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The Chemistry of Protons in Ambient-Temperature Ionic Liquids: Solubility and Electrochemical Profiles of HCl in HCl:ImCl:$AlCl_3$ Ionic Liquids as a Function of Pressure (295 K)

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Abstract: The liquidus region of the HCl:ImCl:$AlCl_3$ ionic liquid system has been determined through manometric measurement of HCl solubility as a function of pressure for $0 < P_{HCl} < 1$ atm at 295 ± 1 K. Analysis of the pressure−composition isotherms thus obtained, in conjunction with spectroscopic data, reveals that dissolution of HCl in these systems is associated with reactions of the general form $HCl(g) + X^-(l) \rightleftharpoons HClX^-(l)$, where $X^- \equiv Cl^-$, HCl_2^-, $H_2Cl_3^-$, $AlCl_4^-$, or $Al_2Cl_7^-$. In the binary HCl:ImCl system, the HCl-derived proton exists as HCl_2^-, $H_2Cl_3^-$, and $H_3Cl_4^-$; the equilibrium constants for the reaction above are 715 ± 76, 3.28 ± 0.05, and 0.74 ± 0.02 atm^{-1} for $X^- \equiv Cl^-$, HCl_2^-, and $H_2Cl_3^-$, respectively. In Lewis acidic HCl:ImCl:$AlCl_3$ melts ($X_{AlCl_3} > X_{ImCl}$), HCl is complexed as the species $AlCl_4{\cdot}HCl^-$ and $Al_2Cl_7{\cdot}HCl^-$. The corresponding equilibrium constants were determined as 0.135 ± 0.001 and 0.109 ± 0.001 atm^{-1} for $X^- \equiv AlCl_4^-$ and $Al_2Cl_7^-$, respectively. In Lewis basic HCl:ImCl:$AlCl_3$ systems, all species with the exception of $Al_2Cl_7{\cdot}HCl^-$ contribute, though the equilibrium constants associated with the reaction above are less well-defined, being dependent on the specific composition of the melt. Liquid phase equilibria such as reported earlier from this laboratory are obtained by combining two or more of the dissolution equilibria above such that molecular HCl does not appear in the result. Electrochemical profiles of HCl dissolved in HCl:ImCl:$AlCl_3$ ionic liquids are reported as a function of HCl pressure for $0 < P_{HCl} < 1$ atm at 295 ± 1 K. In Lewis basic systems, the electroactivity of HCl_2^-, $H_2Cl_3^-$, and $AlCl_4{\cdot}HCl^-$ is observed, while in Lewis acidic systems, two electroactive protic species are present: $AlCl_4{\cdot}HCl^-$ and $Al_2Cl_7{\cdot}HCl^-$. The reduction potential of $Al_2Cl_7{\cdot}HCl^-$ is *ca.* 0.7 to 1.0 V more positive than that of other protic species, confirming that the proton of $Al_2Cl_7{\cdot}HCl^-$ is exceptionally labile. Based on this observation, we conclude that $Al_2Cl_7{\cdot}HCl^-$ is the entity responsible for Brønsted superacidity observed in the Lewis acidic melts. It is demonstrated that the reproducibility of voltammograms requires strict control of the HCl pressure.

Introduction

The chemistry of HCl added to ambient temperature ionic liquids,[1] *e.g.* $AlCl_3$:ImCl ($Im^+ \equiv$ 1-ethyl-3-methyl-1*H*-imidazolium chloride),[2] has been the subject of some investigation.[3−8] For example, it has been demonstrated that when added to the Lewis acidic melts ($X_{AlCl_3} > X_{ImCl}$), HCl behaves as a Brønsted superacid and will protonate a variety of arenes.[9,10] Superacidity was viewed to arise from the ability to maintain a low chloride activity and not from some distinct superacidic species, *i.e.* HCl was considered to be the active agent.

Osteryoung and co-workers have reported evidence for the presence of HCl_2^- and molecular HCl in Lewis basic and acidic $AlCl_3$:ImCl melts, respectively.[5] Interestingly, the infrared stretching frequency and NMR chemical shift of HCl were found to be composition dependent in acidic melts, suggesting some change in the nature of the HCl−solvent interaction. It was proposed that the HCl-derived proton is partitioned according to the reaction[3−5]

$$HCl + Cl^- \rightleftharpoons HCl_2^- \tag{1}$$

Investigations of the HCl:ImCl liquids[4] conducted in this laboratory, however, indicated that reaction 1 was insufficient

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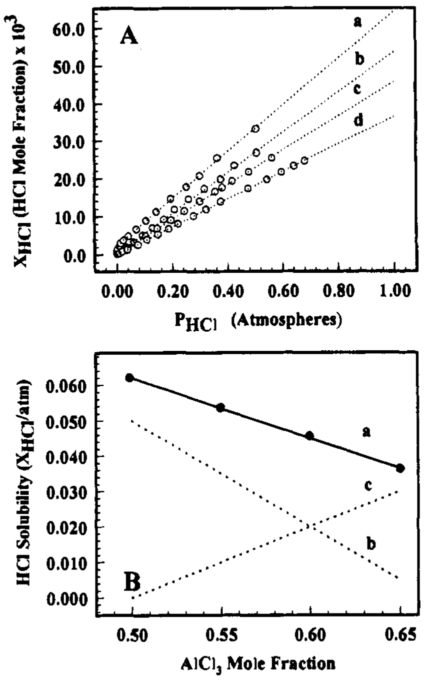

Figure 1. (A) HCl solubilities in near-neutral and Lewis acidic $AlCl_3$:ImCl ionic liquids as a function of P_{HCl}; *binary* $AlCl_3$ mole fraction of progenitor melt (X_{AlCl_3}) equals (a) 0.499, (b) 0.550, (c) 0.600, and (d) 0.650. Solubilities are plotted as *ternary* mole fractions near 295 K. (B) HCl solubility as a function of composition for Lewis acidic $AlCl_3$:ImCl melts: (a) dX_{HCl}/dP_{HCl} *vs* X_{AlCl_3} at ambient temperature; dashed lines are mole fractions ($\times 10^{-1}$) of (b) $AlCl_4^-$ and (c) $Al_2Cl_7^-$ in pure $AlCl_3$:ImCl liquids.

to describe speciation in this system; additional species must exist, *e.g.*[11]

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

Modeling of ^{1}H-NMR data indicated that in the HCl:ImCl system and in strongly Lewis basic $AlCl_3$:ImCl melts (*e.g.* 35 m/o $AlCl_3$), proton speciation is governed largely by the equilibrium

$$H_2Cl_3^- + Cl^- \rightleftharpoons 2HCl_2^- \qquad (3)$$

for which the stoichiometric equilibrium constant was calculated as *ca.* 220 for the HCl:ImCl system. The data were consistent with the presence of larger ions, *e.g.* $H_3Cl_4^-$, in melts of high HCl content though this could not be established unequivocally. Further, the results suggested that molecular HCl does not contribute significantly to proton speciation, a conclusion which was later confirmed by infrared spectroscopy.[12] It was demonstrated that in contrast to the value reported for $AlCl_3$:ImCl melts (*ca.* 10^2 L/mol),[3,6b] the equilibrium constant for reaction 1, K_1, in the HCl:ImCl system is much larger, having a magnitude of at least 10^5 L/mol.[12]

The apparent instability of molecular HCl in the HCl:ImCl system led us to entertain the possibility that in Lewis acidic $AlCl_3$:ImCl melts, HCl might be stabilized as H_2Cl^+, a species believed to arise in the autosolvolysis of liquid HCl,[13] and which would be expected to exhibit superacidic behavior.[11] The formation of H_2Cl^+ is purely analogous to the protonation of an arene and corresponds, in this case, to the self protonation of HCl in the presence of $Al_2Cl_7^-$. Surprisingly, H_2Cl^+ is expected to exhibit intense IR absorptions very near those of HCl itself,[14] and so we believed that further investigation was warranted.

Table 1. Linear Regression Lines for HCl Solubility in Near-Neutral and Lewis Acidic $AlCl_3$:ImCl Melts at Ambient Temperature (295 ± 1 K) and $P_{HCl} \leq 1$ atm

(a) $X_{HCl} = MP_{HCl} + b$

X_{AlCl_3}[a]	M (atm^{-1})	b	R^2
0.499	0.0620 ± 0.0002	0.00227 ± 0.00009	0.9994
0.550	0.0536 ± 0.0007	0.00010 ± 0.00018	0.9982
0.600	0.0456 ± 0.0002	0.00011 ± 0.00005	0.9998
0.650	0.0364 ± 0.0001	−0.00004 ± 0.00004	0.9998

(b) [HCl] = $MP_{HCl} + b$

X_{AlCl_3}[a]	M[b] (mM atm^{-1})	b (mM)	R^2
0.499	588 ± 5	20.2 ± 0.8	0.9995
0.550	523 ± 6	−0.3 ± 1.5	0.9988
0.600	455 ± 2	0.3 ± 0.4	0.9998
0.650	373 ± 1	−1.4 ± 0.4	0.9999

[a] X_{AlCl_3} is the *binary* $AlCl_3$ mole fraction of the initial melt; X_{HCl} is the *ternary* HCl mole fraction of the resulting melt. [b] Calculated assuming constant melt density, see Discussion.

In the current article, we report the solubilites of HCl in HCl:ImCl and several $AlCl_3$:ImCl melts as a function of pressure near ambient temperature. The results indicate that HCl dissolution in HCl:ImCl and $AlCl_3$:ImCl ambient temperature ionic liquids may be described generally in terms of two-phase reactions of the form:

$$HCl(g) + X^-(l) \rightleftharpoons HClX^-(l) \qquad (4)$$

where X^- may be Cl^-, HCl_2^-, $H_2Cl_3^-$, $AlCl_4^-$, or $Al_2Cl_7^-$. We find no evidence for the presence of H_2Cl^+ in any significant quantity. Lastly, we describe a cell which, together with the manostat employed for solubility measurement, allows electrochemical measurements to be performed as a function of pressure. Thus, in tandem with HCl solubility, we report the electrochemical profiles of HCl dissolved in HCl:ImCl:$AlCl_3$ as a function of pressure and composition and consider the bearing of these profiles on the conclusions above.

Results and Discussion

HCl Solubility in Lewis Acidic Systems. Solubilities of HCl in Lewis acidic and near-neutral $AlCl_3$:ImCl melts as a function of HCl pressure, P_{HCl}, are plotted as ternary mole fractions, X_{HCl}, in Figure 1A (295 ± 1 K). The calculated errors were smaller than the indicated markers in all cases. For acidic $AlCl_3$:ImCl melts, HCl solubility is linear in pressure. The equations of the least-squares lines, X_{HCl} *vs* P_{HCl}, are summarized for these melts in Table 1a; those for [HCl] *vs* P_{HCl} are tabulated in Table 1*b*.

The solubility of HCl in Lewis acidic chloroaluminates is linear not only in HCl pressure, but in composition as well. The slopes of the pressure−composition isotherms (dX_{HCl}/dP_{HCl}) from Figure 1A (Table 1) are plotted as a function of melt acidity in Figure 1Ba in which it is seen that the dX_{HCl}/dP_{HCl} are linear in the mole fraction of $AlCl_3$. The mole fraction of HCl as a function of melt composition and HCl pressure may be estimated by the equation

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$$X_{HCl} = \{0.147 \pm 0.002 - (0.170 \pm 0.003)X_{AlCl_3}\}P_{HCl} \quad (5)$$

which was obtained by least-squares fitting of the line in Figure 1Ba ($R^2 = 0.999$). Alternatively, the HCl concentration can be expressed as the linear function

$$[HCl]\ (mM) = \{1.30 \pm 0.03 \times 10^3 - (1.43 \pm 0.06 \times 10^3)X_{AlCl_3}\}P_{HCl} \quad (6a)$$

with a correlation coefficient $R^2 = 0.996$, or by the polynomial

$$[HCl]\ (mM) = \{748 \pm 529X_{AlCl_3} - 1700X^2_{AlCl_3}\}P_{HCl} \quad (6b)$$

with correlation coefficient $R^2 = 1.000$. Equation 6b reproduces the concentrations of Table 1*b* to within 0.5%. The expressions for the HCl concentration (eq 6) are based on the assumption that the density of the melt does not change to within 3 significant figures as HCl is added to the melt. As discussed in the following section, this is a reasonable assumption, particularly at lower pressures (HCl concentrations) and high aluminum chloride contents. Note that for all of the equations above, X_{AlCl_3} is the *binary* mole fraction of aluminum chloride in the Lewis acidic $AlCl_3$:ImCl melt *prior* to equilibration with HCl at pressure P_{HCl}. The HCl mole fraction calculated via eq 5 is a *ternary* mole fraction for the resulting HCl:ImCl:$AlCl_3$ melt.

The linear variation of HCl solubility with pressure (Figure 1A) is not consistent with solvation as cationic species, *e.g.* H_2Cl^+, for which one would expect a higher order pressure dependence [since 2 HCl are consumed per H_2Cl^+ generated]. Further, the dependence of HCl solubility on composition (Figure 1B) is also inconsistent with solvation as H_2Cl^+ for which one would expect HCl solubility to increase with melt acidity. Though one would expect a linear dependence on pressure, solubility as molecular HCl would not be expected to exhibit any particular dependence on melt composition. Additionally, HCl solubility is higher than one might expect for the reactionless dissolution of an inert gas in an inert solvent, and in particular, dissolution of a gas in an ionic liquid.[11] We conclude that the dX_{HCl}/dP_{HCl} are linear in X_{AlCl_3} because the mole fractions of $AlCl_4^-$ and $Al_2Cl_7^-$ are also linear in X_{AlCl_3} (see Figure 1B), and because in a manner analogous to its reaction with Cl^- or HCl_2^- (reactions 1, 2), HCl forms hydrogen-bonded adducts with the chloroaluminate anions:

$$HCl(g) + AlCl_4^-(l) \rightleftharpoons AlCl_4{\cdot}HCl^-(l) \quad (7a)$$

$$HCl(g) + Al_2Cl_7^-(l) \rightleftharpoons Al_2Cl_7{\cdot}HCl^-(l) \quad (7b)$$

These reactions are written so as to acknowledge that a two-phase system is being treated. *Semiempirical* molecular orbital calculations indicate that these reactions are favorable, and in the gas phase are associated with standard free energies of reaction of −42 and −38 kJ/mol, respectively.[14]

Solvation of HCl as hydrogen-bound anionic species accounts for the spectroscopic observations reported by Trulove and Osteryoung, *viz.* that the chemical shift of DCl added to Lewis acidic melts varies approximately linearly with aluminum chloride mole fraction, ranging from 1.61 to 0.90 ppm *vs* TMS for binary aluminum chloride mole fractions of 0.5 and 0.664, respectively.[5] Further, the HCl stretching frequency was observed to be composition dependent, ranging from 2709 cm^{-1} for a near neutral melt to 2762 cm^{-1} for HCl dissolved in an acidic melt ($X_{AlCl_3} = 0.654$).[5] The shift in stretching frequency was attributed[5] to a decrease in the association of the solvent with the HCl dipole. Based on this, the equilibrium constant for the exchange reaction 8, obtained by combining reactions 7*a* and 7*b*, is expected to be greater than unity:

$$AlCl_4^- + Al_2Cl_7{\cdot}HCl^- \rightleftharpoons AlCl_4{\cdot}HCl^- + Al_2Cl_7^- \quad (8)$$

The existence of two distinct HCl environments in the acidic melts provides a facile explanation for spectroscopic data. Interestingly, as Trulove and Osteryoung point out,[5] variations in spectroscopic behavior upon increasing melt acidity occur in conjunction with an increase in Brønsted superacidity of dissolved HCl.[9,10] Reaction 8 indicates that $AlCl_4{\cdot}HCl^-$ will be favored in weakly acidic melts, while $Al_2Cl_7{\cdot}HCl^-$ will dominate in more acidic melts. This suggests that superacidity of HCl dissolved in Lewis acidic chloroaluminates is associated with the species $Al_2Cl_7{\cdot}HCl^-$. It is notable that the reversible protonation of Im^+ in Lewis acidic melts is first order in both $Al_2Cl_7^-$ and HCl.[6]

If we assume that molecular HCl does not exist as such in a significant concentration relative to hydrogen-bonded anions, as demonstrated for the HCl:ImCl system,[11,12] then it is possible to calculate the equilibrium constants corresponding to reactions 7*a* and 7*b*. Since the formation of the anionic species is thermodynamically favorable, and since the chloroaluminate anions exist in high concentrations relative to HCl, this is a good assumption. The low value of the infrared stretching frequency of HCl in the Lewis acidic melts (*ca.* 2700−2760 cm^{-1})[5] relative to that in the gas phase (2990 cm^{-1})[15] or that in inert, nonpolar solvents such as CCl_4 (2834 cm^{-1})[16] suggests that for all intents and purposes, HCl is fully associated in the HCl:ImCl:$AlCl_3$ system. Spectroscopic evidence of this will be discussed in the following section. Under these conditions, it is straightforward to show that the ternary mole fraction of HCl, X_{HCl}, is given by

$$X_{HCl} = K_{A1}X(AlCl_4^-)P_{HCl} + K_{A2}X(Al_2Cl_7^-)P_{HCl} \quad (9)$$

in which the equilibrium mole fractions of $AlCl_4^-$ and $Al_2Cl_7^-$ are functions of composition[17] and pressure,[18] and where the equilibrium constants corresponding to reactions 7*a* and 7*b*, K_{A1} and K_{A2}, respectively, are defined by functions of the form, e.g. for reaction 7*a*:

$$K_{A1} = X(AlCl_4{\cdot}HCl^-)/[X(AlCl_4^-)P_{HCl}] \quad (10)$$

Function 9 was fit to the pressure−composition isotherms for the 55, 60, and 65 m/o $AlCl_3$ melts by means of linear regression in the parameters K_{A1} and K_{A2}. This treatment yielded $K_{A1} = 0.135 \pm 0.001\ atm^{-1}$ and $K_{A2} = 0.109 \pm 0.001\ atm^{-1}$. The correlation coefficient was unity (to 5 significant figures) and the average absolute residual (in X_{HCl}) was 2.4×10^{-4} mole fraction units. Thus the equilibrium constant for the HCl exchange reaction 8 may be calculated as 1.24 ± 0.01.

HCl Solubility in Lewis Basic Systems. Solubilities of HCl in Lewis basic $AlCl_3$:ImCl melts as a function of HCl pressure, P_{HCl}, are plotted as ternary mole fractions, X_{HCl}, in Figure 2A (295 ± 1 K). The pressure−composition isotherms are recast in Figure 2B with HCl contents expressed as the ratio N_{HCl}/N_{Cl}

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[17] The equilibrium constant for the reaction $Al_2Cl_7^- + Cl^- \rightleftharpoons 2AlCl_4^-$ was taken as 10^{17} (see refs 2, 40, and 41).

[18] John L. E. Campbell, Ph.D. Thesis, University of Regina, 1994.

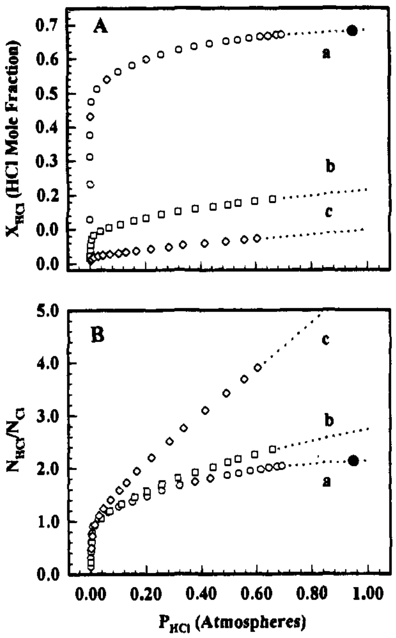

Figure 2. (A) HCl solubilities in Lewis basic $AlCl_3$:ImCl ionic liquids as a function of P_{HCl}; *binary* $AlCl_3$ mole fraction of progenitor melt (X_{AlCl_3}) equals (a) 0.000, *i.e.* HCl:ImCl system, (b) 0.451, and (c) 0.490. Solubilities are plotted as *ternary* mole fractions near 295 K. (B) Pressure–composition isotherms for HCl:ImCl:$AlCl_3$ systems (295 K): (a) N_{HCl}:51:49, (b) N_{HCl}:55:45, and (c) N_{HCl}:N_{ImCl}:0. Vertical axis is in units of N_{HCl}/N_{Cl} (see text). The solid circle in curve a is a datum from ref 11.

where N_{HCl} is the number of moles of HCl and N_{Cl} is the number of moles of available chloride, *i.e.* that over and above chloride required for neutralization of $AlCl_3$. Note that although the chloroaluminate melts achieve higher values of N_{HCl}/N_{Cl}, they contain smaller mole fractions of HCl relative to the HCl:ImCl system (Figure 2). For example, near ambient pressure the 55:45 melt has an N_{HCl}/N_{Cl} ratio of *ca.* 2.5 while for the 51:49 melt N_{HCl}/N_{Cl} is in excess of 5 equiv. For the HCl:ImCl system, density was not observed to be highly dependent on composition, ranging from 1.16 to 1.15 g/cm^3 for low and high HCl content melts, respectively. For the purposes of the manometry calculations, melt density was therefore taken as 1.15_5 g/cm^3. For Lewis basic $AlCl_3$:ImCl melts it was found that the introduction of HCl to molar concentrations has little effect on the density of the melt. For example, the saturation of $AlCl_3$:ImCl (45:55) with HCl resulted in a change in density from 1.27_7 to 1.27_3 g/cm^3, *i.e.* the introduction of HCl to a concentration of *ca.* 2 M has little effect on melt density.

The similarity of pressure–composition isotherms and NMR chemical shift *vs* composition curves[11] suggests that speciation of HCl added to the highly Lewis basic chloroaluminate melts is similar to that of the HCl:ImCl system and involves the formation of HCl_2^-, $H_2Cl_3^-$, and perhaps $H_3Cl_4^-$. This is confirmed by the infrared spectrum[18] of a 45:55 $AlCl_3$:ImCl melt saturated with HCl which exhibits the same very broad band [assigned to $H_2Cl_3^-/H_3Cl_4^-$] observed[12] for HCl:ImCl. Notably, however, this spectrum also exhibits a much weaker, broad band near 2700 cm^{-1}. Trulove and Osteryoung observed a similar band in spectra of HCl dissolved in $AlCl_3$:ImCl melts and attributed it to molecular HCl.[5] However, that this band is not observed in spectra of HCl:ImCl melts at comparable pressures indicates that it corresponds to $AlCl_4{\cdot}HCl^-$, *i.e.* the 2700-cm^{-1} band is observed only in the presence of *both* HCl *and* $AlCl_4^-$. Thus, HCl exists in these systems *only* when associated with anionic species. We conclude that in Lewis basic chloroaluminates, HCl may exist as HCl_2^-, $H_2Cl_3^-$, possibly $H_3Cl_4^-$, and $AlCl_4{\cdot}HCl^-$. In accord with the treatment of the Lewis acidic systems, this suggests that for the Lewis basic ternary system, HCl dissolution should be considered in terms of the two-phase equilibria 7*a* and

$$HCl(g) + Cl^-(l) \rightleftharpoons HCl_2^-(l) \qquad (11a)$$

$$HCl(g) + HCl_2^-(l) \rightleftharpoons H_2Cl_3^-(l) \qquad (11b)$$

$$HCl(g) + H_2Cl_3^-(l) \rightleftharpoons H_3Cl_4^-(l) \qquad (11c)$$

The equilibrium constant for reaction 7*a* (K_{A1}) is given by eq 10. Those for reactions 11 (K_{H1}, K_{H2}, K_{H3}) are given by expressions of the form, *e.g.* for K_{H1}:

$$K_{H1} = X(HCl_2^-)/[X(Cl^-)P_{HCl}] \qquad (12)$$

Based on the appropriate mass/charge balance equations and the equilibrium expressions 12, it is straightforward to show that the ratio $N_{HCl}/N_{Cl} = X_{HCl}/(X_{ImCl} - X_{AlCl_3})$ is given by[18]

$$\frac{N_{HCl}}{N_{Cl}} = \frac{P_{HCl}}{X_{ImCl} - X_{AlCl_3}}\left\{K_{H1}X(Cl^-) + 2K_{H1}K_{H2}X(Cl^-)P_{HCl} + 3K_{H1}K_{H2}K_{H3}X(Cl^-)P^2_{HCl} + \frac{K_{A1}X_{AlCl_3}}{1 + K_{A1}P_{HCl}}\right\} \qquad (13)$$

which, according to the conclusions of this section, is expected to describe the pressure–composition isotherms of Figure 2B (N_{HCl}/N_{Cl} *vs* P_{HCl}). Thus it should be possible to fit eq 13 to these isotherms and thereby extract the equilibrium constants K_{Hn}.

The appropriate function of the form of equation 12 was fit to the HCl:ImCl isotherm of Figure 2Ba by means of nonlinear regression in the parameters K_{H2} and K_{H3}; K_{H1} was constrained[19] such that $K_{H1}/K_{H2} = 218$, *i.e.* the equilibrium constant for reaction 3 calculated[11] from NMR data. Such a treatment yields that for HCl:ImCl melts, $K_{H1} = 715 \pm 76$, $K_{H2} = 3.28 \pm 0.05$, and $K_{H3} = 0.74 \pm 0.02$; the fit was associated with a standard error of 0.0065 and an average absolute residual of 0.005 N_{HCl}/N_{Cl} units. Anion fractions for Cl^-, HCl_2^-, $H_2Cl_3^-$, and $H_3Cl_4^-$ can be calculated on the basis of these equilibrium constants.[18] For HCl mole fractions as high as 0.55 to 0.6, speciation is governed almost exclusively by reaction 3.

It cannot be assumed that K_{H1}, K_{H2}, and K_{H3} in the $AlCl_3$:ImCl system are the same as in HCl:ImCl; this is due to differences in ionic interactions which may distinguish the two systems. It does seem reasonable to assume that K_{A1} is the same in basic and acidic melts, *i.e.* 0.135 atm^{-1}. Constraining K_{A1} to this value, and fitting of 13 to the isotherms for the Lewis basic $AlCl_3$:ImCl melts yields, for the $X_{AlCl_3} = 0.45$ melt (Figure 2Bb), $K_{H1} = 542 \pm 12$, $K_{H2} = 2.83 \pm 0.07$, and $K_{H3} = 0.73 \pm 0.03$. For the $X_{AlCl_3} = 0.49$ melt (Figure 2Bc), the values 372 ± 26, 3.62 ± 0.21, and 0.6 ± 0.5 were obtained. The standard errors (s_r) and average absolute residuals (R) were 0.00958 and

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[19] The reason for constraining K_{H1} in this way is based on the precision of the data. The formation of HCl_2^- is dominant for $X_{HCl} < 0.5$ and for low pressures. Because the equilibrium HCl pressure varies over such a narrow range in this region, and because these low pressures cannot be measured accurately and with precision using the instrumentation employed, *i.e.* a mercury manometer, it is unreasonable to attempt to extract K_{H1} from these data. In contrast, the NMR data (δ *vs* X_{HCl}) are intrinsically better suited to the determination of this parameter because the data span a wider and more accurately sampled domain in which the formation of HCl_2^- is dominant, *e.g.* δ for the acidic proton varies through more than 1 full ppm unit for $X_{HCl} < 0.5$ and δ can be accurately measured to 3 or 4 significant figures.

0.007, respectively, for the 45 m/o melt, and 0.0245 and 0.012 for the 49 m/o melt. Thus, the pressure–composition isotherms of the Lewis basic chloroaluminates yield poorer fits than that obtained for the HCl:ImCl isotherm. This is expected since the precision of the solubility data is lower than that for HCl:ImCl melts, *i.e.* total HCl contents are smaller in the case of $AlCl_3$:ImCl melts. As is the case for the HCl:ImCl system, the determination of K_{H1} from pressure–composition isotherms is prone to error[19] and so the equilibrium constants above should be regarded with caution. A fit of NMR data[11] for solutions of HCl in a strongly basic $AlCl_3$:ImCl melt (35 m/o $AlCl_3$) yielded $K_3 = K_{H1}/K_{H2} = 100 \pm 60$, in qualitative agreement with the above values. Thus proton speciation in Lewis basic HCl:ImCl:$AlCl_3$ melts is similar to that in the HCl:ImCl system, with HCl_2^- predominating in the presence of excess chloride, and $H_2Cl_3^-$, $H_3Cl_4^-$, and $AlCl_4{\cdot}HCl^-$ becoming significant at higher HCl pressures. The relative magnitudes of the formation constants for these species indicate that the order of their formation is as listed above. It must be borne in mind, however, that in weakly basic melts, *e.g.* 49 m/o $AlCl_3$, $AlCl_4{\cdot}HCl^-$ can dominate proton speciation due to the high concentrations of $AlCl_4^-$. Also, because of the relatively lower concentrations of HCl_2^-, the potential for formation of $H_nCl_{n+1}^-$ decreases with increasing X_{AlCl_3}.

In Lewis basic melts, HCl dissolved in excess of 2–3 equiv (Figure 2B) exists as $AlCl_4{\cdot}HCl^-$. The difference[12] in the apparent values of the formation constant of HCl_2^- (reaction 1) in HCl:ImCl and $AlCl_3$:ImCl can now be fully understood. Values of K_1 reported for $AlCl_3$:ImCl melts at 30–90 °C are of the order of 10^2 L mol^{-1},[3,6b] as opposed to a minimum value of *ca.* 10^5 estimated for HCl:ImCl melts.[12] The difference lies in the presence of $AlCl_4^-$ which allows the generation of $AlCl_4{\cdot}HCl^-$. Formation of this species in the presence of high concentrations of $AlCl_4^-$, *i.e.* weakly basic melts, would disfavor the formation of $H_2Cl_3^-$ and HCl_2^- as discussed above so that the *apparent* value of K_1 would be reduced as observed by Trulove *et al.*[3] Indeed, the value calculated by these investigators is more likely related to the equilibrium

$$AlCl_4{\cdot}HCl^- + Cl^- \rightleftharpoons HCl_2^- + AlCl_4^- \qquad (14)$$

and is thus distinct from the HCl_2^- formation constant (reaction 1) in HCl:ImCl ionic liquids.

We observed previously that the chemical shift of HCl_2^- appears lower in the basic chloroaluminate melts than in HCl:ImCl.[11] This may be explained in terms of the exchange of proton between HCl_2^- and $AlCl_4{\cdot}HCl^-$, *i.e.* reaction 14, Though K_{A1} (reaction 7a) is much smaller than the formation constant of HCl_2^- (reaction 1), high concentrations of $AlCl_4^-$ allow the formation of sufficient $AlCl_4{\cdot}HCl^-$ so as to alter the observed chemical shift. The chemical shift of HCl in a near-neutral melt is small relative to that of HCl_2^- (1.6 ppm[5] *vs* 13.6 ppm[11]) and is attributable to $AlCl_4{\cdot}HCl^-$. Thus small concentrations of $AlCl_4{\cdot}HCl^-$ will have a marked effect on the observed chemical shift (population-weighted average).[11]

Electrochemical Profiles in Lewis Acidic HCl:ImCl:$AlCl_3$. Square-wave voltammograms as a function of P_{HCl} for a Lewis acidic melt having an initial (before HCl addition) binary aluminum chloride mole fraction of 0.550 are illustrated in Figure 3A. The generation of two prominent reduction peaks near +0.8 and 0 V as HCl is successively added to the melts is clearly evident. Previous workers have stated that proton electrochemistry in ambient-temperature melts, particularly Lewis acidic melts, is not reproducible.[8,20] In contrast, electrochemical results described here were, in general, fully reproducible. This is owing to careful control of HCl pressure. For example, Noël *et al.* added proton to Lewis acidic melts as $ImHCl_2$[4] and observed that peak currents and reduction profiles decreased with time.[8] Sahami and Osteryoung observed similar results when water was added to Lewis acidic $AlCl_3$:BuPyCl melts (BuPy = *n*-butylpyridinium).[20] Considering the variability of electrochemical profiles with P_{HCl}, irreproducibility is not surprising given failure to control this variable.

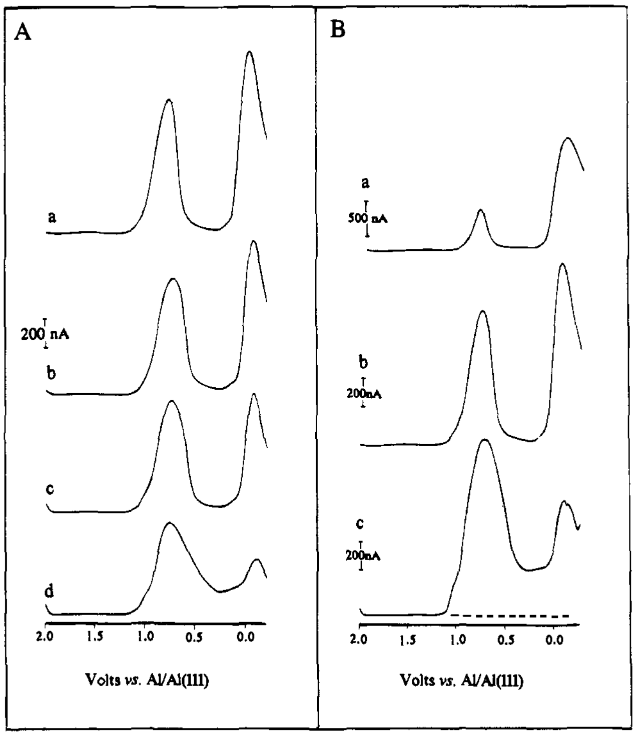

Figure 3. Square-wave voltammograms of HCl dissolved in Lewis acidic $AlCl_3$:ImCl as a function of (A) HCl pressure [$X_{AlCl_3} = 0.550$; P_{HCl} = (a) 0.501, (b) 0.443, (c) 0.363, (d) 0.271 atm] and (B) composition [(a) $X_{AlCl_3} = 0.516$, $P_{HCl} = 0.628$; (b) $X_{AlCl_3} = 0.550$, $P_{HCl} = 0.501$; (c) $X_{AlCl_3} = 0.600$, $P_{HCl} = 0.737$ atm—the dashed line in c approximates response after addition of excess methyl aluminum sesquichloride].

Voltammograms of acidic melts equilibrated with 0.5 to 0.75 atm of HCl as a function of melt composition are illustrated in Figure 3B. It is clear that the magnitudes of the two reduction peaks are inversely related to melt acidity, *i.e.* that near 0 V is dominant in weakly acidic melts while that near +0.8 V dominates in more acidic melts. In the case of the X_{AlCl_3} = 0.60 melt, the 0 V reduction is distinct only at HCl pressures in the upper regions of the experimental range. In highly acidic melts, *e.g.* 65 m/o $AlCl_3$, the 0 V reduction is not observed as a distinct peak regardless of the HCl pressure. These results clearly indicate that the 0 and +0.8 V reductions correspond to the species $AlCl_4{\cdot}HCl^-$ and $Al_2Cl_7{\cdot}HCl^-$, respectively:

$$AlCl_4{\cdot}HCl^- + e \rightleftharpoons {}^1/_2H_2 + Cl^- + AlCl_4^- \qquad (15)$$

$$Al_2Cl_7{\cdot}HCl^- + e \rightleftharpoons {}^1/_2H_2 + Cl^- + Al_2Cl_7^- \qquad (16)$$

Reaction between Cl^- and $Al_2Cl_7^-$ acts so as to shift the potential of the latter reaction in a positive direction. The addition of an excess of methyl aluminum sesquichloride to the melt whose voltammogram is illustrated in Figure 3Bc resulted in obliteration of the HCl reduction waves as approximated by the dashed line.

Representative cyclic voltammograms for HCl dissolved in several acidic melts are illustrated in Figure 4. Voltammograms

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(20) Sahami, S.; Osteryoung, R. A. *Anal. Chem.* **1983**, *55*, 1970–1973.

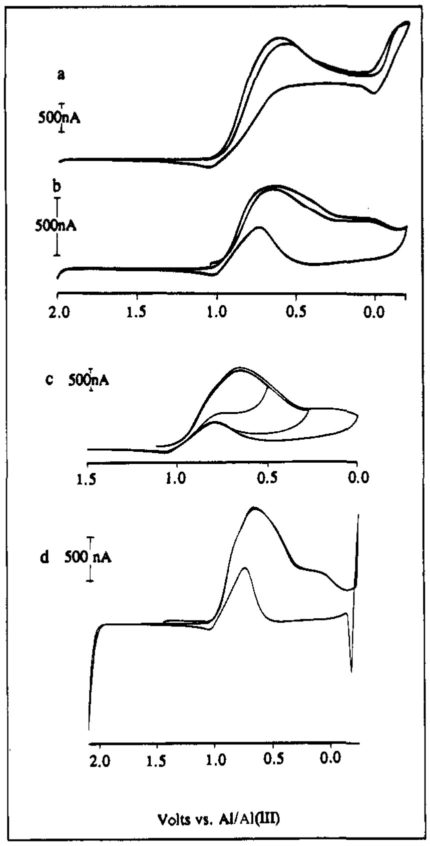

Figure 4. Representative cyclic voltammograms of HCl dissolved in Lewis acidic $AlCl_3$:ImCl as a function of composition and HCl pressure: (a) $X_{AlCl_3} = 0.550$, $P_{HCl} = 0.363$; (b) $X_{AlCl_3} = 0.550$, $P_{HCl} = 0.114$; (c) $X_{AlCl_3} = 0.600$, $P_{HCl} = 0.393$; (d) $X_{AlCl_3} = 0.600$, $P_{HCl} = 0.236$ atm; scan rate, $\nu = 100$ mV/s.

such as that illustrated in Figure 4a are typical of weakly acidic melts, or moderately acidic melts at higher HCl pressures, and correspond to square-wave voltammograms such as those in Figure 3a. Voltammograms such as that of Figure 4d are typical of highly acidic melts or melts under low HCl pressures and correspond to square-wave voltammograms such as those in Figure 3Bc. In all of these voltammograms, the wave with peak potential near +0.7 V corresponds to the reduction of $Al_2Cl_7{\cdot}HCl^-$; in Figure 4a, the reduction near 0 V corresponds to that of $AlCl_4{\cdot}HCl^-$. The 0 V reduction is clearly more reversible than that at +0.7 V, as expected for reactions 15 and 16, respectively, *i.e.* the former exhibits a small but distinct anodic peak, while the latter does not. Both reductions become more reversible at higher scan rates, consistent with following homogeneous reactions, H_2 evolution in both cases, and reaction of Cl^- with $Al_2Cl_7^-$ in the case of $Al_2Cl_7{\cdot}HCl^-$ reduction. Peak currents for cyclic and square-wave voltammograms were linear in P_{HCl} up to pressures of 0.3−0.4 atm and deviated negatively from linearity at higher pressures.

Cyclic voltammograms for highly acidic melts and for less acidic melts at low HCl pressures, *i.e.* Figures 4b, 4c, and 4d, are interesting. Upon scan reversal at 0 V, a sharp drop in current is observed indicating passivation of the electrode. In the subsequent scan toward *positive* potentials, however, *reduction* (of $Al_2Cl_7{\cdot}HCl^-$ presumeably) resumes indicating reactivation of the electrode. Comparison of Figures 4c and 4d indicates that Al deposition is not responsible for passivation. Figure 4c indicates that passivation becomes more severe when reduction of $Al_2Cl_7{\cdot}HCl^-$ is allowed to proceed at more negative potentials. These voltammograms are highly reminiscent of those for the oxidation of formic acid and methanol on metallic electrodes,[21−25] and for the reduction of nitrous oxide in alkaline solution.[26] This suggests that under some conditions, *i.e.* high Lewis acidity or low HCl pressure, the reduction of $Al_2Cl_7{\cdot}HCl^-$ generates an adsorbed product which passivates the electrode surface and desorbs as the potential is scanned anodically through the +0.8 V region. Similar results were obtained with a gold electrode. The process, whatever its actual nature, remains poorly understood. *Most significantly, voltammetry of HCl dissolved in acidic melts is reproducible only if the HCl pressure is controlled so that the liquid phase concentration remains constant.*

Electrochemical Profiles of Lewis Basic HCl:ImCl:AlCl₃ Melts. In a previous communication, we reported preliminary results concerning the electroactivity of HCl added to Lewis basic $AlCl_3$:ImCl melts.[27] It was demonstrated that the addition of excess HCl to Lewis basic melts, *i.e.* $N_{HCl} > N_{Cl}$, buffers the latter near Lewis neutral, and that at least two electroactive species are present. Addition of HCl generates HCl_2^- which undergoes reduction near −0.3 to −0.4 V.[27]

$$HCl_2^- + e \rightarrow {}^1/_2H_2 + 2Cl^- \qquad (17)$$

As the HCl content was increased beyond $N_{HCl}/N_{Cl} = 1$, a second, more positive reduction was observed near −0.2 V. On the basis of its reduction potential relative to that of HCl_2^-, we assigned the more positive reduction to that of $H_2Cl_3^-$:[27]

$$H_2Cl_3^- + e \rightarrow {}^1/_2H_2 + HCl_2^- + Cl^- \qquad (18)$$

In the current work, the cathodic limit of a 40:60 HCl:ImCl melt was observed near −0.4 V *vs* Al/Al(III), and shifted positively by *ca.* 200 mV when the melt was saturated with HCl, *i.e.* so that the predominant protic species changes from HCl_2^- to $H_2Cl_3^-$. This is consistent with the assignments of reactions 17 and 18 above. For dilute solutions of HCl (less than *ca.* 50 mM) in strongly basic $AlCl_3$:ImCl (45 m/o $AlCl_3$), peak currents (HCl_2^- reduction) are linear in the square root of the scan rate and peak potentials are linear in the logarithm of the scan rate. This behavior is consistent with an irreversible diffusion-controlled reaction.[28] At higher HCl concentrations, however, E_p *vs* $\ln(\nu)$ deviated significantly from linearity, consistent with the existence of coupled homogeneous reactions, *e.g.* evolution of hydrogen from the liquid to the gas phase. This was substantiated by the fact that the ratio $i_{p,c}/i_{p,a}$ was observed to decrease with increasing scan rate. Gas bubbles are evolved during the reduction and hence it is probable that irreversibility is owing to the insolubility of hydrogen in the melt.

Cyclic and square-wave voltammograms of HCl dissolved in a weakly basic $AlCl_3$:ImCl melt (49.5 m/o $AlCl_3$) are illustrated as a function of pressure in Figure 5. Prior to the introduction of HCl, the voltammograms were featureless in the region between Cl^- oxidation (*ca.* +1.1 V) and Im^+

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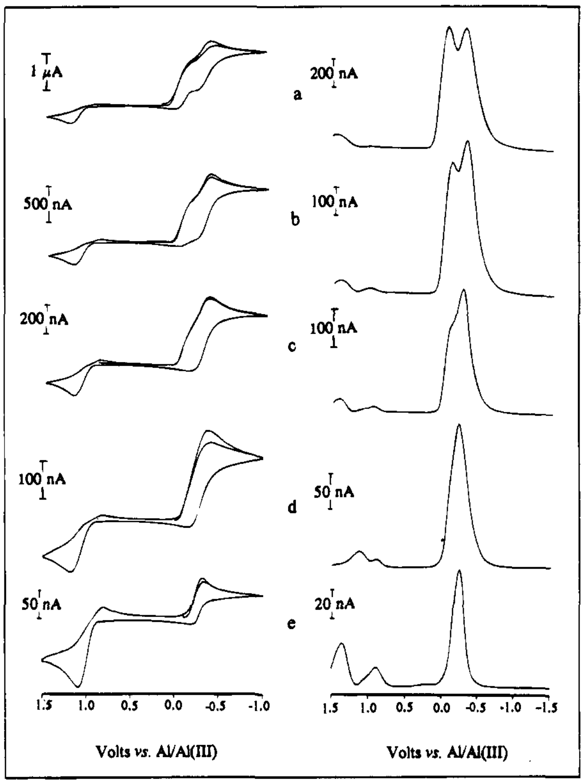

Figure 5. Cyclic and square-wave voltammograms of HCl dissolved in weakly basic $AlCl_3$:ImCl as a function of pressure; $X_{AlCl_3} = 0.495$: P_{HCl} (a) 0.233, (b) 0.111, (c) 0.043, (d) 0.0134, and (e) 0.002 atm; corresponding values of N_{HCl}/N_{Cl} are 1.96, 1.26, 0.741, and 0.459 for a through d, respectively; scan rate = 100 mV/s.

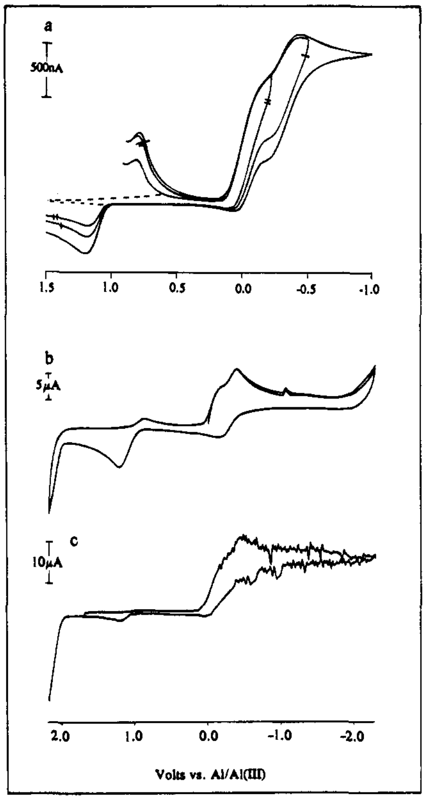

Figure 6. Cyclic voltammograms of HCl dissolved in weakly basic $AlCl_3$:ImCl melts: (a) as a function of cathodic limit, $X_{AlCl_3} = 0.495$, $P_{HCl} = 0.233$ atm, $N_{HCl}/N_{Cl} = 1.96$, scan rate = 100 mV/s, initial potential 900 mV; (b, c) near-neutral $AlCl_3$:ImCl melts as a function of pressure, $X_{AlCl_3} = 0.499$, P_{HCl}: (b) 0.150 and (c) 0.21 atm; scan rate 100 mV/s.

reduction (*ca.* −2.2 V). At low HCl pressures, e.g. Figure 5e, $P_{HCl} = 0.02$ atm, the reduction of HCl_2^- is observed near −0.2 V *vs* Al/Al(III). Similar to the 49 m/o $AlCl_3$ melt,[27] the onset of a second wave at more positive potentials is evident as the pressure is increased; this is clearly evident in the square-wave voltammogram of Figure 5a. It is tempting to assign the more positive reduction to that of $H_2Cl_3^-$. However, since $AlCl_4{\cdot}HCl^-$ is also reduced near 0 V *vs* Al/Al(III), it is probable that the more positive reduction contains a substantial contribution from this species. As discussed previously, it is expected that in weakly basic melts, the concentration of $AlCl_4{\cdot}HCl^-$ may exceed that of $H_2Cl_3^-$ or, for that matter, HCl_2^-.

Based on its potential and apparent dependence on the presence of proton, we initially assigned the +0.8 V reduction (Figure 5) to molecular HCl. However, it has become clear that in basic melts, protic species are always reduced at more negative potentials, *i.e.* less than about 0 V. It appears that the +0.8 V wave corresponds to the reduction of chlorine generated by the oxidation of chloride in the preceding anodic scan. The ratio $i_{p,a}/i_{p,c}$ for these processes decreases with increasing scan rate. This is consistent with a following homogeneous reaction,[29] probably that of chlorine with Im^+.[30] However, as demonstrated in the previous communication,[27] the +0.8 V wave is sometimes observed without a preceding chloride oxidation; if in the absence of chloride, and immediately following the +0.8 V reduction, the scan direction is switched to positive, a chloride oxidation wave is observed near +1.0 V. Thus the +0.8 V reduction does in fact generate chloride. It is conceivable that when a scan is terminated anodically, chlorine may remain adsorbed to the surface of the electrode and is reduced in a subsequent cathodic scan. This would require that the adsorbed chlorine be stable with respect to reaction with Im^+. Suffice it to say that this issue remains unresolved.

The situation is further complicated by the presence of a reduction of unknown origin and transient behavior. For example, consider the voltammograms of Figure 6a. Cathodic scans from +0.9 V exhibit a prominent reduction wave near +0.8 V. This wave behaves differently from that described above in several respects: (1) if after scanning through the +0.8 V reduction the scan direction is immediately changed to anodic, *i.e.* without scanning through the reductions more negative than 0 V, chloride oxidation is not observed, and the +0.8 V wave is absent in a following cathodic scan (dashed line Figure 6a); (2) the peak current for the +0.8 V wave increases if the electrode is allowed to remain quiescent in the melt, and varies in an unpredictable fashion when the melt is stirred. The wave remains after HCl is exhaustively pumped from the melt and is sometimes observed in freshly prepared melts. Though the identity of the species associated with this wave remains a mystery, the results above indicate that it is distinct from that associated with the +0.8 V reduction of Figure 5. Its behavior is consistent with the deposition of some sort of film which is irreversibly reduced at +0.8 V, in contrast to the +0.8 V wave of Figure 5 which corresponds to a reversible reduction to chloride.[27] The presence of two quasireversible couples in the range of 0 to −0.5 V is clearly evident in the voltmmograms of Figure 6a, as is the fact that the quantity of chloride generated is dependent on the extent of these reductions.

Voltammograms of HCl dissolved in a very weakly basic $AlCl_3$:ImCl melt ($X_{AlCl_3} = 0.499$) are illustrated in Figures 6b,c. Under *ca.* 0.15 atm of HCl (Figure 6b), the cyclic voltammo-

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Table 2. Hydrogen Bond Acceptor Strengths and Correlation with Chemical Properties

$$\mathrm{HCl(g)} + \mathrm{X^-(l)} \rightleftharpoons \mathrm{HClX^-(l)}$$

X^-	K	Lewis acidity of X^-	Brønsted[c] acidity of $HClX^-$	reduction potential of $HClX^-$ (V)
Cl^-	715 ± 76^a	basic	H_0 ca. −1	ca. −0.4
HCl_2^-	3.28 ± 0.05^a	↕	H_0 ca. −3	ca. −0.2
$H_2Cl_3^-$	0.72 ± 0.02^a		↕	
$AlCl_4^-$	0.135 ± 0.001^b			ca. 0
$Al_2Cl_7^-$	0.109 ± 0.001^b	acidic	H_0 ca. −14 to −18	ca. +0.7

[a] As measured for HCl:ImCl melts. [b] As measured for Lewis acidic $AlCl_3$:ImCl melts. [c] H_0 = Hammett acidity function, refs 9, 10, and 18.

gram is similar to that for the $X_{AlCl_3} = 0.49$ and 0.495 melts, with a window of about 4.4 V. Under *ca.* 0.21 atm of HCl (Figure 6c), the voltammogram is distorted by gas (H_2) desorption processes, and the chloride oxidation wave is less prominent. The latter might be due to passivation by hydrogen, or by a following chemical reaction which consumes chloride produced during the reduction, *e.g.* reaction 14. $AlCl_4{\cdot}HCl^-$ is reduced near 0 V (reaction 15); chloride generated in this reaction would react with $AlCl_4{\cdot}HCl^-$ diffusing toward the electrode, giving rise to HCl_2^- (*via* reaction 14), which is subsequently reduced near −0.4 V (Figure 6b).

Conclusions

The nature of HCl dissolution in HCl:ImCl and $AlCl_3$:ImCl ambient temperature ionic liquids is compactly summarized by the general two-phase reaction 4.[31] Equilibrium constants for this reaction are summarized in Table 2 along with several trends in behavior with which they may be associated. As we progress through the series $X^- \equiv Cl^-$, HCl_2^-, $H_2Cl_3^-$, $AlCl_4^-$, and $Al_2Cl_7^-$, a general change from strongly Lewis basic to strongly Lewis acidic species is recognized. This change correlates with the respective K values which represent the relative abilities of the X^- to act as hydrogen bond acceptors, *e.g.* Cl^- is a strong acceptor while $Al_2Cl_7^-$ is a very weak acceptor. For the purposes of discussion, each species $HClX^-$ may be considered as a proton coordinated to two anions, *e.g.* for $X^- \equiv HCl_2^-$ we may envision $HClX^-$ as Cl^-- - -H^+- - -$ClHCl^-$. The lability of the "central" proton is dependent upon the strength by which it is bound to the anionic components, which in turn is reflected by the magnitude of K. Thus as we descend through the series, K decreases and is accompanied by an increase in the lability of the proton as manifested by more positive reduction potentials and increasing Brønsted acidity. For example, the Hammett acidity function, H_0, for an HCl saturated HCl:ImCl melt is about 2 units more negative than that for a chloride rich melt, *i.e.* Cl^-- - -H^+- - -$ClHCl^-$ ($H_2Cl_3^-$) is more acidic than Cl^-- - -H^+- - -Cl^- (HCl_2^-);[18] the acidity of the HCl:ImCl system is comparable to that of dilute aqueous HCl (1−10 M, H_0 *ca.* 0 to −4).[32] In considering $HClX^-$ with $X^- \equiv Al_2Cl_7^-$, one can imagine for purposes of illustration that $Al_2Cl_7{\cdot}HCl^-$ may be viewed as its structural isomer: $AlCl_4^-$- - -H^+- - -$AlCl_4^-$.[33] The relative inability of $AlCl_4^-$ to act as a hydrogen bond acceptor ($K = 0.135$ atm^{-1}) results in an exceptionally labile proton which exhibits Brønsted superacidity (H_0 *ca.* −14 to −18)[9,10] and a very positive reduction potential.

Some spectroscopic trends are also evident as we descend through the series of Table 2. For example, the principal infrared absorptions increase in frequency from below 1000 cm^{-1} for[5,12,34] HCl_2^- to about 2700 cm^{-1} for[5] the chloroaluminate adducts; in the gas phase molecular HCl exhibits a vibrational frequency of 2990 cm^{-1}.[15] The ^{1}H-NMR chemical shift of the HCl derived proton decreases from *ca.* 13.6 ppm for HCl_2^-, to *ca.* 8.6 ppm for $H_2Cl_3^-$, to *ca.* 1.6 ppm for $AlCl_4{\cdot}HCl^-$, to *ca.* 0.9 ppm for $Al_2Cl_7{\cdot}HCl^-$; the shift for gas phase HCl is *ca.* 0.7 ppm.[3,11,35] In other words, as the hydrogen bond accepting ability of X^- decreases, the HCl unit of $HClX^-$ behaves, spectroscopically, more like molecular HCl. This is evidence of the relatively weak (*cf.* HCl_2^- *etc.*) interaction between HCl and the chloroaluminate ions.

The K values of Table 2 reflect the ability of the X^- to engage in hydrogen bonding not only with HCl but also with the ring protons of Im^+.[12,36] The ability of the anion population to form such bonds with Im^+ plays a major role in the determination of melt structure. As we progressively replace the anion population of the melt with the anions Cl^-, HCl_2^-, *etc.*, cation−anion interactions are diminished as reflected by the K's, and viscosities are expected to decrease as observed experimentally.[11,37] Indeed, hydrogen bonding plays an important role in determining the chemical *and* physical properties of these systems.

The results of this investigation indicate that there is, in fact, a superacidic species other than molecular HCl, namely $Al_2Cl_7{\cdot}HCl^-$. That such a species exists allows *termolecular* protonation reactions, such as the protonation of arenes,[9,10] to be written as more plausible *bimolecular* reactions:

$$\mathrm{Al_2Cl_7{\cdot}HCl^-} + \mathrm{Ar} \rightleftharpoons 2\mathrm{AlCl_4^-} + \mathrm{ArH^+} \qquad (19)$$

Finally, it must be stated unequivocally that though the two-phase equilibria 4 describe HCl *dissolution*, they do not represent HCl *speciation* in the liquid phase. Such equilibria, *e.g.* reactions 3, 8, and 14, are obtained by combining several dissolution equilibria in such a way that molecular HCl, since it does not exist as such in the liquid phase, does not appear in the result, *i.e.* only ionic species are allowed in the liquid phase. For example, in HCl:ImCl liquids for which $X_{HCl} >$ *ca.* 0.55 ($P_{HCl} >$ *ca.* 0.1 atm), proton speciation is best described by the equilibrium

$$\mathrm{H_3Cl_4^-} + \mathrm{HCl_2^-} \rightleftharpoons 2\mathrm{H_2Cl_3^-} \qquad (20)$$

for which the stoichiometric equilibrium constant may be obtained as 4.43 ± 0.14 from the dissolution equilibria of Table 2.

Experimental Section

General Procedures. All manipulations involving 1-ethyl-3-methyl-1*H*-imidazolium chloride (ImCl), aluminum chloride, and liquids derived from these components were performed in "airless" glassware or in a drybox under an atmosphere of dry argon or nitrogen as described previously.[11] For manometric solubility measurements, a commercial cylinder of high purity HCl (Matheson, Semiconductor

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[31] We previously published an approximate phase diagram exhibiting the liquid phase region of the ternary system.[11] From the data illustrated in Figures 1A and 2A, this region has now been more accurately defined.[18]

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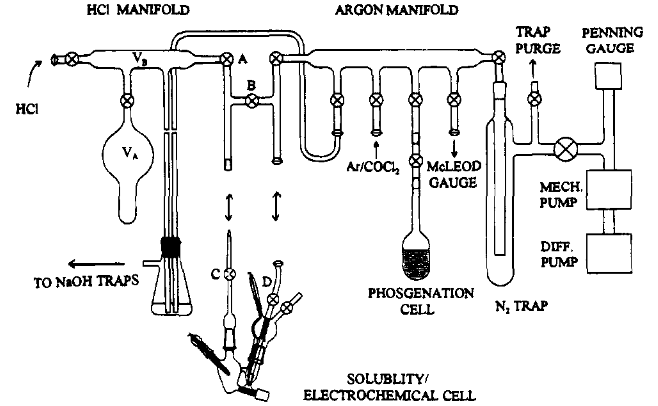

Figure 7. Manostat/vacuum line for phosgene/high-vacuum treatment of melts and manometric determination of HCl solubility.

Grade, 99.995%) was employed; this was used as received. Phosgene was used as received (Matheson). Infrared spectra were acquired as described previously.[12] Where necessary, HCl:ImCl melt densities were measured using a bottle of volume 1.32 ± 0.01 cm^3. After weighing before and after filling the bottle with melt, its composition was determined as described previously.[11] In some instances melt densities were determined by weighing of 1.00- or 10.00-mL samples in volumetric flasks.

$AlCl_3$:ImCl melts were prepared in the glovebox, placed in the phosgenation cell, transferred to the vaccum line, and treated with phosgene followed by high vacuum according to the method of Noël *et al.*[8] ***CAUTION*: Phosgene ($COCl_2$) is extremely poisonous and should be handled only in well-designed apparatus assembled in an efficient fume hood.** In the case of acidic $AlCl_3$:ImCl melts, the melt was heated to 70 °C, saturated with phosgene,[38] and stirred for 0.5 h before the excess phosgene was purged (argon) from the apparatus and passed through several gas washing towers charged with aqueous NaOH (10% w/v). The melt was then evacuated and the phosgenation/evacuation procedure repeated twice. After the last addition of phosgene, the melt was stirred for 2–3 h prior to evacuation. Following evacuation to a pressure less than 0.1 Torr, the diffusion pump was engaged and the melt pumped overnight to a residual pressure of *ca.* 5×10^{-6} Torr as measured with a Penning guage.

Ternary melts consisting of ImCl, the Lewis acid $AlCl_3$, and the Brønsted acid HCl were most commonly prepared by the manometric addition of high purity HCl to known masses of $AlCl_3$:ImCl melts of well-defined composition as described below. In order to evaluate the effect of HCl dissolution on melt density, ternary melts were prepared by gravimetric combination of the binary liquids $AlCl_3$:ImCl and HCl:ImCl, each of well-defined composition, and the density of the resulting melts was determined as described above.

Gas Manifold/Manostat and Variable-Pressure Cell. The gas manifold/manostat used for HCl solubility measurements is illustrated in Figure 7 and consists, for the most part, of an HCl manifold connected to an argon manifold, each with its own mercury manometer. All stopcocks were of the high vacuum variety with grease seals rated to 10^{-7} Torr. The manometers were arranged side by side so as to allow a direct comparison of pressures in the two manifolds. The solubility/variable pressure electrochemial cell is illustrated in Figure 8. The melts in the reference and bulk compartments communicated by means of a thin film of electrolyte formed between the mated halves of a 5/12 standard taper ground joint seated at the base of the former compartment. Provision was made to afford additional separation of the two compartments by including a threaded Teflon stopcock. Not shown in the figure is a small port for addition of reagents to the bulk compartment. All ground joints of the HCl manifold and solubility cell were sealed with black wax, and in the case of ball joints, a fillet of evaporation-cured silicone rubber (Dow Corning) was added, so as to ensure a leak-free system. After evacuating the HCl side of the apparatus to less than 0.005 Torr, allowing several hours for outgassing, and closing stopcocks joining it to the argon manifold, a full vacuum could be maintained for several days without any increase in pressure detectable at the manometer.

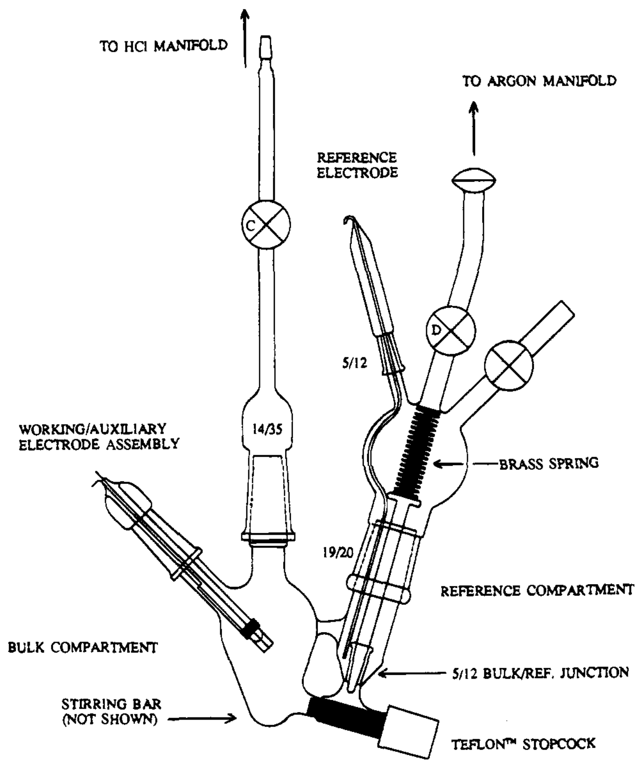

Figure 8. Variable-pressure cell for solubility determination in tandem with electrochemical measurements.

Procedure for Measurement of HCl Solubility. Prior to transfer to the glovebox and filling with phosgenated melt, the variable-pressure cell was evacuated for several hours, flame-dried on the vacuum line, and weighed to ±0.01 g. For acidic and neutral melts, 17 to 20 cm^3 of melt was used; for 49 and 45 m/o $AlCl_3$ melts, volumes of 7 to 10 cm^3 were used; in the case of the 0 m/o $AlCl_3$ melt, *i.e.* HCl:ImCl, the cell was filled with ca. 6 g of solid ImCl. After being filled with melt, the cell was removed from the glovebox, weighed, and attached to the manostat with black wax. The mass of melt contained in the bulk compartment was calculated to ±0.01 g from weighing data and its volume was calculated using the density data of Fannin *et al.*[37] The reference compartment was filled with electrolyte via cannulum (see following section).

With the bulk and reference compartments of the variable-pressure cell sealed (stopcocks C and D, see Figures 7 and 8), the rest of the apparatus was evacuated to a pressure <0.005 Torr and then pressurized with argon. This was repeated several times so as to completely replace the atmosphere inside the apparatus with dry argon. The stopcocks joining the variable-pressure cell to the manifold (C and D) were then opened, as was the stopcock separating the bulk and reference compartments. The apparatus was then slowly evacuated at such a rate that the pressure on either side of the reference junction was the same at all times so as to avoid mixing of the bulk and reference melts. After evacuating to a pressure of *ca.* 0.01 Torr, the apparatus was pressurized slowly to about 100 Torr with dry argon; this ensured the removal of any void spaces in the bulk–reference junction which arise during outgassing of the melts. Background cyclic and/or square-wave

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[38] At 70 °C, aluminum chloride–phosgene adducts are expected to be unstable[39] so that added phosgene remains available for reaction with oxide-containing species. Using an acidic $AlCl_3$:ImCl melt (65 m/o $AlCl_3$, 30 g) it was established that no detectable change in composition occurred during the evacuation, *i.e.* no loss of aluminum chloride could be detected to ±0.01 g. After 4–5 phosgenations of acidic melts had been performed in this way, however, a thin film of aluminum chloride was observed in the cold trap. Based on the total volume of the melts involved, this did not indicate a significant deviation of their compositions from initial aluminum chloride mole fractions (to 3 significant figures).

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voltammograms were acquired, the bulk-reference junction closed, and the system was again evacuated to a pressure of less than 0.005 Torr. The volume of melt in the bulk compartment was corrected for the volume remaining in the bulk−reference junction. The melt was then stirred *in vacuo* for several hours so as to ensure complete removal of dissolved gases.

Following the evacuation period, the stopcock joining the bulk compartment to the HCl manifold (stopcock C) was closed, and a quantity of HCl (99.995%) was admitted to the HCl manifold. After equilibration of the HCl to ambient temperature (295 ± 1 K), its pressure was measured relative to the argon manifold manometer; the latter compartment was maintained at a pressure of less than 0.005 Torr as measured with a McLeod guage. The HCl manifold and variable-pressure cell were subsequently connected by opening the bulk compartment stopcock C, and the melt was allowed to equilibrate with the HCl while being stirred. During equilibration the HCl pressure above the melt was observed to decrease rapidly, with 95% of the reduction in pressure being observed to occur within the first few minutes. Times allowed for equilibration ranged from 2 to 12 h. After equilibration, the HCl pressure was again measured, and HCl taken up by the melt was calculated as the difference between the HCl originally dispensed in the manifold and that remaining in the manifold and the gas-phase volume of the bulk compartment. The cell was then sealed from the manifold, and after evacuating the latter a fresh sample of HCl, at a higher pressure, was dispensed into the manifold and the process repeated until a pressure of between 0.5 and 0.7 atm was reached, at which point the experiment was terminated. The melt was then subjected to electrochemical studies.

Electrochemstry. Cyclic and square-wave voltammograms were acquired with a Bioanalytical Systems Inc. BAS-100A electrochemical analyzer. Parameters for acquisition of square-wave voltammograms were as follows: AC amplitude 25 mV, frequency 15 Hz, step height 4 mV. All potentials were measured against an Al wire (Aldrich, 99.995%, 1.0 mm diameter) immersed in an $AlCl_3$:ImCl melt saturated with aluminum chloride (*ca.* 66.7 m/o $AlCl_3$, $X_{AlCl_3} = 0.667$). The working/auxiliary electrode assembly consisted of a 100 μm Pt wire (Aldrich, 99.99%) sealed in a Pyrex tube so as to afford a Pt disk. In electrochemical studies, the melt was equilibrated with the desired pressure of HCl during which time the HCl and argon manifolds were separated and the bulk−reference junction stopcock was closed. Following equilibration of the melt with HCl, the argon manifold (to which the reference compartment is connected) was pressurized with argon until the HCl and argon pressures were equal. Once this was ensured, the bulk−reference junction stopcock was opened, and electrochemical measurements made.

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Supporting Information Available: Details of the calibration of the variable-pressure cell and manostat, calculation of dissolved HCl, construction of the working and reference electrodes, the origins of eqs 9 and 13 and the method for calculation of the concentrations of solution species, infrared spectra of Lewis basic melts containing HCl, and a plot of anion fractions for HCl:ImCl as a function of pressure and composition (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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