with respect to the solute center due to the solute field (orientational redistribution).
- Finally, the liquid around the solute polarizes the solute itself, changing its electronic and geometrical structure; for an ionic liquid, such contribution is not to be neglected.

When a chemical reaction is involved (such as formation of a metal complex), things get more complicated. We can subdivide the process of solubilization of a metal salt (MX) in

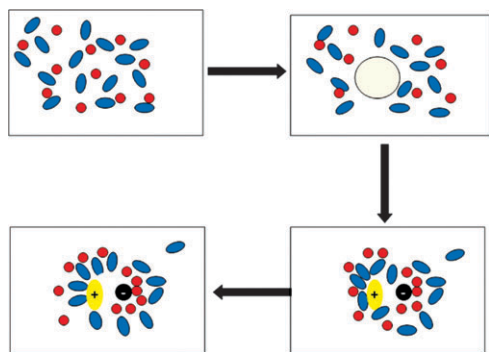
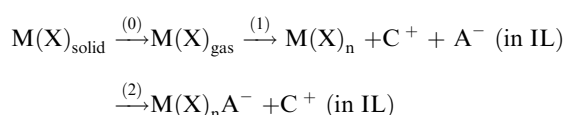


Fig. 2 Step by step representation of the elementary actions necessary to dissolve a metal salt (represented as a cation and an anion) in a ionic liquid (red circles cations, blue ellipses anions).

an IL bearing an anion able to coordinate more or less strongly the metal center in the following way, which will turn useful to analyze the thermodynamics of solvation:



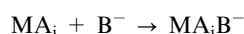
Since passage (0) is independent of the nature of the liquid, the ruling aspects are the ease of bringing the neutral complex in solution (1) and the possible coordination reactions that the complex may undergo when solubilized (typically, the coordination of a further anion).²⁹ To better understand the phenomenon, we will analyze the process by explicitly accounting for each contribution to the free energy:

1. In the first passage, the contribution comes from the solvation free energy of the neutral complex, which in turn is given by two separate addenda: the solute–solvent interaction energy and the solute polarization induced by the solvent.

2. In the second passage, contribution comes from the formation of a chemical bond, from the change in solvation free energy given by the modification of the number of reactant and product species in solution and from the rise of entropy due to the merging of two species into a single one (that, in a liquid, we assume to be negligible).

The energies involved in these processes have to be considered: formation of a metal–small ionic ligand bond to give a charged complex typically gives a (negative) energy ranging from -50 to -100 kcal mol⁻¹, while dissolution of a neutral (ionic) complex in a room-temperature ionic liquid gives positive excess free energies of about 50–25 kcal mol⁻¹. (The excess free energy of an ion constituting the liquid is usually negative, ranging from -20 to -40 kcal mol⁻¹.³⁰) The extent of solute polarization energy by a unfunctionalized IL is considerably lower, giving a contribution of 1–10 kcal mol⁻¹.

From these considerations, it appears that the driving force for solubilization is the ease of formation of the charged complex in solution, often referred to as the “addition reaction”³¹:



as already noticed experimentally; in other words, the more the equilibrium of the addition reaction is shifted towards the products, the more metal could be solubilized in the liquid.

To give a more quantitative insight to such consideration, we will here analyze the thermodynamics of formation of negatively charged homoligand complex ($[\text{MA}_{i+1}]^-$, $\text{A} = \text{B}$) and of heteroligand complex ($[\text{MA}_i\text{B}]^-$, $\text{A} \neq \text{B}$) from the neutral complex MA_i in both gas phase and IL solution with the help of DFT calculations. Calculations are here referred to one of the simplest cases, the insertion of AlCl_3 and $\text{Al}(\text{NO}_3)_3$ in the ionic liquid $[\text{mmim}]\text{Cl}$; we do not consider here the formation of different anionic or neutral species.

From the data reported in Table 1, it emerges that the formation of the charged complex is strongly favoured, having a reaction energy ranging from -40 to -70 kcal mol⁻¹ in the gas phase. The same reaction energy is raised to less negative values by the solubilization process, due mainly to the loss of the solute–solvent contribution due to the bare ligand ion (which is strongly negative), but nevertheless remains strongly negative (about -40 kcal mol⁻¹). The more remarkable thing to be noticed is that the mixed valence complex with chloride has a formation energy less favourable than the homo-complex; this is not surprising, since it is well known that the stability of mixed complexes is usually much lower than that of the parent homoligand complexes when the ligands differ in denticity, geometry or kind of bonding (ionic vs. covalent, or σ vs. π).²⁵

This observation can help in understanding why solubility of transition metal salts is so high in ILs with the same anion, as recently observed by us;¹² metal triflates, acetates, nitrates and bistriflimides show a high solubility in ILs bearing the same anion but they are characterized by a low dissolution ability in ILs bearing a different anion (for example, metal bistriflimides are low soluble in $[\text{bmim}][\text{NO}_3]$). If the solubilization passes through the addition reaction and formation of the charged species, such formation is consistently augmented when the charged complex is a homoligand one (Fig. 3). Complexation of a metal center with the same anion, if the center has not reached its complete coordination number, leads to a symmetric and stable anionic complex. Complexation of a metal center with an anion of different denticity leads to an unsymmetric anionic complex, in which orbital mixing (and thus stabilization by ligand–metal interaction) is less effective, leading to unstable species; this is particularly destabilizing if the parent neutral complex has reached its full coordination number, since the denticity displayed by ligands of the same kind has to change. The greater ease of formation of the complex thus favors the transfer of a larger amount of metal into the liquid.

The relevant solubility of metal chloride in dicyanamide-based ILs is not consistent with this model.¹⁵ However, dicyanamide is a peculiar anion with a high basicity, coordination ability and distinctive shape. These features give the corresponding ILs the ability to build up, with metallic cations, three-dimensional networks which could be responsible of the high solubility of metal chlorides. It is noteworthy that the redox potentials of both of $\text{Cu}^{2+}/\text{Cu}^{1+}$ and $\text{Cu}^{1+}/\text{Cu}^0$ couples in $[\text{emim}][\text{N}(\text{CN})_2]$ occurs at more negative values than those observed in $[\text{emim}][\text{Tf}_2\text{N}]$, in agreement with the fact that dicyanamide is a more basic coordinating ligand and complexes Cu^{2+} and Cu^{1+} stronger than $[\text{Tf}_2\text{N}]^-$ anion does.³²

Table 1 Electronic energies (in kcal mol⁻¹) and excess solvation free energies (in parentheses, only for solvated species) for the reactants and products involved in the homoligand and heteroligand addition reaction

	Neutral complex	Anionic ligand	Anionic complex
$\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^-$ (gas phase)	-314.27	-84.18	-467.62
$\text{Al}(\text{NO}_3)_3 + \text{Cl}^- \rightarrow \text{Al}(\text{NO}_3)_3\text{Cl}^-$ (gas phase)	-1844.21	-84.18	-1966.47
$\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^-$ (ionic liquid)	-313.97 (+ 52.62)	-84.18 (-49.06)	-462.59 (+ 23.05)
$\text{Al}(\text{NO}_3)_3 + \text{Cl}^- \rightarrow \text{Al}(\text{NO}_3)_3\text{Cl}^-$ (ionic liquid)	-1830.05 (+ 50.80)	-84.18 (-49.06)	-1969.47 (+ 27.49)

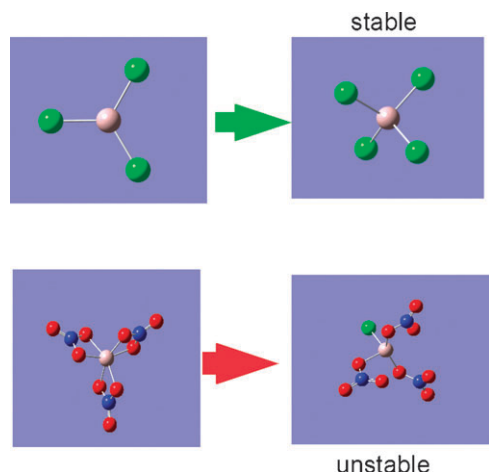


Fig. 3 A simple example on how the anionic complex formation in ILs can be affected by the parent coordinating anion (Al = pink; Cl = green; O = red; N = blue).

Physico-chemical properties of metal-containing ILs

After loading an ionic liquid with a non-negligible quantity of a transition metal ion, the resulting material is expected to show markedly different overall physico-chemical properties with respect to the pure IL. Here, we will focus on the most important ones, keeping in mind the current applications of IL-based systems: viscosity, conductivity, diffusivity and so on. All these properties are nevertheless related to the degree of fluidity of the ionic liquid, and thus indirectly to how much the liquid system temperature lies towards the melting or glass transition temperature. For this reason, the solid-liquid transition temperature will be the first property examined.

Considering the different situations of metal salts in ILs depending on the medium's coordinating ability, at least two limiting situations can be envisaged for unfunctionalized ILs: addition of the metal salt to an IL having a highly coordinating anion or to a IL having a "solvating" low coordinating anion.

Addition of metal halides (AlCl₃, ZnCl₂, FeCl₃, SnCl₂ and so on) to pyridinium, imidazolium and ammonium chlorides gives ILs whose physico-chemical properties are determined by the form and composition of the complex anion. The effect of anionic composition on melting points, glass transition points, and viscosity of haloaluminate ILs has long been recognized;³³ the combination of halide salts with AlCl₃ reduces melting points through the formation of eutectic compositions. In particular, in the case of 1-methyl-3-ethylimidazolium chloride/aluminium trichloride ([emim]Cl/AlCl₃) viscosity remains practically constant at values significantly lower than the starting IL, until the amount of [emim]Cl is below 50%.

However, when [emim]Cl exceed 50 mol%, the absolute viscosity begins to increase. This latter dramatic increase in viscosity, which is correlated with the growth in chloride ion concentration, has been attributed to the hydrogen bonding ability of chloride ions with imidazolium cation. The formation of the metal complexes ([emim]Cl below 50%) therefore decreases at least in this case viscosity reducing the hydrogen bond ability of the anion³⁴ and the Coulombic forces inside the IL, as a consequence of the lower charge density of the Al_nCl_m⁻ anions. The correlation between viscosity and anion form in the case of metal chloride complexes has been extensively discussed³⁵ in terms of ion : hole size ratio by Abbott *et al.*

Although the mixtures of metal salts in ILs bearing low coordinating anions have been scarcely investigated, nevertheless it has been shown that at least ILs composed by binary mixtures of alkali bistriflimides have melting temperatures markedly lower (of about 60 °C) than the ones of the parent monoalkaline salts, their phase diagram showing the formation of an eutectic point near to equimolar composition.³⁶ It is then possible to imagine that the insertion of single-charged transition metal could actually lower the melting temperature of the starting pure ionic liquid, and thus indirectly modify the transport properties, by loosening the lattice packing through the presence of molecules or atoms acting as defects. Each consideration about transport properties of the mixture should then be made after proper knowledge of its melting temperature. In this context, it is noteworthy that the addition of LiBF₄ to 1-methyl-3-ethylimidazolium tetrafluoroborate, [emim][BF₄], modifies significantly the thermal properties of the medium;³⁷ at concentrations of LiBF₄ above 0.5 M, crystallization/melting peaks disappeared, whereas the glass transition temperatures shifted to higher values with increasing LiBF₄ concentration. The addition of LiBF₄, moreover, affects ionic conductivity and the self-diffusion coefficients of the individual components that decrease on increasing LiBF₄ concentration, whereas viscosity increases. A similar behavior of conductivity and viscosity as a function of lithium concentration was observed³⁸ also in the case of lithium bistriflimide/1,3-dimethyl-3-propylimidazolium bistriflimide mixture.

The modification of transport properties, at first, can be often interpreted in terms of the extent of Coulomb interactions of the added ion, with respect to the starting ions; adding a small cation like Li⁺, with a strong Coulomb interaction, increases the viscosity of the melt and subsequently decreases the conductivity, while quaternary ammonium salts with their widely distributed charge have the opposite effect.³⁹ A more detailed analysis of the behavior of all these properties (thermal properties, ionic conductivity, viscosity and self-diffusion coefficients) as a function of the added salt, evidences

that these systems do not have simple solution dynamics although generally a correlation with the metal salt concentration can be envisaged.

On the other hand, even more complicated systems are the binary mixtures of ILs-metal salts, without a common anion. It has been recently reported⁴⁰ that LiTf_2N solutions in $[\text{bmim}][\text{SCN}]$ have a rather peculiar behavior, with a non-monotonic behaviour of conductivity as a function of concentration. In these systems, an optimal lithium salt concentration (maximum conductivity) is found at about 0.3 M, while the viscosity increases monotonically with salt addition. Such behavior reminds us that in IL systems usually the Stokes–Einstein and Nernst–Einstein relation does not hold,⁴¹ and thus the electrical transport properties can in principle be decoupled from the bulk and molecular mass ones. Furthermore, it must be always considered that if small amounts of halides arising from metathesis reactions are able to markedly affect transport properties of “pure” ILs, the more relevant amounts of anions arising from the added metal salt (when this has a different anion and it is soluble!) must certainly affect the physico-chemical properties of the corresponding binary ionic liquid-metal salt mixtures in a way that probably depends on metal anion and changes on changing this parameter.

Conclusions

In conclusion, in this article we have given an overview of the mechanisms through which it is possible to dissolve relevant amounts of metal cations in ILs, evidencing on the basis of structural considerations and physico-chemical parameters how the coordinating power of the IL anion can affect not only important properties of the resulting solutions (such as melting point, conductivity, viscosity, ion diffusivity and so on) but also the electrochemistry of the dissolved metal. We have also evidenced how the binary ionic liquid–metal salt mixtures having low coordinating anions represent practically an as yet un-investigated area in the ionic liquid universe despite their potentiality. A “naked” or “low coordinated” metal can find important applications in electrochemistry, catalysis, material sciences, and in the development of new devices. An explanation of the common ion effect in promoting dissolution of metal salts in ILs has been given considering the solvation mechanism of ionic liquids.

References

- 1 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.
- 2 T. Welton and P. Wasserscheid, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2008.
- 3 C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.*, 2005, **18**, 275.
- 4 S. Lee, *Chem. Commun.*, 2006, 1049; J. H. Davis Jr, *Chem. Lett.*, 2004, **33**, 1072.
- 5 V. I. Părvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615.
- 6 K. Driesen, P. Nockemann and K. Binnemans, *Chem. Phys. Lett.*, 2004, **395**, 306; K. Binnemans, *Chem. Rev.*, 2007, **107**, 2592.
- 7 F. Endres, A. P. Abbott and D. R. MacFarlane, *Electrodeposition from Ionic Liquids*, Wiley-VCH, Weinheim, 2008.
- 8 W. Simka, D. Puszczuk and G. Nawrat, *Electrochim. Acta*, 2009, **54**, 5307.

- 9 L. Barchi, U. Bardi, S. Caporali, M. Fantini and A. Scrivani, *Prog. Org. Coat.*, 2010, **67**, 146.
- 10 W. Kunz and P. Turq, *J. Phys.: Condens. Matter*, 1990, **2**, SA151.
- 11 J. Van Erkel, P. Bressenens, M. C. Marinus and R. J. M. Creusen, WO2009 11577; T. Li, National Meeting Washington, USA, 16 August 2009, p. ANYL-331.
- 12 R. G. Gale, B. Gilbert and R. A. Osteryoung, *Inorg. Chem.*, 1979, **18**, 2723.
- 13 Z. F. Fei, D. B. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe and P. J. Dyson, *Organometallics*, 2007, **26**, 1588.
- 14 Z. F. Fei, T. J. Geldbach, D. B. Zhao and P. J. Dyson, *Chem.–Eur. J.*, 2006, **12**, 2122.
- 15 X. Han and D. W. Armstrong, *Acc. Chem. Res.*, 2007, **40**, 1079.
- 16 C. Chiappe, M. Malvaldi, B. Melai, S. Fantini, U. Bardi and S. Caporali, *Green Chem.*, 2010, **12**, 77.
- 17 P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987.
- 18 A. E. Visser, R. P. Swatowski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis Jr. and R. D. Rogers, *Environ. Sci. Technol.*, 2002, **36**, 2523.
- 19 N. Papaiconomou, J.-M. Lee, J. Salminen, M. von Stosch and J. M. Prausnitz, *Ind. Eng. Chem. Res.*, 2008, **47**, 5080.
- 20 P. Nockemann, B. Thijs, N. Postelmans, K. Van Hecke, L. Van Meervelt and K. Binnemans, *J. Am. Chem. Soc.*, 2006, **128**, 13658.
- 21 M. J. Deng, P. Y. Chen, T. L. Leing, I. W. Sun, J. K. Chang and W. T. Tsai, *Electrochem. Commun.*, 2008, 213.
- 22 P. M. van der Werff, S. R. Batten, P. Jensen, B. Moubarald, K. S. Murray and J. D. Cashion, *Cryst. Growth Des.*, 2004, **4**, 503.
- 23 H. Mehdi, K. Binnemans, K. Van Hecke, L. Van Meervelt and P. Nockemann, *Chem. Commun.*, 2010, **46**, 234.
- 24 G. H. Tao, Y. Huang, J. A. Boaz and J. M. Shreeve, *Chem.–Eur. J.*, 2008, **14**, 11167.
- 25 M. J. Earle, U. Hakala, B. J. McAuley, M. Nieuwenhuyzen, A. Ramani and K. R. Seddon, *Chem. Commun.*, 2004, 1368.
- 26 A. V. Mudring, A. Babai, S. Arenz and R. Giernoth, *Angew. Chem., Int. Ed.*, 2005, **44**, 5485.
- 27 S. Tang, A. Babai and A. V. Mudring, *Angew. Chem., Int. Ed.*, 2008, **47**, 7631.
- 28 Q. Liu, M. H. A. Janssen, F. van Rantwijk and R. A. Sheldon, *Green Chem.*, 2005, **7**, 39.
- 29 M. P. Jensen, J. Neufeind, J. V. Beitz, S. Skantakumar and L. Soderholm, *J. Am. Chem. Soc.*, 2003, **125**, 15466.
- 30 S. Bruzzzone, M. Malvaldi and C. Chiappe, *J. Chem. Phys.*, 2008, **129**, 074509.
- 31 Y. Marcus and I. Eliezer, *Coord. Chem. Rev.*, 1969, **4**, 273.
- 32 T. I. Leong, I. W. Sun, M. J. Deng, C. M. Wu and P. Y. Chen, *J. Electrochem. Soc.*, 2008, **155**, F55.
- 33 J. S. Wilkes, A. J. Levisky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263; A. A. Fannin Jr, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. J. Vaughn, J. S. Wilkes and J. L. Williams, *J. Phys. Chem.*, 1984, **88**, 2614.
- 34 R. A. Mantz and P. C. Trulove, *Viscosity and Density of Ionic Liquids*, in *Ionic Liquids in Synthesis*, ed. P. Wasserscheid and T. Welton, Wiley-VCH, 2003.
- 35 A. P. Abbott, G. Capper, D. L. Davies and R. Rasheed, *Inorg. Chem.*, 2004, **43**, 3447.
- 36 K. Kubota, T. Nohira, T. Goto and R. Hagiwara, *Electrochem. Commun.*, 2008, **10**, 1886.
- 37 K. Hayamizu, Y. Aihara, H. Nokagawa, T. Nukuda and W. S. Price, *J. Phys. Chem. B*, 2004, **108**, 19527.
- 38 S. Seki, Y. Ohno, Y. Kobayashi, H. Miyashiro, A. Usami, Y. Mita, H. Tokuda, M. Watanabe, K. Hayamizu, S. Tsuzuki, M. Hattori and N. Terada, *J. Electrochem. Soc.*, 2007, **154**, A173.
- 39 M. Egashira, S. Okada, J. Yamaki, N. Yoshimoto and M. Morita, *Electrochim. Acta*, 2005, **50**, 3708.
- 40 Z. P. Rosol, N. J. German and S. M. Gross, *Green Chem.*, 2009, **11**, 1453.
- 41 W. Xu and C. A. Angell, *Science*, 2003, **302**, 422.