Structural Features and Properties of Metal Complexes in Ionic Liquids: Application in Alkylation Reactions

Cinzia Chiappe, Tiziana Ghilardi, and Christian Silvio Pomelli

Abstract Metal-containing ionic liquids (ILs) represent a promising sub-class of "charged" liquids which increase the tunability of ILs combining the properties of common organic salts with magnetic, photophysical/optical or catalytic properties of the incorporated metal salts. In ILs lacking of coordinating groups on cation dissolution of metal salts is generally associated with the coordination of the metal cation with IL anion(s). Here we report on the anionic speciation of metals in ILs having either highly or poorly coordinating anions and we discuss some peculiar properties of these systems in the light of their structural features.

Contents

Abbreviations

[bmim]$^+$ 1-Butyl-3-methylimidazolium
[C$_3$mpip]$^+$ N,N-propylmethylpiperidinium
[C$_4$mpyr]$^+$ N,N-butylmethylpyrrolidinium

C. Chiappe (✉), T. Ghilardi, and C.S. Pomelli
Dipartimento di Farmacia Università di Pisa, via Bonanno 33, 56126 Pisa, Italy
e-mail: cinziac@farm.unipi.i

[emim]$^+$	1-Ethyl-3-methylimidazolium
[Et$_3$NH]$^+$	Triethylammonium
[omim]$^+$	1-Octyl-3-methylimidazolium
[Tf$_2$N]$^-$	bis(Trifluoromethanesulfonyl)imide
ILs	Ionic liquids

1 Introduction

Ionic liquids (ILs) are a relatively recent class of ionic compounds which have many potentialities in synthesis, (bio)catalysis, separation processes, electrochemistry as well as in material sciences and for the development of new electrical and electro-chemical devices [1]. Usually constituted by an organic cation and a polyatomic anion, ILs are characterized by melting points near or below room temperature. ILs have also a negligible vapour pressure, a high thermal stability, a nonflammable nature [2] and a good solvent power. Since cations and anions can exert practically all types of interactions with solutes (coulombic interactions, hydrogen bonding, π–π stacking), ILs can solubilize a large variety of organic, inorganic compounds and polymeric materials. Moreover, their physico-chemical properties, such as melting temperature and hydrophilicity/hydrophobicity, can be simply tuned by changing the structure of the cations and anions: for instance, ILs can be designed to make them immiscible in water or in certain organic solvents [3]. The incorporation of specific functional groups into the chemical structure of constituent ions can be used to confer a desired chemical or physical property on the resulting ILs, commonly defined task-specific ionic liquids. It is noteworthy that these peculiar features can be transferred also onto solid surfaces through the formation of self-assembled monolayers of properly functionalized ILs.

Metal-containing ILs represent a promising sub-class of "charged" liquids which combine the properties of the common ILs with magnetic, photophysical/optical or catalytic properties of the merged metal salts [4, 5]. ILs that contain salts of palladium, ruthenium, platinum, gold, aluminium (but also iron, nickel, zinc or copper) have been used with success in catalysis. The use of ILs in catalysis is generally related to their ability to dissolve at least small amounts of metal salts, often favouring the formation of transient "active" species and, contemporane-ously, avoiding the leaching of the metal salt during product extraction. This latter feature increases indeed the possibility of recycling the catalyst, and many excellent accounts and reviews have already been published on this topic [6–10].

Moreover, the ability of ILs to dissolve ions (in particular, large amounts of metal salts) is of great interest also in other fields of chemistry, such as electro-chemistry and material sciences: ILs that contain metal salts are used in batteries, photovoltaic cells and in electrical devices or sensors. Metallic materials having specific characteristics (thin films, nanostructures and others) can be obtained by electrodeposition of metal salts dissolved in appropriate ILs [11]. Of course the addition of metal salts to common ILs modifies the physico-chemical properties of

these latter: this approach can therefore be considered a promising alternative to the use of mixtures of ILs or ILs-organic solvents to extent the tunability of these neoteric media [12].

Here, we explore some aspects related to the coordination environment surrounding metal cations in pure ILs as function of IL structure in order to understand how this feature can affect the main physico-chemical properties of the multi-ion systems and the possibility for their application.

2 Solvation of Metal Salts in Ionic Liquids

Solubility of metal salts in classical ILs depends strongly on IL cation–anion structure: it can be very low, in particular in ILs with poorly coordinating anions. The presence of specific polar functional groups (COOH, OH, CN) on cation or strongly coordinating anions (Cl^-, SCN^- and so on) generally increases metal salts solubility as well as eventual traces of water. The presence of water is an important variable to be considered in this contest since also hydrophobic ILs are able to capture quickly relevant amounts of water from atmosphere [13].

IL structure determines, however, not only the metal salt dissolution ability but also the coordination environment around the metal and, consequently, metal activity and reactivity.

The starting point for understanding reactivity and selectivity of processes carried out in metal-containing ILs requires indeed a detailed knowledge of the coordination structure of metal cations in this special class of solvents.

In water or polar solvents the solubilization of an electrolyte is the consequence of the ability of the solvent molecules to separate and "solvate" the single ions; a solution of metal salts in molecular solvents consists of solvated ions and their combinations (ion pairs or solvent-separated ion pairs). In ILs, salt solubility is primarily governed by the coordination of the IL ions to the metal centre and, in particular in the absence of specific coordinating groups in IL cation, the anionic components of the IL play a fundamental role during the dissolution affecting both the kinetic and thermodynamic of the process [4].

The coordination structure of the metal centre is indeed determined by the degree of metal-IL anion interaction which can be considered a process in competition with the interaction between IL cation and its counterion.

The process of solubilization of a metal salt (MX) in an IL, possessing an anion able to coordinate (more or less strongly) the metal centre, can be schematized as a three-step process:

$$M(X)_{solid} \xrightarrow{(0)} M(X)_{gas} \xrightarrow{(1)} M(X)_n + C^+ + A^-$$

$$\downarrow (2)$$

$$IL = [C][A] \qquad\qquad M(X)_n A^- + C^+$$
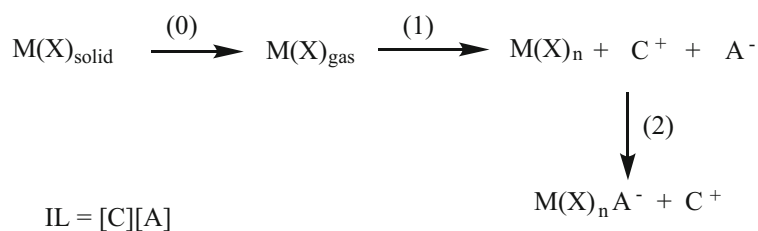
where the step (0) is practically independent by the IL nature, whereas step (1) and (2) are related to the transfer of the salt in solution and subsequent possible coordination reactions (for instance, the coordination of a further anion). Since the formation of bond between a metal centre and a small mono-dentate anion to give a charged complex typically gives a (negative) energy ranging from -50 to -100 kcal mol^{-1}, while the dissolution of a neutral salt, M(X), in an IL gives a positive excess free energy of about 25–50 kcal mol^{-1} and the extent of solute polarization energy by an unfunctionalized IL is considerably lower, about 1–10 kcal mol^{-1}, it is possible to deduce that the driving force for solubilization of a metal salt in an IL is the formation of the charged complex in solution, arising from an "addition reaction."

Since in a pure IL we expect to find the formed charged complex of the metal solvated by the IL cation (generally a mono charged species) the metal complexes with a single negative charge should be preferred for electrostatic reasons. This aspect, together with the coordination properties of the anion (mono- bi- or polydentate species), determines the coordination number (see below), which must be coherent also with the coordination number of the metal ion.

A remarkable point to be stressed is that calculations show that the stability of mixed complexes is usually much lower than that of the homocomplexes [4], in particular when the ligands differ in denticity, geometry, or type of bonding. This observation can support some experimental data showing that the solubility of transition metal salts in ILs sharing the same anion is significantly higher than that in ILs having a different anion. Metal triflates, acetates, nitrates, and bis(trifluoro-methanesulfonyl)imides ([Tf$_2$N]$^-$) show indeed a high solubility in ILs possessing the corresponding anion, and they are characterized by a low dissolution ability in ILs bearing a different anion (for example, metal bis(trifluoromethanesulfonyl)imides are poorly soluble in [bmim][NO$_3$]) [4].

Chlorometallate ILs are easily obtained via direct mixing of a metal chloride with an organic chloride salt and the physico-chemical properties, as well as their Lewis acidity and catalytic ability, depend on both the nature of the merged metal salt and the ratio of the metal chloride to organic chloride salt. However, mixed complexes can be present in solution and their formation, even as transient species, may be determinant for some specific applications of the metal. Tetrahedral mixed tetrahaloaluminates (III), tetrahaloferrates (III), and tetrahalogallates(III) (for example, [AlCl$_3$Br]$^-$, [FeCl$_3$Br]$^-$, [GaCl$_3$Br]$^-$) can be obtained by dissolution of the corresponding trichlorides (MCl$_3$) in the proper halide ILs; however, complex stability strongly depends on halide nature. The ^{27}Al NMR spectra show indeed that [AlCl$_3$Br]$^-$ anion is the dominant species in the [C$_8$mim]Br–AlCl$_3$ sample, whereas the [C$_8$mim]I–AlCl$_3$ mixture is characterized by three peaks corresponding to [AlCl$_4$]$^-$, the dominant anion, [AlCl$_3$I]$^-$ and [AlCl$_2$I$_2$]$^-$, respectively [14]. On the other hand, tetrahedral mixed complexes including halides and pseudohalides (such as NCS$^-$) have been reported for aluminium(III) and iron(III), [(MCl$_3$)NCS]$^-$ where M = Al(III) or Fe(III) [15]. Actually, also mixed complexes involving anions with significantly different shapes and dimensions, such as bis(trifluoromethanesulfonyl)imide and chloride, have been reported, at least as transient species. In particular, it has been shown that even if the addition of AlCl$_3$ to pyrrolidinium, piperidinium or imidazolium bis(trifluoromethanesulfonyl)imides ([C$_4$mpyr][Tf$_2$N], [C$_3$mpip][Tf$_2$N],

Fig. 1 ILs with metal
chelate anions
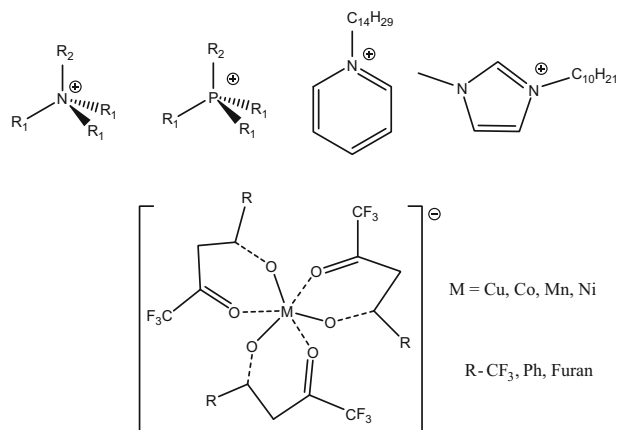
and [bmim][Tf$_2$N]) gives, depending on composition and temperature, phase separation due to the formation of Al(Tf$_2$N)$_3$ (lower phase) and the homocomplex [AlCl$_4$]$^-$ (upper phase), these species arise from the disproportionation of the initially formed mixed complexes, [AlCl$_x$(Tf$_2$N)$_{4-x}$]$^-$ (where x may be 3 or 4) [16, 17]. These transient species present relevant properties, as shown by the fact that while aluminium deposition doesn't occur with [AlCl$_4$]$^-$ in chloroaluminated ILs, this process can be performed in the above reported mixtures and the mixed complex [AlCl$_3$(Tf$_2$N)]$^-$ has been proposed as the electroactive aluminium-containing species. A similar behaviour has been attributed to [AlCl$_2$(Tf$_2$N)$_2$]$^-$ [18].

Finally, it is necessary to mention that hydrophobic ILs composed of simple organic cations (ammonium, phosphonium, pyridinium and imidazolium) having as counteranion chelate anions of monovalent transition metal (Mn, Co, Ni, Cu) have been recently prepared, characterized and used as catalysts in oxidation reactions [19] (Fig. 1).

3 Coordination Structure of Transition Metal Salts in Ionic Liquids

It is well known that in the case of halometallates the coordination chemistry of the anion and, consequently, the Lewis acidity of the resulting IL can be modified by tuning the ratio of metal chloride to organic chloride (generally expressed as mole fraction of metal chloride, χ_{MCl_x}).

Equations (1–3) show the acid−base reactions that occur when an organic chloride salt (IL = [cat]Cl) and AlCl$_3$ are mixed.

$$[cat]Cl + AlCl_3 \rightleftarrows [cat][AlCl_4] \tag{1}$$

$$[cat][AlCl_4] + AlCl_3 \rightleftarrows [cat][Al_2Cl_7] \tag{2}$$

$$[cat][Al_2Cl_7] + AlCl_3 \rightleftarrows [cat][Al_3Cl_{10}] \tag{3}$$

When χ_{AlCl_3} is 0.5, $[AlCl_4]^-$ is practically the sole anionic species present in solution; however, in systems with $\chi_{AlCl_3} > 0.5$ multinuclear chloroaluminate anions are formed which are in equilibrium each other. In the presence of an excess of organic chloride salt ($\chi_{AlCl_3} < 0.5$) the resulting ILs are Lewis basic systems becoming neutral at $\chi_{AlCl_3} = 0.5$ and Lewis acidic at $\chi_{AlCl_3} > 0.5$ [20]. The tunable and variable acidity of these salts is therefore determined by the molar fraction of the Lewis acid, a parameter that strongly affects also all the physico-chemical and thermal properties of the resulting melts. Anionic speciation based on analogous equilibria has been reported also for many other chlorometallate systems, such as chloroferrate(III), chloroindanate(III) and chlorogallate(III).

On the other hand, the existence of several anions and equilibria has been reported also for systems arising by the addition of Me(II) salts ($ZnCl_2$, $CuCl_2$, $SnCl_2$ and $FeCl_2$) to organic chloride salts although, at least for some of these metals, the nature of the predominant species is still the object of debate. On the basis of fast atom bombardment mass spectra (FAB-MS) of the $ZnCl_2$–[emim]Cl mixtures it was reported [21] the formation of the $ZnCl_3^-$ ion under basic conditions (excess of chloride anion), a result subsequently confirmed [22] by Lecocq et al. through NMR and MS analyses. On the contrary, an anion speciation based exclusively on Cl^-, $[ZnCl_4]^{2-}$, $[Zn_2Cl_6]^{2-}$, $[Zn_3Cl_8]^{2-}$ and $[Zn_4Cl_{10}]^{2-}$ anions has been reported in a more recent investigation [23], whereas the Raman spectra of proper mixtures of [bmim]Cl and $ZnCl_2$ appeared to suggest the presence of $[ZnCl_4]^{2-}$ as the main ionic species at $\chi_{ZnCl_2} < 0.3$ [24]. A different speciation has been proposed for dissolution of $SnCl_2$ in chloride-based ILs [25]. In this case, when the anionic speciation of the resulting chlorostannate(II) liquids has been investigated in both solid and liquid states, no evidence was collected for the existence of $[SnCl_4]^{2-}$ within the entire range of χ_{SnCl_2}, although such anion was reported [26] in the literature for chlorostannate(II) organic salts crystallized from organic solvents. Both liquid and solid systems contained $[SnCl_3]^-$ in equilibrium with Cl^-, when χ_{SnCl_2} was < 0.50, $[SnCl_3]^-$ in equilibrium with $[Sn_2Cl_5]^-$, when χ_{SnCl_2} was > 0.50, and only $[SnCl_3]^-$ when $\chi_{SnCl_2} = 0.5$.

Finally, in the case of $CuCl_2$ in [bmim]Cl the presence under specific conditions of the trigonal and deformed tetrahedral copper(II) chloride coordination complexes, $[CuCl_3]^-$ and $[CuCl_4]^{2-}$ respectively, has been proposed on the basis of both experimental (XPS, UV–Vis and EPR) and DFT calculations [27].

Although the above reported examples are related to metal salts in ILs having strongly coordinating anions, anionic speciation can occur also in weakly coordinating ILs, such as bis(trifluoromethylsulfonyl)imide-based ILs. This "innocent" anion can act as a monodentate ligand coordinating the metal directly through either an N or O atom or as a bidentate ligand chelating the metal ion via O, O or O, N atoms to give stable six-membered chelate rings. The coordination via two oxygen atoms, each placed on a different sulfonyl group, assures, however, a remarkable flexibility due to some structural features of this anion and, therefore, it should be preferred. In particular, this kind of coordination guarantees the fact that: (1) the rotation of the CF_3SO_2 moieties around the N–S bonds allows to modify distance and relative orientation of
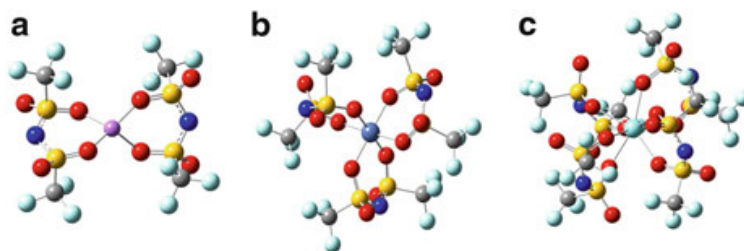
Fig. 2 (**a**) $[Li(Tf_2N)_2]^-$; (**b**) $[Ni(Tf_2N)_3]^-$; (**c**) $[Y(Tf_2N)_4]^-$ complexes. In all complexes the ligands ($[Tf_2N]^-$) are in *trans* conformation and the CF_3 groups are arranged to form a sort of belt, probably due to an interligand dispersive interaction

the two chelating oxygen atoms thus favouring the adoption of the preferred coordination geometry of the metal cation; (2) the presence of 2 equiv. oxygen atoms on each sulfonyl group adds further geometrical flexibility; and (3) free rotation of the CF_3 groups can reduce the sterical hindering in the coordination complex.

Furthermore, considering that each metal cation is characterized by a peculiar charge (M) and a preferred coordination number (N), and that in common bis (trifluoromethylsulfonyl)imide-based ILs the dissolution of single charged species should be favoured with respect to uncharged or multicharged species [28], since bis(trifluoromethylsulfonyl)imide is a mono charged anion and a bivalent ligand, coordination complexes of the type $[M^{+M}(Tf_2N)_{N/2}]^{-1}$ should be the most stable. This is the situation characterizing single charged metals in tetrahedral coordination complexes, typical example (Li(I)), double charged metals in octahedral coordination complexes, typical examples Ni(II), Co(II), Zn(II), Cu(II) and so on, or triple charged metals in square antiprism coordination complexes, typical example Y(III). In Fig. 2, an optimized structure for each of the above-mentioned coordination complexes $[M^{+M}(Tf_2N)_{N/2}]^{-1}$ is reported.

The stability of these coordination complexes with respect to the neutral salts determines the chemical and electrochemical behaviour of these solutions as well as their surface properties. The coordination of the metal cation with the IL anion and the interaction of the arising complex with the counteranion (IL cation) strongly affects the metal ion distribution inside the IL and at the IL/air surface [12, 27, 29] thus determining the IL properties in the bulk and at the interface.

X-ray photoelectron spectroscopy (XPS), a technique able to provide information about elemental and chemical state of a sample, has been employed in the last years not only to investigate the surface of solid materials, including metals and metal compounds, but also of metal-containing ILs [12]. Since the species present in ILs are highly mobile in comparison with solid ionic compounds, the surfaces show phenomena such as surface segregation and enrichment, preferential orientation, and others in much larger extent than crystalline or amorphous solids. In the case of "pure" ILs surface often presents peculiar characteristics, such as the enrichment of the cation alkyl chains at the expense of the polar cation head groups and the anions. It is noteworthy that the enhancement effect depends on alkyl chain length and anion size, and more in particular, it is most evident for the smallest anions and least pronounced for the largest anions [30, 31]. On these bases, it is reasonable to expect that systems constituted by metal ions dissolved in ionic

liquids, because of the larger number of chemical species present in such ionic mixtures, may be characterized by structural differences between bulk and surface. In fact, the presence of complexation equilibria can lead to the simultaneous existence of several anions having different size and therefore affinity toward the liquid/gas interface. It is noteworthy that in these systems, slight variations in IL/metal ratio can dramatically change the surface composition with important consequence when ILs are used for surface processes, for example in the ILs chemistry on supported materials (supported IL phase, SILP).

3.1 Coordination Structure and Physico-Chemical Properties

Addition of metal halides ($AlCl_3$, $ZnCl_2$, $FeCl_3$ and so on) to organic chlorides gives ILs whose physico-chemical properties are determined by anion speciation. The effect of anionic composition on melting point, glass transition temperature, viscosity, and conductivity has long been recognized. In the case of 1-methyl-3-ethylimidazolium chloride/aluminium trichloride ([emim]Cl/$AlCl_3$) viscosity remains practically constant at values significantly lower than the starting IL, until the amount of [emim]Cl is below 50 mol%, however, when [emim]Cl exceed 50 mol%, the absolute viscosity begins to increase [2]. This increase in viscosity, which is related to the increase in chloride ion concentration, has been attributed to hydrogen bonding between chloride ion and imidazolium cation. The formation of the metal complexes ([emim]Cl below 50 mol%) therefore decreases, at least in this case, the viscosity reducing the hydrogen bond ability of the anion and the Coulombic forces inside the IL, as a consequence of the lower charge density of the $Al_nCl_m^-$ anions. Moreover, on the basis of a more recent investigation in which density, viscosity and conductivity of 1-butyl-3-methylimidazolium and 1-hydrogen-3-methylimidazolium chloroaluminates, [bmim]Cl–$AlCl_3$ and [Hmim]Cl–$AlCl_3$, have been determined varying the molar composition in the temperature range 293.15–343.15 K, it has been inferred [32] that not only the hydrogen bonding but also the structural geometry of the formed complexes and cation/anion interaction have a significant effect on the physico-chemical properties of these liquids. An analogous behaviour of viscosity, i.e. high viscosity values in the case of very basic compositions (excess of chloride) and a dramatic decrease with increasing Lewis acid concentration, was observed also in the case of chlorostannates(II) (the investigated system was [omim]Cl–$SnCl_2$), the minimum viscosity value for this system being at $\chi_{SnCl_2} = 0.5$ [25].

Furthermore, it is noteworthy that for this class of metal-containing ILs (imidazolium chlorometallates) an interesting and not predictable correlation has been found between chlorometallate compositions, i.e. anion speciation, and Lewis acidity using the Gutmann acceptor number [33].

Although the mixtures of metal salts in ILs bearing weakly coordinating anions have been scarcely investigated, it is nevertheless known to researchers working in ILs chemistry that the unwanted presence in bis(trifluoromethylsulfonyl)imide-based ILs of even small amounts of $LiTf_2N$, arising from the metathesis reaction,
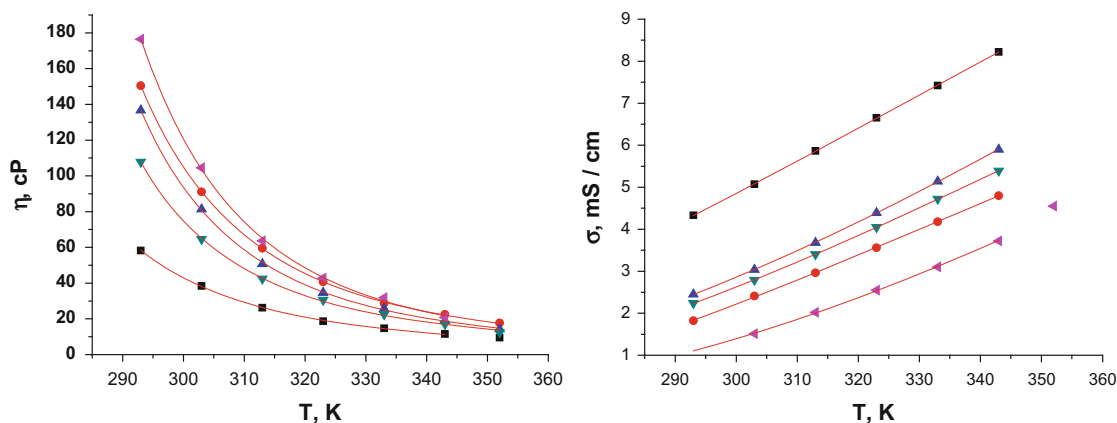
Fig. 3 Temperature dependence of viscosity and conductivity for [bmim][Tf$_2$N] (*black square*); [bmim][Tf$_2$N]/Co(Tf$_2$N)$_2$ (*red circle*); [bmim][Tf$_2$N]/Cu(Tf$_2$N)$_2$ (*blue triangle*); [bmim][Tf$_2$N]/Ni(Tf$_2$N)$_2$ (*green inverted triangle*) and [bmim][Tf$_2$N]/Al(Tf$_2$N)$_3$ (*pink right-pointing triangle*). At 0.1 mol fraction of Me(Tf$_2$N)$_n$

dramatically decreases the melting temperature of the resulting IL and modifies its physico-chemical properties (viscosity, conductivity, hydrophobicity, polarity and so on). Generally, the presence of the metal salt increases viscosity and decreases conductivity with respect to the pure IL and the entity of the effect is determined by the metal cation nature. In contrast with chloride-based ILs, the interaction between cations and anions in organic bis(trifluoromethylsulfonyl)imide is very low and probably moderately affected by the formation of the metal complexes which can, however, modify the packing ability of the system and the "holes" availability. Fig. 3 illustrates the temperature dependence of viscosity and conductivity for some [bmim][Tf$_2$N]-Me(Tf$_2$N)$_n$ (Me = Cu, Co, Al, Ni) mixtures, at $\chi_{Me(Tfl_2N)_n} = 0.1$.[1]

It is noteworthy that both these properties are strongly affected by the temperature; however, while viscosities of the investigated [bmim][Tf$_2$N]-Me(Tf$_2$N)$_n$ (Me = Cu, Co, Al, Ni) mixtures at relatively high temperatures (340–350 K) converge towards the values of the pure IL, conductivities remain parallel and always significantly lower than the pure IL.

4 Application of Halometallates in Synthesis: Alkylation Reactions

Since the earlier development of chloroaluminate ILs in the 1960s, halometallates have been largely used as replacements for conventional acid catalysts for many different applications [34]. In particular, as a consequence of the industrial interest, the petroleum industry has been by far the largest applicant of this kind of ILs; alkylations of arenes (Friedel–Crafts reaction) and alkanes (in particular, of isobutane with 2-butene for the production of high-octane gasoline) have been widely

---

[1] Unpublished results from this laboratory.

investigated (from 2005 more than 50 patents have been published on alkylation with chloroaluminate-based ILs!). The high potential of ILs as alkylating catalysts is best expressed by the fact that an industrial alkylation plant in China is now running with an IL as catalyst [35] and the use of ILs was also studied by several companies (e.g. by the IFP in a pilot plan) although specific details have been not reported up to now.

Wilkes first reported [36] the Friedel–Crafts reactions of aromatic substrates, such as benzene, toluene, chlorobenzene and nitrobenzene in [emim]Cl–AlCl₃: with the exception of nitrobenzene the aromatic substrates were efficiently alkylated. Subsequently, chloroaluminate ILs have been extensively tested as solvents and catalysts for alkylation of other aromatic systems, such as naphthalene and anthracene [37, 38] and, more recently, also other halometallate-based ILs have been investigated [38] for the same reaction.
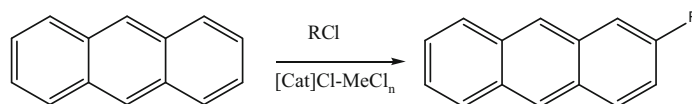

In particular, in 2006 Yin et al. [39] reported the syntheses of diphenylmethane and its derivatives through Friedel–Crafts benzylation of benzene and derivatives with benzyl chloride through the use, for the first time, of the moisture-stable [bmim]Cl/ZnCl₂, [bmim]Cl/FeCl₃, and [bmim]Cl/FeCl₂ systems as solvents and catalysts. Easy separation of the reaction products, increased reaction rates with respect to conventional molecular solvents, and high selectivity towards monoalkylated products were obtained in these media under specific conditions.
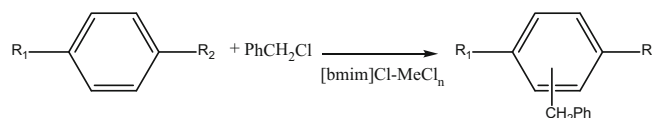
Recently, also the moisture-stable chloroindanate ILs have been used [40] as versatile catalysts for the reaction of phenols with alkenes, obtaining high conversions to alkylated phenols with high selectivities. However, the supposition that moisture-stable chlorometallates can always substitute chloroaluminate-based ILs does not found a general agreement from the literature. Indeed, their lower Lewis acidities have been reported to be an important detrimental factor in some reactions: for example, in the case of anthracene alkylation [38], it has been stressed that [emim]Cl/AlCl₃ gave the best results in terms of both yield (74.5%) and selectivity (82.9%).

Inspired by the outstanding strong Lewis acidity of chloroaluminate ILs, Chauvin et al. firstly investigated the use of [bmim]Cl–AlCl₃ as catalysts in another important refinery process, the isobutane alkylation with light alkenes to obtain branched alkanes [41]. Despite the fact that the alkylate products obtained in chloroaluminate-based ILs alone were characterized by a relatively low content of octane components and a low trimethylpentane/dimethylhexane ratio [41], also

other chloroaluminate systems have been studied [14, 42–44] as catalysts for this reaction. It is noteworthy that, according to the accepted mechanism, in this case strong Brønsted acids are the catalytic species which can be generated from the interaction between a strong Lewis acid and a Brønsted acid; in the case of [bmim] Cl–AlCl$_3$ they arise from the interaction of Lewis acidic chloroaluminates ([Al$_2$Cl$_7$]$^-$ or [Al$_3$Cl$_{10}$]$^-$) with HCl. Acidic protons are indeed inherently present in halogenoaluminate ILs due to the reaction of AlCl$_3$ with the IL cation or traces of water, if the preparation is done in a not very dry atmosphere. Since acidity is a crucial parameter in alkylation, which can be controlled by the molar fraction of the Lewis acid and the addition of "electron donating substances", various additives including metal chlorides, organosulfur compounds and *tert*-butyl halides, were investigated to improve the catalytic performance of the chloroaluminate ILs in this reaction [42–45].
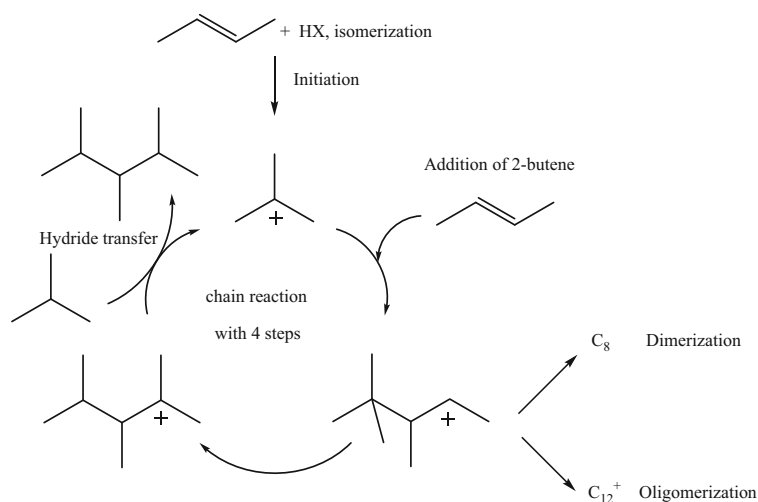
In this contest, interesting results have been recently obtained by addition of acid cation exchange resins (dry or with small amount of water) or 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate ([(HO$_3$Sbu)mim][HSO$_4$]) to the catalytic medium, 1-octyl-3-methylimidazolium bromide–aluminium chloride, [omim]Br–AlCl$_3$. Under optimized conditions, a content of desired trimethylpentanes (up to 64%) and thus an octane number (RON up to 96) comparable or higher than that with H$_2$SO$_4$ [46] were obtained. First of all, it is noteworthy that [omim]Br–AlCl$_3$ was chosen because the anionic species formed, [AlCl$_3$Br]$^-$ or [Al$_2$Cl$_6$Br]$^-$, show higher Lewis acidity compared to complexes containing only chloride as halogenide. Furthermore, a Brønsted acid able to give highly acidic protons was added. In particular, in the case of 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate ([(HO$_3$Sbu)mim][HSO$_4$]), the reaction of the Lewis acidic haloaluminate with the sulfonic group of the functionalized IL leads to a dimeric structure generating superacid protons which can react with either the hydrogensulfate or the [Al$_2$Cl$_7$]$^-$ anion species. The Lewis acid is able to react with hydrogensulfate to give HCl and another highly acidic proton. On the other

hand, HCl interacts with the $[Al_2Cl_7]^-$ anion leading to $H[AlCl_4]$ which is regarded as a superacid.
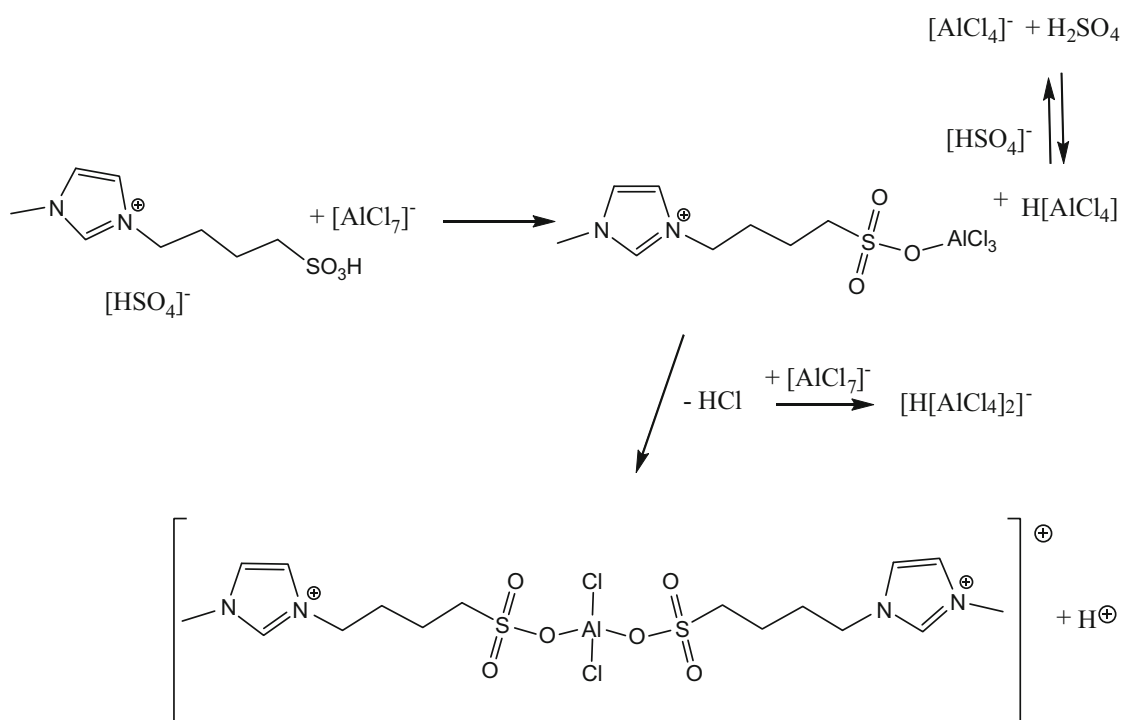
Thus, on the basis of these latter results the possibility to control the Brønsted acidity by forming superacidic IL species or superacidic species in ILs, via protic additives, appears a particularly promising approach to obtain high yields and selectivities in isobutane alkylation. However, the efficiency of this reaction is also determined by reaction conditions (temperature, stirring, paraffin/olefin ratio and residence parameters). Recent kinetic studies, carried out in reactors with and without stirring, have shown [47] that the biphasic alkylation of light olefins with *i*-paraffins using chloroaluminate ILs as catalysts is an extremely fast reaction, leading to a low effectiveness factor of the IL catalyst. In a well-mixed reactor the effective reaction rate is determined by the size of the interphase and of the characteristic length of the diffusion in the IL phase, the thickness of an IL film or the diameter of the IL droplets dispersed in the organic phase [48].

Although chloroaluminate ILs are the most investigated systems for this reaction, recently also chlorogallate ILs have been tested [49]. These latter ILs are more resistant to hydrolysis than the analogous chloroaluminate ones and are characterized by a Lewis acidity comparable or slightly higher than those of chloroaluminate ILs having analogous compositions. In particular, a series of triethylammonium-based chlorogallate ILs with a variety of Lewis acidity have been applied to isobutane alkylation. The triethylammonium chloride–gallium trichloride ($[Et_3NH]Cl–GaCl_3$) with $\chi_{GaCl_3} = 0.65$ displayed a potential catalytic activity and the addition of CuCl (5% mol) dramatically enhanced the alkylation reaction; also in this case, up to 70.1% C8 selectivity and 91.3 RON were achieved under selected conditions (0.5 MPa, 900 r min^{-1}, 15 min, 288 K).

5   Conclusions

Ionic liquids containing metal salts represent a fascinating world in the ILs universe that can open up new possibilities in important areas such as catalysis, electrochemistry and material science. The physico-chemical properties of the included metals and the structural organization of the ionic systems arising from the interaction between the "appropriate IL" and the metal salt can give new materials, catalysts and solvents. Bulk and surface properties of ILs containing a metal cation can be substantially modified changing IL anion (more or less coordinating anions can give ILs having completely different properties and abilities) and IL/metal salt ratio, although also the IL cation, in particular when functionalized, can contribute to this purpose.

References

1. Plechkova NV, Seddon KR (2008) Applications of ionic liquids in the chemical industry. Chem Soc Rev 37:123
2. Wasserscheid P, Welton T (2008) Ionic liquids in synthesis, 2nd edn. Wiley-VCH, Weinheim
3. Chiappe C, Pieraccini D (2005) Ionic liquids: solvents properties and organic reactivity. J Phys Org Chem 18:275
4. Chiappe C, Malvaldi M (2010) High concentrated solutions of metal cations in ionic liquids: current status and future challenges. Phys Chem Chem Phys 12:11191
5. Binnemans K (2007) Lanthanides and actinides in ionic liquids. Chem Rev 107:2592
6. Dupont J, de Souza RF, Suarez PAZ (2002) Ionic liquid (molten salt) phase organometallic catalysis. Chem Rev 102:3667
7. Wasserscheid P, Keim W (2000) Ionic liquids-new "Solutions" for transition metal catalysis. Angew Chem 39:3772
8. Pârvulescu VI, Hardacre C (2007) Catalysis in ionic liquids. Chem Rev 107:2615
9. Lee JW, Jang HB, Shin JY, Chun YY, Song CE, Lee S (2010) Toward understanding the origin of positive effects of the ionic liquids on catalysis: formation of more reactive catalysis and stabilization of reactive intermediates and transition. Acc Chem Res 43:985
10. Dyson PJ, Geldbach TJ (2005) Metal catalysed reactions in ionic liquids. Springer, Dordrecht
11. Endres F, Abbott AP, MacFarlane DR (2008) Electrodeposition from ionic liquids. Wiley-VCH, Wienheim
12. Chiappe C, Pomelli CS, Bardi U, Caporali S (2012) Interface properties of ionic liquids containing metal ions: features and possibilities. Phys Chem Chem Phys 14:5045
13. Di Francesco F, Calisi N, Creatini M, Melai B, Salvo P, Chiappe C (2011) Water sorption by anhydrous ionic liquids. Green Chem 13:1712
14. Yoo K, Namboodiri VV, Varma RS, Smirniotis PG (2004) Ionic liquid-catalyzed alkylation of isobutane with 2-butene. J Catal 222:511
15. Algra G, Balt S (1983) Reversible substitution reactions of tetrahedral tetrahaloferrates(III) with thiocyanate. Inorg Chim Acta 75:179
16. Rodopoulos T, Smith L, Horne MD, Rüther T (2010) Speciation of aluminium in mixtures of the ionic liquids [C3mpip][NTf2] and [C4mpyr][NTf2] with AlCl3: an electrochemical and NMR spectroscopy study. Chem Eur J 16:3815
17. Eiden P, Liu Q, El Abedin SZ, Endres F, Krossing I (2009) An experimental study of the aluminium species present in mixtures of AlCl3 with the ionic liquids [BMP]Tf2N and [EMIm]Tf2N. Chem Eur J 15:3426

18. Rocher NM, Izgorodina EI, Rüther T, Forsyth M, MacFarlane DR, Rodopoulos T, Horne MD, Bond AM (2009) Aluminium speciation in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsufonyl)amide/AlCl$_3$ mixtures. Chem Eur J 15:3435

19. Zhang P, Gong Y, Lv Y, Guo Y, Wang Y, Wang C, Li H (2012) Ionic liquids with metal chelate anions. Chem Commun 48:2334

20. Piao LY, Fu X, Yang YL, Tao GH, Kou Y (2004) Alkylation of diphenyl oxide with α-dodecene catalyzed by ionic liquids. Catal Today 93:301

21. Hsiu S, Huang J-F, Sun I-W, Yuan C-H, Shiea J (2002) Lewis acidity dependency of the electrochemical window of zinc chloride-1-ethyl-3-methylimidazolium chloride ionic liquids. Electrochim Acta 47:4367

22. Lecocq V, Graille A, Santini CC, Baudouin A, Chauvin Y, Basset JM, Arzel L, Bouchu D, Fenet B (2005) Synthesis and characterization of ionic liquids based upon 1-butyl-2,3-dimethylimidazolium chloride/ZnCl$_2$. New J Chem 29:700

23. Estager J, Nockemann P, Seddon KR, Swadźba-Kwaśny M, Tyrrell S (2011) Validation of speciation techniques: a study of chlorozincate(II) ionic liquids. Inorg Chem 50:5258

24. Alves MB, Santos VO, Soares VCD, Suarez AZ, Rubin JC (2008) Raman spectroscopy of ionic liquids derived from 1-n-butyl-3-methylimidazolium chloride and niobium chloride or zinc chloride mixtures. J Raman Spectrosc 39:1388

25. Currie M, Estager J, Licence P, Men S, Nockemann P, Seddon KR, Swadźba-Kwaśny M, Terrade C (2013) Chlorostannate(II) ionic liquids: speciation, Lewis acidity, and oxidative stability. Inorg Chem. doi:10.1021/ic300241p

26. Yin RZ, Yo CH (1998) Structural and optical properties of the (CnH$_2$n + 1NH$_3$)2SnCl$_4$ (n = 2, 4, 6, 8, and 10) System. Bull Korean Chem Soc 19:947

27. Caporali S, Chiappe C, Ghilardi T, Pomelli CS, Pinzino C (2012) Coordination environment of highly concentrated solutions of Cu(II) in ionic liquids through a multidisciplinary approach. Chemphyschem 14:1885

28. Chiappe C, Pomelli CS (2013) Computational studies on organic reactivity in ionic liquids. Phys Chem Chem Phys 15:412

29. Chiappe C, Malvaldi M, Melai B, Fantini S, Bardi U, Caporali S (2010) An unusual common ion effect promotes dissolution of metal salts in room-temperature ionic liquids: a strategy to obtain ionic liquids having organic–inorganic mixed cation. Green Chem 12:77

30. Kolbeck C, Cramer T, Lovelock KRJ, Paape N, Schulz PS, Wasserscheid P, Maier F, Steinrück HP (2009) Influence of different anions on the surface composition of ionic liquids studied using ARXS. J Phys Chem B 113:8682

31. Maier F, Cremer T, Kolbeck C, Lovelock KRJ, Paape N, Schulz PS, Wasserscheid P, Steinrück HP (2010) Phys Chem Chem Phys 12:1905

32. Zheng Y, Dong K, Wang Q, Zhang J, Lu X (2013) Density, viscosity and conductivity of Lewis acid 1-butyl- and 1-hydrogen-3-methylimidazolium chloroaluminate ionic liquids. J Chem Eng Data. doi:10.1021/je3004904

33. Estager J, Oliferenko AA, Seddon KR, Swadźba-Kwaśny M (2010) Chlorometallate(III) ionic liquids as Lewis acidic catalysts: a quantitative study of acceptor properties. Dalton Trans 39:11375

34. Welton T (2004) Ionic liquids in catalysis. Coord Chem Rev 248:2459

35. Liu Z, Zhang R, Xu C, Xia R (2006) Oil Gas J 104:52

36. Boon JA, Levisky JA, Pflug JL, Wilkes JS (1986) Friedel-Crafts reactions in ambient-temperature molten salts. J Org Chem 51:480

37. Blanco CG, Banciella DC, González Azpíroz MD (2006) Alkylation of naphthalene using three different ionic liquids. J Mol Catal A 253:203

38. Chen M, Luo Y, Li G, He M, Xie J, Li H, Yuan X (2009) Alkylation of anthracene to 2-isopropylanthracene catalyzed by Lewis acid ionic liquids. Korean J Chem Eng 26:1563

39. Yin D, Li C, Tao L, Yu N, Hu S, Yin D (2006) Synthesis of diphenylmethane derivatives in Lewis acidic ionic liquids. J Mol Catal A 245:260

40. Gunaratne HQN, Lotz TJ, Seddon KR (2010) Chloroindanate(III) ionic liquids as catalysts for the alkylation of phenols and catechol with alkene. New J Chem 34:1821

41. Chauvin Y, Hirschauer A, Olivier H (1994) Alkylation of isobutane with 2-butene using 1-butyl-3-methylimidazoliumchloride aluminium-chloride molten-salts as catalysts. J Mol Catal 92:3508
42. Zhang J, Huang CP, Chen BH, Li JW, Li YX (2008) Alkylation of isobutane and butane using chloroaluminate imidazolium ionic liquid. Korean J Chem Eng 25:982
43. Liu Y, Hu RS, Xu CM, Su HQ (2008) Alkylation of isobutane with 2-butene using composite ionic liquid catalysts. Appl Catal A Gen 346:189
44. Huang CP, Liu ZC, Xu CM, Chen BH, Liu YF (2004) Effects of additives on the properties of chloroaluminate ionic liquid catalyst for alkylation of isobutene and butane. Appl Catal A Gen 277:41
45. Aschauer S, Schilder L, Korth W, Fritschi S, Jess A (2011) Liquid-phase isobutane/butane-alkylation using promoted Lewis-acidic IL-catalysts. Catal Lett 141:1405–1419
46. Bui TLT, Korth W, Aschauer S, Jess A (2009) Alkylation of isobutane with 2-butene using ionic liquids as catalyst. Green Chem 11:1961
47. Aschauer SJ, Jess A (2012) Effective and intrinsic kinetics of the two-phase alkylation of i-paraffins with olefins using chloroaluminate ionic liquids as catalyst. Ind Eng Chem Res 51:16288
48. Schilder L, Maass S, Jess A (2013) Effective and intrinsic kinetics of liquid-phase isobutane/2-butene alkylation catalyzed by chloroaluminate ionic liquids. Ind Eng Chem Res 52:1877
49. Qi XX, Ying ZG, Zhong CJ (2012) Chlorogallate(III) ionic liquids: synthesis, acidity, determination and their catalytic performances for isobutene alkylation. Sci China Chem 55:1547