

1-Methyl-3-ethylimidazolium Hydrogen Dichloride: Synthesis and Application to the Study of Protons in Ambient-Temperature Chloroaluminate Ionic Liquids

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The syntheses of 1-methyl-3-ethylimidazolium hydrogen dichloride (ImHCl₂) and its deuterium analogue (Im²HCl₂) and their use as proton/deuterium donors in ambient-temperature chloroaluminate melts are described. The material exists as a liquid at room temperature and has been characterized by ¹H NMR spectroscopy. ImHCl₂ is itself an ambient-temperature molten salt composed of the Im⁺ cation and HCl₂⁻ anion. The ²H NMR chemical shifts of species derived from Im²HCl₂ in 1-methyl-3-ethylimidazolium chloride/aluminum chloride melts lead us to suggest that HCl interacts with a second chloride in basic melt solutions, whereas it is more weakly complexed in acidic melt solutions. The quantitative addition of a proton by ImHCl₂ is demonstrated by use of pulse voltammetry.

Introduction

Mixtures of AlCl₃ with 1-methyl-3-ethylimidazolium chloride (ImCl) form liquids at or below room temperature over a wide composition range. A considerable body of work has dealt with the physical and chemical properties of these ionic liquids.¹ In several cases, solute chemistry has been affected by the presence of impurities derived from residual water, most recently in a study of Mo dimers² and oxide³ present in ImCl and AlCl₃ used to make the melts.

Several previous studies have dealt with the chemistry of these impurities. The qualitative aspects of water chemistry have been investigated by using ¹⁷O NMR spectroscopy.⁴ This work indicated that both oxide (Al-O) and hydroxide (Al-OH) species, which may also contain Cl⁻, were present in melt solutions containing water. The presence of hydroxide-containing species has also been indicated by infrared spectroscopy.⁵ In order to obtain more concrete information on the species present in solution, means must be found to manipulate, in a well-defined manner, the chemistry of the oxy- and hydroxychloroaluminate species present. The simplest ways of doing this are by varying the composition of the melt and the concentration of protons present in the melt. The former is straightforward whereas the latter requires appropriate reagents for addition and removal of protons to and from solutions.

We have previously described⁶ the use of the reagent ethylaluminum dichloride for the removal of protons. Protons can be added to the melt in a variety of ways. Addition of water results in an increase in the proton concentration, as shown by Sahami and Osteryoung.⁷ However, it is obvious that the oxide concentration will also be altered by addition of water. Furthermore, quantitative addition of protons by water addition is difficult since some HCl evolves during the dissolution process. Hydroquinone has been used as a proton donor in these melts,^{8,9} but it is electrochemically active and undergoes complexation with acidic species in the melt. Finally, we have used gaseous HCl to drive the oxide/hydroxide equilibria fully to the hydroxide side.⁴ However, HCl is difficult to use as a reagent for the quantitative addition of protons to the melt.

We describe here the synthesis and application of 1-methyl-3-ethylimidazolium hydrogen dichloride (ImHCl₂), a simple

reagent for the quantitative addition of protons to chloroaluminate melts.

Experimental Section

The synthesis and purification of 1-methyl-3-ethylimidazolium chloride was carried out as previously reported.¹⁰ AlCl₃ was purified by sublimation in a bomb tube as described elsewhere.¹¹ The synthesis of ImHCl₂ was carried out by passage of HCl over ImCl in a Schlenkware flask. The flask was initially kept in a dry ice/ethanol bath and alternatively frozen and thawed. After all of the solid ImCl dissolved in the liquid formed upon thawing, the HCl flow was halted and the vessel was carefully evacuated. Bubbles of gas emerged from solution for a time. After the gas evolution ceased, the flask was transferred into the drybox and used. The product, ImHCl₂, was a colorless liquid. The change of weight upon conversion of ImCl to ImHCl₂ (0.242 g of ImCl yielded 0.300 g of product; theoretical yield is 0.302 g) was consistent with the addition of 1 HCl per ImCl. The product was further analyzed by a potentiometrically monitored titration of a weighed amount of ImHCl₂ in an aqueous solution with AgNO₃. A 1.47 × 10⁻³ mol amount of ImHCl₂ reacted with 2.90 × 10⁻³ mol of Ag⁺ (98% of that expected on the basis of the stoichiometry of ImHCl₂). The ¹H NMR spectrum (see below) indicated that no water was present in the product, and the spectrum contained a peak not seen in the spectrum of 1-methyl-3-ethylimidazolium chloride which we presume to be that of the HCl₂⁻ ion. The integration of this peak relative to that of the proton in the 2-position on the imidazole ring is approximately 0.98, supporting the stoichiometry indicated. The deuterium dichloride analogue of ImHCl₂, Im²HCl₂, was prepared in the same manner, substituting ²HCl gas for HCl.

²H NMR experiments were performed using a JEOL FX-270 NMR spectrometer operating at 41.37 MHz. ¹H NMR spectra were measured with a JEOL FX-90Q spectrometer operating at 89.55 MHz. All chemical shifts reported are relative to TMS. All NMR samples were prepared in a drybox (Vacuum Atmospheres Corp.) with a recirculating He atmosphere. Water and oxygen content were kept below 5 ppm each. Solutions were loaded into NMR tubes that were capped and sealed with Parafilm in the drybox.

Electrochemical measurements were performed by using a three-electrode cell with a Pt indicator electrode (BAS Inc.; area 0.020 cm²), an Al-wire counter electrode, and an Al-wire reference electrode dipped into a 1.5:1.0 AlCl₃:ImCl melt separated from the bulk solution by a glass frit. An EG&G PARC 273 potentiostat controlled by a DEC PDP-8/e computer, as previously described,¹² was used for electrochemical measurements. Normal-pulse voltammetry measurements were carried out with stirring between pulses to restore the boundary conditions on the solid electrode used. The Pt surface was also pretreated by potentiostating the electrode at +1.1 V, on the Cl⁻ oxidation wave, for 1.5 s after each pulse. A long waiting period, typically 15 s, with stirring for 2.8 s, was interposed between the pretreatment step and the next pulse. This pretreatment results in a considerable improvement in the voltammetric behavior of the proton-containing species present in basic melts. In acidic melts, a similar treatment is not feasible since the Cl₂ gas evolved reacts

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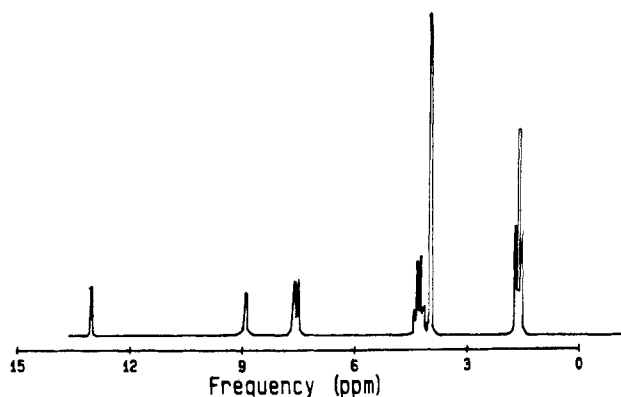


Figure 1. ^1H NMR spectrum of neat ImHCl_2 .

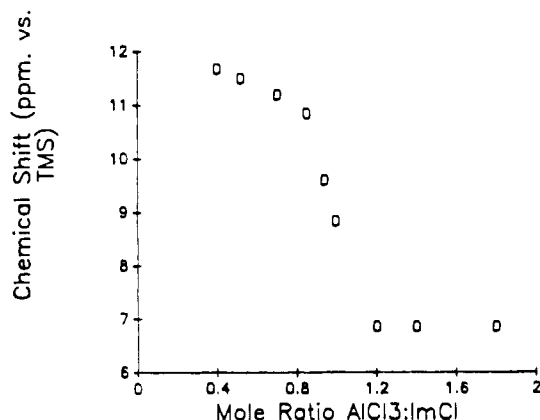


Figure 2. ^2H chemical shift vs melt composition (200 mM Im^2HCl_2).

rapidly with the Im^+ cation,¹³ resulting in the liberation of protons.

Results and Discussion

The ^1H NMR spectrum of pure ImHCl_2 is shown in Figure 1. The spectrum observed is quite similar to that of an $\text{ImCl}/\text{AlCl}_3$ melt with the exception of the line furthest downfield at 13.02 ppm. Evidence has led us to assign this line to the HCl_2^- ion. The HCl_2^- ion is known to exist at low temperatures in various cases.^{14,15} In our case, the large downfield chemical shift, similar to that found for salts formed from reaction of HCl with nitrogen bases,¹⁶ and the stoichiometric evidence detailed above lead us to believe that the HCl_2^- ion is present in the liquid formed by reaction of ImCl with HCl .

The ^2H spectra of solutions of Im^2HCl_2 in $\text{AlCl}_3/\text{ImCl}$ melts have a single line if no oxide is present. The chemical shift of this line is markedly dependent on melt composition. In acidic melts, a peak is observed at 6.9 ppm vs TMS. This line shifts downfield as the melt is made basic. In a 0.4:1.0 $\text{AlCl}_3:\text{ImCl}$ melt, the chemical shift of the deuterium line is 12 ppm vs TMS. The chemical shifts observed for 200 mM solutions of Im^2HCl_2 in $\text{AlCl}_3/\text{ImCl}$ melts as a function of melt composition are shown in Figure 2.

It is evident from the data shown in Figure 2 that the presence of chloride in the melt causes a marked downfield shift of the ^2H line. This suggests that protons interact strongly with a second chloride ion, forming the $^2\text{HCl}_2^-$ ion in solution. The deuterium

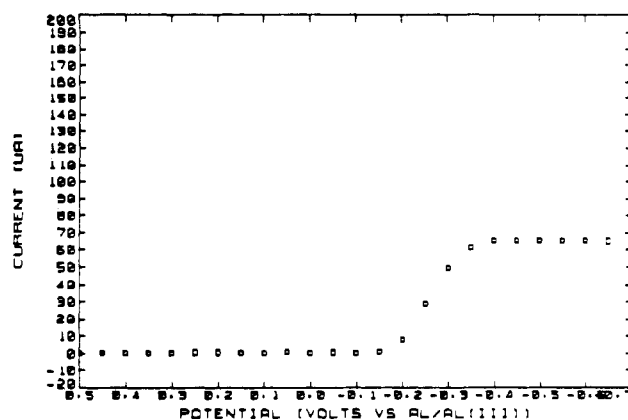
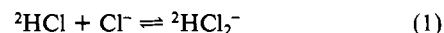


Figure 3. Normal-pulse voltammogram of 200 mM ImHCl_2 added to a 0.8:1.0 melt (Pt electrode).

chemical shift observed for a solution of Im^2HCl_2 in very basic melts is similar to that observed for the HCl_2^- proton in pure ImHCl_2 . Indeed, even for moderately basic melts, the deuterium chemical shift is far downfield. Thus, it may be suggested deuterons (and/or protons) in basic melt solutions are exchanging rapidly between two sites in the equilibrium



In basic melts, equilibrium 1 is shifted to the right since the chloride concentration is high. The existence of undissociated HCl in acidic melts is inferred from the conclusion of Lipsztajn et al. that the proton-containing species is undissociated HCl in neutral melts and from the invariant chemical shift observed for Im^2HCl_2 added to an acidic melt.⁸

A typical normal-pulse voltammogram for ImHCl_2 added to a basic melt is shown in Figure 3. A plot of limiting current for reduction of the proton-containing species in a basic melt versus $t_p^{-1/2}$, where t_p is the pulse width, is linear and has an intercept near the origin (slope $65.7 \mu\text{A s}^{1/2}$; y intercept $-8.2 \mu\text{A}$; correlation coefficient 0.999). Thus, the current on the plateau is diffusion limited.

A plot of the limiting current for the reduction of the proton-containing species in a basic melt versus concentration of added ImHCl_2 is also linear (slope $2.76 \mu\text{A mM}^{-1}$; y intercept $8.88 \mu\text{A}$; x intercept -3.2 mM ; correlation coefficient 0.999). The negative intercept of this plot indicates the initial concentration of a proton-containing impurity as ca. 3 mM.

The variation of the limiting current with $t_p^{-1/2}$ and with the concentration of ImHCl_2 experiments was used to estimate values for the diffusion coefficient of the proton-containing species; values of D obtained were 7.2×10^{-7} and $6.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively, for these experiments. These numbers are in reasonable accord with that previously reported, $4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, for the reduction of the proton-containing species in a 0.8:1 $1-n$ -butylpyridinium chloride/aluminum chloride containing melt;⁷ in this latter case the protonic species was added as H_2O . However, we are unsure if the oxide present in the melt has any effect on the diffusion coefficients, and additional work is being carried out to address this point.

The new compounds ImHCl_2 and its deuterium analogue, Im^2HCl_2 , are thus useful proton/deuterium donors for application in room-temperature chloroaluminates. Since we have shown EtAlCl_2 to be a proton removal reagent,⁶ we now have clean and quantitative means of adjusting the proton concentration in the melts. These reagents are being exploited in our ongoing study of the chemistry of water in the melt and in other areas.

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