Proton Speciation in Ambient-Temperature Chloroaluminate Ionic Liquids

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Proton speciation in ambient-temperature chloroaluminate ionic liquids, composed of 1-ethyl-3-methylimidazolium chloride (ImCl) and aluminum chloride has been examined by ^{2}H NMR and FT-IR spectroscopies. In oxide free basic melts (excess ImCl), two proton-containing species, HCl and HCl_2^-, exist which are in an equilibrium that strongly favors the formation of the dichloride ion. In oxide free acidic melts (excess $AlCl_3$) HCl is the only proton-containing species. There is a single aluminum hydroxychloride species in acidic melts containing oxides, and there is at least one aluminum hydroxychloride species in basic melts containing oxides.

Introduction

Chloroaluminate molten salts, composed of mixtures of aluminum chloride with either *N*-butylpyridinium chloride, BuPyCl, or 1-ethyl-3-methylimidazolium chloride, ImCl, are liquid at or below ambient temperature over a wide range of compositions. These mixtures are unique ionic solvents whose anionic composition can be manipulated by varying the relative amounts of $AlCl_3$ and organic chloride.[1–3] When $AlCl_3$ is in excess the resulting melts contain $AlCl_4^-$ and $Al_2Cl_7^-$, a Lewis acid, and are referred to as acidic. Melts prepared with an excess of the organic chloride contain $AlCl_4^-$ and Cl^-, a Lewis base, and are basic. The melt containing equimolar amounts of $AlCl_3$ and organic chloride is referred to as a neutral melt because $AlCl_4^-$ is the only anion present.

Initially, the ambient-temperature chloroaluminate molten salts were thought to be aprotic and totally anhydrous.[4–7] However, subsequent studies showed this not to be the case.[8,9] The extremely hygroscopic organic chlorides used in these melts, when prepared by normal methods, are invariably contaminated by small quantities of water. When the organic chlorides are mixed with $AlCl_3$, the resulting melts contain millimolar quantities of both oxide and proton impurities.[10,11] The ubiquitous nature of these impurities and their reactivity toward solutes necessitate a clear understanding of their chemistry if the ambient-temperature chloroaluminates are to be routinely employed as solvents. As part of an ongoing effort in our laboratory, this manuscript describes further studies of proton speciation in the $AlCl_3$–ImCl melts.

The characterization of the proton containing species in the ambient-temperature chloroaluminate molten salts has been the subject of a variety of studies.[8,9,12–21] Initial work in the $AlCl_3$–BuPyCl melts by Sahami and Osteryoung[8] showed that the electrochemistry of proton, added as water, or as HCl, was indistinguishable in both acidic and basic melts. Lipsztajn et al.,[14] using hydroquinone as a proton donor, studied the electrochemistry of proton in the $AlCl_3$–ImCl melts. They proposed that in slightly basic melts proton existed as undissociated HCl, and when they compared their electrochemical results with those of Sahami and Osteryoung,[8] they concluded that the dissolution of water in basic melts produced two HCl molecules. However, these conclusions were somewhat at odds with the infrared work of Tait and Osteryoung[13] which indicated that the addition of water to both acidic and basic melts generated aluminum hydroxychlorides.

Franzen et al.[18] employed secondary ion mass spectrometry (SIMS) to investigate the anionic species in the chloroaluminate melts. The only proton containing anion identified for both acidic and basic melts was $Al_2Cl_6OH^-$. Wicelinski et al.[19] used fast atom bombardment mass spectrometry (FAB-MS) to further investigate the anionic species in the melts. In acidic melts, in addition to $Al_2Cl_6OH^-$ observed with SIMS, two additional hydroxychloroaluminates, $AlCl_3OH^-$ and $Al_3Cl_7O_2H^-$, were detected. In the basic melts no proton-containing anions were observed. The unusually high concentrations of oxide-containing anions observed in both the SIMS and FAB-MS studies resulted from water contamination both before and during the experiments. Consequently, the researchers in both studies were unable to determine if the hydroxides observed were initially present in the melts or resulted from fragmentation and/or reactions with traces of moisture in the system.

Zawodzinski and Osteryoung,[15] using ^{17}O NMR spectroscopy, investigated the chemistry of oxide and hydroxide species generated from the addition of water to the $AlCl_3$–ImCl melts. They demonstrated that oxide in acidic melts was partitioned

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between three species, two oxychloroaluminates and one hydroxychloroaluminate, in slow exchange. The relative amounts of each species depended on the amount of water added and the melt composition. In basic melts the oxy- and hydroxychloroaluminate species were in fast exchange giving a single ^{17}O resonance, the chemical shift of which depended on the amount of water added. In a later study, Zawodzinski and Osteryoung,[21] using improved techniques for proton addition and removal,[16,17] manipulated the proton concentrations and the melt compositions to model the oxy- and hydroxychloroaluminate species in the melts. Incorporating their results with the data from previous mass spectral studies,[18,19] they concluded that in the basic melts $Al_2Cl_6OH^-$ was the only hydroxychloroaluminate present. Their results for the acidic melts also indicated the presence of a single hydroxychloroaluminate; however, they were not able to unambiguously determine this species, so they presented two possible hydroxychloroaluminates, $Al_2Cl_6OH^-$ and $Al_3Cl_9OH^-$, of which they favored the former.

By employing 1-ethyl-3-methylimidazolium hydrogen dichloride ($ImHCl_2$) as a reagent for the quantitative addition of proton to the melts, Zawodzinski and Osteryoung[17] were able to study the chemistry of proton in the absence of large amounts of oxides. (In this study adventitious oxide impurities were not removed, and consequently, the oxide concentration in their melts was 5–10% of the added proton concentration.) The ^2H NMR of deuteron in the $AlCl_3$–ImCl melts gave a single line with a chemical shift that showed a marked dependence on melt composition. In very basic melts the deuteron line fell at 12 ppm vs TMS (7.5 ppm vs D_2O). As the melt was made less basic, the line shifted upfield. When the melt was made acidic the chemical shift remained constant, independent of acidity, at 6.9 ppm vs TMS (2.4 ppm vs D_2O). The strong dependence of the chemical shift in basic melts suggested the presence of two deuteron-containing species, ^2HCl and $^2HCl_2^-$, in fast exchange. From these results they proposed that deuteron, and also proton, speciation in the absence of large amounts of oxides could be described by the following equilibrium:

$$^2HCl + Cl^- \rightleftharpoons {}^2HCl_2^- \qquad (1)$$

Increasing chloride concentration in basic melts shifts eq 1 toward the formation of the $^2HCl_2^-$ ion. In neutral and acidic melts the absence of chloride ion leaves ^2HCl as the sole deuteron-containing species.

Smith and co-workers[10,22] studied the acidity of proton in acidic $AlCl_3$–ImCl melts. From the level of protonation of a series of arene bases they found that proton, added as HCl(g), was a Brønsted superacid similar, or greater, in strength to liquid HF at 0 °C ($H_0 = -15.1$). They found the strength of this superacid increased with increasing melt acidity. They proposed that proton in acidic melts existed as undissociated HCl and that the enhanced acidity of HCl in acidic melts was not due to any direct interaction with $Al_2Cl_7^-$ but instead resulted from the extremely low chloride activity in acidic melts which is maintained by the presence of $Al_2Cl_7^-$.

In the present work, NMR and infrared spectroscopies are used to further study proton speciation in the $AlCl_3$–ImCl melts. Recently it has become possible to cleanly and effectively remove initial oxide and proton impurities from $AlCl_3$–ImCl melts.[11] We have employed these methods to study the proton species present in oxide free basic and acidic melts. We describe here ^2H NMR measurements in oxide free melts that support the overall conclusions of Zawodzinski and Osteryoung.[17] However, we offer a correction to their assignment of the acidic melt ^2HCl chemical shift dependence. We also present FT-IR measurements which confirm the presence of HCl_2^- and HCl in oxide free basic melts and HCl in oxide free acidic melts. Finally, we describe ^2H NMR experiments which present further evidence for the existence of hydroxychloroaluminates in both basic and acidic melts.

Experimental Section

The synthesis and purification of ImCl was performed by a modified version of the procedure of Wilkes et al.[7] A total of 500 g of 1-methylimidazole (99%, Aldrich) was dried over CaH_2, and then 350 mL of liquid was vacuum distilled into a 1.2-L custom-built pressure bottle. The pressure bottle was fabricated from heavy walled tubing and had a top made from a No. 25 Ace-Thred (Ace Glass). Approximately 750 mL of ethyl chloride (99%, Matheson) was condensed into a flask containing 5 g of P_2O_5. After the ethyl chloride was dried over the P_2O_5 for several hours, 700 mL was condensed into the pressure bottle containing the 1-methylimidazole. The pressure bottle was then closed off and the mixture allowed to stir at room temperature for a period of 10 days to 2 weeks. The reaction was complete when the crude white ImCl precipitated. The pressure bottle with crude ImCl was transferred into a drybox where the excess ethyl chloride was carefully removed. The crude ImCl was then dissolved in a minimum of dry acetonitrile. The ImCl was precipitated by slowly adding the acetonitrile solution to dry toluene while stirring vigorously. After the ImCl was filtered, traces of toluene were removed by heating the ImCl above its melting point, 100 °C, and evacuating to <1 torr for 4–8 h. Normally, 400–500 g of clean white product was obtained from the above procedure.

The $AlCl_3$ used in ambient-temperature molten salts was purified by sublimation in a sealed glass bomb tube containing aluminum wire and sodium chloride.[3,7] Basic melts were prepared by slowly mixing weighed amounts of $AlCl_3$ and ImCl. The basic melts were then treated with phosgene and evacuated to remove oxide and proton impurities.[11] Acidic melts were prepared by first making a slightly basic melt (0.99:1.0) and treating the melt with phosgene and vacuum. $AlCl_3$ was then added to obtain the desired acidic melt. When an exactly neutral melt (1.0:1.0) was required, a slightly basic melt (i.e. 0.99:1.0) was first prepared and proton and oxide impurities removed.[11] Cyclic voltammetry was then used to monitor the melt electrochemical limits as small amounts of aluminum chloride were slowly added. A neutral melt was reached when the chloride oxidation wave disappeared and the $Al_2Cl_7^-$ reduction wave was not yet observed.

The presence of water and oxide impurities in the melts leads to some uncertainty in the concentration of the melt ionic species.[11] This error is significant only when ion concentrations are small, as is the case in slightly basic and slight acidic melts. To minimize this source of error for melts near neutral, a neutral melt was first prepared as described above. Using this neutral melt, slightly acidic melts with known $Al_2Cl_7^-$ concentrations and slightly basic melts with known Cl^- concentrations were prepared by addition of weighed amounts of $AlCl_3$ and ImCl, respectively. All melts between 0.95:1.0 and 1.1:1.0 were prepared by this method.

1-Ethyl-3-methylimidazolium hydrogen dichloride ($ImHCl_2$) and its deuterated analogue 1-ethyl-3-methylimidazolium deuterium dichloride (Im^2HCl_2) were used in the $AlCl_3$:ImCl melts as quantitative sources of proton and deuteron, respectively.[17] $ImHCl_2$ was prepared by reacting HCl(g) with ImCl. Im^2HCl_2 was prepared in the same manner as $ImHCl_2$ by substituting ^2HCl for HCl. We have found that the stoichiometry of the $ImHCl_2$ (and Im^2HCl_2) prepared by this method is variable. It is, in fact, more accurate to represent $ImHCl_2$ as $ImCl(HCl)_n$, where n ranges from 0.8 to 1.4. Consequently, each batch of $ImHCl_2$ and Im^2HCl_2 was analyzed to determine its stoichiometry. This analysis was performed by dissolving a weighed amount of $ImCl(HCl)_n$ in distilled water and titrating it with standardized NaOH. The end point was determined potentiometrically using a glass electrode. In addition, the isotopic purity of the Im^2HCl_2 was determined by comparing the ^1H NMR peak for the residual HCl_2^- with the other melt resonances. Normally, the Im^2HCl_2 was greater than 99% enriched.

1-Ethyl-3-methylimidazolium-2,4,5-d_3 chloride (ImCl-d_3) was prepared by a base catalyzed hydrogen–deuterium exchange with D_2O using the procedure of Dieter et al.[23] Following preparation, the crude ImCl-d_3 was dissolved in acetonitrile and filtered to remove small amounts of residual KCl. ^1H NMR analysis showed the ImCl-d_3 to be >95% deuterated at the 2-, 4-, and 5-positions on the imidazolium ring. The 1-ethyl-3-methylimidazolium-2,4,5-d_3 hydrogen dichloride (ImCl-d_3(HCl))

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was prepared using ImCl-d_3 in the procedure described above for the preparation of $ImHCl_2$.

All melt preparation was performed in a Vacuum Atmospheres drybox. The drybox atmosphere of nitrogen (99.995%, prepurified grade, Linde) was circulated through a Vacuum Atmospheres Model MO-40 inert gas purifier. The quality of the drybox atmosphere was normally evaluated using a 25-W bulb with the tungsten filament exposed. An acceptable atmosphere was one in which the bulb would burn for at least 14 days; this was indicative of oxygen and water levels less than 5 ppm.[24]

NMR samples were prepared in the drybox, pipetted into NMR tubes, and then capped and sealed with Parafilm. Melt samples for ^1H NMR were pipetted into 5-mm tubes fitted with precision coaxial inserts (Wilmad Glass Co.). Melt samples for ^2H NMR were placed into 10-mm tubes (Wilmad Glass Co.). The NMR samples of acidic melts saturated with ^2HCl were placed in 10-mm tubes, which were 9-in. long with a constriction at 8 in. (Wilmad Glass Co.). These NMR tubes were filled with melt in the drybox, attached to a vacuum line, saturated with ^2HCl, and then sealed. ^1H chemical shifts were referenced to 0.1% TMS in $CDCl_3$ (MSD Isotopes) in the coaxial insert. Natural abundance D_2O in water was the reference for the ^2H NMR and was assigned a value of 0 ppm. Referencing was performed by substitution, and all ^2H NMR spectra were acquired with the spectrometer unlocked. The ^1H and ^2H NMR experiments were performed using a Varian VXR-400S, operating at 399.952 and 61.395 MHz, respectively.

Infrared data were collected using a MIDAC high-resolution FT-IR spectrometer. The spectrometer employed a TGS detector and a Nernst glower source. All spectra were acquired at 4-cm^{-1} resolution with a total of 100 scans acquired per spectrum. Water vapor and CO_2 were removed from the sample compartment by continuous purging with dry nitrogen. The temperature of the sample compartment was 30 ± 1 °C. The sample cell and handling procedures used were the same as those employed by Tait and Osteryoung.[13]

Results and Discussion

NMR Studies of Proton in Oxide Free Melts. Zawodzinski and Osteryoung[17] presented data showing the effect of melt composition on the ^2HCl chemical shift. These data, after the referencing was changed to D_2O and the melt composition was corrected for the addition of chloride from the Im^2HCl_2, are shown in Figure 1a. We repeated this experiment, and the data are shown in Figure 1b. All of our melts were treated prior to use to remove adventitious oxide and proton impurities.[11] In the basic melts ^2HCl was added as Im^2HCl_2. The melt compositions were then corrected for the addition of Cl^- from the Im^2HCl_2. The acidic melts were saturated at 30 °C with 1 atm of ^2HCl gas.[25] From gravimetric analysis the concentration of ^2HCl in all the acidic melts was found to be ca. 200 mM.

The two sets of data for the basic melts presented in Figure 1 are similar. Like Zawodzinski and Osteryoung[17] we observed a single deuterium line in all basic melts, which indicates that there is fast chemical exchange between all deuterium-containing species present. However, the chemical shifts for the data of Zawodzinski and Osteryoung[17] are consistently less than our data. Some of this difference may be due to temperature. Zawodzinski and Osteryoung[17] obtained their data at 90 °C versus 30 °C for our data. The deuteron equilibrium (eq 1) shifts toward formation of ^2HCl with increasing temperature.[26] Since ^2HCl is the upfield resonance, an increase in temperature would lead to a shift in the population weighted average resonance toward higher fields. However, the magnitude of the temperature dependence of the $^2HCl_2^-/^2HCl$ equilibrium is relatively small and can account for at most a few tenths of a ppm difference in the most basic melts.[26] The primary cause for the difference in the two sets of basic melt chemical shift data appears to result from the fact that the melts used by Zawodzinski and Osteryoung[17] were not treated to remove oxide impurities and as such probably contained 5–15 mM oxides. The addition of Im^2HCl_2 would lead to some if not all of the oxide impurities being converted to deuteroxides. The chemical shift of the deuteroxide in the basic melt appears to be less than the $^2HCl_2^-$ chemical shift (see below). Consequently, the population-weighted average chemical shift would be upfield of a melt without oxides.

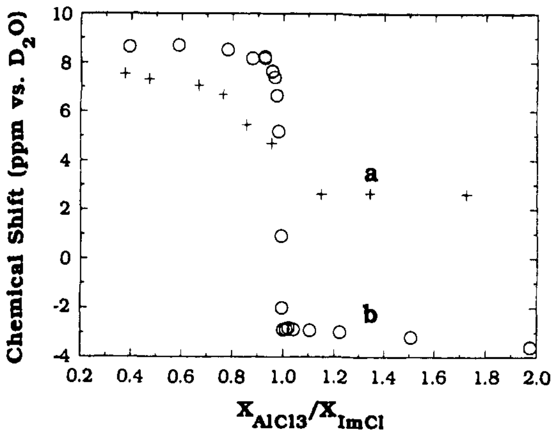

Figure 1. Plots of ^2HCl chemical shift versus mole ratio: (a) data from Zawodzinski and Osteryoung[17] (+), with 200 mM ^2HCl (added as Im^2HCl_2) at 90 °C; (b) data from the present work (○), with spectra obtained at 30 °C and 98 mM ^2HCl (added as Im^2HCl_2) for melts <1.0 and ca. 200 mM ^2HCl (added as 1 atm $^2HCl(g)$) for melts ≥1.0.

In the acidic melts, Zawodzinski and Osteryoung[17] gave the chemical shift of ^2HCl as 2.4 ppm. Our initial ^2H NMR studies of ^2HCl in acidic melts appeared to agree with this assignment with the exception of the neutral melt where we found the chemical shift of ^2HCl to be −2.9 ppm. This inconsistency lead us to conduct more detailed experiments which eventually showed that the peak assigned to ^2HCl at 2.4 ppm was, in fact, deuterium at the 4,5-position on the imidazolium cation ring. Further experiments with time-resolved FT-IR spectroscopy demonstrated that deuterium from ^2HCl was exchanging with protium at the 4,5-position of the imidazolium ring. The details of this hydrogen–deuterium (H–D) exchange on Im^+ will be described elsewhere.[27]

During the experiments of Zawodzinski and Osteryoung,[17] enough time apparently elapsed between sample preparation and spectral acquisition for all the ^2HCl to be converted to HCl. Thus, they only observed the deuterium signal from the ^2H-4,5 on the imidazolium ring. In our experiments we were able to obtain chemical shift data for ^2HCl in the acidic melts by acquiring our spectra as soon as the samples were prepared. These data showing the actual dependence of the ^2HCl chemical shift on acidic melt composition are shown in Figure 1b. Interestingly, the ^2HCl chemical shift does not remain constant through the acidic melt region, but shifts from −2.9 to −3.6 ppm going from a 1.0:1.0 to a 1.976:1.0 melt (Table I), respectively. The upfield shift in the ^2HCl resonance is toward the gas phase value.[28] This indicates an increase in charge density on the deuterium and a corresponding increase in covalent character of the ^2H–Cl bond. From this one may infer that ^2HCl becomes less solvated as the melt acidity increases.

For our data (Figure 1b) the overall chemical shift difference between $^2HCl_2^-$ (most basic melt) and ^2HCl (neutral melt) is ca. 11.6 ppm (Table I). This difference is similar to the ^1H NMR chemical shift difference found for HCl_2^-/HCl in various nonaqueous solvents.[29,30]

Although, as discussed above, there were some errors in their results, the conclusions drawn by Zawodzinski and Osteryoung[17]

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[25] $^2HCl(g)$ is rapidly lost from acidic melts after the addition of Im^2HCl_2. Consequently, the only method of introducing a constant concentration of deuteron into acidic melts was to saturate the melts with ^2HCl in the NMR tubes at a specific partial pressure of ^2HCl and then seal the tube.

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Table I. NMR Chemical Shift Data for Proton-Containing Species in the $AlCl_3$–ImCl Melts

proton species	chem shift, ppm ^1H vs TMS[a]	 ^2H vs D_2O[b]	 ^{17}O vs $H_2{}^{17}O$[a]
HCl_2^-	12.997[c]	8.44[c]	
HCl (1.0:1.0 melt)	1.610[c]	−2.90	
HCl (1.976:1.0 melt)		−3.60	
$Al_2Cl_6OH^-$ (basic)			25.0[d]
acidic "AlOH" ($Al_2Cl_6OH^-$ or $Al_3Cl_9OH^-$)		0.86	44[e]
			49.7[f]

[a] Data obtained at 90 °C. [b] Data obtained at 30 °C. [c] The chemical shift was obtained from a fit of basic melt data.[26] [d] Reference 21. [e] Reference 11. [f] Reference 15.

about the deuteron (and proton) equilibrium in $AlCl_3$–ImCl melts were essentially correct. In the absence of oxides the deuteron equilibrium is described by eq 1. In the basic melts $^2HCl_2^-$ and ^2HCl are in fast exchange under equilibrium control, and in acidic melts ^2HCl is the only deuteron-containing species present.

Proton in Melts Containing Oxides. In $AlCl_3$–ImCl melts containing oxides at least one and possibly two additional proton-containing species exist, $Al_2Cl_6OH^-$ in basic melts and $Al_2Cl_6OH^-$ or $Al_3Cl_9OH^-$ in acidic melts.[21] To further study these hydroxychloroaluminate ions a series of basic and acidic melts were prepared containing 100 mM D_2O. The addition of D_2O to these melts resulted in the formation of a precipitate which, with stirring overnight at 50 °C, dissolved. The ^2H NMR spectra of basic melts ranging from 0.80:1.0 to 0.99:1.0 at temperatures from 7 to 90 °C in all cases showed a single line. The position of this peak was dependent on chloride concentration and temperature. The effect of lower chloride concentration or increasing temperature was to shift the peak upfield. These results suggest that fast chemical exchange is taking place between all of the deuteron environments.

The addition of water has been shown to generate HCl and aluminum oxide and hydroxide moieties.[13,15] Previous ^{17}O NMR studies[15,21] in basic melts indicated that these three species are in the equilibrium

$$Al_2OCl_5^- + HCl \rightleftharpoons Al_2Cl_6OH^- \qquad (2)$$

under fast exchange conditions. Also, as discussed above, $^2HCl_2^-$ and ^2HCl (eq 1), in the absence of oxides, are in fast chemical exchange. Thus, the observation of a single ^2H NMR peak for basic melts with added D_2O is consistent with rapid exchange between the three deuteron-containing species, $^2HCl_2^-$, ^2HCl, and $Al_2Cl_6O^2H^-$. Because of the uncertainty in the concentration and the presence of rapid exchange, the exact ^2H NMR chemical shift of $Al_2Cl_6O^2H^-$ could not be determined. However, the deuteroxide species in acidic melts appears to be either the same as in the basic melts or differs by only one $AlCl_3$ (i.e. $Al_3Cl_9O^2H^-$).[21] Consequently, the chemical shift of $Al_2Cl_6O^2H^-$ in basic melts should be close to that observed for the deuteroxide in acidic melts (see below).

The ^2H NMR spectra of the acidic melts containing D_2O exhibited lines for ^2H-4,5, from the H–D exchange reaction, and, normally, a small ^2HCl peak. In addition a new resonance at 0.86 ppm was observed. The presence of a single deuteriooxychloroaluminate ion is in agreement with earlier ^{17}O NMR studies.[15,21] We assigned this new peak to the acidic deuteriooxychloroaluminate ion. For convenience we will represent this species as "AlO^2H" because of the ambiguity as to its exact nature.[21] The chemical shift of "AlO^2H" remained essentially constant in all of the acidic melts studied. However, the relative integrated intensity of the "AlO^2H" resonance decreased with respect to the H–D exchange peak (^2H-4,5) at 2.4 ppm as the melt acidity increased. The observation of both ^2HCl and "AlO^2H" peaks in these melts indicates that the rate of chemical exchange is slow between ^2HCl and "AlO^2H". This is also in agreement with the ^{17}O NMR observations of slow exchange between the three acidic melt oxide species.[15,21] A summary of NMR chemical shift data for proton-containing species in the $AlCl_3$–ImCl melts is given in Table I.

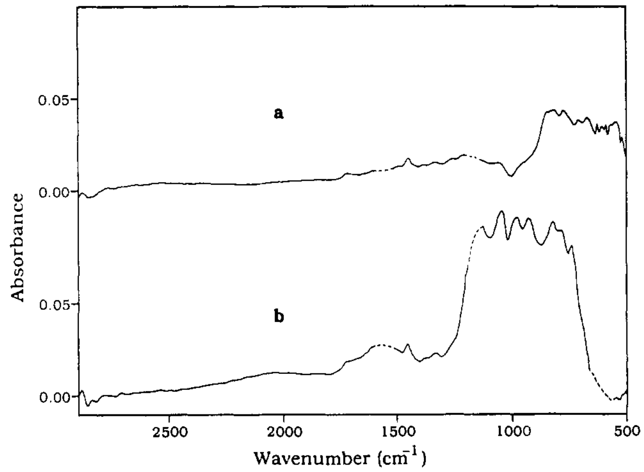

Figure 2. IR spectra of a 0.394:1.0 melt at 30 °C containing (a) 98.6 mM ^2HCl (added as Im^2HCl_2) and (b) 122.4 mM HCl (added as $ImHCl_2$). Spectra are background subtracted and smoothed. Dashed lines represent regions of severe interference.

Infrared Studies of Proton in $AlCl_3$–ImCl Melts. Tait and Osteryoung[13] examined the IR spectra of melts containing proton added as water. These studies were limited with respect to proton chemistry because of the presence of oxides generated from water. Therefore, in conjunction with the above ^2H NMR studies, the infrared spectra of proton and deuteron in oxide free acidic and basic melts were examined.

A series of background subtracted infrared spectra of proton and deuteron in oxide free basic and acidic melts were obtained. The spectrum of the silicon window cell containing the original melt before the addition of proton (or deuteron) was used as the background. In general, the background subtraction worked well except for those silicon and melt absorbances greater than ca. 1 AU where the subtraction resulted in a confused differential. To enhance the clarity of several of the figures presented in this manuscript these regions were replaced with dashed lines that best approximated the proton (deuteron) absorbances. In addition, all background subtracted spectra were smoothed using an 11-point second-order Savitsky–Golay algorithm. Both proton and deuteron spectra were obtained so that the isotopic shift in absorption bands could be used to identify features due to proton- (deuteron-) containing species. In all cases proton was added as $ImHCl_2$, and deuteron was added as Im^2HCl_2. However, for consistency all proton and deuteron concentrations are given in terms of HCl and ^2HCl, respectively. The melt compositions are then corrected for the chloride added from the $ImHCl_2$ or Im^2HCl_2.

The infrared spectrum of a 0.394:1.0 melt containing 98.6 mM ^2HCl is shown in Figure 2a, and the spectrum of the same melt containing 122.4 mM HCl is displayed in Figure 2b. The broad absorbances exhibited by the spectra in Figure 2 are characteristic of hydrogen dihalide ions in solution.[31-35] The absorption features and isotopic shift of the spectra in Figure 2a,b are essentially the same as those of $^2HCl_2^-$ and HCl_2^-, respectively, in nonaqueous solvents.[31] Therefore, we may conclude that hydrogen dichloride ion is one form of proton (deuteron) present in the oxide free basic melts.

There is considerable uncertainty in choosing the band centers for the broad absorbances of HCl_2^- and $^2HCl_2^-$ in basic melts;

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(31) Evans, J. C.; Lo, G. Y.-S. *J. Phys. Chem.* **1966**, *70*, 11–19.
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(34) Evans, J. C.; Lo, G. Y.-S. *J. Phys. Chem.* **1967**, *71*, 3942–3947.
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Table II. HCl_2^- and $^2HCl_2^-$ Absorption Features in Basic $AlCl_3$–ImCl Melts and Acetonitrile[a]

basic $AlCl_3$–ImCl[b]			acetonitrile[b,c]			
HCl_2^-	$^2HCl_2^-$	$H/^2H$	HCl_2^-	$^2HCl_2^-$	$H/^2H$	assignt
2014 (vw, vb)			2040 (vs, b)			$2\nu_2$
1562 (w, b)	1192 (vw, vb)	1.31	1600 (w, b)	1170 (w)	1.37	$2\nu_3$
~1140 (s, b) ~984 (s, b)	~752 (s, b)		~1150 (s, b) ~950 (s, b)	~780 (s, b)		ν_2
~802 (s, b)	~563 (s, b)	1.42	800 (s, b)	560 (s, b)	1.43	ν_3

[a] Abbreviations: vw = very weak; w = weak; s = strong; b = broad; vb = very broad; $2\nu_2$ = first overtone bending mode; $2\nu_3$ = first overtone asymmetric stretch; ν_2 = doubly degenerate bending mode; ν_3 = asymmetric stretch. [b] All absorbances in cm^{-1}. [c] Data obtained from ref 31.

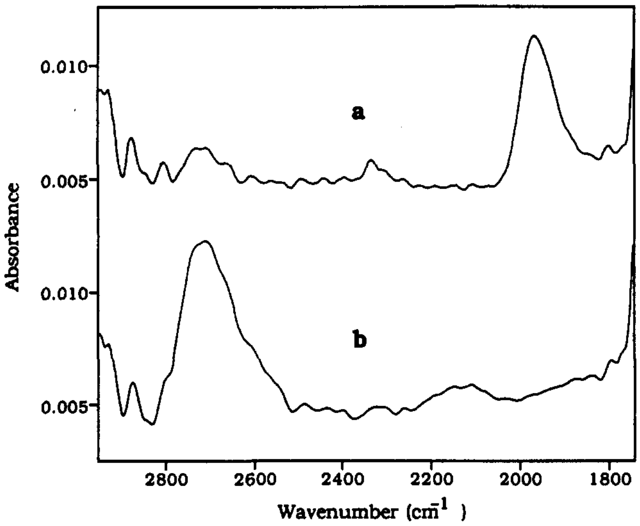

Figure 3. IR spectra of slightly basic melts containing (a) 12.5 mM Cl^- and 98.9 mM ^2HCl (added as Im^2HCl_2) and (b) 13.2 mM Cl^- and 125.6 mM HCl (added as $ImHCl_2$). Spectra were obtained at 30 °C. Data are background subtracted and smoothed.

Table III. HCl and ^2HCl Fundamental Vibration Bands in $AlCl_3$–ImCl Melts and in Various Solvents

	ν, cm^{-1}			
solvent	HCl	^2HCl	$H/^2H$	ref
CCl_4	2834	2054	1.380	*a*
CCl_2CCl_2	2830	2051	1.380	*a*
1.887:1.0[c] $AlCl_3$:ImCl	2762	2002	1.380	*b*
C_6H_6	2758	2004	1.376	*a*
1.194:1.0[c] $AlCl_3$:ImCl	2721			*b*
0.997:1.0[d] $AlCl_3$:ImCl	2709	1972	1.374	*b*
$C_6H_6NO_2$	2693			*e*
CH_3CN	2542	1851	1.373	*c*

[a] Reference 36. [b] This work. [c] Melt containing ca. 200 mM HCl (^2HCl) added as $ImHCl_2$ (Im^2HCl_2). [d] Melt containing ca. 100 mM HCl (^2HCl) added as $ImHCl_2$ (Im^2HCl_2). [e] Reference 37.

this is especially true for the band of absorbances from 1170 to 740 cm^{-1} for HCl_2^- and from 870 to 510 cm^{-1} for $^2HCl_2^-$. The overall features of the HCl_2^- and $^2HCl_2^-$ bands were constant throughout the basic melt region. However, the interference from the melt background varied with melt composition. Consequently, spectra from a wide range of basic melts were used to determine the infrared bands for HCl_2^- and $^2HCl_2^-$ listed in Table II. Even so the assignments of the bending (ν_2) and asymmetric stretching (ν_3) modes are at best approximate. For comparison the absorbance features for HCl_2^- and $^2HCl_2^-$ in acetonitrile are also given in Table II. The work of Evans and Lo[31] showed that the dichloride ion in acetonitrile exists as a linear molecule with the hydrogen symmetrically placed between the two chlorides. The close similarities between the HCl_2^- and $^2HCl_2^-$ bands in the basic melts and in acetonitrile leads us to conclude that the dichloride ions in the melts also exists as a linear symmetrical species.

The infrared spectra of 98.9 mM ^2HCl in a 0.9973:1.0 melt (12.5 mM Cl^-) and 125.6 mM HCl in a 0.9971:1.0 melt (13.2 mM Cl^-) are shown in parts a and b of Figure 3, respectively. The shape, position, and isotopic shift of the bands in Figure 3 are characteristic of hydrogen chloride.[36–44] Hydrogen chloride was the only proton containing species observed in an oxide free, very slightly basic melt; this is in agreement with the ^2H NMR data presented above and with the conclusions made by Smith et al.[10] The HCl and ^2HCl fundamental vibration bands from Figure 3 and two other acidic melts are given in Table III. For comparison the vibration bands of hydrogen chloride in several solvents are also given in Table III. The shape and isotopic shift of the hydrogen chloride band remained relatively constant throughout the acidic melts. However, the position of the band shifted toward higher wavenumbers as the melts were made more acidic. The shift in HCl vibration frequency to higher wavenumbers for the solvents in Table III has been attributed to a decrease in the association of the solvent with the HCl dipole.[38] Consequently, the increase in the HCl vibration frequency with increasing melt acidity seems to indicate a significant decrease in the interaction of the solvent with HCl. A similar conclusion was reached from the upfield shift in the ^2HCl resonance at higher [$Al_2Cl_7^-$] (see above). Interestingly, this decrease in solvent interaction occurs in conjunction with an increase in the Brønsted superacidity of HCl.[10,22] However, the relationship between these two phenomena is still not clear.

The above data confirm the presence of HCl and HCl_2^- in the $AlCl_3$:ImCl melts. To demonstrate the equilibrium between these two species infrared spectra were obtained for 124 mM HCl in basic melts containing 210, 78, 31, and 13 mM Cl^-. Figure 4 shows this family of spectra. The presence of two isosbestic points at 2820 and 2350 cm^{-1} is indicative of an equilibrium between HCl and HCl_2^-.[41] Figure 4 also demonstrates that in basic melts the proton equilibrium (eq 1) strongly favors the formation of HCl_2^-, and only under conditions of very low chloride concentrations are significant amounts of HCl present; these observations are in complete agreement with the ^2H NMR data presented above.

Recent work has shown that there is extensive hydrogen bonding between the imidazolium ring hydrogens and chloride ion in basic $AlCl_3$–ImCl melts.[23,42,43] The HCl_2^- ion can also act as a hydrogen-bond acceptor.[30,44,45] Thus, it seemed possible that HCl_2^- ion could also be involved in hydrogen-bond interactions with the imidazolium cation. To investigate this further a basic

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(45) The HCl_2^- ion has been shown to hydrogen bond with one or more HCl molecules to form $Cl(HCl)_n^-$ ions.[30,44]

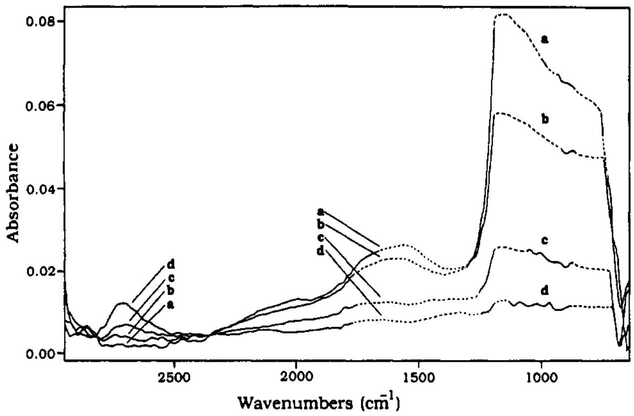

Figure 4. IR spectra of 124 mM HCl in basic melts containing (a) 210 mM Cl^-, (b) 78 mM Cl^-, (c) 31 mM Cl^-, and (d) 13 mM Cl^-. Spectra were obtained at 30 °C. Data were background subtracted and smoothed. Dashed lines represent areas of severe interference.

melt (0.394:1.0) prepared from $AlCl_3$ and 1-ethyl-3-methylimidazolium-2,4,5-d_3 chloride (ImCl-d_3) was made 112.6 mM in HCl, added as ImCl-d_3(HCl). A second nondeuterated basic melt (0.396:1.0) containing 122.4 mM HCl was also prepared. The IR spectra of these two melts are shown in Figure 5. If significant hydrogen bonding existed there should be some isotopic shift in the band maxima for HCl_2^- in the $AlCl_3$:ImCl-d_3 melt (Figure 5b). However, the bands in the two spectra in Figure 5 appear to be essentially the same. Also if the HCl_2^- ion were involved in hydrogen bonds one would expect to see absorbance features of an unsymmetrical ion (unless of course both chlorides were equally involved in hydrogen bonds to Im^+); however, as discussed above, this is not the case. It is possible that, for the spectra in the very basic melts shown in Figure 5, the high concentration of chloride ion may bind most of the available hydrogen-bonding sites, and, consequently, hydrogen-bonding of HCl_2^- may be more important in less basic melts. However, the IR spectrum of HCl_2^- remains constant throughout the basic melts (see above), indicating no appreciable change in solvation. Thus, the data presented above show no evidence of significant hydrogen-bonding between HCl_2^- ion and the imidazolium cation.

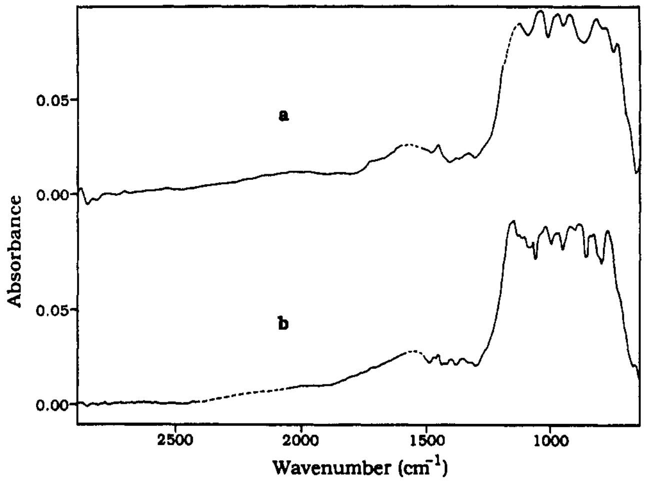

Figure 5. IR spectra of (a) a 0.394:1.0 $AlCl_3$:ImCl melt with 122.4 mM HCl (added as $ImHCl_2$) and (b) 0.396:1.0 $AlCl_3$:ImCl-d_3 melt with 112.6 mM HCl (added as ImCl-d_3(HCl)). Spectra were obtained at 30 °C. Data are background subtracted and smoothed. Dashed lines represent areas of severe interference.

Conclusion

Proton in oxide free basic melts exists as either HCl_2^- or HCl. The equilibrium between these two species strongly favors HCl_2^- except in those basic melts with very low chloride ion concentrations. The HCl_2^- ion exhibits spectral features of a linear symmetrical species, and it does not appear to be involved in hydrogen bonds to the imidazolium cation. In acidic oxide free melts, HCl is the only proton-containing species. In acidic melts containing oxides there exists a single hydroxychloroaluminate, and in basic melts containing oxides there is at least one hydroxychloroaluminate species.

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