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Infrared and Variable-Temperature ^{1}H-NMR Investigations of Ambient-Temperature Ionic Liquids Prepared by Reaction of HCl with 1-Ethyl-3-methyl-1*H*-imidazolium Chloride

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HCl:ImCl ambient-temperature ionic liquids have been investigated through infrared and variable-temperature ^{1}H-NMR spectroscopy as a function of HCl mole fraction (Im$^+$ ≡ 1-ethyl-3-methyl-1*H*-imidazolium). The infrared spectrum of the dihydrogen trichloride ion, $H_2Cl_3^-$, has been observed, apparently for the first time. The absence of significant molecular HCl as earlier proposed, is confirmed. Thermodynamic parameters for the reaction $H_2Cl_3^- + Cl^- \rightleftharpoons 2HCl_2^-$, in which all species are solvated, have been estimated by VT-NMR: ΔH and ΔS were determined as -22.8 ± 1.0 kJ mol^{-1} and -31.8 ± 2.9 J K^{-1} mol^{-1} respectively. The minimum value of the equilibrium constant for the reaction $HCl + Cl^- \rightleftharpoons HCl_2^-$, is estimated to be on the order of 10^4–10^5 L mol^{-1}, considerably larger than that in molecular solvents. Im$^+$ ring proton resonances have a marked dependence on the anion fractions of Cl$^-$, HCl_2^-, and $H_2Cl_3^-$, with Im–H$_2$ being the most strongly affected. VT-NMR spectra of Im$^+$ indicate that for $X_{HCl} < 0.5$, all three ring protons are involved in cation–anion interactions while for $X_{HCl} > 0.5$, Im–H$_2$ is dominant in mediating these. We have interpreted these results in terms of hydrogen-bonded aggregates of anions and cations, the nature of which depends on the ability of the anion population to form hydrogen bonds with Im$^+$. At the extremes we suggest that these aggregates may range from extended structures involving hydrogen bonding to all three ring protons, to ion-pairs involving hydrogen bonding via Im–H$_2$.

Introduction

Campbell and Johnson[1a,b] have recently reported evidence indicating that, in HCl:ImCl ionic liquids[1c] and in the Lewis basic region of the ternary system HCl:ImCl:AlCl$_3$, proton speciation is governed substantially by the equilibrium

$$H_2Cl_3^- + Cl^- \rightleftharpoons 2HCl_2^- \qquad (1)$$

The stoichiometric equilibrium constant for reaction 1 was determined through ^{1}H-NMR measurements as 218 ± 25 for HCl:ImCl melts at 297 K. The maximum solubility of HCl in the HCl:ImCl system ($P_{HCl} \leq 1$ atm) was found to correspond to an HCl mole fraction of about 0.67, *i.e.* the stoichiometry of $H_2Cl_3^-$. Though it could not be demonstrated unequivocally whether or not larger anions, *e.g.* $H_3Cl_4^-$, contribute significantly at high HCl contents, the data were consistent with this possibility. It was concluded that molecular HCl probably does not contribute significantly to proton speciation in these systems. In the current paper, we report infrared spectra which provide direct confirmation of these conclusions. Although species of the form $H_nCl_{n+1}^-$ have been suggested to exist in several systems,[1d–g] the spectra reported here constitute the first spectroscopic observation of $H_2Cl_3^-$, and perhaps $H_3Cl_4^-$.

Reaction 1 may be rewritten in the form

$$Im^+H_2Cl_3^- + Im^+Cl^- \rightleftharpoons 2Im^+HCl_2^- \qquad (1a)$$

so as to emphasize that each anion is solvated to some extent; reaction 1a does not necessarily imply simple electrostatic ion-pair formation, but cation–anion interactions in general, whatever these might be, hydrogen bonding, for example. The physical and spectral properties of the AlCl$_3$:ImCl system have a marked dependence on composition. The viscosity decreases sharply as the AlCl$_3$ mole fraction increases toward 0.5, and only slightly as it increases thereafter.[2] Similar, albeit purely qualitative, observations were made during investigations of the HCl:ImCl system.[1] ^{1}H- and ^{13}C-NMR chemical shifts,[3–5] and infrared frequencies[6] of Im$^+$ have composition dependencies similar to that of melt viscosity. Previous work with the AlCl$_3$:ImCl system has shown that the chemical shifts of the Im$^+$–H$_{2,4,5}$ ring protons have a strong dependence on composition and can be related to the anion fractions (α) of the available counterions, in this case Cl$^-$, $AlCl_4^-$, and $Al_2Cl_7^-$.[3,4] Clearly, these spectral changes are manifestations of cation–anion interactions which govern the composition-dependent structure of the melts and hence their physical properties. Considerable evidence exists for a hydrogen bonding interaction between Im–H$_2$ and anions in the melt and for ImCl in CH$_3$CN.[5] Ion pair formation has been suggested on the basis of infrared data.[6] Wilkes and co-workers proposed a model of melt structure in which each Im$^+$ ion may interact with two anions, forming oligomeric stacks of alternating cations and anions; the anions are located above and below Im$^+$ ions with the latter species arranged in parallel planes.[3,4,7] This model does not recognize hydrogen-bonding interactions as being significant, though presumably such interactions could take place between stacked oligomers. By means of semiempirical MO calculations,

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Dymek *et al.* have shown that it is possible to account for infrared results by assuming a model in which each Im^+ cation is hydrogen-bonded to three anions (Cl^-) via the protons at the 2, 4, and 5 positions of the ring.[8] The crystal structure of ImCl indicates that each Im^+ has three chloride ions as nearest neighbors and in positions which suggest hydrogen bonding to the three ring protons.[8] The crystal structure of the corresponding iodide is characterized by hydrogen bonding between iodide and $Im-H_2$.[9]

In the current work it is shown that in analogy to the $AlCl_3$:ImCl system, ^1H-NMR chemical shifts of Im^+ ring protons can be related to the anion fractions of Cl^-, HCl_2^-, and $H_2Cl_3^-$. Variable-temperature (VT) ^1H-NMR data have been acquired in order to estimate thermodynamic parameters for reaction 1a in the HCl:ImCl system. Temperature dependencies of the Im^+ ring proton resonances determined as a function of melt composition are illuminating regarding cation interactions in HCl:ImCl ionic liquids.

Experimental Section

Materials. 1-Ethyl-3-methyl-1*H*-imidazolium chloride (ImCl) was synthesized as described previously.[1a] Anhydrous HCl was prepared by the reaction of concentrated hydrochloric and sulfuric acids (ACS Reagent grade). The resulting HCl was dried by passage through a column of aluminum chloride which had been purified by sublimation as described previously.[1a] Anhydrous DCl was prepared in an analogous fashion from D_2SO_4 (Aldrich, 99.5 atom % D) and DCl (37% by weight in D_2O, Aldrich, 99.5 atom % D). HCl:ImCl and DCl:ImCl ionic liquids were prepared by the slow addition of HCl/DCl to a known mass of ImCl; this reaction was conducted in "airless" glassware under an atmosphere of dry argon (HP). The HCl content of the melt was estimated from the mass before and after addition. All further manipulations were performed in a nitrogen-filled glovebox as described elsewhere.[1a] Where necessary, melt densities were measured using a density bottle of volume 1.32 ± 0.01 cm^3.

Infrared Spectroscopy. Infrared spectra were acquired with a Perkin-Elmer Series 1600 FT-IR spectrophotometer. The sample cell consisted of two NaCl plates between which were placed two layers of polyethylene film, each having a thickness of *ca.* 0.1 mm. In the case of high HCl content melts, failure to include polyethylene results in dissolution of the NaCl plates. After recording background spectra of the empty cell, a single drop of melt sample was placed between the polyethylene windows; this operation was performed in the glove box. In the case of melts with HCl mole fractions less than 0.5, the polyethylene layers were omitted. All spectra were background subtracted and are shown unsmoothed. Since the samples were run as thin films without spacers, sample thickness, and hence absorbances, were not highly reproducible. For this reason, absorbance axes have been neglected in the spectra, allowing only qualitative interpretation.

VT-NMR Spectroscopy. Variable temperature (297–347 K) ^1H-NMR spectra of HCl:ImCl ionic liquids were acquired with a Bruker AC 200 MHz spectrometer. The samples were contained in sealed glass capillaries which were placed in standard 5 mm NMR tubes and bathed in DMSO-d_6. All shifts are referenced to TMS. Temperatures are accurate to ±0.5 K.

Results and Discussion

Infrared spectra of HCl:ImCl melts are illustrated as a function of composition in Figure 1. Infrared spectra of chloride-rich HCl:ImCl and DCl:ImCl ionic liquids appear in parts a, b, and e of Figure 1, respectively. Of principal interest is the broad absorption band centered near 1000 cm^{-1} which corresponds to the linear, symmetric HCl_2^- ion.[10,11] This band is similar to that recently reported by Trulove and Osteryoung for solutions of HCl in Lewis basic AlCl:ImCl melts,[11] and is observed to shift to lower frequencies upon substitution with deuterium (Figure 1e). Though the DCl_2^- absorption is ill-defined in the spectrum shown in Figure 1e, the decrease/increase in intensity near 1000/600 cm^{-1} is clear (protium[Figure 1b]/deuterium[Figure 1e]). Evans and Lo noted that the deuterium spectra were associated with a lower intrinsic absorption intensity;[10] our results, and those of Trulove and Osteryoung, are in agreement in this respect.

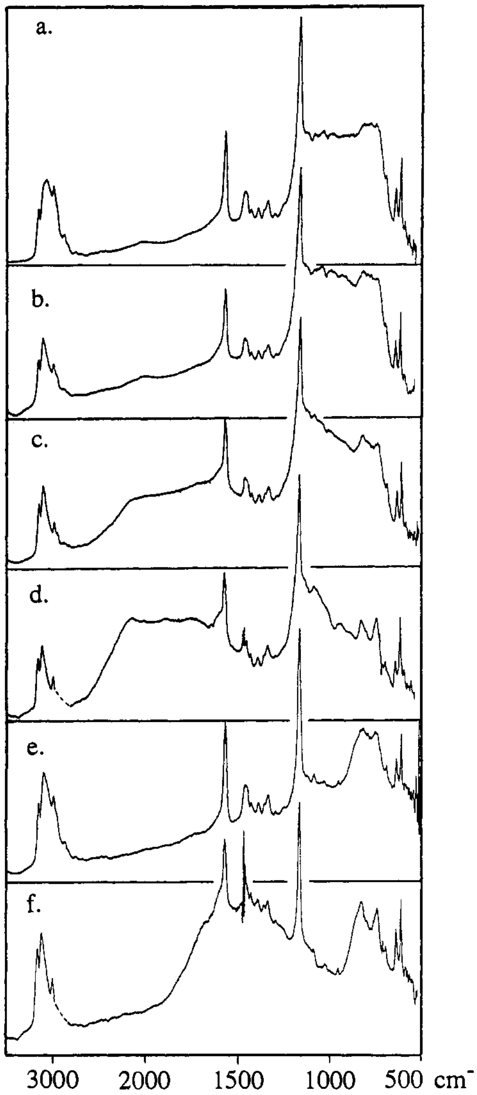

Figure 1. Infrared absorption spectra of HCl:ImCl and DCl:ImCl ionic liquids as a function of composition: X_{HCl} = (a) 0.39, (b) 0.49, (c) 0.59, (d) 0.67; X_{DCl} = (e) 0.45, (f) 0.66. All spectra were acquired at ambient temperature (298 K).

Infrared spectra of chloride-deficient HCl:ImCl and DCl:ImCl (*ca.* 2:1) ionic liquids are illustrated in parts c, d, and f of Figure 1, respectively. It was not possible to fully subtract the CH stretching absorption corresponding to the polyethylene background. For this reason, and for the sake of clarity, the region from 3000–2850 cm^{-1} has been replaced by a dashed line. Similar subtraction errors are observed near 1500 (*e.g.* Figure 1f) and below *ca.* 600 cm^{-1}. The 2:1 HCl:ImCl melt (Figure 1d) exhibits an extremely broad absorption band centered near 1800–1900 cm^{-1}, and other broad absorptions at 1086 and 943 cm^{-1}. All of these absorptions shift to lower frequencies upon substitution with deuterium (Figure 1f). The high frequency band can be assigned to $H_2Cl_3^-$, the dihydrogen trichloride ion. *Ab initio* molecular orbital calculations[12] indicate that the most intense IR bands of $H_2Cl_3^-$ and $D_2Cl_3^-$ (C_{2v}) should occur near 2000 and 1400 cm^{-1} respectively, in excellent agreement with the spectra of Figure 1. Of particular importance is the absence of any

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Table 1. Infrared Absorption Frequencies and Assignments (cm^{-1}) for HCl:ImCl Ionic Ligands

0.64:1 HCl:IMCl		2:1 HCl:ImCl		
freq	intens[a]	freq	intens	assignt
		Imidazolium Cation		
3144	m	3149	m	aromatic C–H str
3086	s, vb	3103	s, b	aromatic C–H str
2983	m	2987	m	aliphatic C–H str
2947	w, sh	2959	w	aliphatic C–H str
		2942	w	aliphatic C–H str
3868	w, b	2878	vw, b	interaction bands
2823	vw, sh	2827	vw, b	interaction bands
2739	vw, vb	2740	vw, vb	combination
2670	vw, vb	2670	vw, vb	ring str overtone
1573	s	1572	s	ring str sym
1462	m, b	1465	m	ring str sym
1428	vw	1428	vw	Me C–H b asym
1388	w	1388	w	Me C–H b asym
1345	vw, sh	1345	vw, sh	Me C–H b sym
1336	w	1336	w	ring str sym
1299	vw	1299	vw	ring C–H b sym
1236	vw, sh	1236	vw, sh	ring b overtone
1172	vs	1170	vs	ring str sym
1120	w, sh	1120	w, sh	ring C–H i/p b
1090	w	1090[b]	w	ring C–H i/p b
1038	vw	1030[b]	vw	combination
960[b]	w	960[b]	w	C–H i/p b
824	m, b	826	m, b	C–H i/p b
757	w, b	749	m, b	ring o/p b asym
700	vw	700	vw	combination
646	m	646	m	ring b asym
621	ms	620	ms	ring b asym
597	mw	597	mw	ring b asym
		Proton Anions (See Text)		
2026	w, vb			HCl_2^- overtone ($2\nu_2$)
		2200–1600 several vb bands: 2144, 1890, 1744	vs	$H_2Cl_3^-$, $H_3Cl_4^-$?
1150–750	s, several vb bands			HCl_2^- (ν_2, ν_3)
		1086	s, vb	HCl_2^-?, $H_nCl_{n+1}^-$?
		942	m, vb	

[a] s, m, w, v, b, and sh stand for strong, medium, weak, very, broad, and shoulder respectively. [b] Observed only in spectra of DCl:ImCl melts.

significant absorption which might be associated with molecular HCl (broad absorbances in the range 2600–2800 cm^{-1}).[11] This is in agreement with the view[1a] that molecular HCl does not contribute significantly to proton speciation in HCl:ImCl melts; *i.e.*, HCl is extensively solvated in these systems. This is also true for AlCl:ImCl melts for which chloride is in excess, *i.e.* basic melts.[13]

Infrared absorption frequencies and relative intensities for chloride-rich and chloride-deficient melts are summarized in Table 1. Assignments of Im$^+$ vibrations are based on those of Tait and Osteryoung.[6] Assignments for the HCl_2^- and $H_2Cl_3^-$ ions appear at the bottom of Table 1. Evans and Lo observed the ν_2 and ν_3 fundamentals of HCl_2^- as strong, broad absorptions at 1150/950 and 800 cm^{-1} respectively (HCl_2^- in CH_3CN).[10] For Lewis basic $AlCl_3$:ImCl, Trulove and Osteryoung observed these at 1140/984 and 802 cm^{-1}.[11] Weak, broad absorbances at 2040 and 1600 cm^{-1} in CH_3CN[10] and at 2014 and 1562 cm^{-1} in Lewis basic $AlCl_3$:ImCl[11] were assigned to the first overtones of ν_2 and ν_3 respectively. In the present work, the 984-cm^{-1} absorption was observed, though the 1140-cm^{-1} absorption and the ν_3 band and its overtone are obscured by the Im$^+$ absorptions. In benzene,[10] the ν_1 mode was observed as a weak, broad absorption near 240 cm^{-1}, beyond the limits of the present investigation.

Table 2. VT-^{1}H-NMR Data for the Acidic Proton in HCl:ImCl Ionic Liquids: Chemical Shift of Acidic Proton as a Function of Temperature (ppm vs TMS)

	VT-^{1}H-NMR data					
X_{HCl}[a]	297 K	307 K	317 K	327 K	337 K	347 K
0.375	13.519	13.471	13.420	13.366	13.316	13.258
0.473	13.265	13..193	13.118	13.039	12.960	12.875
0.493	13.083	12.996	12.923	12.842	12.761	12.677
0.498	12.989	12.897	12.815	12.742	12.661	12.575
0.500	12.909	12.824	12.738	12.651	12.560	12.465
0.512	12.752	12.682	12.604	12.524	12.439	
0.528	12.329	12.261	12.198	12.132	12.061	11.989
0.570	11.102	11.065	11.025	10.981	10.936	10.883
0.579	10.845	10.808	10.769	10.727	10.685	10.639
0.586	10.670	10.635	10.597	10.556	10.514	10.470

[a] Determined using abductive network[14]; see text.

It is not clear whether or not the bands at 1086 and 943 cm^{-1} (Figure 1d) arise from HCl_2^- or from $H_2Cl_3^-$. On the basis of the melt composition ($X_{HCl} = 0.67$), assignment of these bands to hydrogen dichloride would imply the existence of larger anions in the melt, *i.e.* to account for the total HCl content. We have suggested that such ions, *e.g.* $H_3Cl_4^-$, might contribute to speciation in the Lewis basic ambient-temperature systems,[1a] though the correspondence of the upper limit of HCl solubility with the stoichiometry of $H_2Cl_3^-$ suggests, circumstantially at least, that contribution of larger species is probably minimal. In the $AlCl_3$:ImCl system, however, $Al_3Cl_{10}^-$ becomes significant near 2:1 stoichiometry, and so we should suspect that in HCl:ImCl melts, $H_3Cl_4^-$ may reach significant concentrations near the upper limit of HCl solubility. Notably, the calculated vibrational spectrum for the $H_2Cl_3^-$ ion (C_{2v}) does not exhibit strong absorption intensities below 1500 cm^{-1},[12] though here the symmetry of $H_2Cl_3^-$ need not be restricted to C_{2v}, the minimum energy gas-phase geometry. Suffice it to say that the presence or absence of larger anions cannot be confirmed on the basis of the present data. For this reason, unequivocal assignments of the 1086- and 943-cm^{-1} bands (Table 1) cannot be made.

Thermodynamic Parameters for Reaction 1a. Variable-temperature ^{1}H-NMR data for the acidic proton (HCl:ImCl systems) are tabulated in Table 2. For VT samples, melt compositions were estimated from the chemical shifts of the acidic proton and the three Im$^+$ ring protons. This was effected through synthesis of an abductive network[14] which correlated the binary HCl mole fraction, X_{HCl}, with δ's for the 4 proton environments (data from Figure 3 of this paper and Figure 2 of ref 1a). The network estimated X_{HCl} with an uncertainty less than ±0.002 unit (mole fraction). The data of Table 2 were then used to fit a function based on the assumption of rapid exchange in accord with reaction 1

$$\delta_{obs} = (1/X_{HCl})\{X(HCl_2^-)\delta(HCl_2^-) + 2.0X(H_2Cl_3^-)\delta(H_2Cl_3^-)\} \quad (2)$$

in which the mole fractions (X) and chemical shifts (δ) are as defined previously.[1a] The concentration of each anion can be determined from X_{HCl} and $X(HCl_2^-)$. The latter quantity can be calculated from the expression

$$X(HCl_2^-)^2 + \{2K/(4-K)\}\{(1 - X_{HCl})X(HCl_2^-) - X_{HCl}(1 - {}^3/_2X_{HCl})\} = 0 \quad (3)$$

which arises from application of the appropriate mass and charge balance equations to the expression for the stoichiometric equilibrium constant corresponding to reaction 1. The equilibrium constant is included in the form $K = \exp\{(1/R)(\Delta S - \Delta H/T)\}$.

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The model encompassed by eqs 2 and 3 was fit to the data in terms of the variable parameters $\delta(\mathrm{HCl_2}^-)$, $\delta(\mathrm{H_2Cl_3}^-)$, ΔH, and ΔS. A total of 89 (X_{HCl}, δ_{obs}, T) data points were employed: 59 from Table 2 (297–347 K), and 30 from previous[1a] work (297 K). Nonlinear regression afforded ΔH and ΔS as -22.8 ± 1.0 kJ mol^{-1} and -31.8 ± 2.9 J K^{-1} mol^{-1} respectively, corresponding to $\Delta G^{297\mathrm{K}} = -13.3 \pm 1.9$ kJ mol^{-1}, in agreement with the value of -13.3 ± 0.3 kJ mol^{-1} calculated from 297 K data[1a] ($K = 218 \pm 25$, 16 data points). The shifts of $\mathrm{HCl_2}^-$ and $\mathrm{H_2Cl_3}^-$ were calculated as 13.54 ± 0.02 and 8.58 ± 0.01 ppm respectively, indistinguishable from those calculated from 297 K data alone (30 data points). The average absolute residual was less than 0.03 ppm/data point, and the correlation coefficient R^2 was 0.9995.

Assumptions inherent in the fit of ΔH and ΔS include the following: (1) regardless of the HCl mole fraction (X_{HCl}), each protic anion may be considered to occupy a distinct environment which remains more or less constant over the range of X_{HCl}, *i.e.* so that the δ of each environment may be considered constant for all X_{HCl}, and (2) for a given environment, δ is independent of temperature, at least to the extent that changes in δ_{obs} are due more to changes in the ratio of the environments than to changes in the shifts of the environments themselves. Though these are quite reasonable assumptions, it is acknowledged that some error must arise from their adoption. The concurrence of parameters obtained from VT data (297–347 K) and those obtained from 297 K data is encouraging regarding the viability of performing the fit outlined above. This agreement also suggests that over the range of composition employed in the VT study ($0.37 < X_{\mathrm{HCl}} < 0.59$) proton speciation is adequately defined by reaction 1; *i.e.*, larger anions do not contribute significantly. This conclusion stems from the fact that K^{297} was initially determined[1a] for $0.38 < X_{\mathrm{HCl}} < 0.51$, over which reaction 1 most certainly governs proton speciation exclusively. At the extremes of temperature employed in this study, the anion fractions of $\mathrm{HCl_2}^-$ and $\mathrm{H_2Cl_3}^-$ in 1:1 HCl:ImCl are *ca.* 0.88 and 0.06 at 297 K, and 0.80 and 0.10 at 347 K. Thus at the highest temperature employed, about 20% of proton exists as dihydrogen trichloride. Reference to this melt as $\mathrm{ImHCl_2}$ is therefore misleading as far as proton speciation is concerned.

Estimation of The Formation Constant for $\mathrm{HCl_2}^-$ in HCl:ImCl Systems. The absence of significant molecular HCl in an HCl-saturated melt (X_{HCl} *ca.* 0.67 under *ca.* 0.94 atm HCl, Figure 1d) makes it possible to establish minimum values of the equilibrium constants for the reactions

$$\mathrm{HCl} + \mathrm{Cl}^- \rightleftharpoons \mathrm{HCl_2}^- \tag{4a}$$

$$\mathrm{HCl} + \mathrm{HCl_2}^- \rightleftharpoons \mathrm{H_2Cl_3}^- \tag{4b}$$

the difference of which is simply reaction 1. The maximum value for the Henry law constant (${}^{\mathrm{max}}K_{\mathrm{H}}$), corresponding to the gas–liquid equilibrium

$$\mathrm{HCl(g)} \rightleftharpoons \mathrm{HCl(1)} \tag{5}$$

can be estimated based on the assumption that the maximum solubility of HCl (ambient pressure, 30 °C) is about 200 mM, *i.e.* the value reported for acidic $\mathrm{AlCl_3}$:ImCl melts.[11] Considering the infrared data (Figure 1d), this is likely an overestimate, and hence ${}^{\mathrm{max}}K_{\mathrm{H}}$ may be taken as 0.2 mol L^{-1} atm^{-1}.

For a melt equilibrated with HCl at pressure P_{HCl}, the maximum liquid phase concentration of molecular HCl is given by

$${}^{\mathrm{max}}C_{\mathrm{HCl}} = P_{\mathrm{HCl}}\,{}^{\mathrm{max}}K_{\mathrm{H}}\ (\mathrm{mol\ L^{-1}}) \tag{5a}$$

In highly basic melts reaction 1a is driven far to the right so that $\mathrm{H_2Cl_3}^-$ can be neglected in the calculation of the anion fractions of Cl^- and $\mathrm{HCl_2}^-$. In order to estimate minimum values of the $\mathrm{K_4}$, we prepared an HCl:ImCl melt of 1:1 stoichiometry and evacuated it to pressure P_{HCl} at ambient temperature (296–298 K). After one hour of pumping the pressure over the melt dropped to 0.025 Torr. The melt compartment was sealed from the line and stirred for several hours during which time no change in pressure could be detected at a mercury manometer. However, since the readability of such a manometer is limited to about 0.1 Torr, we can conclude only that P_{HCl} was within the range 0.025–0.1 Torr. The melt density was determined as 1.16 g cm^{-3} and its composition was determined as $X_{\mathrm{HCl}} = 0.340$ by means of the titrimetric procedure described previously.[1a] Calculating the concentrations of Cl^- and $\mathrm{HCl_2}^-$ from X_{HCl} (3.4 and 3.6 mol L^{-1} respectively), and ${}^{\mathrm{max}}C_{\mathrm{HCl}}$ from eq 5a by confining P_{HCl} to the range above, affords ${}^{\mathrm{min}}K_{4\mathrm{a}}$ in the range of 4×10^4 to 1.6×10^5 L mol^{-1}. Using this result in the expression $K_{4\mathrm{a}}/K_{4\mathrm{b}} = K_{1\mathrm{a}} = 2.2 \times 10^2$ yields ${}^{\mathrm{min}}K_{4\mathrm{b}}$ as 1.8×10^2 to 7.3×10^2 L mol^{-1}. In further support of these estimates, we consider an analogous experiment involving the preparation of an HCl:ImCl melt for which $X_{\mathrm{HCl}} = 0.665$; such a melt can be prepared for P_{HCl} near ambient (*ca.* 0.95 atm).[1a] The melt density is about 1.15 g cm^{-3}, and using the previously determined[1a] value for $K_{1\mathrm{a}}$, one can calculate that the equilibrium concentrations of $\mathrm{HCl_2}^-$ and $\mathrm{H_2Cl_3}^-$ are on the order of 0.1 and 5 mol L^{-1} respectively. Estimating the maximum concentration of molecular HCl as 0.2 M, one calculates the minimum value of $K_{4\mathrm{b}}$ as 2.5×10^2, and hence that of $K_{4\mathrm{a}}$ as 5.5×10^4, in agreement with the ranges calculated above. We previously reported that a direct search simulation of NMR data according to the equilibria shown in (4), was optimized for $K_{4\mathrm{a}}$ (stoichiometric) on the order of 10^5.[1b] Values of $K_{4\mathrm{a}}$ reported for $\mathrm{AlCl_3}$:ImCl melts at 30–90 °C are on the order of 10^2 L mol^{-1}.[13] The reason for this large difference is not clear, though we have previously indicated[1a] that the determination[13] of $K_{4\mathrm{a}}$ from NMR data in Lewis basic chloroaluminates is prone to error due to the presence of $\mathrm{H_2Cl_3}^-$; as the ratio of total HCl to available chloride increases, that of $\mathrm{H_2Cl_3}^-$ is also expected to increase. NMR data employed for the calculation of $K_{4\mathrm{a}}$ included melts for which the proton concentration exceeded that of the available chloride, *e.g.* $[\mathrm{Cl}^-] = 76$ mM, $[\mathrm{H}^+] = 100$ mM[13] so that some $\mathrm{H_2Cl_3}^-$ might be present.

In molecular solvents such as nitrobenzene and tetrachloroethane, $K_{4\mathrm{a}}$ is on the order of 5×10^2 L mol^{-1};[15,16] we have argued previously that in ionic liquids such as HCl:ImCl and $\mathrm{AlCl_3}$:ImCl, $K_{4\mathrm{a}}$ should assume a larger value.[1a] The calculated ${}^{\mathrm{min}}K_{4\mathrm{a}}$ indicates that in the case of HCl:ImCl ionic liquids, this is indeed true. In contrast, Trulove *et al.* have reasonably argued[13] that the small value of $K_{4\mathrm{a}}$ for Lewis basic $\mathrm{AlCl_3}$:ImCl melts, might be attributed to the enhanced ability of these melts to solvate chloride (relative to molecular solvents), though it is not immediately apparent why HCl:ImCl and $\mathrm{AlCl_3}$:ImCl liquids should behave so differently in this respect. It is likely that the difference lies in the presence of $\mathrm{AlCl_4}^-$ which is capable of forming a hydrogen bond with HCl (gas phase);[12] $\mathrm{Cl{-}H{-}{-}{-}AlCl_4}^-$ is analogous to $\mathrm{HCl_2}^-$, in which one chloride is replaced by tetrachloroaluminate. Formation of such a species in the presence of high concentrations of $\mathrm{AlCl_4}^-$, *i.e.* weakly basic melts, would shift reactions 4a and 4b so as to disfavor the formation of $\mathrm{H_2Cl_3}^-$ and $\mathrm{HCl_2}^-$ so that the apparent value of $K_{4\mathrm{a}}$ would be reduced as observed by Trulove *et al.*[13] Indeed, the latter value is more likely related to the equilibrium

$$\mathrm{Cl{-}H{-}{-}{-}AlCl_4}^- + \mathrm{Cl}^- \rightleftharpoons \mathrm{HCl_2}^- + \mathrm{AlCl_4}^-$$

It is notable that K determined for reaction 1 in 35:65 $\mathrm{AlCl_3}$:ImCl appeared smaller than that in HCl:ImCl melts, though this

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(15) Herbrandson, H. F.; Dickerson, R. T., Jr.; Weinstein, J. *J. Am. Chem. Soc.* **1954**, *76*, 4046.

(16) Fujiwara, F. Y.; Martin, J. S. *J. Chem. Phys.* **1972**, *56*, 4091–4097.

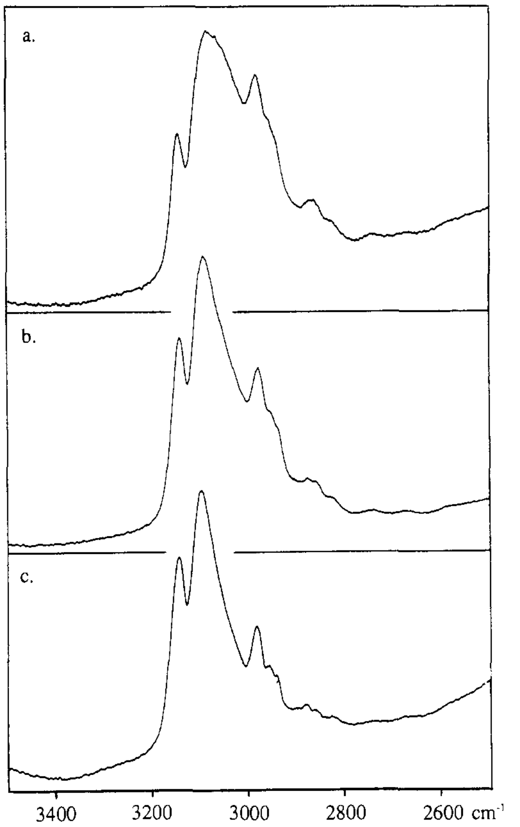

Figure 2. C-H stretching region of HCl:ImCl ionic liquids as a function of composition: X_{HCl} = (a) 0.39, (b) 0.49, (c) 0.59.

could not be demonstrated conclusively within the accuracy of the experiment.[1a] Additionally, the formation of HCl–chloroaluminate adducts is consistent with shifts in IR frequencies and NMR chemical shifts observed for HCl in acidic $AlCl_3$:ImCl systems.[11] The role of species such as Cl–H---$AlCl_4^-$ will be discussed in the context of HCl solubility in the ternary HCl:ImCl:$AlCl_3$ system to be reported in a subsequent paper.

Ionic Interactions in the HCl:ImCl System. ΔH for the gas phase reaction 1 has been estimated as −46 kJ mol^{-1} by means of *ab initio* MO calculations.[12] Comparison to that calculated for the condensed phase reaction 1a reveals a considerable contribution from solvation. One concludes that the interaction of chloride with Im^+ is more exothermic than that of the protic ions. The Im^+ C–H stretching region "interaction bands" observed[6,7] in the corresponding chloroaluminate systems are observed in HCl:ImCl melts, though in contrast to the $AlCl_3$:ImCl system, these bands persist to some extent as the HCl mole fraction increases from 0.5 (see Figure 2). For X_{HCl} = 0.59 (Figure 2c) the aromatic C–H stretching absorptions near 3150 and 3100 cm^{-1} clearly remain broadened compared to those in $AlCl_3$:ImCl melts for which the chloride concentration is negligible. In the latter system these bands do not extend beyond the range of *ca.* 3100–3200 cm^{-1} (Figure 4c of ref 7). Interaction bands in the range 2800–2900 cm^{-1} persist for acidic HCl:ImCl melts (*e.g.* Figure 2c) but are absent in the corresponding chloroaluminate melts. These results indicate that the protic anions also interact with Im^+, albeit less strongly than the chloride ion. Overall trends in shifts of peak frequencies with melt composition are consistent with those observed for the $AlCl_3$:ImCl systems; frequency shifts were interpreted in terms of ion-pair formation.[6]

For the HCl:ImCl system, the chemical shifts of the Im^+ ring protons, and counterion fractions are illustrated as a function of composition in Figure 3 (297 K), in which it is apparent that the Im^+ ring proton shifts are most strongly dependent on the fraction of chloride ion. The H_2 proton is most strongly affected, though H_4 and H_5 are also involved, in agreement with results for $AlCl_3$:ImCl.[5] Notably, chemical shifts of the ring protons in acidic melts are somewhat larger in the HCl:ImCl system compared to those in the $AlCl_3$:ImCl system. This suggests that the protic ions effect greater deshielding of the ring protons than do chloroaluminate species. The observed shift for each of the ring protons can be fitted to a function of the form

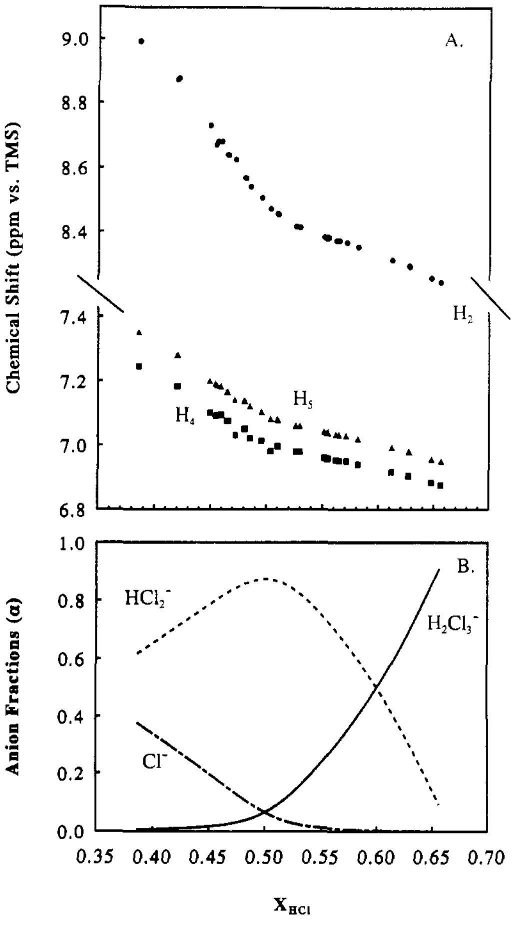

Figure 3. A. Variation of Im^+ ring proton chemical shifts with X_{HCl}. B. Anion fractions. All data were acquired at 297 K.

$$\delta_{obs} = \delta_1\alpha_1 + \delta_2\alpha_2 + \delta_3\alpha_3 \qquad (6)$$

which corresponds to an ion-pair model in which each Im^+ cation interacts with a single anion; the quantities α_1, α_2, and α_3 are the anion fractions of Cl^-, HCl_2^-, and $H_2Cl_3^-$ respectively. The δ's are the chemical shifts of the ring proton in the ion-pair environment. The extended H-bonded aggregate model of Dymek *et al.* would correspond to the three equations of the form above, one for each ring proton. The fit of eq 6, however, cannot be distinguished from that of

$$\delta_{obs} = \delta_{11}\alpha_1^2 + 2\delta_{12}\alpha_1\alpha_2 + \delta_{22}\alpha_2^2 + 2\delta_{23}\alpha_2\alpha_3 + \delta_{33}\alpha_3^2 \qquad (7)$$

corresponding to the oligomeric stacking model of Wilkes and coworkers. Each term corresponds to a distinct environment in which Im^+ interacts with two anions. A term corresponding to the environment δ_{13} was not included, as the maximum value of $\alpha_1\alpha_3$ is less than 0.004. Distinction between the stacked oligomer and ion-pair/extended H-bonded aggregate models would be possible only if several of the δ's could be held constant at known values. Nevertheless, the fits to these equations are instructive in that the changes in the fitted shifts with the various environments are indicative of the relative abilities of the anions to interact with Im^+. The results of fits for Im–H_2, Im–H_4, and Im–H_5 tabulated in Table 3 indicate, as might be expected, that this ability decreases in the order Cl^- > HCl_2^- > $H_2Cl_3^-$, *e.g.* shifts in the HCl_2^- (δ_2 or δ_{22}) and $H_2Cl_3^-$ (δ_3 or δ_{33}) environments are

Table 3. Results of Nonlinear Fit of Im^+ Ring Proton Chemical Shifts to Equations 6 and 7

environment	$Im–H_2$	$Im–H_4$	$Im–H_5$
	Equation 6		
δ_1	10.04 ± 0.04	7.69 ± 0.02	7.83 ± 0.01
δ_2	8.39 ± 0.01	6.97 ± 0.00	7.05 ± 0.00
δ_3	8.27 ± 0.01	6.87 ± 0.01	6.94 ± 0.00
	Equation 7		
δ_{11}	9.86 ± 0.30	7.88 ± 0.14	8.01 ± 0.06
δ_{12}	9.26 ± 0.08	7.30 ± 0.04	7.41 ± 0.02
δ_{22}	8.47 ± 0.02	7.03 ± 0.01	7.12 ± 0.00
δ_{23}	8.33 ± 0.03	6.94 [illegible] 0.01	7.01 ± 0.01
δ_{33}	8.27 ± 0.02	6.86 ± 0.01	6.93 ± 0.00
R^2 (eq 6/eq 7) av:	0.997/0.997	0.999/0.999	1.000/1.000
abs residual	0.01/0.01	0.007/0.005	0.004/0.003
S_r[b]	0.018/0.018	0.01/0.008	0.006/0.004

[a] ppm/data point. [b] Standard error of regression.

not widely different, but are considerably lower than those in the Cl^- (δ_1 or δ_{11}) environment. That chloride interacts more strongly with Im^+ than either of the protic anions is obvious from the fact that if one converts the chloride ions in ImCl to HCl_2^-, liquefication takes place!

Further insight into anion–cation interactions is available from an examination of the temperature dependence of the Im^+ ring proton resonances. For a given value of X_{HCl} the variation of $\delta(Im–H_2)$, $\delta(Im–H_4)$, or $\delta(Im–H_5)$ with temperature approximates a linear function ($R^2 > 0.99$) with slope $d(\delta(Im–H_i))/dT$. The $d(\delta(Im–H_i))/dT$ values are plotted as a function of X_{HCl} in Figure 4A. The anion fractions are also highly linear in temperature (for a given value of X_{HCl}); the $d\alpha/dT$ values are plotted as a function of X_{HCl} in Figure 4B. The behavior of the $d(\delta(Im–H_i))/dT$ (Figure 4A) is determined by two competing factors, namely the temperature dependence of anion fractions (Figure 4B) and the temperature dependence of cation–anion interactions. An increase in temperature shifts reaction 1 to the left; interaction of chloride with Im^+ results in deshielding of the ring protons and $d(\delta(Im–H_i))/dT$ is positive. However, since dissociation is characterized by a positive entropy change, cation–anion interactions are diminished with increasing temperature so that the ring protons experience greater shielding, *i.e.* $d(\delta(Im–H_i))/dT$ is negative. The sign of the observed $d(\delta(Im–H_i))/dT$ will depend on the relative contributions of these processes. Only for $X_{HCl} <$ *ca.* 0.45, where α_{Cl^-} is significant, is cation–anion dissociation dominant in determining the sign of the $d(\delta(H_i))/dT$. It is notable that it is also this region in which the $d(\delta(Im))/dT$ for H_2, H_4, and H_5 are not widely different. As X_{HCl} approaches or exceeds 0.5, however, $d(\delta(Im))/dT$ for H_2 diverges from that of H_4 and H_5, suggesting a general change in the nature of interactions determining the $\delta(Im)$. One presumes that in the oligomeric stacking model of Wilkes and coworkers, interactions may also take place between adjacent oligomeric stacks of alternating anions and cations. This would most likely occur via hydrogen bonding of anions in one stack, to Im^+ ring protons in adjacent stacks. We suggest that the most accurate model of melt structure is probably a hybrid of the Wilkes and Dymek models and that hydrogen bonding is the key interaction. The range over which the average hydrogen-bonded supramolecular structure extends through space is determined largely by the ability of the anion population to form hydrogen bonds. Extended aggregates are favored in the presence of high concentrations of chloride which, relative to the protic species, is most strongly polarizing by virtue of its higher charge density. When the chloride concentration becomes insignificant, the formation of hydrogen-bonded ion pairs may become more important in determining the structure of the melt, and hence its physical properties, *i.e.* viscosity, *etc.* The behavior of the $d(\delta(Im–H_i))/dT$ for $X_{HCl} > 0.5$ suggests that $Im–H_2$ is the principal mediator of ion-pair formation. This is expected since $Im–H_2$ is the most acidic ring proton. It has recently been reported, for example, that in the salts $Im_2[MCl_4]$ (M ≡ Co, Ni), all three ring protons are hydrogen-bonded to chlorine, with $Im–H_2$ forming the shortest hydrogen bond.[17]

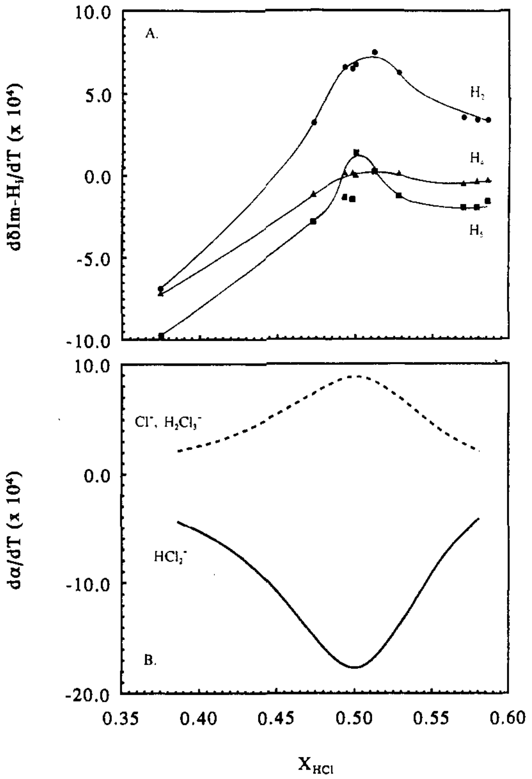

Figure 4. A. Temperature dependence of Im^+ ring proton chemical shifts, $d(\delta(Im–H_i))/dT$ *vs* X_{HCl}. B. Temperature dependence of anion fractions, $d\alpha/dT$ vs X_{HCl}. Data were generated using thermodynamic parameters calculated for reaction 1a.

The conclusions of earlier work[1a] concerning proton speciation in ambient-temperature molten salts have been confirmed spectroscopically, and thermodynamic parameters for reaction 1a have been evaluated for HCl:ImCl melts. It must be recognized that since these parameters contain a substantial contribution from solvation, they would be affected by the presence of tetrachloroaluminate, and thus do not apply to solutions of HCl in Lewis basic chloroaluminate melts. Minimum values for the formation constants of HCl_2^- and $H_2Cl_3^-$ (eq 4a,b) in HCl:ImCl ionic liquids have been established as *ca.* 10^4–10^5 and 5×10^2 L mol^{-1} respectively. Im^+ ring proton chemical shifts have composition dependencies similar to those observed for the $AlCl_3$:ImCl system. Ionic interactions in the HCl:ImCl system lead to the formation of hydrogen-bonded aggregates of anions and cations, the nature and extent of which depend on the ability of the anion population to form hydrogen bonds with Im^+.

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