THE CHEMISTRY OF WATER IN AMBIENT-TEMPERATURE CHLOROALUMINATE IONIC LIQUIDS: NMR STUDIES
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ABSTRACT

$^{17}$O NMR spectroscopy has been used to study the species formed upon addition of water to room-temperature molten salts composed of mixtures of AlCl$_3$ with 1-methyl, 3-ethyl imidazolium chloride (ImCl) at various mole ratios. In basic melts, a single resonance peak is observed; in acidic melts, 3 separate peaks are observed and the nature of the various $^{17}$O sites can be deduced.

$^2$H NMR has been employed to study the chemistry of protons in these melts. DCI interacts with a second chloride ion in basic melts whereas it interacts only weakly in acidic melts.

INTRODUCTION

Room-temperature ionic liquids composed of mixtures of A1C1$_3$ and organic chloride salts, RCl (R = N-(1-butyl)-pyridinium cation (BuPy$^+$) or 1-methyl, 3-ethyl imidazolium cation (Im$^+$)), have been used as solvents for a wide variety of chemical studies (1). These molten salts have several desirable properties including a high chloride ion activity for basic (molar excess RCl) melt compositions, high Lewis acidity, and nearly aprotic conditions. However, residual protons and oxide present in the melt have been found to have significant effects on the chemistry of certain solutes (2,3,4,5,6). Since these impurities are nearly always present, it is important to understand their chemistry.

A titration procedure for the determination of oxide impurities in melts (1,6) has been developed using Ti(IV), which shows two voltammetric reduction waves, the first due to the reduction of the hexachlorotitanate anion and the second to the reduction of the titanium oxytetrachloride anion. Surprisingly, the addition of water to a solution of Ti(IV) with a known oxide content shifted the equilibrium between TiCl$_6^{2-}$ and TiOCl$_4^{2-}$ away from the oxychloro-complex (5). This was believed to be due to the formation of an Al-OH containing species. Subsequent infrared work (7) indicated that an -OH moiety is indeed formed upon addition of water to both basic and acidic melts.
The reduction on a Pt electrode of protons from water added to melts was studied (8) and it was shown that limiting currents increased linearly with increasing water concentration in basic melts. Less current was observed for an equivalent amount of water added to an acidic melt. Finally, the addition of water to nearly neutral melts apparently results in a release of 2 protons per water molecule (9).

As part of an ongoing effort to study the chemistry of water in the room-temperature chloroaluminate melts, we have used $^{17}$O and $^2$H NMR of water added to the melt to obtain information on the speciation of oxide and protons. We find that these techniques allow a qualitative description of water chemistry in chloroaluminate melts.

EXPERIMENTAL

The preparation, purification, and handling of melt components and solutions are fully described elsewhere (10). Water enriched to 20 or 30% $^{17}$O was obtained from Cambridge Isotope Labs and was used as received. The synthesis of ImDCl$_2$ was similar to that of the $^1$H analog, (11).

$^{17}$O and $^2$H NMR spectra were measured using a JEOLCO FX-270 NMR spectrometer operating at 36.54 or 41.7 MHz. Proton decoupling was carried out using broad-band, pseudo-random noise decoupling. All $^{17}$O spectra were obtained at 90°C since baseline resolution of all spectral lines could be obtained at this temperature.

RESULTS AND DISCUSSION

$^{17}$O NMR spectra of solutions of water in acidic melts consist (generally) of three peaks as shown in Figure 1. The relative intensities of these peaks vary with composition (Figure 1) and concentration (Figure 2). As the mole ratio of AlCl$_3$ to ImCl is increased, the peak furthest downfield (Peak C) increases in relative intensity. The peak at 49.7 ppm (Peak A) is the most intense peak in the spectrum in melts less acidic than approximately 1.5:1.0. The intensity of the peak at 73 ppm (Peak B) decreases as the melt composition is made more acidic and is nearly negligible in very acidic melts.

Figure 3 is a plot of the total integrated intensity of the three lines observed in a 1.2:1.0 melt with various concentrations of added H$_2$O. The linearity of the plot implies that peaks A, B, and C account for all of the water added. The relative intensity of Peak A increases sharply with increasing concentration while that of Peak B...
increases gradually with concentration. The relative intensity of Peak C decreases as the concentration of water is increased.

The spectrum shown in Figure 4 is that which results when HCl gas is bubbled through the solution whose spectrum is shown in Figure 1a. Addition of this proton donor results in the disappearance of peaks B and C, implying that peak A corresponds to oxygen present in a hydroxy-chloroaluminate species. The highly acidic nature of the medium leads us to infer that protons and AlCl$_3$ units (from Al$_2$Cl$_7$) compete for oxide sites and that peaks B and C are for oxygen atoms in bridging environments between aluminum atoms. This is further supported by the downfield chemical shift of these two lines relative to peak A, due to additional AlCl$_3$ moieties surrounding the O nucleus, and by the observed composition dependence of their intensities. By the same token, Peak C must correspond to a more highly substituted environment than Peak B.

O-bridging oxychloroaluminate species have been proposed for high temperature chloroaluminate melts (12) and have been shown to exist by crystallographic investigations of inorganic salts formed with the oxychloroaluminate as a counterion (13). Preliminary attempts at fitting the $^{17}$O data discussed above to models which take into account the stoichiometry of all species formed suggest that species similar to those in references 12 and 13 are formed and concur with the qualitative conclusions reached above.

Spectra of dissolved water at several concentrations in a basic melt are shown in Figure 5. In all cases, a single line is observed. However, the position of the peak shifts with increasing water concentration. The effect of bubbling HCl through a solution of water in a basic melt is to shift the peak upfield. As in the acidic melts, the peak which results is inferred to be due to an "Al-OH" moiety. Fast chemical exchange between two or more oxygen environments, probably "Al-O" and "Al-OH" moieties, is indicated by the presence of a single peak with a variable chemical shift. The observed concentration dependence then indicates that the "Al-O" moiety is the predominant oxide environment at low concentrations while "Al-OH"-containing species are more important at higher concentrations. This suggests that the discrepancy between the infrared (7) and electrochemical (9) results is due to the higher water concentrations used in the former case relative to those typically employed in the neutral melt amperometric titration technique utilized in the latter case. These results also provide direct evidence for the type of equilibrium used to explain the behavior of the Ti(IV) system upon addition of H$_2$O. In the latter experiment, relatively large H$_2$O concentrations were added to the titanium solutions.

Further information on water chemistry in the chloroaluminate melts can be obtained from $^1$H NMR studies of D$_2$O added to the melt.
We have also synthesized the DC1 salt of ImCl, (11), hereafter referred to as ImDClp, for use as a proton donor. $^2$H spectra of ImDCl solutions in basic and acidic melts are shown in Figure 6. The "DC1" resonance peak, the major peak in the spectrum, shifts downfield as the melt is made more basic. This is due to the interaction of DC1 with a second chloride ion in basic melts, probably in an H-bonding interaction, effectively forming DC1$^-$ ions. The proton chemical shift of the corresponding HCl$^-$ ion in the ImHCl$_2$ liquid is 13 ppm relative to TMS. In acidic melts, protons are present as free or weakly complexed HCl.

The $^2$H spectrum of a 50 mM solution of D$_2$O in an acidic melt is shown in Figure 7. In addition to the DC1 peak, there is a second D-containing species present. This is the "Al-OH" species discussed above. Spectra of D$_2$O in basic melts have but a single peak. This is probably due to fast chemical exchange, as discussed above.

In conclusion, $^1$H and $^2$H NMR studies have enabled us to deduce the nature of the speciation in H$_2$O solutions in melts. In acidic melts, three oxygen containing species are formed; one hydroxychloroaluminate and two O-bridged oxychloroaluminate species. In basic melts, rapid exchange precludes determination of the exact number of species formed, but we can qualitatively conclude that an oxychloroaluminate, probably in a terminal environment, and a hydroxychloroaluminate are present, with the latter species being the predominant form at high water concentrations. $^2$H NMR studies of protonic environments suggest that protons are present as DCl in acidic melts, but are strongly associated with a second chloride in basic melts.

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Fig. 1. $^{17}$O NMR spectra of 50 mM solutions of H$_2$O in (a) 1.2:1 melt and (b) 1:73:1.0 melt.

Fig. 2. Plot of relative intensities (integrated intensity for peak divided by total integrated intensity) for the three peaks as a function of water concentration in a 1.2:1.0 AlCl$_3$:ImCl melt.
Fig. 3. Plot of total integrated intensity (sum of integrated intensities for individual peaks in spectrum) as a function of concentration of water added to a 1.2:1.0 AlCl₃:ImCl melt.

Fig. 4. Spectrum of solution from Figure 1(a) after bubbling HCl through it.

Fig. 5. Spectra of water at various concentrations in a 0.8:1.0 melt (a) 50 mM; (b) 200 mM.
Fig. 6. Spectra of 50 mM solutions of ImDCI₂ in (a) 0.88 and (b) 1:32:1.0 melts.

Fig. 7. Spectrum of a 50 mM solution of D₂O in a 1:32:1.0 melt.