Articles

Speciation of the Proton in Ambient-Temperature Molten Salts[†]

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Received November 25, 1992

Ionic equilibria associated with acidic protons present in HCl:ImCl (Im$^+$ ≡ 1-ethyl-3-methyl-1H-imidazolium) ionic liquids (0.38 < HCl mole fraction, X_{HCl} < 0.67) have been investigated by ^{1}H-NMR spectroscopy (200 MHz, 297 K). We conclude that proton speciation in these liquids is governed largely by the reaction $H_2Cl_3^- + Cl^- \rightleftharpoons 2HCl_2^-$, for which the stoichiometric equilibrium constant has been evaluated as 218 ± 25; the concentration of molecular HCl is small or negligible relative to that of the anionic species. Virtually identical behavior was observed in an AlCl$_3$:ImCl (AlCl$_3$ mole fraction = 0.35) ionic liquid. As in the case of the HCl:ImCl system, it was found that, maximally, 2 equiv of HCl (relative to available chloride ion) could be introduced into the AlCl$_3$:ImCl liquid under ambient conditions. On the basis of these observations, and those of other workers, we have constructed an approximate phase diagram for the ternary system HCl:ImCl:AlCl$_3$ near ambient temperature and with HCl pressure less than 1 atm. Depending on the activity of Al$_2$Cl$_7^-$, the behavior of protic species in this system may range from that of a weak Lewis acid to that of a Bronsted superacid.

Introduction

Ambient-temperature molten salts generated by the reaction of an organic base with a Lewis acid have been widely investigated in a number of laboratories (for reviews see refs 1–4). Though a variety of organic base/Lewis acid systems have been investigated, 1-ethyl-3-methyl-1H-imidazolium chloroaluminates (AlCl$_3$:ImCl) have been found to combine high conductivity and low viscosity with a wide electrochemical window.[6,7] A great deal of work conducted with these liquids involves electrochemical investigations; notably, a variety of transition metal complexes which are unstable in other media may be studied in ambient-temperature melts.[8–10] Near ambient temperature, the AlCl$_3$:ImCl system forms a single liquid phase for AlCl$_3$ mole fractions in the range *ca.* 0.33–0.67.[1] The Lewis acidity of the system can be varied through a wide range depending on the proportions of organic base and Lewis acid from which it is prepared; AlCl$_3$ mole fractions less than 0.5 afford a basic melt, while those greater than 0.5 afford an acidic medium. The acid/base behavior of the melts is controlled largely by reaction 1, which is believed to

$$Al_2Cl_7^- + Cl^- \rightleftharpoons 2AlCl_4^- \tag{1}$$

adequately describe the speciation of chloroaluminate melts over a wide range of compositions. The equilibrium constant for this reaction is of the order of 10^{17}–10^{18} near ambient temperature,[11,12] and hence in basic melts, the predominant anionic species are AlCl$_4^-$ and Cl$^-$, while in acidic melts, Al$_2$Cl$_7^-$ and AlCl$_4^-$ predominate. In the highly acidic melts, larger aluminum chloride adducts may become significant, *e.g.* Al$_3$Cl$_{10}^-$.

An unavoidable impurity, water reacts with AlCl$_3$:ImCl melts to produce several oxy/hydroxychloroaluminate species and molecular HCl.[13] Consequently, the chemistry of HCl in ambient-temperature melts has received considerable attention. Liquid hydrogen halides (HX; X ≡ Cl, F) are believed[14] to undergo autoionization according to the equilibrium

$$3HX \rightleftharpoons H_2X^+ + HX_2^- \tag{2}$$

giving rise to the finite conductivities of the pure liquids. Liquid HF has a Hammett acidity function (H$_0$) value of about −15.1;[15] addition of SbF$_5$ results in a powerful superacid (H$_0$ *ca.* −30) which is known to contain H$_2$F$^+$ and H$_3$F$_2^+$.[16] The corresponding chloronium ion, H$_2$Cl$^+$, is believed[14] to exist in a few solid compounds and, presumeably, should also exist in the AlCl$_3$:HCl superacids. The existence of this species, however, has never been demonstrated unequivocally. HCl added to liquid ionic chlorides is expected to ionize according to reaction 2 but with an increased association constant appropriate to the temperature and to the degree of electrostatic stabilization afforded by the melt. Where the ionic chloride is Lewis acidic, *e.g.* AlCl$_3$:MCl (M = Li, Na, K, Rb) or AlCl$_3$:ImCl, X(AlCl$_3$) > X(M or Im),

[†] The current paper is a corrected and revised version of paper No. 513, which was originally presented at the Spring 1992 meeting of The Electrochemical Society, Inc., held in St. Louis, MO.[5]

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we anticipate stabilization of H_2Cl^+ and a corresponding superacidity. In the Lewis acidic $AlCl_3$:ImCl system, protons added as HCl behave as Bronsted superacids and will protonate a variety of arenes.[17] Though H_2Cl^+ has yet to be identified, the potential of the Lewis acidic $AlCl_3$:ImCl systems to stabilize cationic species has been noted.[18] Formation of H_2Cl^+ involves protonation of HCl (*i.e.* the latter acts as a base) and is therefore analogous to formation of an arenium ion;[17] proton affinities of hydrogen halides are favorable in this respect.[19,20] It has been suggested that the proton exists as molecular HCl^{21-24} and that superacidity results not from some superacidic species but from the ability to maintain a low chloride concentration according to reaction 1.[17] Conclusive evidence for the existence of HCl in the acidic $AlCl_3$:ImCl system has recently been reported.[25]

Where the ionic chloride is Lewis basic, $X(AlCl_3) < X(M$ or Im), one would expect HCl to be stabilized as HCl_2^- in accord with the reaction

$$HCl + Cl^- \rightleftharpoons HCl_2^- \qquad (3)$$
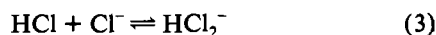
which is believed to describe proton speciation in the $AlCl_3$:ImCl system and in $ImHCl_2$ (1:1 HCl:ImCl), another ambient-temperature melt which results from reaction of ImCl with anhydrous HCl.[21] The equilibrium constant for reaction 3 in nitrobenzene has been reported[26] as 5×10^2 L/mol at 298 K, and hence in the presence of excess chloride the predominant species is the hydrogen dichloride anion. In the Lewis basic $AlCl_3$:ImCl system, k_3 is reported as 67 ± 18 at 363 K.[27] For reviews of the hydrogen dihalides and strong hydrogen bonding, see Tuck[28] and Emsley,[29] respectively.

Although $ImHCl_2$ has been used as a reagent for proton addition, no detailed investigations of the HCl:ImCl system itself, previous to the current work, have appeared in the literature. In the current paper, details and results of an NMR investigation concerning the identity of protic species in this system are reported; these are particularly illuminating regarding proton speciation in the basic regime under ambient conditions, where it is demonstrated that species other than HCl_2^- must exist and that molecular HCl does not contribute significantly. The chemistry of protic species in the ternary, Lewis basic HCl:ImCl:$AlCl_3$ system appears virtually identical to that in HCl:ImCl. On the basis of these observations, we have constructed an approximate phase diagram for the ternary system HCl:ImCl:$AlCl_3$ for ambient temperature and $P_{HCl} < 1$ atm. These results are significant in that, up to the present, only HCl and HCl_2^- have been recognized as protic species in the HCl:ImCl and $AlCl_3$:ImCl systems.

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Experimental Section

Materials. 1-Ethyl-3-methyl-1*H*-imidazolium chloride (ImCl) was prepared by the method of Smith *et al.*[17] affording a 70% yield of ImCl, mp 91.2–91.6 °C (uncorrected). The recrystallization solvent (acetonitrile) was removed from ImCl by heating (70 °C) under vacuum (0.001 mmHg) for 7 days. Aluminum chloride (Fluka, puriss) was further purified by two successive vacuum sublimations from reagent grade Al and NaCl (Fisher, ACS Reagent) which had been prepared by heating at 400 °C for 4 days with alternation between vacuum and an atmosphere of dry HCl or argon. The synthesis of ImCl and the purification of $AlCl_3$ were conducted under an atmosphere of dry argon, and the resulting products were immediately stored in sealed Pyrex ampules under same. All further manipulations were conducted in a glovebox under an atmosphere of dry argon or nitrogen or in "airless" glassware. The glovebox atmosphere was circulated continuously through a Cu furnace and equilibrated over P_2O_5. Anhydrous HCl was prepared by the reaction of concentrated hydrochloric and sulfuric acids under an atmosphere of argon or nitrogen. The resulting HCl was dried by passage through a dry-ice/acetone trap, sparging through drying towers of concentrated H_2SO_4, and, finally, by passage through a column of anhydrous Mg-$(ClO_4)_2$.

Preparation of Melts. The preparation of HCl:ImCl liquids was accomplished by the addition of dry HCl to weighed samples of ImCl. This was performed at such a rate that the temperature of the melt did not exceed *ca.* 30 °C. In some instances, excess HCl was pumped off so as to afford the desired HCl mole fraction (X_{HCl}). The HCl content of these samples was determined by a titrimetric procedure described below. $AlCl_3$:ImCl was prepared by the gradual addition of $AlCl_3$ to a known mass of ImCl; following preparation of the melt, $AlCl_3$ content was obtained from the total mass of the resulting cooled melt. Solutions of HCl in a basic $AlCl_3$:ImCl (35.0 mol % $AlCl_3$) ionic liquid were prepared by the direct addition of dry HCl to freshly prepared chloroaluminate liquids. For these samples, the total HCl content was determined gravimetrically and by integration of NMR signal intensities.

¹H-NMR Spectroscopy. ¹H-NMR spectra (200 MHz) were acquired at 297 K with a Bruker AM 200 NMR Spectrometer. NMR samples were prepared in the glovebox in standard 5-mm NMR tubes, each of which contained a coaxial capillary filled with DMSO-d_6. All spectra are referenced to TMS. In the case of HCl:ImCl, approximately 1 g of melt was added to a previously weighed NMR tube. Following acquisition of NMR spectra, the samples were weighed and analyzed for HCl content by reacting with an excess of aqueous Na_2CO_3 (BDH, AnalR). In the carrying out of this reaction, the NMR tube was opened under the surface of the basic solution so as to ensure complete reaction of HCl contained in the sample; no odor of HCl was detectable during this procedure. The HCl content of the sample was then determined by back-titration of the reaction mixture with standard HCl. Initially, HCl:ImCl samples were prepared gravimetrically, sealed in 1-mm glass capillaries, and immersed in NMR tubes containing a few milliliters of DMSO-d_6. However, poor reproducibility of chemical shift *vs* composition data was observed for these samples; this is attributed to changes in composition during sample preparation, *i.e.* pipet transfers. For this reason, all samples used to acquire composition *vs* chemical shift data were analyzed by the titrimetric procedure outlined above.

Results

Ionic liquids within the HCl:ImCl system were found to exist as such (298 K, maximum P_{HCl} *ca.* 0.94 atm) for HCl mole fractions (X_{HCl}) in the range *ca.* 0.38–0.68, the latter composition having a stoichiometry near 2:1. The value of 0.38 is probably higher than the lower limit. A typical proton NMR spectrum of such a liquid is illustrated in Figure 1 for a melt with $X_{HCl} = 0.47$. The downfield resonance at 13.01 ppm (inset, Figure 1) is ascribed in the literature to the HCl_2^- ion.[21,25] Initially, we reported[5] that for melts with an excess of HCl, *i.e.* $X_{HCl} > 0.5$, a complex transient NMR signal is associated with the acidic proton. However, we have come to the conclusion[51] that this signal is an artifact arising during transfer of melt samples to NMR tubes; because these liquids tend to change composition with pressure changes, several discrete compositions may be generated as the sample is pipetted into the NMR tube. The existence of such gradients was ruled out, initially, on the basis of the fact that the "complex" resonance was observed only for
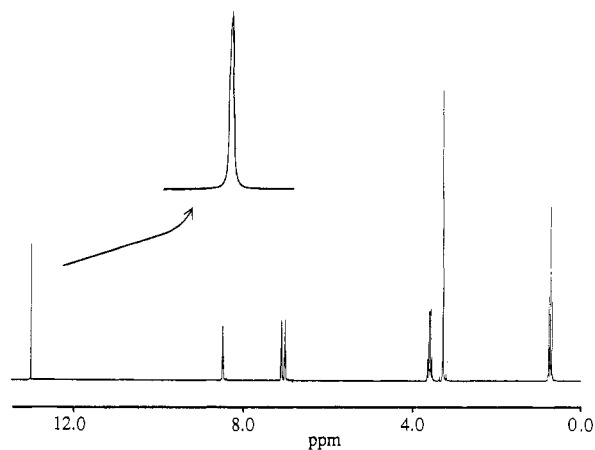
Figure 1. Typical ^{1}H-NMR spectrum of a chloride-rich HCl:ImCl ionic liquid (X_{HCl} = 0.47). The inset shows an expansion of acidic proton resonance at 13.01 ppm.
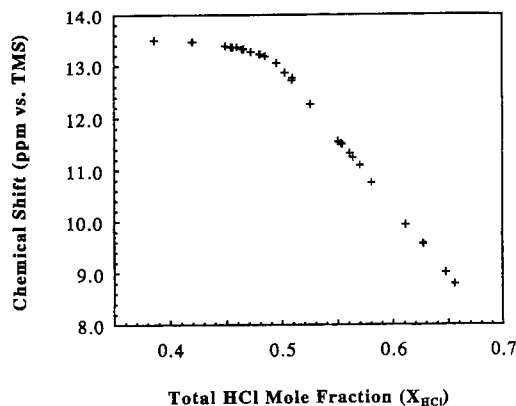

Figure 2. Chemical shift of acidic proton as a function of HCl mole fraction in HCl:ImCl ionic liquids.

the acidic proton, Im$^+$ resonances being unaffected. We now attribute this to the much greater sensitivity of the acidic proton shift to melt composition, particularly for X_{HCl} > 0.5 (see below). Our overall conclusions,[5] however, remain unchanged.

The dependence of the chemical shift of the acidic proton on X_{HCl} is illustrated in Figure 2. As the chemical shift varies over a range of *ca.* 5 ppm, it is clear that the proton is engaged in rapid exchange amongst several environments, with that predominating in the chloride-rich range (X_{HCl} < 0.50) being deshielded relative to that in the chloride-deficient compositions. For X_{HCl} < 0.50, the shift is relatively independent of composition suggesting that as the HCl mole fraction increases from its minimum value somewhere below 0.38, HCl reacts with chloride forming HCl$_2^-$ in accord with reaction 3. In light of the reported[26,27] equilibrium constant, this reaction is virtually quantitative so that the observed shift is largely invariant. On the acidic side, however, the signal is observed to migrate upfield with increasing X_{HCl}, suggesting a rapid increase in the concentration of the corresponding environment(s). The relative integrated intensities of the acidic proton and Im$^+$ ring proton resonances were found to correlate well with melt composition. A plot of the ratio of acidic proton and Im-H$_2$ peak areas versus the ratio X_{HCl}:X_{Im} was found to be linear with slope 1.02 ± 0.01 and correlation coefficient R^2 = 0.997.

The reaction of HCl with ImCl is highly exothermic. Notably, this is also the case for the addition of HCl to 1:1 HCl:ImCl. As the HCl content approached 50 mol % during the preparation of a melt, the viscosity of the melt was observed, qualitatively, to decrease considerably. Similar observations were made during the preparation of AlCl$_3$:ImCl melts, for which quantitative measurements of viscosity have been reported.[7]
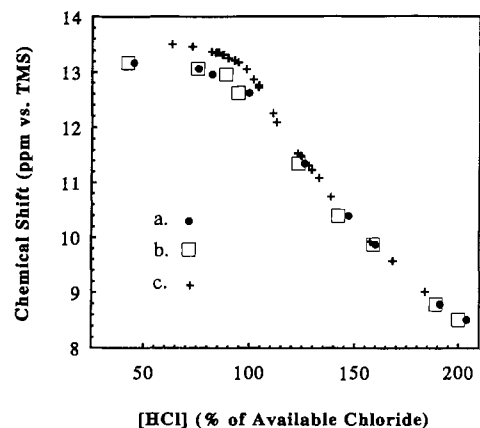

[HCl] (% of Available Chloride)

Figure 3. Chemical shift of acidic proton in a Lewis basic HCl:ImCl: AlCl$_3$ melt as a function of HCl content (expressed a percentage of the available chloride) in 0.65:0.35 ImCl:AlCl$_3$: (a) proton content determined gravimetrically; (b) proton content determined from NMR signal intensity; (c) HCl:ImCl data.

The behavior of protons was also studied in a basic HCl:ImCl: AlCl$_3$ ionic liquid by means of an analogous series of NMR experiments, in which HCl was added to AlCl$_3$:ImCl melts (AlCl$_3$ mole fraction 0.35). The chemical shift of the acidic proton in this melt is plotted as a function of HCl content in Figure 3. The HCl content is expressed as a molar percentage of the chloride available in the basic melt without added HCl, *i.e.* that over and above chloride required for reaction with AlCl$_3$; 100% corresponds to the hydrogen dichloride stoichiometry (HCl:Cl$^-$, 1:1). Inspection of this figure reveals a close resemblance to the curve acquired for HCl:ImCl ionic liquids (Figure 3c). HCl concentrations determined by the relative intensities of NMR signals (Figure 3b) are in reasonable agreement with the gravimetric results (Figure 3a). We were unable to prepare basic melts containing HCl concentrations greater than about 200% of the available chloride. For neutral and acidic chloroaluminates it was found that one cannot introduce sufficient HCl to generate a detectable ^{1}H-NMR signal (this work, ambient temperature). Nor can this be achieved by the addition of ImHCl$_2$; in the case of the acidic melts most of the protons added in this fashion are visibly driven out as HCl. The latter is consistent with the results of other workers.[25]

Discussion

The stabilization afforded by dissolution in a *reactive* solvent is inherently greater than that which might arise through weaker, intermolecular forces, *i.e.* in a more inert solvent. This is reflected in the HCl solubilities summarized in Table I. For solvents of the form R$_2$O (R ≡ H, alkyl), high solubilities are attributable to the formation of onium ions, *e.g.* R$_2$OH$^+$, which may be further solvated. In inert solvents such as CCl$_4$, it is seen that HCl solubilities are markedly lower. Relatively low HCl solubilities in molten inorganic chlorides is evidence of the instability of HCl$_2^-$ at high temperatures (840 °C). The solubility of HCl in the Lewis acidic AlCl$_3$:ImCl system is probably representative of the limited ability of ambient temperature ionic systems to stabilize HCl in its molecular form. It is clear that for 1:1 HCl: ImCl and 35.0:65.0 AlCl$_3$:ImCl, HCl solubilities are consistent with some sort of reactive solvation associated with the evolution of heat, as observed experimentally. We conclude immediately that for X_{HCl} < 0.5, the equilibrium reaction 3 is dominant and lies far to the right.[26,27] As X_{HCl} exceeds 0.5, however, chloride is increasingly unavailable, and additional HCl is consumed in further reaction according to

$$HCl + HCl_2^- \rightleftharpoons H_2Cl_3^- \qquad (4)$$

Table I. Solubilities of HCl (1 atm) in Various Media

	temp (°C)	solubility (mol %)
Reactive Solvents		
water[a]	20	22.6
methanol[b]	18	49.7
diethyl ether[b]	20	40.3
Inert Solvents[c]		
CCl₄	20	1.81
hexane	20	1.97
octane	20	2.96
Ionic Liquids		
NaCl[d]	840	1.23
KCl[d]	840	0.51
MgCl₂[d]	840	3.67
AlCl₃:ImCl, $X(AlCl_3) > 0.5$[e]	30	*ca.* 0.6 w/o
AlCl₃:ImCl, $X(AlCl_3) = 0.350$[f]	25	*ca.* 16 w/o
1:1 HCl:ImCl[g]	25	ca. 34

[a] Reference 47. [b] Reference 48. [c] Reference 49. [d] Reference 50. [e] Reference 25. [f] This work. [g] This work; quoted value is the binary HCl mole fraction *in excess* of 1:1 HCl:ImCl stoichiometry.

or, in general

$$HCl + H_nCl_{n+1}^- \rightleftharpoons H_{n+1}Cl_{n+2}^- \quad (n = 0, 1, 2, ...) \quad (5)$$
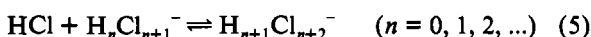
It is notable that the upper limit (298 K, $P < 1$ atm) for X_{HCl} lies somewhere near 0.67 (*cf.* 0.58),[25] which corresponds to the stoichiometry of $H_2Cl_3^-$, *i.e.* 2:1 HCl:ImCl.

Support for these conclusions is found in the literature: one finds that species as outlined above have been reported previously. In a study of the pyridine:HCl system, for example, Shuppert and Angell proposed the existence of anionic HCl aggregates as written in eq 5;[30] the authors comment on the tendency of HCl_2^- to promote the generation of such species. Further evidence for this was also reported by Fujiwara and Martin.[31] McDaniel and Vallee had earlier reported pressure–composition isotherms for $R_4NX:HX$ systems;[32] these data suggested the existence of $H_nCl_{n+1}^-$ ($n > 1$) at low temperatures and/or high pressures. The earliest report of $H_nX_{n+1}^-$ ($n = 2, 3$; X = Cl, Br) appears to be that of Kaufler and Kunz in 1909.[33] In 1914, Ephraim established that the formation and dissociation process is reversible.[34] The fluoride analogues ($n = 2–5$) have been studied in some detail.[35,36]

HCl:ImCl Ionic Liquids: Modeling of Equilibria. For a nucleus engaged in rapid exchange among several environments, the observed chemical shift is given by the population-weighted average of the shifts in each discrete environment. Specifically, for a proton undergoing rapid exchange among HCl and $H_nCl_{n+1}^-$ ($n \geq 1$), the shift is given by

$$\delta_H = (1/X_{HCl})\{X(HCl)\delta(HCl) + \sum nX(H_nCl_{n+1})\delta(H_nCl_{n+1})\} \quad (6)$$

where X_{HCl} is the total HCl mole fraction here defined by

$$X_{HCl} = X(HCl) + \sum nX(H_nCl_{n+1}) \quad (7)$$

$X(HCl)$ and $X(H_nCl_{n+1})$ are the relative mole fractions of the proposed environments, and the δ's are their respective chemical shifts; ionic charges have been omitted for convenience. The binary mole fraction of ImCl, $X_{Im} = 1 - X_{HCl}$, is given by

$$X_{Im} = X(Cl) + \sum X(H_nCl_{n+1}) \quad (8)$$

and the concentrations of the various species are related to one

Table II. Nonlinear Fit of Reaction 10 to Data of Figure 2[a]

	$N = 30$	$N = 16$
β	0.66	0.51
S_r	0.0354	0.0177
R	0.0238	0.0136
k_3/k_4	184 ± 22	218 ± 25
$\delta(HCl_2^-)$	13.58 ± 0.03	13.57 ± 0.02
$\delta(H_2Cl_3^-)$	8.57 ± 0.02	8.30 ± 0.17

[a] N = number of data points, β = maximum value of X_{HCl} employed in data set, S_r = standard error of regression, and R = average residual chemical shift (ppm per data point).

another by stoichiometric equilibrium constants of the following form:

$$k_i = \frac{X(H_nCl_{n+1})}{X(HCl)X(H_{n-1}Cl_n)} \quad (9)$$

Unfortunately, it is not possible to fit chemical shift versus composition data to equilibria involving more than two rapidly exchanging species (see for example, Vinogradov and Linnel[37]); only those limiting forms of the general model implied by eqs 6–9 which involve two protic species can be fit to the data analytically by means of nonlinear regression. It was found indirectly through the use of direct search and abductive network techniques,[5] however, that a fit of the model involving reactions 3 and 4 is sensitive to the ratio k_3/k_4 and is optimized for large values of k_3 and k_4, *i.e.* low concentrations of molecular HCl. Inspection of eqs 3 and 4 reveals that the ratio k_3/k_4 is the equilibrium constant for the reaction

$$H_2Cl_3^- + Cl^- \rightleftharpoons 2HCl_2^- \quad (10)$$

which one immediately recognizes as being analogous to reaction 1, the autosolvolysis reaction in chloroaluminate melts. Hence we are justified in referring to HCl:ImCl melts as either acidic or basic (X_{HCl} greater or less than 0.5) in character. The difference in magnitudes of the equilibrium constants (see below) for reactions 1 and 10 is a reflection of the fact that the Lewis acid behavior [*sic*] of HCl is limited to the formation of strong hydrogen bonds. This parallelism lends support to the view that hydrogen may sometimes be regarded as the simplest metal. Tuck, for example, suggested that the dihydrogen halide ion should be named dihalohydrogen(I) in recognition of the fact that, here, hydrogen is the more electropositive element.[28]

Reaction 10 was fitted to the data by means of nonlinear regression. Two data sets were employed for this purpose. These involved N data points spanning $0.38 \leq X_{HCl} \leq \beta$, where β is the highest value of X_{HCl} in the set. The results of these regressions are summarized in Table II. Residual chemical shifts (calculated – experimental) are maximal in the region where X_{HCl} is greater than 0.5; for $X_{HCl} < 0.5$ and $X_{HCl} > 0.5$, the average absolute residuals were 0.013 and 0.030 ppm, respectively. In addition to the possibility of experimental error in high HCl content melts, this might be attributable to inadequacy of the model (reaction 10) in this region, *i.e.* neglect of reaction 5 and/or the equilibrium

$$HCl(g) \rightleftharpoons HCl(l) \quad (11)$$
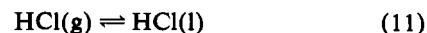
We have neglected this equilibrium in our model, with no justification other than the fact that the amount of HCl above the melt in the NMR tube was insignificant relative to the total HCl contained in the tube and in the spectrometer probe. The best estimate of k_3/k_4 is probably that obtained from the $N = 16$ fit ($\beta = 0.51$), since reaction 10 is expected to contribute exclusively in the domain spanned by these data. This is supported by the standard errors (S_r) and average residuals (R).

The highest HCl mole fraction achieved was 0.681 at *ca.* 0.94 atm of HCl and 298 K, and hence, under these conditions, there

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(36) Hibbert, F.; Emsley, J. *Adv. Phys. Org. Chem.* **1990**, *26*, 255–379.

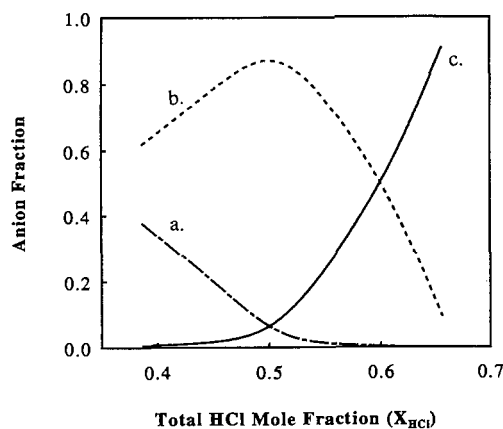(37) Vinogradov, S. N.; Linnel, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold Co.: Toronto, 1971.

Figure 4. Anion fractions as a function of X_{HCl} in HCl:ImCl ionic liquids: (a) Cl⁻; (b) HCl₂⁻; (c) H₂Cl₃⁻.

exists a slight excess of HCl relative to the stoichiometry of $H_2Cl_3^-$. This may be associated with large aggregate anions and molecular HCl though it is not immediately clear how the excess is distributed. In light of the correspondence of the upper limit of X_{HCl} with the stoichiometry of $H_2Cl_3^-$, contribution of these species is probably minimal. The active absorption of HCl by $ImHCl_2$ observed in this work, and the results of other workers,[30-32] tend to support solvation as anionic aggregates. Further, it is possible to fit[52] to the data a more flexible generalization of equilibrium 10:

$$H_nCl_{n+1}^- + (n-1)Cl^- \rightleftharpoons nHCl_2^- \qquad (12)$$
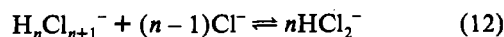
in which the proton is partitioned among hydrogen dichloride and some distribution of anionic species for which the average number of HCl residues is n (>1). Over the range $0.38 < X_{HCl} < 0.66$, such a fit (30 data points) is associated with a smaller standard error than that obtained for reaction 10 (0.0299 vs 0.0354); n was calculated as 2.16 ± 0.06. The residuals of this fit show similar trends in the region $X_{HCl} > 0.5$, and hence it appears likely that relatively large residuals in this region are attributable, at least in part, to experimental error. Suffice it to say that the concentration of molecular HCl is negligible in HCl:ImCl melts of low HCl content and small in high HCl content melts. Anion fractions (α values) have been calculated as a function of X_{HCl} using $k_3/k_4 = 218$; a plot of these values for Cl⁻, HCl_2^-, and $H_2Cl_3^-$ appears in Figure 4. For "stoichiometric" $ImHCl_2$, *i.e.* $X_{HCl} = 0.50$, *ca.* 12% of the total HCl exists as the $H_2Cl_3^-$ ion.

In the fitting of the equilibria 10 and 12 to δ_H vs X_{HCl} data, it was assumed that the shifts of the various species are invariant with respect to the overall ionic environment of the melt. One might anticipate that this assumption is not strictly valid, and so we recognize the possibility that the chemical shift, *i.e.* the magnetic susceptibility, of each discrete species may vary slightly through weak interactions with the medium, *i.e.* solvent effects.[38-41] The variation of the chemical shift of the Im-H₂ proton with X_{HCl} is illustrated in Figure 5a (this work, HCl:ImCl). This behavior was also observed for H₄ and H₅ to a lesser extent. Similar behavior was observed in the AlCl₃:ImCl system by Avent *et al.*[42]

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(42) Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. In *Proceedings of the Seventh International Symposium on Molten Salts*; Hussey, C. L., Flengas, S. N., Wilkes, J. S., Ito, Y., Eds.; The Electrochemical Society Inc.: Pennington, NJ, 1990; pp 98–121.
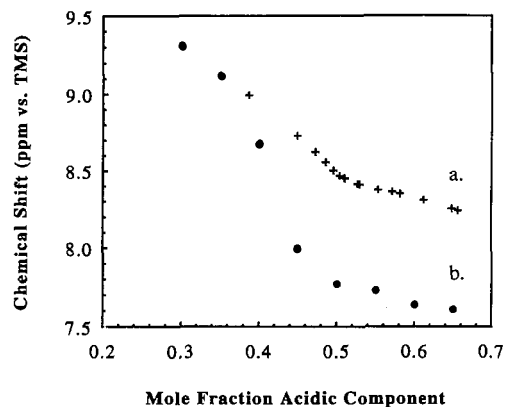

Figure 5. Chemical shift of Im-H₂ proton as a function of acidic component mole fraction for (a) HCl:ImCl and (b) AlCl₃:ImCl ionic liquids (data from ref 43).
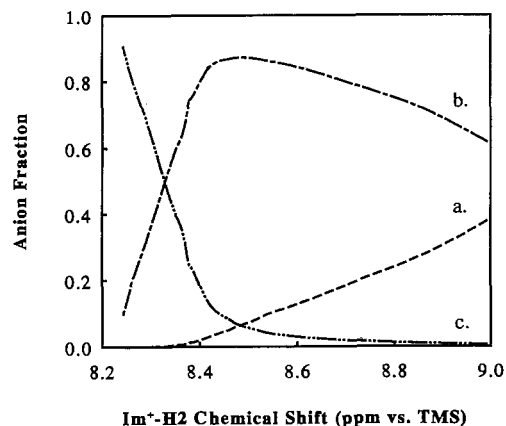

Figure 6. Anion fractions as a function of Im-H₂ chemical shift in HCl:ImCl ionic liquids: (a) Cl⁻; (b) HCl₂⁻; (c) H₂Cl₃⁻.

(see Figure 5b) and by Fannin *et al.*[43] For both HCl:ImCl and AlCl₃:ImCl ionic liquids, the variation in the chemical shift of the Im⁺ ring protons is greatest in the composition range where the rate of change of the chloride concentration is maximal, *i.e.* for acidic component mole fractions less than 0.5. This suggests that the chemical shift of the ring protons is strongly dependent on the chloride ion concentration. Seddon and co-workers concluded that a hydrogen-bonding interaction between the Im⁺ ring protons and anions in the melt is responsible[42] (see also refs 38–41). Interaction between melt constituents raises the important question of whether the protic anions themselves interact with the Im⁺ ring protons, leading to variation of the chemical shifts of all species involved. Figure 6 illustrates the variation of the chemical shift of Im-H₂ with the α values of the various anions present in $ImHCl_2$. Examination of the region in which the chloride ion fraction is negligible reveals that the interaction of Im-H₂ with HCl_2^- and $H_2Cl_3^-$ is much weaker and, hence, should not lead to excessive variation in the chemical shifts of these anions. The absence of strong interactions between HCl_2^- and Im⁺ is supported by the IR results of Trulove and Osteryoung.[25] This suggests that the assumption of invariant chemical shifts of the protic anions is reasonable to a first approximation, so that the equilibrium constant calculated for reaction 10 should be regarded favorably.

In the AlCl₃:ImCl system, melt viscosity[7] and Im⁺ ring proton chemical shifts[43] have a similar dependence on the AlCl₃ mole fraction; both of these observables decrease rapidly as the 1:1 AlCl₃:ImCl (Lewis neutral) composition is approached. Clearly, interactions governing melt viscosity are manifested by the variation in these shifts. It is interesting that the Im⁺ ring proton

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resonances in HCl:ImCl and AlCl₃:ImCl systems have a very similar dependence on the mole fraction of the acidic component (HCl or AlCl₃, Figure 5a,b). By virtue of the similarity of this dependence, we anticipate that viscosity measurements of the HCl:ImCl system would reveal behavior similar to that of the AlCl₃:ImCl system; this was observed qualitatively (this work). Quantitative viscosity measurements, however, are complicated by the tendency of these liquids to change composition during manipulation.

HCl:ImCl:AlCl₃ Ionic Liquids. In the case of the basic AlCl₃: ImCl melt (35.0 mol % AlCl₃) it was also found that, maximally, 2 equiv of HCl relative to the available chloride can be introduced into this liquid. Nonlinear regression of the curves derived by gravimetry and NMR (Figure 3) yield k_3/k_4 values of 110 ± 86 and 101 ± 62, respectively, and hence it is not strictly possible to discern any difference from the value obtained in HCl:ImCl liquids. Admittedly, a larger data set would provide more definite results though inability to measure the HCl content directly (as in the case of HCl:ImCl melts) gives rise to inherently large errors. Qualitatively, the behavior of HCl in both systems appears to be very similar, as reflected by the high HCl solubilities and in the δ_H vs X_H curves. Notably, however, the chemical shift of HCl₂⁻ appears to be somewhat lower in the chloroaluminate melts. We conclude that proton speciation outlined for the HCl:ImCl system also applies to the basic chloroaluminates, *i.e.* HCl:ImCl: AlCl₃, with the total possible proton concentration being limited by the available chloride. Further, we suggest that the decreasing proton chemical shift (of the acidic proton) observed[21,25,27] as one increases the AlCl₃ content of a basic AlCl₃:ImCl melt is due not only to an increase in the concentration of molecular HCl but also to an increase in that of H₂Cl₃⁻, in accord with reaction 10. Neglect of reaction 10 might lead to an erroneous value of k_3. Of course as the free chloride concentration diminishes near the Lewis neutral composition, H₂Cl₃⁻ will decompose generating HCl, and speciation of the proton might be adequately described by reaction 3.

Infrared data reported by Trulove and Osteryoung clearly demonstrate the existence of HCl₂⁻ in melts with an excess of chloride and that of HCl in Lewis acidic melts.[25] Unfortunately, they do not lead to any conclusions regarding H₂Cl₃⁻ in the basic AlCl₃:ImCl system. In all spectra where we might expect to see H₂Cl₃⁻ (slightly basic melts with excess HCl; Figure 4 of ref 25) significant regions were deleted owing to interference. Semiempirical MO calculations (AM1) reveal that H₂Cl₃⁻ should possess C_{2v} symmetry and therefore show nine vibrational modes.[44] On the basis of Herzberg's analysis[45] of carbon suboxide, eight of the vibrational modes of H₂Cl₃⁻ are expected to be IR active, so that some bands may have been obscured in regions of interference. As the number of HCl residues (n) increases, hydrogen bond distances are expected[36,40] to increase so that these residues behave increasingly like molecular HCl and should exhibit HCl-like bands in their IR spectra.

In the Lewis acidic AlCl₃:ImCl system, the acidic proton is manifested by its protonation of arenes,[17] and when melts are prepared with DCl, the signal of the acidic species may be detected[21,25,27] through ²H-NMR; presumeably, this is owing to the low overall ²H concentration and, hence, a greater signal to noise ratio. For HCl:ImCl and basic AlCl₃:ImCl melts, the concentration of the acidic proton is limited only by the availability of chloride and by the potential to form stable species. Owing to low chloride concentrations, and the small equilibrium constant for reaction 11, the total solubility of HCl in acidic chloroaluminates is correspondingly low (Table I). We conclude that unless HCl can form an ionic species, *i.e.* unless HCl can be *stabilized through reactive solvation with the melt*, it simply will not dissolve
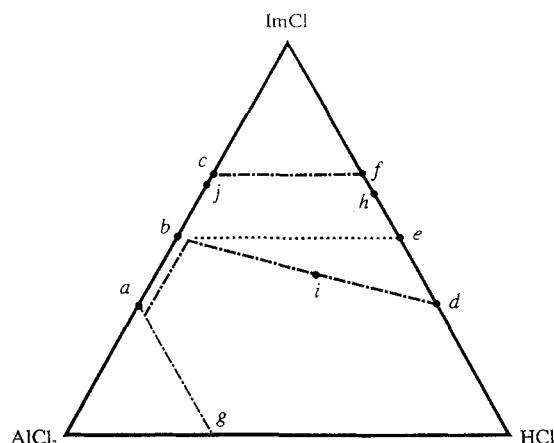

Figure 7. Approximate liquid-phase region for the ternary system HCl: ImCl:AlCl₃ under conditions of ambient temperature and pressure (see text). Points, a, b, e, and d correspond to the compositions (HCl:ImCl: AlCl₃) 0:1:2, 0:1:1, 1:1:0, and 2:1:0.

appreciably. It stands to reason that, in a highly ionic environment, significant electrostatic stabilization is afforded by solvation as an ionic species.

Phase Diagram of the Ternary System HCl:ImCl:AlCl. An approximate phase diagram (see Figure 7) for the ternary system HCl:ImCl:AlCl₃, under conditions of ambient temperature and pressure, may be constructed by engaging several reasonable assumptions which follow directly from the conclusions of this paper and those of earlier workers: (1) In the binary AlCl₃:ImCl system, the AlCl₃ mole fraction ranges from *ca.* 0.33 to 0.67, segment ac. (2) In the binary HCl:ImCl system, the maximum HCl mole fraction is *ca.* 0.68, point d. (3) In ternary melts with ImCl or AlCl₃ mole fractions exceeding *ca.* 0.67, segments cf and ag, a solid phase must exist. (4) In melts for which the AlCl₃ mole fraction is significantly less than that of ImCl, HCl added to the melt is partitioned according to reaction 10; in melts for which the AlCl₃ mole fraction is only slightly less than that of ImCl, it is possible that equilibria 11, 3, and 10 all contribute significantly. (5) In melts for which the AlCl₃ mole fraction exceeds that of ImCl, the proton exists, for the most part, in accord with equilibrium 11. (6) Finally, in systems for which X_{HCl} is greater than twice the quantity $X_{ImCl} - X_{AlCl3}$, a significant gas phase must exist.

Compositions along the segments dh and ij were observed experimentally. Attempts to prepare melts along the line joining the points a and d by the addition of a 2:1 AlCl₃:ImCl melt to a 2:1 HCl:ImCl melt resulted in HCl evolution; the composition of the resulting liquid phase was found along the segment bd (this work). There is at present no evidence for reaction between HCl and AlCl₃, *e.g.* HAlCl₄ is not known. The region bounded by the trapezoid $bcfe$ is Lewis basic in character owing to the high concentration of chloride ion while that bounded by bed is weakly Lewis acidic owing to the activity of H₂Cl₃⁻ (reaction 10). In the vicinity of the segment ab, the system is Lewis acidic, and protic species exhibit Bronsted superacidity. The Lewis/Bronsted behavior of protic species is modulated by the chloroaluminate Lewis acidity; *i.e.*, as the concentration of Al₂Cl₇⁻ becomes sufficiently high, the Lewis acidity of protic species is leveled by that of the much stronger Lewis acid. Hence the ternary system allows the control of melt acidity in the weakly Lewis acidic range. Investigation of the protonating power of HCl:ImCl (X_{HCl} > 0.5) liquids might be illuminating regarding the extent of this range.

Our results with HCl:ImCl and basic HCl:ImCl:AlCl₃ liquids originally[5] led us to entertain several possibilities (other than molecular HCl) for proton speciation in acidic melts. These included HₙCl_{n+1}⁻, generated in accord with the reverse of reaction 12 and H₂Cl⁺, which might arise in the following net reaction:

(44) Campbell, J. L.; Johnson, K. E. Unpublished results.
(45) Herzberg, G. *Infrared and Raman Spectroscopy of Polyatomic Molecules*; D. Van Nostrand Co. Inc.: Toronto, 1945.

$$Al_2Cl_7^- + 2HCl(g) \rightleftharpoons 2AlCl_4^- + H_2Cl^+ \qquad (13)$$

Trulove and Osteryoung have recently reported IR and ^{2}H-NMR evidence which indicates that molecular HCl is definitely present in these melts.[25] The shift of the acidic proton (deuteron) was observed to decrease to 1.6 ppm (vs TMS) as a basic melt was made neutral and further to 0.9 ppm as 2:1 (AlCl$_3$:ImCl) stoichiometry was approached. The gas-phase value for the HCl shift has been reported as 0.68 (corrected to TMS) by Schneider *et al.*[46] In themselves, the NMR observations[25] do not rule out solvation as $H_nCl_{n+1}^-$ since as n increases, the observed shift is expected to approach that of molecular HCl. Moreover, the variation in shift could be explained in terms of the existence of other environment(s) contributing to the HCl signal. However, Trulove and Osteryoung also claim that, in the Lewis acidic AlCl$_3$:ImCl system, HCl solubility is independent of melt acidity, being on the order of 200 mM under ambient conditions.[25] This would seem to rule out significant solvation as $H_nCl_{n+1}^-$ or H_2Cl^+, for which one would expect HCl solubility to be markedly dependent on melt acidity, *i.e.* AlCl$_3$ mole fraction. Exchange of the acidic proton at Im-H$_{4,5}$ has been demonstrated and was

interpreted as a reversible Lewis acid catalyzed protonation of Im$^+$ by HCl.[27] This would constitute solvation of proton as ImH^{2+}.

Modifications of the single-phase liquid region which might arise through the application of nonambient conditions pose interesting possibilities. At high HCl pressures and low temperatures,[37] for example, the segments *bd* and *ab* are expected to shift toward higher values of X_{HCl}, corresponding to a higher molecular HCl concentration, and to larger values of n, *i.e.* $H_nCl_{n+1}^-$. It can be shown that the concentration of $H_nCl_{n+1}^-$ is proportional to the nth power of the HCl pressure and to the chloride ion concentration, so that these species will be significant only for high pressures and/or Lewis basic systems. We suspect that H_2Cl^+ may exist in AlCl$_3$:ImCl melts under some conditions, though clearly only at low concentrations. It is notable that, regardless of the relative concentration of molecular HCl, it remains possible that H_2Cl^+ is responsible for Bronsted superacidity in acidic AlCl$_3$:ImCl ionic liquids. This might also be said of the proposed[27] ImH^{2+} species. We predict that H_2Cl^+ should be stabilized in the presence of very large anions, perhaps under conditions of temperature and/or pressure well-removed from ambient. Ongoing investigations are aimed at refinement of the phase diagram reported here, particularly in the vicinity of the segment *ab*.

Conclusions

Our results indicate that, in being taken up by HCl:ImCl and basic AlCl$_3$:ImCl ionic liquids, HCl is extensively solvated. It has been demonstrated that in addition to hydrogen dichloride, proton speciation under ambient conditions involves the formation of $H_2Cl_3^-$, and perhaps $H_nCl_{n+1}^-$ ($n > 2$). Relative to anionic species, molecular HCl does not contribute significantly to proton speciation in HCl:ImCl and basic AlCl$_3$:ImCl ionic liquids. In the ternary melts, the behavior of protic species may range from that of a weak Lewis acid to that of a Bronsted superacid; this behavior is determined by the activity of the much stronger Lewis acid Al$_2$Cl$_7^-$. It remains to be determined, however, whether molecular HCl is the active superacid species in acidic melts. Further investigations of the ternary system may prove fruitful in this regard.

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(47) Dean, J. A. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill: Toronto, 1992.
(48) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: New York, 1963; Volume I, Part II.
(49) *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longman's, Green and Co.: Toronto, 1956; Supplement II, Part I.
(50) Flengas, S. N.; Block-Bolten, A. In *Advances in Molten Salt Chemistry*; Braunstein, J., Mamantov, G.; Smith, G. P., Eds.; Plenum: New York, 1973; Vol. 2, pp 27–81.
(51) The authors acknowledge reviewers comments which spurred the reevaluation of this possibility.
(52) Though reaction 3 alone cannot account for the high solubility of HCl in HCl:ImCl and AlCl$_3$:ImCl systems, or for heat evolution observed upon addition of HCl to a 1:1 HCl:ImCl melt, it is still possible to fit it to the data with a goodness of fit comparable to that of reaction 10. This is because the fit cannot distinguish between a proton in an HCl environment and that in, e.g., H$_2$Cl$_3^-$; this is related to the result that one cannot fit a model involving more than two rapidly exchanging species.[37] If one performs a fit of reaction 3 to the data, however, its inadequacy is manifested by the shift of molecular HCl, which is obtained as 3.69 ± 0.04 ppm *vs* TMS. This is not consistent with either the gas-phase shift of HCl (0.68 ppm[46]) or the liquid-phase shift reported for the acidic AlCl$_3$:ImCl system (0.9–1.6 ppm[25]). A fit of reaction 3 to the data also shows large residuals for $X_{HCl} > 0.5$, supporting the conclusion that large residues in this region arise from experimental error.