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COMMUNICATION

Do all ionic liquids need organic cations? Characterisation of $[\text{AlCl}_2 \cdot n\text{Amide}]^+ \text{AlCl}_4^-$ and comparison with imidazolium based systemsHadi M. A. Abood,^{ab} Andrew P. Abbott,^{*a} Andrew D. Ballantyne^a and Karl S. Ryder^a

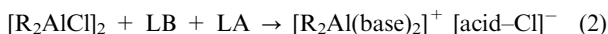
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The addition of a simple amide to AlCl_3 causes the formation of a liquid of the form $[\text{AlCl}_2 \cdot n\text{Amide}]^+ \text{AlCl}_4^-$. The material thus produced is liquid over a wide temperature range, is relatively insensitive to water and has the properties of an ionic liquid. This ionic liquid is shown to be a suitable medium for the acetylation of ferrocene and the electrodeposition of aluminium and demonstrated that quaternary ammonium cations are not always needed to form ionic liquids.

The ubiquitous application of ionic liquids is evidenced through their use in catalysis,¹ electrochemistry,² biotechnology³ and material processing.⁴ One of the only factors linking all of these ionic liquids is the use of organic cations, most of which are nitrogen based with the vast majority containing imidazolium moieties. Metal containing ionic liquids have primarily incorporated the active metal centre as a chloro-metallate anion. Aluminium-based ionic liquids are well known and exemplars using imidazolium and pyridinium chlorides are amongst the first studied ionic liquids.^{5,6} In all cases aluminium forms anionic species including AlCl_4^- and Al_2Cl_7^- .⁷ One issue associated with this is the Lewis acidity and general reactivity of the metal centre which is largely affected by the relative content of the Lewis base in the liquid.

Cationic aluminium complexes are less common than their anionic counterparts and are certainly unknown in ionic liquids. They are generally formed from the reaction of alkyl aluminium halides with a Lewis acid, LA or base, LB^{8–10} e.g.



The area of cationic aluminium complexes has been reviewed by Atwood.¹¹ All of the complexes of this form synthesized to date are solids at ambient temperature.

The majority of ionic liquids are based on quaternary ammonium or phosphonium cations,¹² however it was recently shown that room temperature eutectics could also be formed between ZnCl_2 and simple amides and diols. These form ionic liquids through the disproportionation of ZnCl_2 to

form ZnCl^+ and ZnCl_3^- although they have relatively low conductivities.¹³

In the current study it is shown that AlCl_3 can also undergo disproportionation by forming a complex with acetamide or urea and the complex is liquid at ambient temperature with a 3 to 4 fold higher conductivity than the corresponding zinc chloride eutectics. The AlCl_3 based liquids only form with a limited range of amides and only over a relatively small compositional range.

An AlCl_3 eutectic was made by slowly mixing aluminium chloride (2.1 g, 15.75 mmol) with acetamide (0.93 g, 15.75 mmol) in a Schlenk tube under a blanket of dry nitrogen gas making a 1 : 1 mole ratio. The solids reacted immediately without external heating and reached a temperature of ca. 75 °C. The liquid was left to cool gradually to room temperature producing transparent, yellow colored, free flowing liquid as shown in Fig. 1. This liquid was found to have a density of 1.4 g cm⁻³, a conductivity of 0.804 mS cm⁻¹ and a viscosity of 60 cP at 25 °C. When this liquid was examined by differential scanning calorimetry it underwent a glass transition around -63 °C and was stable up to 100 °C.

An analogous liquid was made using equimolar amounts of urea in place of acetamide (Fig. 1). Numerous amides and polyols were tested and the only other amide that produced a liquid at room temperature was *N,N*-dimethyl urea. Attempts to use tetramethylurea, dimethylformamide and benzamide as the amide did not result in a homogeneous liquid presumably due to their inability to act as complexing agents. No polyols

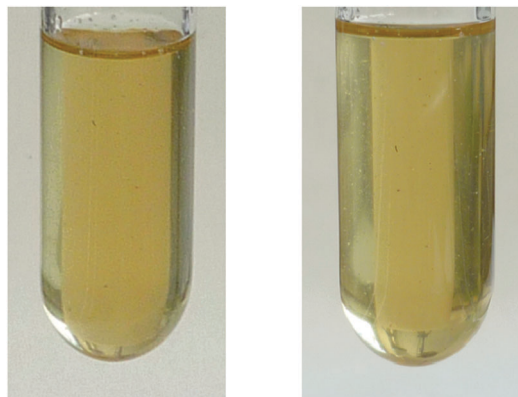


Fig. 1 1 : 1 AlCl_3 -acetamide (left) and 1 : 1 AlCl_3 -urea (right).

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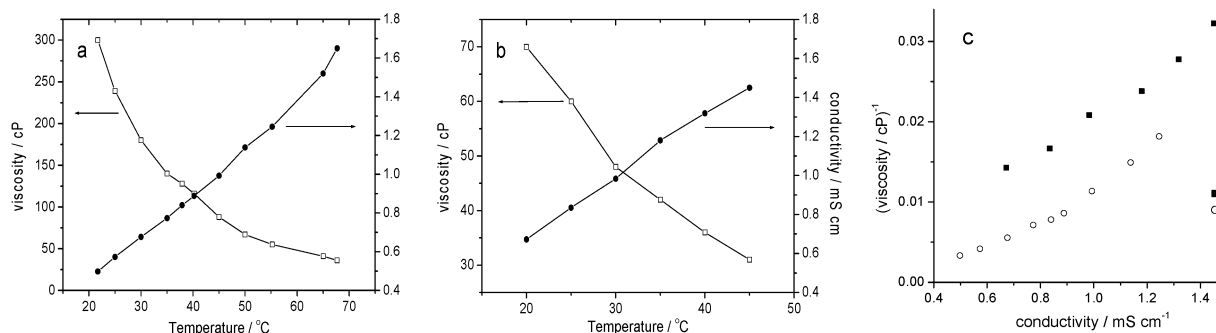


Fig. 2 Plots of viscosity and conductivity as a function of temperature for the 1 : 1 AlCl₃-urea (a), 1 : 1 AlCl₃-acetamide (b) and a plot of fluidity vs. conductivity for both systems (c).

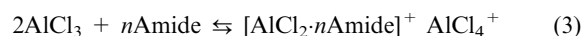
formed homogeneous liquids but instead reacted with AlCl₃ yielding HCl. To characterize the AlCl₃-amide complexes formed a variety of analytical techniques were applied to the liquids. FAB-MS showed several aluminium containing species [AlCl₂(Acet)₂]⁺ (*m/z* = 215) and [AlCl₂(Acet)]⁺ (*m/z* = 156) (or more probably the dimer with bridging ligands). Slight traces of aluminium containing cations were also found with *m/z* = 121 and 179 (which could be [AlCl(Acet)₃]²⁺). There was one primary aluminium containing anionic species AlCl₄⁻ (*m/z* = 169) with only small traces of Al₂Cl₇⁻. Analogous complexes were found using urea as the amide although the signal for [AlCl₂(U)]⁺ was comparatively small compared with the acetamide case. Jacobs and Nöcker showed that the complex [AlCl₂(NH₃)₄]⁺[AlCl₄]⁻ could be formed but this was a solid with a melting point of 150 °C.¹⁴ Similar studies with pyridine and tetrahydrofuran yielded analogous complexes with 4 neutral ligands surrounding the aluminium centre and 2 additional axial chloride ligands *i.e.* an octahedral geometry.^{15,16} The speciation observed from FAB-MS suggests that the lower melting points of these complexes are due to their coordination geometry.

²⁷Al NMR spectroscopy of the liquid shows the presence of 3 main peaks at δ = 101.1, 88.6 and 73.6 ppm. This technique has been used previously to quantify aluminium species in solution.¹⁷ Most previous studies have been made in solution of a molecular solvent and so direct comparison is not possible since the solvent significantly affects the peak position. The peak at 88.6 is thought to correspond to AlCl₄⁻ since it integrates to the size of the other two peaks. Also, the addition of MgCl₂ causes it to increase in size of this peak while the other two decrease in size. It is assumed that the peaks at δ = 101.1 and 73.6 ppm correspond to the complexes [AlCl₂(Acet)₂]⁺ and [AlCl₂(Acet)]⁺ respectively. The integrated areas under these two peaks were found to be 1.6 : 1 which is in close agreement with the signal intensities from FAB-MS. While integration of these two peaks does not give quantitative information about the exact amount of species present this correlation in relative peak intensities can be used for species identification.

The method of complexation can be determined through analysis of the IR spectra of the liquid and pure amide. Significant shifts in the stretching frequencies of the N-H were shifted from 3300 and 3151 in pure acetamide to 3435 and 3361 cm⁻¹ in the eutectic liquid. The C=O stretching

frequencies were shifted from 1673 and 1631 to 1662 and 1557 cm⁻¹. Similar shifts were also observed for the urea-based liquid and these suggest that complexation to the aluminium occurs through the oxygen on the amide.

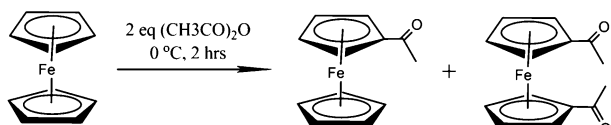
The liquid only forms in the compositional range 1 : 1 < amide:AlCl₃ < 1 : 2. Outside these limits a suspension of either AlCl₃ or amide in the eutectic forms. This is clearly related to the stoichiometry of the amide:AlCl₃ complex; once the AlCl₂⁺ is saturated with amide no further material will dissolve in the liquid. It should however be noted that this is very different from the corresponding ZnCl₂:acetamide complex where the eutectic composition was at 1 : 4 and liquids did not form below a stoichiometry of 1 : 2. It can therefore be concluded that the reaction occurring to produce the aluminium-based ionic liquids is:



The liquids are optically transparent and highly fluid. Fig. 2 shows plots of viscosity and conductivity for the 1 : 1 AlCl₃:acetamide and 1 : 1 AlCl₃:urea as a function of temperature. Comparison of these systems with the imidazolium chloroaluminates for example shows that they have similar but lower conductivities and higher viscosities (1 : 1 3-butyl-1-methyl imidazolium chloride:AlCl₃; viscosity = 27 cP, conductivity 10 mS cm⁻¹). For all of these systems plots of conductivity vs. fluidity are linear since the mobile species are similar in size (Fig. 2c). The properties of these liquids are akin to those of most common ionic liquids.¹² The liquid is qualitatively observed to hydrolyse less readily in moist air than the chloroaluminate liquid. This is in keeping with the report by Atwood *et al.* that crystals of [AlCl₂(THF)₄]⁺[AlCl₄]⁻ could be easily handled in the open laboratory.¹⁶

AlCl₃ is a Lewis acid and has been used in ionic liquids for a range of catalytic reactions.¹² To demonstrate the efficacy of the AlCl₃:amide systems the acetylation of ferrocene was carried out in an analogous method to that published using 1emiml : 2AlCl₃.¹⁸ For this study the reactions were carried out in a Schlenk flask under N₂ at 0 °C for 2 h with subsequent work up by quenching with 2 M HCl solution and extraction with dichloromethane (4 × 25 ml). The individual products were then isolated by column chromatography (Scheme 1).

Table 1 shows the yield of the respective components from the acetylation of ferrocene. The acetylferrocene and



Scheme 1 Acetylation of ferrocene.

Table 1 Percentage yields of products from acetylation of ferrocene with two equivalents of acetic anhydride in liquids of 1 : 1.5 urea : AlCl₃ or 1 : 1.5 acetamide : AlCl₃

	Mole % AlCl ₃	Acetylferrocene	Diacetylferrocene
Urea	40	26	36
Acetamide	40	8	56
emimI : AlCl ₃	50	0	0 ¹⁸
emimI : AlCl ₃	55	89	0 ¹⁸
emimI : AlCl ₃	58	38	38 ¹⁸
emimI : AlCl ₃	67	16	40 ¹⁸
emimI : AlCl ₃	75	9	19 ¹⁸

diacetylferrocene were characterized by ¹H NMR, {¹H}¹³C NMR, elemental analysis, electrospray MS, and IR spectroscopy. Interestingly, the two amide-based liquids show differing reactivity. The urea liquid gave moderate yield of each of the compounds whereas the acetamide liquid gave a yield of 56% of the diacetylated product with low quantities of the monoacetylated intermediate. This latter result is an improvement on that reported for the emim AlCl₃I liquid despite the fact that there is significantly less AlCl₃. The fact that no product was obtained using 1 : 1 emimI : AlCl₃ suggests that AlCl₃I⁻ is not very Lewis acidic. It also suggests that the cationic aluminium containing species is more Lewis acidic than Al₂Cl₇⁻.

Another technological application of aluminium-based ionic liquids has been for batteries or metal deposition.^{19,20} Fig. 3 shows the cyclic voltammogram for the 1 : 1 AlCl₃ : acetamide and 1 : 1 AlCl₃ : urea systems at 25 °C in a 1 mm radius Pt disc electrode. The shape is generally similar to that of the butyl-methyl imidazolium chloride : AlCl₃ system although there is no under-potential deposition presumably due to the lack of Al₂Cl₇⁻.^{19,20} There is also no evident deposition of nano-particulate aluminium²⁰ and the over-potential required to deposit metal is larger than in the imidazolium-based liquid. Electrodeposition of aluminium cannot be carried out from Lewis basic chloroaluminate melts ($x_{\text{AlCl}_3} < 0.5$) and this is thought to be due to the speciation of aluminium which is predominantly AlCl₄⁻. Bulk electrolysis of the 1 : 1 AlCl₃ : acetamide liquid was carried out at 25 °C by applying a constant current of 2 mA cm⁻² with a stable voltage of 0.4 volt was applied between a brass rod cathode (radius = 5 mm) and an aluminium anode for one hour. An adherent, grey metallic coating was obtained on the cathode as shown in Fig. 3 (inset). Electrochemical quartz crystal microbalance showed an electrodeposition efficiency of 97%. The ability to electrodeposit aluminium from these liquids suggests that the cationic species are those predominantly reduced at the electrode surface.

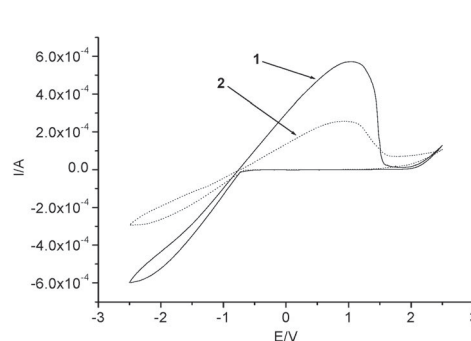


Fig. 3 Cyclic voltammogram of 1 : 1 aluminium trichloride with acetamide (1) and urea (2) at room temperature. (Inset: aluminium coating obtained from bulk deposition (see text for details).)

In conclusion this work has shown that an AlCl₃ : amide eutectic can be created with aluminium containing cations and anions. The physical properties are akin to those of other ionic liquids based on quaternary ammonium cations. These liquids have the advantage that they are easy to prepare and less water sensitive than other aluminium containing liquids.

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