4396 *Inorg. Chem.* **1993**, *32*, 4396–4401

NMR Studies of the Proton Equilibrium in Basic Ambient-Temperature Chloroaluminate Ionic Liquids[†]

Paul C. Trulove,[‡] Dinesh K. Sukumaran,[§] and Robert A. Osteryoung[*]

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Received February 3, 1993[⊗]

In basic mixtures of the molten salt composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride, proton, in the absence of oxides, is partitioned between hydrogen chloride and hydrogen dichloride ion. The equilibrium between these two species has been examined by ^{2}H and ^{1}H NMR spectroscopies. The magnitude of the hydrogen chloride/dichloride equilibrium constant demonstrates that the equilibrium strongly favors the formation of the hydrogen dichloride ion. The ratio of ^{2}H and ^{1}H equilibrium constants at 90 °C gave an equilibrium isotope effect of 0.67 ± 0.26, which indicates that deuterium accumulates in the hydrogen chloride molecule. An equilibrium isotope effect of 0.712 was calculated from hydrogen chloride and hydrogen dichloride vibrational frequencies. Analysis of the temperature dependence of the hydrogen chloride/dichloride equilibrium constant gave values for the enthalpy of reaction, ΔH_{RXN}, and the entropy of reaction, ΔS_{RXN}, of -9.8 ± 0.8 kJ mol^{-1} and 4.8 ± 2.5 J mol^{-1} K^{-1}, respectively. Comparison of the ΔH_{RXN} for the hydrogen chloride/dichloride equilibrium in the melts with values obtained for other solvents suggests that the melt interacts more strongly with chloride ion than with hydrogen dichloride ion.

Introduction

Ambient-temperature chloroaluminate molten salts composed of mixtures of aluminum chloride (AlCl$_3$) with 1-ethyl-3-methylimidazolium chloride (ImCl) are unique ionic solvents which have been employed in numerous chemical and electrochemical studies.[1–3] The anionic composition of these molten salts can be manipulated by varying the relative amounts of AlCl$_3$ and ImCl. Melts prepared with excess AlCl$_3$ contain AlCl$_4^-$ and Al$_2$Cl$_7^-$, a Lewis acid, and are referred to as acidic. When ImCl is in excess, the melts contain AlCl$_4^-$ and Cl$^-$, a Lewis base, and are called basic. A melt prepared from equal molar amounts of AlCl$_3$ and ImCl is referred to as neutral because AlCl$_4^-$, which is essentially Lewis neutral, is the only anion present.

The AlCl$_3$:ImCl melts, when prepared by normal methods, invariably contain small quantities of both oxide and proton impurities.[4–6] These impurities result from contamination of the starting materials with water. Recent studies have demonstrated that the presence of these water-generated impurities in the melts can significantly affect the chemistry of a wide varity of both organic[5,7–10] and inorganic[11,12] species. The ubiquitous nature of these impurities and their reactivity toward other species requires that their chemistry be fully understood if the AlCl$_3$:ImCl melts are to be routinely used as solvents. As a continuation of previous work in our laboratory on the chemistry of oxide and proton species in the AlCl$_3$:ImCl melts, this manuscript describes NMR studies of the proton equilibrium in oxide-free basic melts.

The chemistry of proton in AlCl$_3$:ImCl melts has been the subject of numerous investigations.[4,5,7,13–19] In much of the initial work the melts studied contained significant oxide concentrations because water was used as the reagent for proton addition. This greatly increased the complexity of the melt proton chemistry because of the additional proton/oxide interactions. In an effort to isolate the chemistry of proton from that of oxide, Zawodzinski and Osteryoung[16] developed a new quantitative source of proton, 1-ethyl-3-methylimidazolium hydrogen dichloride (ImHCl$_2$), which did not introduce oxides into the melts. Using ImHCl$_2$ and its deuterated analogue Im^{2}HCl$_2$, Zawodzinski and Osteryoung[16] studied the chemistry of proton in the absence of significant oxide concentrations. (It must be noted that their melts still contained ca. 5–15 mM oxides from the initial contamination of the melt starting materials with water.) They found that the ^{2}H NMR of deuteron in the AlCl$_3$:ImCl melts gave a single line with a chemical shift that varied depending on melt composition. In acidic melts the ^{2}H chemical shift was relatively constant at 6.9 ppm vs TMS (2.4 ppm vs D$_2$O), while in basic melts the ^{2}H

[†] Portions of this work were carried out at the State University of New York, Buffalo, NY 14214.

[‡] Present address: The Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, CO 80840-6528.

[§] Present address: Department of Chemistry, State University of New York, Buffalo, NY 14214.

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1993.

(1) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. 1, pp 55–78.

(2) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185–230.

(3) Osteryoung, R. A. In *Molten Salt Techniques*; Mamantov, G., Marassi, R., Eds.; NATO ASI Series C, Reidel: Dordrecht, The Netherlands, 1987; Vol. 202, pp 329–364.

(4) Zawodzinski, T. A.; Carlin, R. T.; Osteryoung, R. A. *Anal. Chem.* **1987**, *59*, 2639–2640.

(5) Smith, G. P.; Dworkin, A. S.; Pagni, R. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1989**, *111*, 525–530.

(6) Noël, M. A. M.; Trulove, P. C.; Osteryoung, R. A. *Anal. Chem.* **1991**, *63*, 2892–2896.

(7) Smith, G. P.; Dworkin, A. S.; Pagni, R. M.; Zingg, S. P. *J. Am. Chem. Soc.* **1989**, *111*, 5075–5077.

(8) Trulove, P. C.; Carlin, R. T.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4567–4568.

(9) Trulove, P. C.; Carlin, R. T.; Osteryoung, R. A. In *Proceedings of the Seventh International Symposium on Molten Salts*; Hussey, C. L., Flengas, S. N., Wilkes, J. S., Ito, Y., Eds.; The Electrochemical Society: Pennington, NJ, 1990; pp 306–324.

(10) Park, S.-G.; Trulove, P. C.; Carlin, R. T.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3334–3340.

(11) Carlin, R. T.; Osteryoung, R. T. *Inorg. Chem.* **1988**, *27*, 1482–1488.

(12) Carlin, R. T.; Osteryoung, R. T. *Inorg. Chem.* **1988**, *27*, 3675–3677.

(13) Tait, S.; Osteryoung, R. T. *Inorg. Chem.* **1984**, *23*, 4352–4360.

(14) Lipsztajn, M.; Sahami, S.; Osteryoung, R. A. *Inorg. Chem.* **1986**, *25*, 549–551.

(15) Zawodzinski, T. A.; Osteryoung, R. A. *Inorg. Chem.* **1987**, *26*, 2920–2922.

(16) Zawodzinski, T. A.; Osteryoung, R. A. *Inorg. Chem.* **1988**, *27*, 4383–4384.

(17) Franzen, G.; Gilbert, B. P.; Pelzer, G.; Depauw, E. *Org. Mass Spectrom.* **1986**, *21*, 443–444.

(18) Wicelinski, S. P.; Gale, R. J.; Pamidi, K. M.; Laine, R. A. *Anal. Chem.* **1980**, *60*, 2228–2232.

(19) Zawodzinski, T. A.; Osteryoung, R. A. *Inorg. Chem.* **1990**, *29*, 2842–2847.

0020-1669/93/1332-4396$04.00/0

chemical shift moved downfield with increasing melt chloride concentration. In the most basic melts the deuteron line fell at 12 ppm vs TMS (7.5 ppm vs D_2O). Zawodzinski and Osteryoung[16] proposed that the observed variation in ^2H chemical shift with melt composition resulted from the fast exchange between deuterium chloride (^2HCl) and deuterium dichloride ($^2HCl_2^-$). They suggested that the proton, and also deuteron, equilibrium in the absence of oxides can be described by the following reaction:

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

The increase in chloride concentration as the melt becomes more basic shifts eq 1 toward formation of the dichloride ion. Consequently, in the most basic melts (highest chloride concentrations) the observed ^2H chemical shift is primarily that of $^2HCl_2^-$. In neutral and acidic melts the absence of chloride ion moves the equilibrium complete to the left, and therefore, the observed ^2H chemical shift is that of ^2HCl.

We recently reported on the investigation of proton speciation in oxide-free $AlCl_3$:ImCl melts using FT-IR and ^2H NMR spectroscopies.[20] (In this study the melts were treated initially to remove adventitious oxide and proton impurities.[6]) FT-IR measurements showed that HCl and HCl_2^- were the only proton species present in oxide-free basic melts and that HCl was the only proton-containing species in oxide free acidic melts. Furthermore, FT-IR spectra of proton in a series of slightly basic melts demonstrated the equilibrium between HCl and HCl_2^-. The composition dependence of the ^2H NMR chemical shift was similar to that found by Zawodzinski and Osteryoung[16] and, in general, confirmed their overall conclusions about the proton (deuteron) equilibrium in the $AlCl_3$:ImCl melts. In the basic melts there were minor differences in the chemical shifts of the two sets of data; these most likely resulted from the presence of small amounts of oxides in the melts of Zawodzinski and Osteryoung.[16] However, in the acidic melts the two sets of data differed significantly. In a separate study in the acidic melts, we found that deuterium from ^2HCl readily exchanged with protium at the 4,5 position on the imidazolium ring.[21] Thus, the peak at 2.4 ppm vs D_2O originally assigned by Zawodzinski and Osteryoung[16] to ^2HCl was, in fact, the peak for deuterium exchanged on to the imidazolium ring. The actual ^2HCl chemical shift in acidic melts was found to range from −2.9 to −3.6 ppm vs D_2O by going from a 1.0:1.0 to a 1.976:1.0 melt.

The dependence of the ^1H NMR chemical shift on halide concentration has been used to evaluate hydrogen halide/dihalide equilibrium constants in nonaqueous solvents.[22,23] In the present work we apply these techniques to study the hydrogen chloride/dichloride equilibrium (eq 1) in basic oxide-free $AlCl_3$:ImCl melts. ^2H NMR and, when possible, ^1H NMR spectroscopies were used to obtain equilibrium constants and limiting chemical shifts. The equilibrium constants from ^2H and ^1H NMR were compared to determine the presence of an equilibrium isotope effect, and the temperature dependence of the equilibrium constants were used to determine the enthalpy and entropy of reaction.

Experimental Section

Materials. The synthesis and purification of ImCl and $AlCl_3$ were performed as previously described.[1,20,24] Basic melts were prepared by slowly mixing weighed amounts of $AlCl_3$ and ImCl; this was followed by treatment with phosgene and evacuation to remove oxide and proton impurities.[6] A neutral melt (1.0:1.0 mole ratio $AlCl_3$ to ImCl) was prepared from a slightly basic melt (i.e., 0.99:1.0) which had proton and oxide impurities removed. Cyclic voltammetry was used to monitor the melt electrochemical limits as very small amounts of aluminum dichloride were added. A neutral composition (i.e., only Im^+ and $AlCl_4^-$ present) was achieved when the chloride oxidation wave disappeared and the $Al_2Cl_7^-$ reduction wave was not yet observed.

The removal of proton and oxide impurities from the melts resulted in some uncertainty in the concentrations of the melt ionic species (i.e., Im^+, $AlCl_4^-$, Cl^-). This source of error was only significant for those melts where some of the ion concentrations were small, as was the case for the slightly basic melts. In order to minimize this source of error, weighed amounts of ImCl were added to a neutral melt (prepared as described above) to generate slightly basic melts with known Cl^- concentrations. All basic melts with mole ratios greater than 0.95:1.0 were prepared in this manner.

1-Ethyl-3-methylimidazolium hydrogen chloride ($ImHCl_2$) and its deuterated analogue 1-ethyl-3-methylimidazolium deuterium dichloride (Im^2HCl_2) were used in the $AlCl_3$:ImCl melts as a quantitative source of proton and deuteron, respectively. $ImHCl_2$ and Im^2HCl_2 were prepared and analyzed as previously described.[16,20]

Procedures. All melt preparation was performed in a Vacuum Atmospheres drybox. The drybox atmosphere of nitrogen (99.995%, prepurified grade, Linde) was circulated through a Vacuum Atmospheres Model MO 40 inert-gas purifier. The quality of the drybox atmosphere was judged acceptable when the exposed tungsten filament of a 25-W bulb burned for at least 14 days; this was indicative of oxygen and water levels less than 1 ppm.[25]

All NMR samples were prepared in the drybox, pipetted into NMR tubes, and then capped and sealed with parafilm. Melt samples for ^1H NMR were pipetted into 5-mm tubes fitted with precision coaxial inserts (Wilmad Glass Co.). For ^2H NMR, melt samples were placed into 10-mm tubes (Wilmad Glass Co.). ^1H Chemical shifts were referenced to 0.1% TMS in $CDCl_3$ (MSD Isotopes) in the coaxial insert. Natural abundance D_2O in water was used as the reference for the ^2H NMR and was assigned a value of 0 ppm. Referencing for ^2H NMR was performed by substitution, and all ^2H spectra were acquired with the spectrometer unlocked. The ^1H and ^2H NMR experiments were performed using a Varian VXR-400 S spectrometer operating at 399.952 and 61.395 MHz, respectively. The temperature set by the spectrometer was calibrated using ethylene glycol. The error for temperatures ranging from 30 to 90 °C was found to be ±0.5 °C.

For the special case of the spectra of ^2HCl and HCl in a 1.0:1.0 neutral melt, the following procedure was used. A neutral melt (prepared as described above) was placed into a 10-mm NMR tube for ^2HCl or a 5-mm NMR tube for HCl. Both these tubes were 9 in. long with a constriction at 8 in. (Wilmad Glass Co.). In addition, a sealed capillary tube containing $CDCl_3$ with 0.1% TMS was placed into the 5-mm tube to use for lock and referencing. After being filled with melt, these NMR tubes were removed from the drybox and attached to a vacuum line. The melt in the 10-mm tube was then saturated with ^2HCl (>99% ^2H, Cambridge Isotope Laboratories), and the melt in the 5-mm tube was saturated with HCl (99.999%, Matheson). After saturation the NMR tubes were cooled in liquid nitrogen and then sealed with a minitorch.

Analysis of NMR Data. Determination of proton and deuteron equilibrium constants in the basic melts from ^1H and ^2H NMR data, respectively, was accomplished using the Benesi–Hildebrand–Scott (B–H–S) method.[22,26,27] The B–H–S method as applied to our ^1H and ^2H NMR data is given in detail in the Appendix.

Results and Discussion

Hydrogen Chloride/Dichloride Equilibrium in Basic Melts. The NMR specta of proton (deuteron) in oxide-free basic melts, in most cases, exhibit a single line resulting from the fast exchange

---

[20] Trulove, P. C.; Osteryoung, R. A. *Inorg. Chem.* **1992**, *31*, 3980–3985.

[21] Trulove, P. C.; Osteryoung, R. A. In *Proceedings of the Eighth International Symposium on Molten Salts*; Gale, R. J.; Blomgren, G.; Kojima, H., Eds.; The Electrochemical Society: Pennington, NJ, 1992; pp 303–316.

[22] Fujiwara, F. Y.; Martin, F. Y. *J. Chem. Phys.* **1972**, *56*, 4091–4097.

[23] Martin, J. S.; Fujiwara, J. S. *J. Chem. Phys.* **1972**, *56*, 4098–4102.

[24] Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263–1264.

[25] Eubanks, O.; Abbott, F. J. *Anal. Chem.* **1969**, *41*, 1708–1709.

[26] (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707. (b) Scott, R. L. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 787–789.

[27] Green, R. D.; Martin, J. S. *J. Am. Chem. Soc.* **1968**, *90*, 3659–3668.

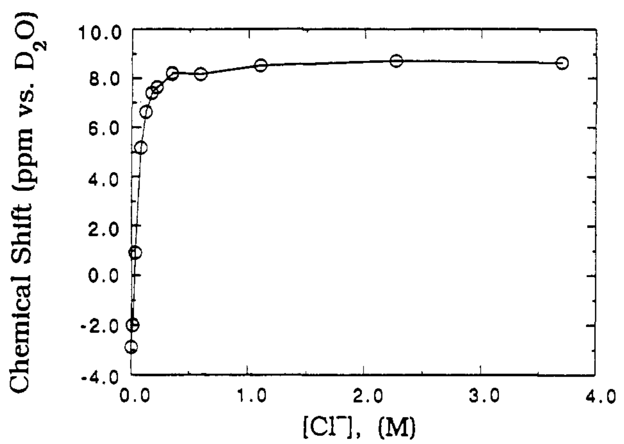

Figure 1. Effect of chloride ion concentration on the ^{2}H NMR chemical shift of 98 mM ^{2}HCl in basic $AlCl_3$:ImCl melts. Data were obtained at 30 °C.

between hydrogen chloride and hydrogen dichloride ion.[28] The observed chemical shift, δ_{obs}, is the population-weighted average chemical shift of these two species. The strong dependence of the ^{2}H NMR chemical shift on chloride ion concentration is shown in Figure 1. The equilibrium constant for the hydrogen chloride/dichloride equilibrium (eq 1) can be determined from the dependence of δ_{obs} on chloride concentration using the Benesi–Hildebrand–Scott (B–H–S)[22,26,27] analysis method. The B–H–S method solves simultaneously for both the equilibrium constant, K_{eq}, and the chemical shift of the dichloride ion, $\delta_{HCl_2^-}$. The B–H–S method was chosen because $\delta_{HCl_2^-}$ was not known initially. However, from analysis of the NMR data (see below) $\delta_{HCl_2^-}$ turns out to be essentially δ_{obs} in the most basic melts (highest chloride concentrations). The B–H–S method requires knowing only the hydrogen chloride chemical shift, δ_{HCl}, the total chloride concentration, $[Cl^-]_T$, and δ_{obs}. δ_{HCl} is readily obtained from the NMR spectrum of a neutral melt saturated with HCl (or ^{2}HCl), $[Cl^-]_T$ is determined from the amounts of ingredients used to make up the melts, and δ_{obs} is the observed quantity.

The ^{1}H and ^{2}H NMR chemical shifts for several of the melts where $[Cl^-]_T < {}^1/_2[H^+]_T$ were greater than the chemical shift which would occur from quantitative formation of HCl_2^-. This suggests that more than one molecule of HCl is complexed to each Cl^-. Multiple ions of the form $Cl(HCl)_n^-$ have previously been reported in pyridine saturated with HCl,[29] and recently the $Cl(HCl)_2^-$ ion has been observed in HCl-rich ImCl:HCl molten salts.[30] Our observations appear to be consistent with systems where 2:1 association was observed (i.e. $Cl(HCl)_2^-$).[22] The effect of multiple ion formation on the NMR chemical shifts decreased with increasing temperature. These effects were not observed in the ^{2}H NMR data above 50 °C; however, for the ^{1}H NMR data some effects were still seen at 90 °C. The B–H–S analysis assumes a 1:1 complex between Cl^- and HCl. Consequently, data where $[Cl^-]_T < {}^1/_2[H^+]_T$ were not used in the analysis.

^{2}H NMR data for the hydrogen chloride/dichloride equilibrium were obtained at 30, 50, 70, and 90 °C. A total of nine melt compositions ranging from 0.984:1.0 to 0.410:1.0 ($[Cl^-]_T$ = 0.076–3.576 M) and containing ca. 100 mM total deuteron were used to evaluate the equilibrium constants. However, for ^{1}H NMR, 90 °C proved to be the only temperature where we were able to observe a sufficient number of proton resonances to perform a reasonable B–H–S analysis. At temperatures lower that 90 °C exchange broadening and interference from the large Im^+ peaks prevented observation of most of the proton resonances. Even at 90 °C melts where $[HCl] \geq [HCl_2^-]$ (i.e. near neutral melts) the rate of chemical exchange slowed sufficiently such that the proton lines were broadened into the baseline noise. Consequently, only seven melt compositions ranging from 0.975:1.0 to 0.410:1.0 ($[Cl^-]_T$ = 0.112–3.576 M) and containing ca. 100 mM total proton were analyzed.

Table I. Equilibrium Constant and Chemical Shift Data for the Hydrogen Chloride/Dichloride Equilibrium in Basic $AlCl_3$:ImCl Melts

$^2HCl_2^-/^2HCl$ Equilibrium

T, °C[a]	$\delta_{^2HCl}$, ppm[b,c]	$\delta_{^2HCl_2^-}$, ppm[c,d]	$\Delta_{^2HCl_2}$, ppm[e]	K_{eq}, L mol^{-1} [e]
30.0	−2.80	8.70	11.51 ± 0.04	82 ± 23
50.0	−2.85	8.57	11.42 ± 0.04	70 ± 19
70.0	−2.87	8.50	11.37 ± 0.05	56 ± 14
90.0	−2.90	8.44	11.33 ± 0.05	45 ± 10

HCl_2^-/HCl Equilibrium

T, °C[a]	δ_{HCl}, ppm[f,g]	$\delta_{HCl_2^-}$, ppm[g,h]	$\Delta_{HCl_2^-}$, ppm[e]	K_{eq}, L mol^{-1} [e]
90.0	1.61	13.00	11.39 ± 0.03	67 ± 18

[a] Temperatures are to ±0.5 °C. [b] Data for ^{2}HCl in neutral melt. [c] Chemical shifts versus D_2O at 30 °C. (To convert referencing to TMS add 4.5). [d] Calculated from $\delta_{^2HCl}$ and $\Delta_{^2HCl_2^-}$. [e] Values are ± one standard deviation. [f] Data for HCl in a neutral melt. [g] Chemical shifts versus TMS. [h] Calculated from δ_{HCl} and $\Delta_{HCl_2^-}$.

The final weighted regression of the ^{2}H and ^{1}H NMR data was quite good; in all cases $R > 0.9999$.[31,32] The results of the B–H–S analysis of the ^{2}H and ^{1}H NMR data along with the limiting chemical shifts are listed in Table I. The values of $\delta_{HCl_2^-}$ and $\delta_{^2HCl_2^-}$ listed in Table I are essentially the same as δ_{obs} at high chloride ion concentrations. This validates the B–H–S analysis and suggests that the chemical shifts observed at high chloride concentrations are characteristic of the pure hydrogen dichloride ions in these melts. The values of K_{eq} shown in Table I are significantly less than the ca. 600 L mol^{-1} reported for the HCl_2^-/HCl equilibrium in tetrachloroethane at 34 °C.[22] The lower values of K_{eq} in the melts may result from stronger solvation of Cl^- and its resulting effect on the hydrogen chloride/dichloride equilibrium (eq 1). In a nonpolar solvent such as tetrachloroethane, the compact negative charge of Cl^- would be poorly solvated; this in turn would make the formation of HCl_2^- more favorable (larger K_{eq}). On the other hand, the strong interaction of Cl^- with the Im^+ cation in the ImCl:$AlCl_3$ ionic liquids (see below) would, correspondingly, make the formation of HCl_2^- less favorable (smaller K_{eq}).

In Table I $\delta_{HCl_2^-}$ is shifted upfield ca. 1 ppm and δ_{HCl} is shifted ca. 0.5 ppm downfield with respect to values reported in tetrachloroethane, methylene chloride, and acetonitrile. Previous work has demonstrated that all important contributions to proton shielding in hydrogen halides and bihalides are directly proportional to hydrogen charge density.[23] Thus, the upfield shift of $\delta_{HCl_2^-}$ in the melts relative to the other solvents indicates an increase in the charge density on the hydrogen atom in HCl_2^-. This would result in weakened hydrogen bonds in HCl_2^- making the formation of dichloride ion less favorable in the melts, which is consistent with the smaller K_{eq}'s observed. The upfield shift in δ_{HCl} is indicative of a decrease in charge density of the hydrogen; this may result from an increase in the HCl dipole due to greater solvation in the melts.

Hydrogen Chloride/Dichloride Equilibrium Isotope Effect. The substitution of deuterium for protium in the dichloride ion affects the HCl_2^-/HCl equilibrium.[33-36] This equilibrium isotope effect

---

(28) Representative NMR spectra of a proton (deuteron) in basic $AlCl_3$:ImCl melts are given in refs 6, 16, and 31.

(29) Shuppert, J. W.; Angell, C. A. *J. Chem. Phys.* **1977**, *67*, 3050–3056.

(30) Campbell, J. L. E.; Johnson, K. E. In *Proceedings of the Eighth International Symposium on Molten Salts*; Gale, R. J.; Blomgren, G.; Kojima, H., Eds.; The Electrochemical Society: Pennington, NJ, 1992; pp 317–334.

(31) Trulove, P. C. Ph.D. Thesis, State University of New York, Buffalo, NY, 1992.

(32) The complete listing of the NMR data used in the B–H–S analysis is given in ref 31.

(33) Szydlowski, J. *Z. Naturforsch., A* **1975**, *30*, 38–43.

(34) Szydlowski, J. *J. Mol. Struct.* **1985**, *127*, 209–215.

for the dichloride ion can be viewed as the following equilibrium:

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

The equilibrium isotope effect, K_{EIE}, for the hydrogen dichloride ion is simply the equilibrium constant for eq 2,

$$K_{\mathrm{EIE}} = \frac{[{}^2\mathrm{HCl_2^-}][\mathrm{HCl}]}{[\mathrm{HCl_2^-}][{}^2\mathrm{HCl}]} = \frac{K_{\mathrm{eq}}({}^2\mathrm{H})}{K_{\mathrm{eq}}({}^1\mathrm{H})} \qquad (3)$$

where $K_{\mathrm{eq}}({}^2\mathrm{H})$ is the equilibrium constant for the $^2\mathrm{HCl_2^-}/^2\mathrm{HCl}$ system and $K_{\mathrm{eq}}({}^1\mathrm{H})$ is the equilibrium constant for the $\mathrm{HCl_2^-}/\mathrm{HCl}$ system.

We are able to compare deuteron and proton equilibrium constants at 90 °C (Table I). The ratio of these two values (eq 3) gives $K_{\mathrm{EIE}} = 0.67 \pm 0.26$. While the standard deviation is large, the equilibrium isotope effect appears to be real, and the magnitude indicates that the equilibrium favors the left side of eq 2. A value of 0.60 ± 0.01 has been found for K_{EIE} of dichloride ion in the gas phase.[36] The surprisingly close agreement between ours and the published value may be coincidence considering the large differences between reactions in solution and the gas phase. However, the published value does confirm the overall direction of K_{EIE} toward accumulation of deuterium in the hydrogen chloride molecule.

A theoretical value for the dichloride ion equilibrium isotope effect can be calculated from the fundamental vibrational frequencies, ν, of the species in equilibrium. With employment of standard statistical thermodynamic arguments, it can be shown that K_{EIE} is given by[37]

$$K_{\mathrm{EIE}} = \exp\left(\frac{-\Delta\epsilon_{\mathrm{zp}}}{\kappa T}\right) \prod_{i=1}^{3N_{\mathrm{HCl_2^-}}-6} \left\{ \frac{\nu'^{i}_{\mathrm{o}}\left[1-\exp\left(\frac{-h\nu'^{i}_{\mathrm{o}}}{\kappa T}\right)\right]}{\nu^{i}_{\mathrm{o}}\left[1-\exp\left(\frac{-h\nu^{i}_{\mathrm{o}}}{\kappa T}\right)\right]} \right\} \times \prod_{j=1}^{3N_{\mathrm{HCl}}-6} \left\{ \frac{\nu'^{j}_{\mathrm{o}}\left[1-\exp\left(\frac{-h\nu'^{j}_{\mathrm{o}}}{\kappa T}\right)\right]}{\nu^{j}_{\mathrm{o}}\left[1-\exp\left(\frac{-h\nu^{j}_{\mathrm{o}}}{\kappa T}\right)\right]} \right\} \frac{\sigma_{\mathrm{HCl_2^-}}\sigma_{\mathrm{HCl}}'}{\sigma_{\mathrm{HCl_2^-}}'\sigma_{\mathrm{HCl}}} \qquad (4)$$

where

$$\Delta\epsilon_{\mathrm{zp}} = \sum_{i=1}^{3N_{\mathrm{HCl_2^-}}-6}\left(\frac{h[\nu'^{i}_{\mathrm{o}} - \nu^{i}_{\mathrm{o}}]}{2}\right) - \sum_{j=1}^{3N_{\mathrm{HCl}}-6}\left(\frac{h[\nu'^{j}_{\mathrm{o}} - \nu^{j}_{\mathrm{o}}]}{2}\right)$$

$\Delta\epsilon_{\mathrm{zp}}$ is the zero-point energy, κ is the Boltzmann constant, h is Plank's constant, σ is the symmetry number and T is absolute temperature. The terms with a superscript (′) are for the deuterium-containing species. Since the symmetry of hydrogen chloride and hydrogen dichloride ion do not change upon deuterium substitution, the final factor in eq 4 reduces to one. Thus, there are essentially three terms in eq 4 contributing to the dichloride ion equilibrium isotope effect, the zero-point energy term, the translational and rotational partition functions, and the vibrational partition functions.[37,38] Use of eq 4 requires all vibrational frequencies to be known; although the symmetrical stretch, ν_1, is not known, we assume it is the same for both $\mathrm{HCl_2^-}$ and $^2\mathrm{HCl_2^-}$.

Table II. Vibrational Frequencies of Hydrogen Chloride and Hydrogen Dichloride Ion in Basic $\mathrm{AlCl_3}$:ImCl Melts[a,b]

	ν_1	ν_2	ν_3
$\mathrm{HCl_2^-}$		1062[c]	802
$^2\mathrm{HCl_2^-}$		752	563
HCl[d]	2709		
^{2}HCl[d]	1972		

[a] Abbreviations: ν_1 = symmetric stretch; ν_2 = doubly degenerate bending mode; ν_3 = asymmetric stretch. [b] All frequencies are in cm^{-1} and were obtained from ref 20. [c] For the doubly degenerate bending mode of $\mathrm{HCl_2^-}$, the average of the two values in ref 20 was used to calculate the K_{EIE}. [d] Frequencies are for hydrogen chloride in a 0.997:1.0 melt.

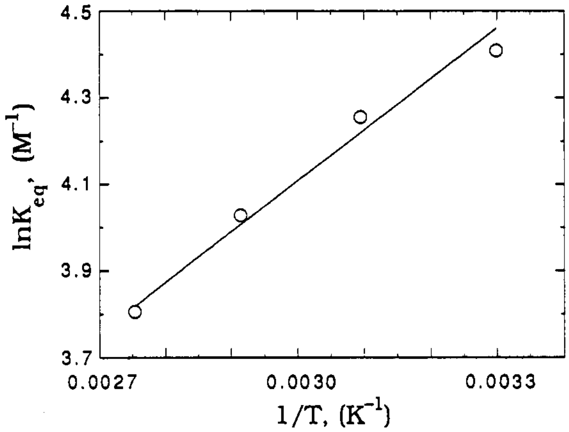

Figure 2. Plot of ln K_{eq} versus $1/T$ for the $^2\mathrm{HCl_2^-}/^2\mathrm{HCl}$ equilibrium.

Employing the vibrational frequencies listed in Table II in eq 4, we obtained a K_{EIE} of 0.712 at 90 °C. This value is well within the error limits of the experimentally determined value (see above) and, therefore, further confirms our initial conclusion that deuterium accumulations in hydrogen chloride. Interestingly, the dichloride ion K_{EIE} arises primarily from rotational and translational partition function ratios and not from zero-point energy differences. This most likely results from the large differences in the moments of inertia for HCl and ^{2}HCl and the fact that these two molecules do not have bending vibrations to contribute to zero-point energy differences.[36]

Thermodynamics of the $^2\mathrm{HCl_2^-}/^2\mathrm{HCl}$ Equilibrium. The temperature dependence of an equilibrium constant is given by[38]

$$\ln K_{\mathrm{eq}} = \frac{\Delta S_{\mathrm{RXN}}}{R} - \frac{\Delta H_{\mathrm{RXN}}}{RT} \qquad (5)$$

where ΔS_{RXN} is the entropy change for the reaction, ΔH_{RXN} is the enthalpy change for the reaction, R is the gas constant, and T is absolute temperature. Thus, a plot of ln K_{eq} versus $1/T$ will allow one to obtain the values of ΔH_{RXN} and ΔS_{RXN}. This plot was made for the $^2\mathrm{HCl_2^-}/^2\mathrm{HCl}$ equilibrium constant data in Table I giving Figure 2. The data were fit using a weighted linear regression ($R = 0.9950$). The weights for the regression analysis were determined from the standard deviations in ln K_{eq}. The standard deviations in the slope and intercept were calculated in the same manner as in the above B–H–S analysis (see Appendix) and were then propagated through the calculations to obtain the standard deviations for ΔH_{RXN} and ΔS_{RXN}. The values obtained for ΔH_{RXN} and ΔS_{RXN} are -9.8 ± 0.8 kJ mol^{-1} and 4.8 ± 2.4 J mol^{-1} K^{-1}, respectively.

---

(35) Szydlowski, J.; Ratajska, W. *J. Radioanal. Nucl. Chem.* **1987**, *109*, 133–138.

(36) Larson, J. W.; McMahon, T. B. *J. Phys. Chem.* **1987**, *91*, 554–557.

(37) Ritche, C. D. *Physical Organic Chemistry: The Fundamental Concepts*, 2nd ed.; Marcel Dekker: New York, 1990; Chapter 8.

(38) Rock, P. A. *Chemical Thermodynamics*; University Science Books: Mill Valley, CA, 1983; Chapter 10.

(39) The equation $\Delta G_{\mathrm{RXN}} = -RT \ln K_{\mathrm{eq}}$ was used to calculate ΔG_{RXN} from the equilibrium constant data in Table I.

(40) Caldwell, G.; Kebarle, P. *Can. J. Chem.* **1985**, *63*, 1399–1406.

(41) Dieter, K. M.; Dymek, C. J.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 2722–2726.

While isotopic substitution does not alter the potential energy surface of a system, it does affect the thermodynamic properties. Consequently, the values for ΔH_{RXN} and ΔS_{RXN} given above differ somewhat from the values for the HCl_2^-/HCl equilibrium. Calculation of the free energy of reaction, ΔG_{RXN}, for the HCl_2^-/HCl equilibrium at 90 °C gives a value ca. 1 kJ mol^{-1} greater than the corresponding ΔG_{RXN} calculated for the $^2HCl_2^-/^2HCl$ equilibrium at the same temperature (i.e. 12.7 vs 11.5 kJ mol^{-1}).[39] Therefore, if there is no large difference in the ΔS_{RXN} for the two equilibria, then ΔH_{RXN} for the HCl_2^-/HCl equilibrium should be ca. 1 kJ mol^{-1} larger than ΔH_{RXN} for the $^2HCl_2^-/^2HCl$ equilibrium.

The value of ΔH_{RXN} for the dichloride ion equilibrium in sulfolane and propylene carbonate has been reported as −33.9 and −10.5 kJ mol^{-1}, respectively.[40] The difference in ΔH_{RXN} between sulfolane and propylene carbonate appears to result from differences in the heats of solvation of the anions. Propylene carbonate solvates HCl_2^- significantly less than Cl^-, while in sulfolane the differences in solvation of the two anions are not as large. This same rational may also explain the relatively small ΔH_{RXN} for the dichloride equilibrium in the basic $AlCl_3$:ImCl melts. It is well-known that Cl^- in basic melts strongly interacts with the imidazolium cation forming hydrogen bonds with the ring hydrogens.[41–43] On the other hand, HCl_2^- shows no evidence of hydrogen bonding to Im^+.[20] Thus, one would expect the heat of solvation for Cl^- to be larger than for HCl_2^-.

The value obtained for ΔS_{RXN} has a large error associated with it, so any conclusions from it must be regarded as tentative. However, the presence of strong H-bonds between Cl^- and Im^+ and their apparent absence between HCl_2^- and Im^+ (see above) would seem to indicate that the positive ΔS_{RXN} results from liberation of solvent molecules (Im^+) upon formation of HCl_2^-.

Conclusions

The hydrogen chloride/dichloride equilibrium constants measured in this study further demonstrate that the equilibrium (eq 1) strongly favors the formation of the dichloride ion. The equilibrium isotope effect for the hydrogen chloride/dichloride ion indicates that deuterium will accumulate in the hydrogen chloride molecule. Finally, the magnitude of the enthalpy of reaction suggests that the melts solvate chloride ion more strongly than hydrogen dichloride ion.

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research.

Appendix

The B–H–S method[22,26,27] as applied to our ^1H and ^2H NMR data is presented below. However, for the sake of simplicity the equations are given with respect to the treatment of the ^1H NMR data with the understanding that the ^2H NMR data were handled in the same manner.

If we assume a 1:1 complex between HCl and Cl^- in the $AlCl_3$:ImCl melts (eq 1), then the equilibrium constant, K_{eq}, for the hydrogen chloride/dichloride equilibrium is given by

$$K_{eq} = \frac{[HCl_2^-]}{[Cl^-][HCl]} \tag{A1}$$

It can be shown that the B–H–S equation for the HCl/HCl_2^- equilibrium is[22,27]

$$\frac{[Cl^-]}{\Delta_{obs}} = \frac{1}{K_{eq}\,\Delta_{HCl_2^-}} + \frac{[Cl^-]}{\Delta_{HCl_2^-}} \tag{A2}$$

The observed proton chemical shift difference, Δ_{obs}, and the limiting proton chemical shift difference, $\Delta_{HCl_2^-}$, are defined as

$$\Delta_{obs} = \delta_{obs} - \delta_{HCl} \tag{A3}$$

$$\Delta_{HCl_2^-} = \delta_{HCl_2^-} - \delta_{HCl} \tag{A4}$$

where δ_{obs} is the observed chemical shift and $\delta_{HCl_2^-}$, and δ_{HCl} are the chemical shifts for HCl_2^- and HCl, respectively. From a linear least-squares fit of eq A2,

$$y = b_1 + b_2 x \tag{A5}$$

where $y = [Cl^-]/\Delta_{obs}$ and $x = [Cl^-]$, we obtain $\Delta_{HCl_2^-}$ and K_{eq}.

Proton is added to the melts as $ImHCl_2$. For the purpose of these calculations each $ImHCl_2$ adds one Cl^- and one HCl. (The $ImHCl_2$ is normally not stoichimetric;[6,20] however, this was taken into account when evaluating the experimental data.) Thus, the total melt chloride concentration, $[Cl^-]_T$, is the sum of the melt chloride concentration, $[Cl^-]_{melt}$, and the chloride added from the $ImHCl_2$, $[Cl^-]_{ImHCl_2}$.

$$[Cl^-]_T = [Cl^-]_{melt} + [Cl^-]_{ImHCl_2} \tag{A6}$$

Initially the equilibrium concentration of Cl^-, $[Cl^-]_{eq}$, is not known. It differs from $[Cl^-]_T$, by the HCl_2^- concentration since the formation of each dichloride ion removes one chloride ion (eq A7). The total proton concentration is generally small in comparison to $[Cl^-]_T$. Consequently $[Cl^-]_T$ is a good first approximation for $[Cl^-]_{eq}$.

$$[Cl^-]_{eq} = [Cl^-]_T - [HCl_2^-] \tag{A7}$$

The analysis of the NMR data began with plotting $[Cl^-]_T/\Delta_{obs}$ versus $[Cl^-]_T$. An initial estimate of $\Delta_{HCl_2^-}$ was obtained from 1/slope of the linear regression of this data.[44] The value of $\Delta_{HCl_2^-}$ was then used to determine $[HCl_2^-]$ by employing the following expression:

$$[HCl_2^-] = [H^+]_T\left(\frac{\Delta_{obs}}{\Delta_{HCl_2^-}}\right) \tag{A8}$$

Here $[H^+]_T$, the total proton concentration in the oxide-free basic melts, is the sum of the concentrations of hydrogen chloride, [HCl], and hydrogen dichloride ion, $[HCl_2^-]$. The values of $[HCl_2^-]$ were then used in eq A6 to determine $[Cl^-]_{eq}$.

The NMR data was then replotted using $[Cl^-]_{eq}$ and an improved value for $\Delta_{HCl_2^-}$ obtained. This, in turn, was used to revise the values for $[Cl^-]_{eq}$. This iterative procedure was repeated until the values of $\Delta_{HCl_2^-}$ and K_{eq} converged.

After convergence was reached with the nonweighted least-squares analysis, the errors in the data were incorporated and the procedure was repeated using a weighted least-squares analysis. The standard deviations in the ^2H and ^1H NMR data, $\sigma\delta_{obs}$, were conservatively estimated to be ±0.1 and ±0.01 ppm, respectively. The estimated error in $[Cl^-]_{eq}$, $\sigma[Cl^-]_{eq}$, was ±0.005 M. The variance in the y_i's, $(\sigma y_i)^2$, in eq A5 is given by

$$(\sigma y_i)^2 = \frac{(\sigma[Cl^-]_{eq})^2}{(\delta_{obs} - \delta_{HCl})^2} + \frac{[Cl^-]_{eq}^2[(\sigma\delta_{obs})^2 + (\sigma\delta_{HCl})^2]^2}{(\delta_{obs} - \delta_{HCl})^4} \tag{A9}$$

---

[42] Dymek, C. J.; Stewart, J. J. P. *Inorg. Chem.* **1989**, *28*, 1472–1476.

[43] Abdul-Sada, A. K.; Al-Juaid, S.; Greenway, A. M.; Hitchcock, P. B.; Howells, M. J.; Seddon, K. R.; Welton, T. *Struct. Chem.* **1990**, *1*, 391–394.

[44] The regression analysis of our data was performed using the program KaleidaGraph on a Macintosh microcomputer: KaleidaGraph, Version 2.02, 1986–1989, Abelbeck Software. Distributed by Synergy Software (PCS Inc.), 2457 Perkiomen Avenue, Reading, PA 19606; manual Chapters 7 and 8.

In weighted least squares the weight given to each data point, w_i, is commonly the reciprocal of the variance.[45] However, to simplify the regression analysis the reciprocal of the variance was divided by the reciprocal of the mean variance, $1/\overline{(\sigma y)}^2$, to give weights for each y_i.

$$\frac{1/(\sigma y_i)^2}{1/\overline{(\sigma y)}^2} = w_i \tag{A10}$$

For weights derived from eq A10

$$\sum w_i = n \tag{A11}$$

where n is the number of points. Using these w_i's, a weighted regression was performed on the data from the final nonweighted iteration above. As before, $\Delta_{HCl_2^-}$ was used to generate improved values for $[Cl^-]_{eq}$ and the weighted regression run a last time giving the final values for $\Delta_{HCl_2^-}$ and K_{eq}. The determination of the errors in the values of $\Delta_{HCl_2^-}$ and K_{eq} is described below.

In the B–H–S analysis there is often a fortuitous coincidence of the data points to the best fit line.[27] The resulting very small errors in the slope, σb_2, and intercept, σb_1, are not indicative of the experiments that generated the points. Therefore, the error contributions from the observable quantities were incorporated into the evaluation of σb_2 and σb_1.

The variance in y_i (eq A9) was included in the calculation of the weighted residual sum of squares (RSS)[46,47]

$$\mathrm{RSS} = \sum w_i\{[y_i - (b_1 + b_2x_i)]^2 + (\sigma y_i)^2\} \tag{A12}$$

The weighted residual mean square, σ^{*2}, is given by

$$\sigma^{*2} = \frac{\mathrm{RSS}}{n-2} \tag{A13}$$

where $n - 2$ is the degree of freedom. The variances for the slope and intercept are then

$$(\sigma b_2)^2 = \sigma^{*2}\left\{\frac{n}{n\sum w_ix_i^2 - (\sum w_ix_i)^2}\right\} \tag{A14}$$

$$(\sigma b_1)^2 = \sigma^{*2}\left\{\frac{\sum w_ix_i^2}{n\sum w_ix_i^2 - (\sum w_ix_i)^2}\right\} \tag{A15}$$

Finally, the standard deviations for $\Delta_{HCl_2^-}$ and K_{eq} were obtained from

$$(\sigma\Delta_{HCl_2^-})^2 = \frac{(\sigma b_2)^2}{b_2^4} \tag{A16}$$

$$(\sigma K_{eq})^2 = \frac{(b_2)^2}{b_1^2} + \frac{b_2^2(\sigma b_1)^2}{b_1^4} \tag{A17}$$

---

(45) Caulcutt, R.; Boddy, R. *Statistics For Analytical Chemists*; Chapman and Hall: New York, 1983; Chapter 8.

(46) Weisberg, S. *Applied Linear Regression*; Wiley: New York, 1985; Chapter 1.

(47) Worthing, A. G.; Geffner, J. *Treatment of Experimental Data*; Wiley: New York, 1943; Chapter 11.