

# PROPERTIES AND APPLICATIONS OF CHLOROALUMINATE AS ROOM TEMPERATURE IONIC LIQUID

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*Ionic liquids are emerging as new solvents and have wide applications in various fields. One of the important class of ionic liquid is chloroaluminate, whose properties can be tailored by varying the concentration of aluminium chloride and is miscible in all proportions with organic liquids. In this report we review the properties and applications of chloroaluminate room temperature ionic liquid.*

*Keywords: Ionic liquid, chloroaluminate, room temperature melt*

## INTRODUCTION

In general an ionic liquid is a liquid that consists only of ions. However, this term includes an additional special definition to distinguish it from the classical definition of a molten salt [1,2]. While a molten salt is generally refer to a high melting highly viscous and very corrosive medium. Whereas, ionic liquids are liquid at room temperature ( $< 373$  K) and have relatively low viscosity. The apparently somewhat arbitrary line drawn between molten salts and ionic liquids at melt temperature of 373.8 K can be justified by the abrupt improvements in the range of applications for liquid salts below this temperature. Even though some samples are known in which high temperature salt melts have been successfully used as reaction media for synthetic application [3] only a liquid range below 373.8 K can enable the versatile substitution of conventional organic solvents by liquids. The development of ionic liquid goes back to 1914. First research efforts dealt with the synthesis of ethylammonium nitrate [4]. This salt is liquid at room temperature but usually contains a small amount of water (200-600 ppm) [5,6]. The first ionic liquids with chloroaluminate ions were developed in 1948 by Hurley and Wier at the Rice Institute in Texas as bath solutions for electroplating aluminium

[7,8]. However these systems were not studied until the late 1970s when the groups of Oster Young and Wilkes rediscovered them.

For the first time they succeeded in preparing room temperature liquid chloroaluminate melts [9,10]. Research and development concentrated mainly on electrochemical applications at this time. As early as 1967 a publication by Swain et al described the use of tetra-*n*-hexylammonium benzoate as a solvent for kinetic and electro chemical investigations. Even though the liquid salt was a hemihydrate at room temperature, this research work had a pioneering significance because of quantitative determination of the ionization strength of the ionic medium. In the early 1980s Seddon and Hussey generally started with electrochemical aspects of the relevant transitions metal complexes, [11,12,13,14] followed by spectroscopic and complex chemistry experiments [15,16]. The first publications in ionic liquids as a new reaction media and catalysts for organic synthesis appeared at the end of 1980s. Acidic ionic liquids with chloroaluminate ions proved to be effective Friedel Crafts catalysts [17]. Phosphonium halide melts were used successfully in nucleophilic aromatic substitution reactions [18].

The purity of the system is essential for many solvent applications and for characterization of

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their physical and chemical properties. Preparation of chloroaluminate room temperature ionic liquid involves the mixing of solid aluminium chloride with solid 1-ethyl-3-methylimidazolium chloride, (ImCl). Mixing solids together results in exothermic reaction and generation of a clear, colourless liquid which is the room temperature molten salt. If the mole ratio of  $\text{AlCl}_3$ :ImCl is greater than, less than or exactly equal to 1.00:1.00, the solvents are Lewis acidic, basic or neutral accordingly.

### Preparation

Preparation of the haloaluminate (III) ionic liquids is simple. An imidazolium or pyridinium halide salt is mixed directly with the appropriate aluminium (III) halide in the ratios necessary to generate the composition required. Upon mixing an exothermic reaction occurs with the solid melting into a liquid. If the mixture is allowed to get too hot, hot spots occur and decomposition of the component may occur [19], which will lead to degradation of the ionic liquid. Many workers prefer to add the ingredients to a small amount of the liquid from a previous preparation. This allows efficient stirring and heat dissipation. Spectroscopically pure ionic liquids require that the aluminium (III) chloride be sublimed before use. However recently commercial aluminium (III) chloride has been used to prepare a solvent that was used for synthesis and without apparent loss of functionality [20]. However it must be noted that the introduction of proton and oxide impurities can have drastic effect on the chemistry of the chloroaluminate ionic liquid.

### Characteristic properties of chloroaluminate room temperature ionic liquid density

The dependence of density of the ionic liquid on the type of the cation and anion can be illustrated clearly by the example of chloroaluminate and bromoaluminate melts. A comparison of chloroaluminate melts with different cations reveals an almost linear relationship between the density and the length of the N-alkyl chain on the imidazolium cation [21].

The density of 1,3-dialkylimidazolium tetrachloroaluminate melts depends on the type of both alkyl groups. It can be concluded that the density of comparable ionic liquid decreases as the bulkiness of the organic cation increases. Slight structural changes in the cation allow a fine adjustment of the density. Varying the anion results in more obvious effects in several cases. With bromoaluminate it was possible to achieve unusual densities for common organic solvents [22]. Density measurements of ionic liquids with triflate or trifluoroacetate ions confirmed the more general result that a certain density range is established by the choice of anion within which a fine adjustment is possible for careful choice of the cation [23].

### Viscosity

The viscosity of ionic liquid is essentially determined by their tendency to form hydrogen bonds and by their strength of their VanderWaals interactions. The effect of hydrogen bonding becomes clear when for example the viscosities of chloroaluminate melts of different compositions are compared. Dependence of the dynamic viscosity  $\eta[\text{cp}]$  of two 1,3-dialkylimidazolium tetrachloroaluminate melts on the mole fraction of aluminium (III) chloride at 531 K.  $x(\text{AlCl}_3) < 0.5$  is a result of the formation of hydrogen bonds between the hydrogen atoms of the imidazolium cation and the basic chloride ion. This statement is supported by IR [24] and X-ray spectroscopy [25], ROESY-NMR and theoretical calculations [26]. In acidic mixtures, however the anions  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  are present in which the negative charge is delocalized. This leads to the formation of weaker hydrogen bonds and much lower viscosity. In addition viscosity of different hydrophobic ionic liquids with 1-n-butyl-3-methylimidazolium ions emphasizes the interplay between the VanderWaals interactions with hydrogen bonds. It is apparent that the stronger VanderWaals interactions result in higher viscosity of the ionic liquid. The structure of the cation also influences the viscosities of the ionic liquid. The lowest viscosities are usually obtained for the melts with 1-ethyl-3-methylimidazolium ion, in

which the side chain with sufficient mobility is combined with a low molar mass. Longer or fluorinated alkyl chains result in higher viscosities because of stronger VanderWaals interactions. The viscosity of ionic liquids can be lowered drastically in some cases by only slight increases in temperature or by addition of small amounts of organic solvents [27,28].

### Acidity and co-ordination ability

The acidity and the co-ordination properties of ionic liquids are essentially determined by the nature of its anion. Many intermediate levels between strongly basic, strongly acidic, strongly co-ordinating and practically non-co-ordinating can be realized by a careful choice of the anion [29]. In this context those ionic liquids have to be mentioned which form of anions do they possess whether neutral anion (eg.  $\text{AlCl}_4^-$ ) or an acidic anion (eg.  $\text{Al}_2\text{Cl}_7^-$ ) or a basic anion (eg.  $\text{Cl}^-$ ) by addition of a Lewis acid ( $\text{AlCl}_3$ ). Chloroaluminated melts are designated as basic when the molar ratio of  $\text{AlCl}_3$  is smaller than 0.5. A neutral melt is referred to as the one in which  $\text{AlCl}_3$  ratio is exactly 0.5 [30]. Finally an acidic chloroaluminate melt is one in which the  $\text{AlCl}_3$  ratio is larger than 0.5.

Two further phenomena in the field of acid/base chemistry of ionic liquids deserve to be mentioned. These are so-called "latent acidity" and 'super acidity' of protons in ionic liquids. The latent acidity of ionic liquids arises when weak bases are added to buffered neutral chloroaluminate melts. For example such melts are formed by adding an excess of alkali metal chloride to an acidic chloroaluminate melt. A buffered melt is one in which the neutrality of the melt is maintained by reaction of excess alkali metal chloride when acidic  $\text{AlCl}_3$  is added. The latent acidity of this neutral system becomes noticeable when a weak base such as *N,N*-dimethyl aniline, pyrrole or acetyl ferrocene is added. An adduct is formed with the added base and  $\text{AlCl}_3$  with precipitation of alkali metal chloride. This reaction is not observed in the absence of excess alkali metal cations. The super acidity is observed when strong mineral acids are dissolved in acidic chloro-

aluminate ionic liquids [31]. The acid strength of a superacid can be compared with those of conventional superacids. The superacid properties of protons in acidic chloroaluminate melts have been explained by the reaction between the dissolved  $\text{HCl}$  and the acidic species in the melt, which releases protons with extremely low solvation and therefore high reactivity. In contrast to the common superacid systems superacid ionic liquids are much easier and safer to handle [17]. They could be very promising alternatives to the normal superacids.

### Handling and availability

The handling of ionic liquids depends on the stability of the anion towards hydrolysis. Systems with chloroaluminate anions must be classified as extremely hygroscopic and labile towards hydrolysis. More difficulties arise when traces of water in chloroaluminate melts react with the anions of the melt to release superacid protons. These cause unwanted side reactions and possess a considerable potential for corrosion. Since the preparation of an anhydrous chloroaluminate melt is difficult, the level of tolerable impurities has to be determined for each application. To sum up handling and stability of chloroaluminate ionic liquid cannot be easily assessed, but it is mainly dependent on the nature of the anion. Although it is possible to use standard Schlenk techniques and most workers in this field prefer the use of high integrity glove boxes too. All glass apparatus is used and PTFE is preferred lubricant for ground-glass joints. The equipment should be thoroughly cleaned and dried before use. In our experience the use of glassware washed with acetone often leads to discoloration of the liquids particularly in acidic compositions. It is well known that acetone is difficult to remove from glassware, even with prolonged heating. The discoloration is possibly caused by Lewis acid catalyzed condensation reaction of the acetone with trace amounts of unreacted imidazole in the ionic liquid, such reactions are well known for the related pyrroles.

Little is known of the toxic effects of chloroaluminate ionic liquids. In a study of the effects of basic ( $\text{X}(\text{AlCl}_3) = 0.40$ )  $[\text{emim}]\text{Cl}/\text{AlCl}_3$  ionic

liquid on the skin of rats [32], it was shown that the ionic liquid induced significant skin irritation leading to ulceration in severe cases. Penetration of epidermis of toxic material assumed to be aluminium (III) chloride and a damage to the underlying cells was observed. It was shown that washing the exposed area of skin with water led to a reduction in the degree of damage incurred. This study demonstrated that this ionic liquids are potentially hazardous.

### Chloroaluminate species

Upon fusion aluminium chloride almost doubles the volume giving a low electrical conductance ( $< 3 \times 10^{-7} \Omega \text{ cm}^{-1}$ ) [33]. X-ray analysis of the pure metal reveals molecular liquid consisting of  $\text{Al}_2\text{Cl}_6$  [34] dimers comprising of tetrahedra sharing edge. However when mixed with chloride salts melts formed are conducting indicating of the presence of ions [35].

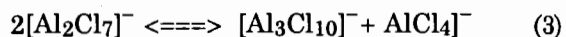
Raman, [36,37]  $^{27}\text{Al}$  NMR, [28] and mass spectra [38,39] all indicate that when  $X(\text{AlCl}_3) \leq 0.5$  in a pure ionic liquid,  $[\text{AlCl}_4]^-$  is the only chloroaluminate species present. These observations confirm the formation of the single compound  $[\text{cat}][\text{AlCl}_4]^-$  (where  $\text{cat} = [\text{emim}]^+$  or  $[\text{n-bpy}]^+$  that is indicated by the local maxima in the phase diagram of the chloroaluminate systems. When  $X(\text{AlCl}_3) = 0.5$  ions with the aluminium coordination number greater than four do not form, and excess  $\text{Cl}^-$  ions remain uncoordinated.

$^{27}\text{Al}$  NMR spectra of  $[\text{n-bpy}][\text{Cl}][\text{AlCl}_3]$  ionic liquids as a function of composition [40] at temperatures in the region 553-823 K consist of a single peak, which broadens considerably as more aluminium (III) chloride is added. At temperatures of 923 K and 1033 K the spectrum of a  $x(\text{AlCl}_3) = 0.58$  ionic liquid resolved into two peaks, one broad and the other sharp, attributable to  $[\text{Al}_2\text{Cl}_7]^-$  and  $[\text{AlCl}_4]^-$ , respectively. Similar results have been obtained for  $[\text{emim}][\text{Cl}][\text{AlCl}_3]$  ionic liquids [41]. Negative-ion FAB mass spectra of  $[\text{emim}][\text{Cl}][\text{AlCl}_3]$  ionic liquids have also shown peaks due to both  $[\text{AlCl}_4]^-$  and  $[\text{Al}_2\text{Cl}_7]^-$  ions. [42] X-ray diffraction studies of the  $[\text{n-bpy}][\text{Cl}][\text{AlCl}_3]$  ionic liquids ( $x(\text{AlCl}_3) = 0.5$  and  $0.67$ ) demonstrate the

presence of the tetrahedral  $[\text{AlCl}_4]^-$  ion and the  $[\text{Al}_2\text{Cl}_7]^-$  ion constructed from two corner-sharing  $(\text{AlCl}_4)$  tetrahedra. [43].

Unambiguous evidence for the presence of the  $[\text{Al}_3\text{Cl}_{10}]^-$  ion in  $[\text{emim}][\text{Cl}][\text{AlCl}_3]$  ionic liquids has been provided by the negative-ion FAB mass spectrum ( $X(\text{AlCl}_3) = 0.66$ ) [44] and by the infrared spectrum ( $X(\text{AlCl}_3) = 0.75$ ,  $T = 473 \text{ K}$ ). In addition, the infrared spectrum demonstrated the presence of the molecular species  $[\text{Al}_2\text{Cl}_6]$  indicating that it is unlikely that chloroaluminate species heavier than  $[\text{Al}_3\text{Cl}_{10}]^-$  make any contribution to the structure of these ionic liquids at any composition.

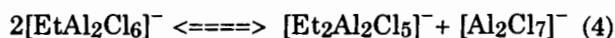
Clearly, the chemistry of these chloroaluminate ionic liquids is dependent upon the specific composition of the ionic liquid. The anionic chemistry of the addition of a chloride salt to aluminium (III) chloride can be described simply by the following reactions [Equations 1-3].



The equilibrium constant for Equation 2 has been measured several times for both the  $[\text{emim}][\text{Cl}][\text{AlCl}_3]$  and  $[\text{n-bpy}][\text{Cl}][\text{AlCl}_3]$  systems and is determined in the range from  $10^{-16}$  to  $10^{-17}$  at 313 K [45-47]. Heerman and D'Olieslager [48] measured potentiometric titration curves for  $[\text{n-bpy}][\text{Cl}][\text{AlCl}_3]$  ionic liquids containing a large excess of aluminium (III) chloride and calculated the equilibrium constant for Equation 3 to be  $2.09 + 0.06 \times 10^{-13}$  at 313 K.

In the ionic liquid, an analogy is often made between equilibrium and the autosolvolysis reaction of water. Since  $\text{Cl}^-$  is a Lewis base and  $[\text{Al}_2\text{Cl}_7]^-$  and  $[\text{Al}_3\text{Cl}_{10}]^-$  are both Lewis acids, the Lewis acidity or basicity of the ionic liquid may be manipulated by altering its composition. This leads to a nomenclature of the liquids in which compositions with an excess of  $\text{Cl}^-$  are called basic, those with an excess of  $[\text{Al}_2\text{Cl}_7]^-$  are called acidic, and those at the compound formation point are called neutral.

$^{27}\text{Al}$  NMR spectra of the closely related ethylchloroaluminate system  $[\text{emim}]\text{Cl}^-\text{EtAlCl}_2$  have also been measured and used to propose the presence of  $[\text{EtAlCl}_3]^-$  ions and molecular  $[\text{Et}_2\text{Al}_2\text{Cl}_4]^-$  in neutral compositions of the ionic liquid with an additional small amount of  $[\text{Et}_2\text{Al}_2\text{Cl}_5]^-$  in acidic compositions [36]. However, both  $^1\text{H}$  NMR and Raman spectroscopy of  $[\text{bmim}]\text{Cl}^-\text{EtAlCl}_2$  ionic liquids have shown that the distribution of the ethylchloroaluminate species follows the same pattern as it is found for chloroaluminate ionic liquids [49,50]. Hence, in basic ionic liquids  $\text{Cl}^-$  and  $[\text{EtAlCl}_3]^-$  ions are found, in moderately acidic ionic liquids  $[\text{EtAlCl}_3]^-$  and  $[\text{Et}_2\text{Al}_2\text{Cl}_5]^-$  ions are present, and in highly acidic compositions  $[\text{Et}_3\text{Al}_3\text{Cl}_7]^-$  and  $[\text{Et}_2\text{Al}_2\text{Cl}_4]^-$  become important components. Similar results are found for ionic liquids [51]. This simple model of the ethylchloroaluminate ionic liquids does not, however, give the full picture. Closer inspection of the Raman spectra of acidic  $[\text{bmim}]\text{Cl}^-\text{EtAlCl}_2$  ionic liquids reveals that the ions  $[\text{AlCl}_4]^-$  and  $[\text{EtAl}_2\text{Cl}_6]^-$  and the molecular species  $\text{Et}_2\text{AlCl}$  and  $\text{Et}_3\text{Al}_2\text{Cl}_3$  are present hence, exchange of ethyl and chloride ligands must be taking place, e.g.,



### Reactions with water

Aluminium (III) halides are extremely sensitive to even the smallest amounts of water. Hence, when water is added to a chloroaluminate ionic liquid of any composition, an exothermic reaction occurs with the evolution of  $\text{HCl}$ . The reaction produces oxide- and proton-containing species, both of which can interact with other solutes.

### Oxide containing species

$^{17}\text{O}$  NMR spectra of the  $[\text{emim}]\text{Cl}^-\text{AlCl}_3$  ionic liquids with added  $\text{OH}_2$  show a single signal in basic compositions, the chemical shift of which is dependent on the amount of  $^{17}\text{OH}_2$  added and the exact composition of the ionic liquid [52]. If proton impurity is removed by the addition of ethylaluminum (III) dichloride, [27] then a single resonance appears, the chemical shift of which is both composition and concentration independent. These

data suggest that in basic ionic liquids, there is a single chlorooxoaluminate species that, in the presence of proton, is in equilibrium with a chlorohydroxoaluminate species with the former being dominant at lower concentrations of oxide.

Negative-ion FAB mass spectra of basic  $[\text{emin}]\text{Cl}^-\text{AlCl}_3$  and  $[\text{n-bpy}]\text{Cl}^-\text{AlCl}_3$  ionic liquids show the presence of  $[\text{Al}_2\text{Cl}_5\text{O}]^-$  ions, [53] and the chlorooxoaluminate species are clearly seen in the  $^{17}\text{O}$  NMR spectra. However, no hydroxo-containing species was observed in particular, there is no evidence for the presence of  $[(\text{AlCl}_3(\text{OH}))]^-$  ion. The absence of  $[(\text{AlCl}_3(\text{OH}))]^-$  in the FAB experiments indicate the initial reaction of the basic ionic liquid with water. At higher concentrations of protons or hydroxyl ions, a second reaction becomes important, leading to the formation of the hydroxo species, possibly  $[(\text{AlCl}_3(\text{OH}))]^-$ .

In acidic ionic liquids, the  $^{17}\text{O}$  NMR spectra [54] clearly show three oxide-containing species whose relative concentrations are sensitive to both the precise composition of the ionic liquid and the amount of  $^{17}\text{OH}_2$  added. Again, using  $\text{EtAlCl}_2$  to remove the proton, one of these can be shown to be a chlorohydroxoaluminate species  $[(\text{Al}_2\text{Cl}_6(\text{OH}))]^-$ . The other two signals were attributed to  $[\text{Al}_2\text{Cl}_5\text{O}]^-$  and  $[\text{Al}_3\text{Cl}_6\text{O}_2]^-$  ions.

Negative-ion FAB mass spectra of oxide-free  $[\text{emim}]\text{Cl}^-\text{AlCl}_3$  ionic liquids have been recorded and the hydrolysis of the liquids in the spectrometer was observed [55]. After 30 min in the spectrometer, six oxide-containing ions were visible in the spectrum. The formation of  $[\text{Al}_3\text{Cl}_{10}\text{O}]^-$  ions (the structure of which has been determined crystallographically [56] directly from  $[\text{Al}_3\text{Cl}_{10}]^-$  was clearly demonstrated, as was that of  $[\text{Al}_2\text{Cl}_5\text{O}]^-$  from  $[\text{Al}_2\text{Cl}_7]^-$ . These initial reactions were shown to be followed by others, leading to  $[(\text{Al}_2\text{Cl}_6(\text{OH}))]^-$  as the dominant chlorohydroxoaluminate ion and to  $[\text{Al}_4\text{Cl}_9\text{O}_2]^-$ ,  $[\text{Al}_3\text{Cl}_7\text{O}(\text{OH})]^-$  and  $[\text{Al}_3\text{Cl}_6\text{O}_2]^-$  ions when the amount of water is increased.

Given that the amount of water added in the NMR experiment is likely to have been much greater than the amount that the ionic liquid was

exposed inside a high-vacuum mass spectrometer and that mass spectrometry is sensitive to the smallest amounts and these observations do not necessarily contradict each other.

Since the presence of water is ubiquitous, in even the most carefully controlled systems oxide impurities are always present. However, it has been clearly demonstrated that phosgene will remove all oxide contamination from both basic and acidic chloroaluminate ionic liquids [57]. It has also been shown that the solid, bis(trichloromethyl) carbonate (triphosgene), will do the same, at least in basic compositions [58].

### Proton containing species

The discovery of the superacidic behavior of acidic compositions of the chloroaluminate ionic liquids, protons become superacidic has stimulated a considerable amount of interest in their speciation [59,60]. The Bronsted acidity varies as both a function of proton concentration and precise composition of the ionic liquid, with Hammett acidities of upto - 18 for the most acidic ionic liquids.

In basic oxide-free [emim]Cl<sup>+</sup>AlCl<sub>3</sub><sup>-</sup> ionic liquids, the formation of the (HCl<sub>2</sub>)<sup>+</sup> ion has been clearly demonstrated over a range of compositions and concentrations [61-62] .

Some workers have claimed that in oxide-free acidic chloroaluminate ionic liquids, HCl is the only proton containing species [12] whereas the formation of the hydrogen-bonded species [AlCl<sub>4</sub>HCl]<sup>-</sup> and [Al<sub>2</sub>Cl<sub>7</sub>HCl] have also been suggested [63]. It is likely, since it has been shown that [AlCl<sub>4</sub>]<sup>-</sup> and [Al<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> are only poor hydrogen-bond acceptors, [64] that the bond is relatively weak. Hence, it would probably be a mistake to think of the species as long-lived isolable ions. It is better to view the situation as highly dynamic, with the HCl being solvated by the best hydrogen-bond acceptor ions available in the ionic liquid.

In addition to these protic species, ionic liquids with oxide impurities have been shown to contain chlorohydroxoaluminate ions [65-67].

Complete removal of proton-containing impurities from the chloroaluminate ionic liquids has been demonstrated using ethylaluminium dichloride. Care is required and the EtAlCl<sub>2</sub> must be titrated into the ionic liquid, because an excess of this reagent cannot be removed. Moreover, EtAlCl<sub>2</sub> must be handled with caution. However, it has more recently been shown that it is possible to remove all proton impurity from both basic and acidic ionic liquids by prolonged (overnight) evacuation (10<sup>-6</sup>-10<sup>-7</sup> Torr) [68]. This also confirms that free HCl is present in the liquids, as it is the species that is actually removed.

Complete removal of contamination of the ionic liquids by the adventitious water present in, even the best, anhydrous systems can now be achieved by first treating with phosgene [60-65] or triphosgene [65-72] and then evacuating overnight [73-76].

### Transition-metal halide chemistry

One of the most common use of the halogenoaluminate ionic liquids is the investigation of the spectroscopy and electrochemistry of transition-metal halide complexes, and the area has been well reviewed. Much of this work has focused on the precise measurement of redox couples or electronic absorption spectra rather than the in situ preparation of the ions used and is not of direct relevance to this review. However, these ionic liquids have been shown to stabilize a variety of species that usually demonstrate only transient existence in most solvents, and a number of species have been observed in solution for the first time.

When MoCl<sub>5</sub> or [Et<sub>4</sub>N][MoCl<sub>6</sub>] are dissolved in a basic chloroaluminate ionic liquid, a one-electron reduction to the [MoCl<sub>6</sub>]<sup>-</sup> ion (confirmed by electronic absorption spectroscopy) is observed [77]. Clearly, the species that is found in the ionic liquid is the product of the spontaneous reduction of Mo(V) to [MoCl<sub>6</sub>]<sup>2-</sup>. This species cannot usually be observed in solution because either it hydrolyses in water, it yields to coordination by the solvent in polar solvents, or its salts are



insoluble in nonpolar solvents. Similarly, if  $\text{WCl}_6$  or  $\text{KWCl}_6$  are dissolved in a basic ionic liquid, identical solutions of the complex  $[\text{WCl}_6]$  are formed which can be reduced to  $[\text{WCl}_6]^{2-}$  and  $[\text{WCl}_6]^{3-}$ . The W (III) metal-bonded cluster ion  $[\text{W}_2\text{Cl}_9]^{3-}$  [78] undergoes a one-electron oxidation to give  $[\text{W}_2\text{Cl}_9]^{2-}$  but on exhaustive electrolysis yields  $[\text{WCl}_6]^{2-}$ . This is proposed to be the result of the disproportionation of the  $[\text{W}_2\text{Cl}_9]^{2-}$  ion in the presence of excess chloride ion in the ionic liquid.

A wide range of chlorometalate species have been observed in the chloroaluminate ionic liquids. In basic ionic liquids, well-defined anionic halogeno-metalate species were formed in all cases [79].

Not surprisingly, several people have used the ionic liquids as solvents for the electrodeposition of metals. Aluminium has been deposited from a variety of ionic liquids, [80] as have a number of other metals [81]. The chloroaluminate ionic liquids have also been used to deposit several aluminium-transition-metal alloys [82]. Neat [emim] Cl at 1473 K has even been used to deposit a Bi-Sr-Ca-Cu superconductor [83]. When aluminium (III) chloride containing ionic liquids were used, aluminium is co-deposited with the alloy.

Despite the widespread interest in the ionic liquids as solvents for halogenometalate species, very few chemical transformations of these complexes have been studied in the ionic liquids. The only real exception to this has been the investigation of the oxo-exchange chemistry.

### Organic reactions in chloroaluminate (III) ionic liquids - Electrophilic substitutions

It is not surprising that electrophilic aromatic substitutions were the first organic reactions to be investigated in the room temperature chloroaluminate ionic liquids [84]. The high concentration of chloroaluminate species coupled with the good solubility of simple arenes in the acidic ionic liquids makes them ideal solvents for these reactions, and it is possible to combine their function as a solvent and a catalyst. Of the arenes tested by reaction with 1-chloropropane, only

nitrobenzene failed to react. As with conventional systems, polyalkylation was common, e.g., reaction between an excess of chloroethane and benzene led to the formation of a mixture of mono di, tri, tetra penta and hexa substituted products. Polyalkylation can be minimized by use of a large excess of the arene but not totally eliminated. Basic ionic liquids do not provide adequate catalytic activity for alkylation and acylation reactions to occur.

In order to Friedel-Crafts reactions to occur, it is necessary to form an electrophile in the ionic liquid. Luer and Bartak [85] demonstrated that even in a moderately acidic ionic liquid, dissolution of chlorotriphenylmethane leads to the formation of the triphenylmethyl carbonium ion.

Reactions with 1-chloropropane and 1-chlorobutane lead to the formation of products resulting from secondary carbonium ions, which implies that alkylation occurs via the dissociated carbonium ions [86]. Mixing benzene and hexamethylbenzene in an acidic ionic liquid did not lead to a transfer of methyl groups and the formation of toluene, xylenes, mesitylenes, etc., cannot be observed. It is shown that there is no dissociation of the methyl substitutes when the ionic liquid does not contain protic impurities.

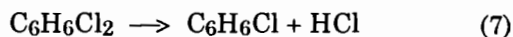
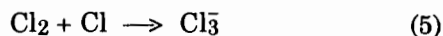
Friedel-Crafts acylation reactions of aromatic compounds have also been carried out in the ionic liquids [87]. For the reaction of acetyl chloride with benzene, it was determined that the rate at which acetophenone was produced was dependent on the Lewis acidity of the ionic liquid, which is in turn dependent on the ionic liquid composition. The reaction between acetyl chloride and the acidic ionic liquid was followed by  $^1\text{H}$ NMR.

The alkylation of the coal has been investigated in pyridinium chloride ionic liquid ( $X(\text{AlCl}_3)=0.65$ ) [88]. The coal chosen for the study was a high sulfur, high volatile carbon bituminous coal and the alkylating agent employed was 2-propanol. Auto alkylation of 2-propanol yielded a series of high molecular weight polymers most of which are non volatile. No alkylating pyridines from reaction with the ionic liquid itself were formed. Reaction between demineralized coal and 2-propanol was

attempted and the Friedel Craft's alkylation was accompanied by depolymerization of coal.

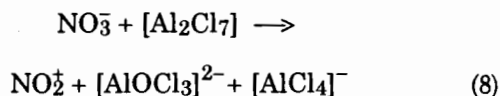
Isobutane alkylation has also been investigated in ionic liquids. Again it was adjustable nature of Lewis acidity of the systems that made them attractive [89]. The process involved a reaction mixture consisting of isobutane, butane and 2-butene in a  $[\text{bmin}]\text{Cl}^- \text{AlCl}_3$  ionic liquid. The products of the reaction included 2,2,4-trimethylpentane, 2,5-dimethylhexane, light ends (C5-C7 isoparaffins) and heavy ends (C9+ isoparaffins). The rate and selectivity of alkylation reaction was found to be dependent on precise composition of the ionic liquid. In an investigation of the electrochemical oxidation of hexamethylbenzene in mixtures of acidic ( $X(\text{AlCl}_3) = 0.67$ ) ethylpyridinium bromide-aluminium III chloride in benzene, [90] it was found that a product mixture containing penta, tetra and trimethyl benzene and diphenylmethane was formed. The authors postulated that the mixture was formed by a series of Friedel Craft's reaction initiated by a two electron oxidation of hexamethyl benzene.

Proposed mechanism of chlorination of benzene in a basic  $[\text{emim}]\text{Cl}^- \text{AlCl}_3$  ionic liquid.



Carbo cations are not the only electrophile that can be generated by chloroaluminate ionic liquids and both chlorination and nitration have been observed in  $[\text{emin}]\text{Cl}^- \text{AlCl}_3$  ionic liquids. Chlorination occurs in both acidic and basic ionic liquids but not in pure molten  $[\text{emim}]\text{Cl}$  which indicate chloroaluminate ions are required for the reaction to occur. In both the reactions the primary product was chlorobenzene. In acidic compositions large amounts of two dichlorobenzene isomers were synthesized. In basic compositions there was no formation of polychlorobenzene but significant amounts of tetra chlorocyclohexane isomers and hexachlorohexane isomers were observed.

Nitration of aromatic compounds in  $[\text{emin}]\text{Cl}^- \text{AlCl}_3$  ionic liquid used  $\text{KNO}_3$  as source of  $\text{NO}_2^+$  which acts as electrophile and resulted in 55% yield of nitrobenzene.  $\text{NH}_3\text{NO}_3$  and  $\text{NO}_2\text{BF}_4$  also tried as nitrating agent but gave much lower yields.



### Reactions with protons in acidic chloroaluminate ionic liquids

It has been demonstrated that protons present in  $[\text{emin}]\text{Cl}^- \text{AlCl}_3$  ionic liquids are superacidic with Hammett acidities upto -18 [91]. Hence they are expected to be highly reactive. Initial investigations showed the ability of  $[\text{emin}]\text{Cl}^- \text{AlCl}_3\text{-HCl}$  systems to protonate aromatic substrates and generate cationic species. Anthracene has been shown to exchange deuterium with  $\text{DCl}$  in acidic  $[\text{emin}]\text{Cl}^- \text{AlCl}_3$  ionic liquids [28]. It is therefore not surprising that the  $[\text{emim}]^+$  cations undergo H-D exchange in acidic  $[\text{emin}]\text{Cl}^- \text{AlCl}_3$  solutions of  $\text{DCl}$  [92].

Since the exchange occurs by electrophilic substitutions at 4- and 5- positions of the imidazolium ring rather than the 2- position which has a greater positive charge. Carbocation formation by protonation of arenes has been observed by UV and NMR studies for a number of substrates in trimethyl sulfonium bromide-chloroaluminate and trimethyl sulfonium bromide-aluminium bromide ionic liquids with added  $\text{HBr}$  [93].

Polyphenylene can be prepared by electropolymerization of benzene in neutral and acidic ionic liquids [94]. Varying the precise composition of the ionic liquid had a minimal effect on the polymerization potential, suggesting that there is a little interaction between benzene and chloroaluminate ionic liquids. This reaction has also been carried out in a novel  $[\text{n-bpy}]\text{Cl}^- \text{AlCl}_2(\text{OC}_2\text{H}_5)$  Ionic liquid [95]. Protons in acidic chloroaluminate ionic liquids have been known to catalyse the formation of oligomers with molecular weights characteristic of a cationic reaction from



olefins. Attempts to avoid this reaction lead to the first preparation of alkyl chloroaluminate ionic liquids [96]. The electrochemical oligomerization of ethene in three room temperature ionic liquids [n-bpy]Cl<sup>+</sup>AlCl<sub>3</sub><sup>-</sup>, [pyH]Cl<sup>+</sup>AlCl<sub>3</sub><sup>-</sup> and [emin]Cl<sup>+</sup>AlCl<sub>3</sub><sup>-</sup> have been investigated [97]. Electrochemical polymerisation has been utilized to synthesize polyaniline using [emin]Cl<sup>+</sup>AlCl<sub>3</sub><sup>-</sup> ionic liquids [98]. The electrochemical polymerization of benzene and pyrrole to yield a high conducting free standing film has been reported using chloroaluminate - AlCl<sub>3</sub> -room temperature melt by Trivedi.[99]

### Organometallic reactions in chloroaluminate ionic liquids.

Another interesting Friedel Craft's reaction performed in room temperature ionic liquids is the acylation of ferrocene [100]. The acylation of ferrocene with acetic anhydride in [emin]Cl<sup>+</sup>AlCl<sub>3</sub><sup>-</sup> ionic liquid and in the liquid clathrate prepared from the addition of toluene to the ionic liquid was investigated. Interestingly the authors used commercial chloroaluminate without further purification to prepare the ionic liquids. It was claimed that monoacetyl ferrocene was the only product of the acylation reaction with high yields.

Arene exchange reactions of ferrocene are well known to be catalysed by aluminium III chloride. Hence acidic (X(AlCl<sub>3</sub>) = 0.65) and [bmim]Cl<sup>+</sup>AlCl<sub>3</sub><sup>-</sup> ionic liquid has been used to prepare a number of arene from ferrocene [101]. The ionic liquid acts both as Lewis acid and solvent. The reductive carbonylation of titanocene dichloride (C<sub>p</sub><sub>2</sub>TiCl<sub>2</sub>) in an acidic (X(AlCl<sub>3</sub>) = 0.65) and [emim]Cl<sup>+</sup>AlCl<sub>3</sub><sup>-</sup> ionic liquid lead to the formation of a metal-carbon bond [102]. A reducing mixture has been prepared by adding sodium metal to the ionic liquid. This lead to the precipitation of aluminium from the ionic liquid in a more reactive form compared to commercial granular aluminium.

### Transition metal mediated

In homogenous catalysis the solvent can often control the course of a reaction by affecting reaction rates and improving chemo-, regio-, stereo-, and enantioselectives of reaction products. In transition metal-based catalysis it is important

for the solvent to stabilize the active catalytic species but remain unreactive toward the active catalytic site i.e to behave as a non conductor solvent. Hence acidic composition of the chloroaluminate ionic liquids, with either poor co-ordinating anions, offer potentially exciting novel medium for catalysis.

### Olefin dimerization

The chloroaluminate ionic liquids were first used as solvents for the dimerization to propene to hexene using nickel II complexes as the catalysts [103]. In these reactions the product hexenes separated from the ionic liquid phase and could easily be removed by decantation. It was found that only catalysts with a nickel - carbon bond were active and the products were contaminated by cationic side reaction. By using ethyl aluminium dichloride based ionic liquids both of these problems were avoided. This allowed a greater number of potential catalysts to be employed for the reaction, particularly nickel phosphene dihalides.

Cationic (-nickel II complexes containing phosphene ligands are useful catalysts for dimerization of propene in solution in chlorinated or aromatic hydrocarbons. A number of air-stable NiCl<sub>2</sub> 2L complexes (L = P(Bu<sub>3</sub>), P(cyclohexyl)<sub>3</sub> and pyridine have been successfully used as catalysts for regio selective dimerization of propene in chloroaluminate and ethyl chloroaluminate ionic liquids.

### Olefin polymerization

In two studies of titanium chemistry in chloroaluminate ionic liquids to which alkyl chloroaluminate drying agents had been added, ethene polymerization has been observed. When AlEtCl<sub>2</sub> and TiCl<sub>4</sub> are added to an acidic (X(AlCl<sub>3</sub>) = 0.52) ionic liquid, a deep red colored solution is formed which will polymerize ethene to give poly(ethene) with a melting point in the region of 393 K- 403 K chloroaluminate [104]. Better yields were obtained with solutions of C<sub>p</sub><sub>2</sub>TiCl<sub>2</sub> in the same composition ionic liquid with Al<sub>2</sub>Me<sub>3</sub>Cl<sub>3</sub> acting as the alkylating agent [105].

Interestingly neither  $C_{p2}Zr_2Cl_2$  or  $C_{p2}HfCl_2$  were catalytically active in the ionic liquids.

### Olefin hydrogenation

Another example of the use of this system is the catalytic hydrogenation of cyclohexene by rhodium complexes [106,107]. The use of an acidic chloroaluminate ionic liquid ( $X(AlCl_3) = 0.54$ ) leads to the polymerization of cyclohexene. However upon dissolving Wilkinson's catalyst in basic ( $X(AlCl_3) = 0.45$ ) ionic liquid, the cyclohexene undergoes hydrogenation [108,109,110].

### In batteries

Room temperature molten salts consisting of 1-methyl-3-propylimidazolium chloride and aluminum chloride have been examined as possible electrolytes for a room temperature design of the sodium/metal chloride battery; however, the coulombic efficiency of the sodium couple is less than 95%. This work examines the reduction and oxidation efficiency of the sodium couple from a 1-methyl-3-propylimidazolium chloride/aluminium chloride neutral melt. Most of the work was performed on a tungsten substrate using cyclic voltammetry. The coulombic efficiency of the sodium couple was improved by treating the melt with gaseous HCl using a closed electrochemical cell which allowed for quantification of the effect of HCl on the electrochemical behavior of sodium. Thionyl chloride was also found to induce sodium plating and stripping in 1-methyl-3-propylimidazolium chloride/aluminum chloride melts. Optical microscopy was used to examine the surface of the tungsten electrode during sodium deposition, open-circuit periods, and sodium stripping. In comparison for the stability of sodium in two other imidazolium melts, (1,2-dimethyl-3-propylimidazolium chloride and 1-methyl-2-ethylimidazolium chloride) the 1-methyl-3-propylimidazolium chloride system was found to have the widest stability.

### Lithium in chloroaluminate molten salts

Addition of protons to buffered neutral  $AlCl_3:MEIC:LiCl$  (MEIC-1-methyl-3-ethyl imidazolium chloride) melts allows elemental lithium to

be deposited and stripped at a 250  $\mu m$  tungsten electrode. In basic melts elemental lithium appears to be stable for long times with and without addition of protons. In addition the maximum lithium anodization current density achieved in basic melts is higher than that in the buffered neutral melts [111,112,113.]

Vanadium halide and oxyhalides in chloroaluminate room temperature ionic liquid were studied by David et al recently. They found that  $V_2O_3$ ,  $V_2O_4$  and  $VOSO_4$  are insoluble while  $V_2O_5$  and  $Na_3VO_4$  are slightly soluble with solubility limits of less than 5 mM. A new ionic liquid was formed using  $VOCl_3$  as the Lewis acid instead of  $AlCl_3$ .

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