Acidity of HCl in Neutral Buffered Chloroaluminate Molten Salts

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Abstract: The Brønsted acidity of HCl in neutral buffered $AlCl_3$:1-ethyl-3-methylimidazolium chloride (EMIC) melts has been compared to the Brønsted acidity of HCl in acidic (55 mol % $AlCl_3$) melts. The acidities were compared using the spectrophotometric indicator method. Arenes were used as the weak indicator bases. The acidity of HCl in the neutral buffered melts was found to be dependent on both the type of buffering agent (LiCl, KCl, and NaCl) and on the concentration of the metal cation in the melt. An enhancement in Brønsted acidity of HCl is observed in the neutral buffered melts, although to a lesser degree than that in the acidic melts. A Hammett acidity function was determined for a NaCl (originally 55 mol % $AlCl_3$) buffered melt and a LiCl (originally 55 mol % $AlCl_3$) buffered melt. For a HCl (1 atm)/NaCl/$AlCl_3$:EMIC (originally 55 mol % $AlCl_3$) buffered melt, $H_o = -11.3$. $H_o = -12.7$ for a HCl (1 atm)/LiCl/$AlCl_3$:EMIC (originally 55 mol % $AlCl_3$) buffered melt.

Introduction

During the past decade, investigations have revealed that HCl acts as a Brønsted superacid when dissolved in an acidic chloroaluminate molten salt.[1,2] Chloroaluminate ionic liquids, or molten salts, are prepared by combining aluminum chloride ($AlCl_3$) and an organic chloride, in this case 1-ethyl-3-methylimidazolium chloride (EMIC).[3] A melt is considered acidic, basic, or neutral depending on whether the mole ratio of $AlCl_3$ to EMIC is greater than, less than, or equal to unity. An acidic melt may be buffered to neutrality by addition of an alkali metal chloride, MCl, where the reaction

$$MCl(s) + Al_2Cl_7^- \rightleftharpoons M^+ + 2AlCl_4^- \quad K \gg 1 \qquad (1)$$

takes place.[4] Melts are commonly buffered with LiCl, NaCl, and KCl. The condition for neutrality is (where EMI^+ is 1-ethyl-3-methylimidazolium cation)

$$[EMI^+] + [M^+] = [AlCl_4^-] \qquad (2)$$

The excess alkali chloride is insoluble once the melt is neutralized, and thus provides a solid buffer.

Previously, we showed that the neutral buffered melts possess a chemical behavior termed "latent acidity", which is not present in unbuffered neutral melts.[5] Acetylferrocene (B:), a weak Lewis base, was used as the probe molecule to observe this behavior. Acetylferrocene forms an $AlCl_3$ adduct in acidic melts. It was found that acetylferrocene also forms an $AlCl_3$ adduct in the neutral buffered melt, whereas it does not in a neutral unbuffered or basic melt.[5] The additional driving force for this reaction apparently results from the precipitation of the solid MCl:

$$AlCl_4^- + M^+ + B: \rightleftharpoons B{:}AlCl_3 + MCl(s) \qquad (3)$$

The extent of latent acidity is controlled by the concentration of M^+ ions present in the neutral buffered melt and hence depends on the $Al_2Cl_7^-$ content of the melt from which it is prepared.[6]

Smith and co-workers concluded that HCl (1 atm) in acidic (55 mol % $AlCl_3$) melts is a Brønsted superacid on the same order of acidity as 100% HF ($H_o = -15.1$).[2] The strong Lewis acid $Al_2Cl_7^-$, present in acidic melts, acts as a Cl^- sink, providing the driving force for the enhanced acidity of the HCl.

$$Al_2Cl_7^- + HCl \rightleftharpoons 2AlCl_4^- + H^+ \qquad (4)$$

We wished to determine if the neutral buffered melts would also exhibit an enhancement in the Brønsted acidity of HCl. The driving force for the enhanced acidity of HCl in the neutral buffered melts could also be provided by the precipitation of the alkali metal chloride from solution.

$$M^+ + HCl \rightleftharpoons MCl(s) + H^+ \qquad (5)$$

In this work, the acidity of HCl in neutral buffered $AlCl_3$:1-ethyl-3-methylimidazolium chloride melts has been quantified and compared to the acidity of HCl in acidic (55 mol % $AlCl_3$) melts. The spectrophotometric indicator method was used to compare the acidity of HCl in melts of various compositions and in the quantification of the acidity of HCl. This method measures the extent of protonation of weakly basic indicators in an acid solution using UV-vis spectroscopy in terms of the ionization ratio ($[BH^+]/[B]$).

$$B + H^+ \rightleftharpoons BH^+ \qquad (6)$$

If a reaction similar to eq 3, for a Lewis base, takes place in the neutral buffered melt, then in the presence of a Brønsted

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

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acid such as HCl the reaction

$$M^+ + HCl + B \rightleftharpoons MCl(s) + BH^+ \tag{7}$$

with an equilibrium constant given by

$$K = \frac{[BH^+]}{[B][HCl][M^+]} \tag{8}$$

could conceivably take place due to the latent acidity effect. If so, we would expect an enhanced Bronsted acidity and the ionization ratio to be linearly dependent on the [HCl] and $[M^+]$ in the neutral buffered melt.

The melts exhibit a wide UV window (down to 240 nm) making it possible to observe both the protonated and unprotonated forms of the base. Arenes were used as weak indicator bases in order to directly compare these results to those of Smith and co-workers in the acidic melts.

Experimental Section

Melt Preparation. Aluminum chloride and 1-ethyl-3-methylimidazolium chloride were prepared as previously described.[7-10] Melts were made by mixing weighed amounts of $AlCl_3$ and EMIC to produce a slightly basic melt (0.97:1.00). Proton and oxide impurities were then removed by treatment with high vacuum and phosgene.[11,12] *CAUTION: Phosgene ($COCl_2$) is an extremely posionous gas and should be handled in a operating fume hood in a well-ventilated room. It is also advisable to wear an acidic gas respirator whenever working with the gas.* Acidic melts were prepared by first making a basic melt and removing impurities as described above. A weighed amount of $AlCl_3$ was then added to the basic melt to obtain the desired acidity. Neutral buffered melts were prepared by adding excess LiCl, NaCl, or KCl to an acidic melt. LiCl (Aldrich, 99.99+ %), NaCl (Aldrich, 99.999%), and KCl (Aldrich, 99.999%) were dried by heating to 399 °C below 1×10^{-3} torr for 4 days. All melt preparation was done in a nitrogen-filled Vacuum Atmospheres drybox. Combined oxygen and water concentrations were maintained at a concentration of less than 5 ppm.

Chemicals. All aromatic hydrocarbons were used as received from Aldrich. Protonation studies were conducted using HCl(g) (Air Products, electronic grade); the HCl(g) was used as received. Phosgene (Matheson) used to remove oxide in the melts was used as received.

Preparation of Arene Solutions. Arene solutions were prepared by stirring a weighed amount of arene in a weighed amount of melt. The molar concentration of the arene was determined from the density of the melt for acidic and basic melts and from the density of an unbuffered neutral melt (1.2943 g/mL) for the neutral buffered melts. A single large batch of arene solution was made for each set of experiments to minimize error. The arene solution of interest was prepared and used within 36 h to avoid any chance of decomposition of the arene in the melt. The concentration was varied depending on the arene in order to keep the absorbance for the bands of interest between 0.1 and 1.0 absorbance units.

Protonation of the Base. After the solution was prepared, approximately 3 mL of melt was transferred by pipet to the side arm of the protonation cell (Figure 1). A stir bar is placed in the bulb at the end of the side arm. A quartz insert and its holder were then lowered into the cell, and the vacuum stopcock was closed to the outside atmosphere. The cell was removed from the drybox and attached to a vacuum line designed for the determination of HCl pressure over the melt.[13] The cell was slowly evacuated to avoid excessive bubbling of the melt. The cell was then isolated from the vacuum, and HCl was introduced. The melt was stirred in the side arm under the HCl pressure of interest. An instanteous color change was observed in the melts upon the introduction of HCl. After the HCl pressure reaches equilibrium, the melt remained under the equilibrated pressure for 10 min of additional reaction time. The protonation cell assembly was then removed from the line. The melt was poured into the cell, and the spectra were taken.

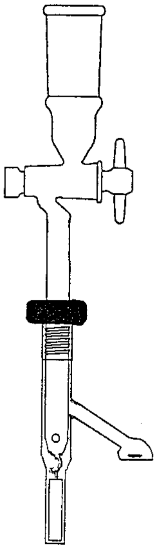

Figure 1. Protonation cell.

Spectroscopic Measurements. Optical absorption spectrophotometry was performed on a Hewlett Packard Model 8452A diode array spectrophotometer. Quartz rectangular fluorimeter cells (1 cm path lengths) with quartz block inserts were purchased from Wilmad Glass Co. and modified (see Figure 1). Modifications included adding a 24/40 joint which made it possible to attach the cell to the vacuum line, a vacuum stopcock to maintain an inert atmosphere above the melt during transfer out of the drybox and onto the vacuum line, and a side arm. The side arm provided a place for the melt to stir under the HCl(g) pressure of interest. Care should be taken not to make the side arm too long. The cell assembly must fit in the spectrophotometer in both directions in order to take measurements at both path lengths. If the side arm is too short, however, it is easier to make a mistake during evacuation of the melt and bubble or foam part of the melt into the cell.

For several of the arenes used in the study, it was necessary to have two path lengths available at the same time. The need for two path lengths arises if only a percentage of the arene has been protonated after the addition of HCl(g). A very small effective path length (0.005 cm) was necessary for the protonated arene due to its relative large molar absorpitivity. A larger effective path length (0.1 cm) was necessary for the unprotonated arene due to its relatively small molar absorpitivity. Effective cell path lengths were calibrated following the methods described in NBS Special Publication 260-54, U.S. Department of Commerce/National Bureau of Standards: Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard−SRM 935. All experiments were conducted at 24 ± 1 °C.

Results and Discussion

Effect of Varying Melt Composition on the Relative Acidity of HCl in the Melt. Figure 2 represents a typical series of spectrum taken for hexamethylbenzene at various pressures of HCl. As the pressure of HCl increases, the absorbance of the protonated form of the base observed at 285 and 396 nm

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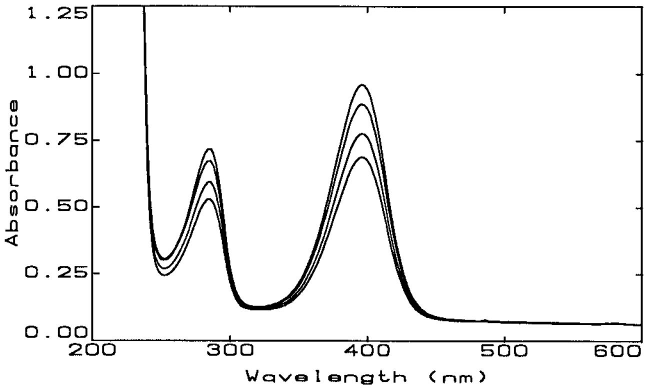

Figure 2. Absorption spectra of hexamethylbenzene in LiCl (60 mol % $AlCl_3$) buffered melt. Protonated forms of the base at 285 and 396 nm can be seen increasing as the pressure of HCl is increased (268, 348, 442, 760 mmHg).

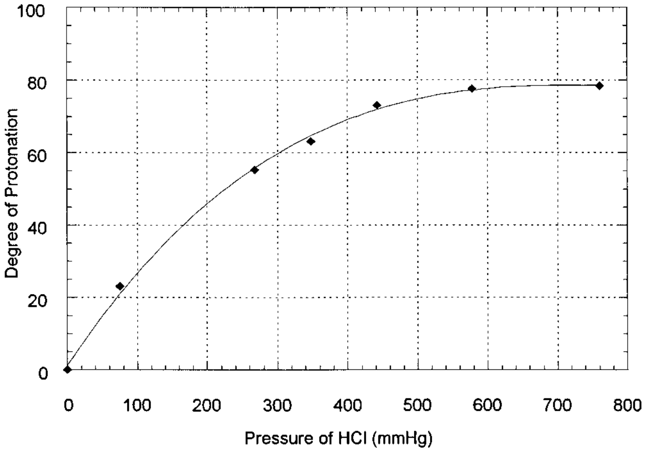

Figure 3. Degree of protonation of hexamethylbenzene versus pressure of HCl (mmHg) in a LiCl buffered melt, originally 60 mol % $AlCl_3$.

increases. The unprotonated form of the base cannot be seen in these spectrum due to its small molar absorptivity. If the concentration of the protonated base is calculated at each pressure for the absorbance band at 396 nm and divided by the total initial concentration of base in the melt, then the degree of protonation is obtained. An increase in pressure results in an increase in the degree of protonation (see Figure 3).

At a given pressure, the relative acidity of HCl in the neutral buffered melts was found to be dependent on the specific type of alkali metal cation, M^+. Acidic melts were buffered with LiCl, NaCl, and KCl. Figure 4 shows the effect of the metal cation on the relative acidity of HCl in various neutral buffered melts. Using 9,10-dimethylanthracene ($pK_B = 6.4$ in HF) as the indicator base, one can observe the change in the degree of protonation versus pressure for each buffering agent. Using the degree of protonation as an indicator for the acidity of HCl in the various melts, the effect of the cation on the acidity of HCl in the neutral buffered melts can be ranked: LiCl buffered > NaCl buffered ≫ KCl buffered. This work is in agreement with research in our laboratory in which Guttman acceptor numbers (AN) were used as a measure of the relative Lewis acidities of the various neutral buffered melt systems. Using triethylphosphine oxide as the probe molecule, the same order of acidities was found.[14]

In addition to being dependent on the type of metal cation in the melt, the acidity of HCl was also found to be dependent on the concentration of M^+ in solution. The metal cation concentration in a neutral buffered melt is approximately equal to the initial $Al_2Cl_7^-$ concentration in the melt before buffering. Figure 5 shows the effect of changing the initial $Al_2Cl_7^-$ concentration and buffering with the same alkali metal chloride. The degree of protonation is larger for the melts that were originally 60 mol % $AlCl_3$ than for the melts that were originally 55 mol % $AlCl_3$. The larger the M^+ concentration the larger the degree of protonation observed at a given HCl(g) pressure, regardless of which buffering agent is employed.

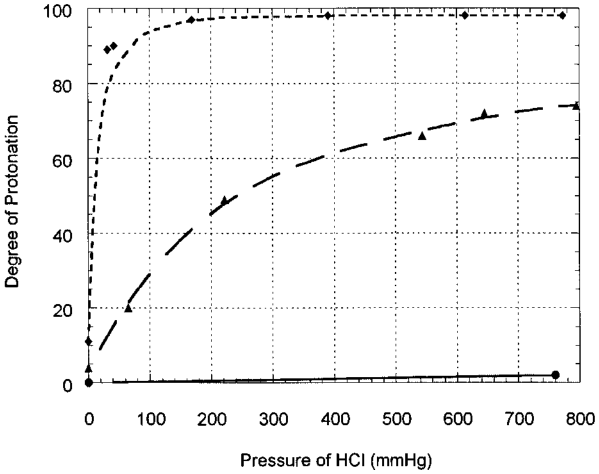

Figure 4. Degree of protonation of 9,10-dimethylanthracene versus pressure of HCl (mmHg) for various neutral buffered melt systems, all originally 55 mol % $AlCl_3$ (LiCl - - -, NaCl — — —, KCl —).

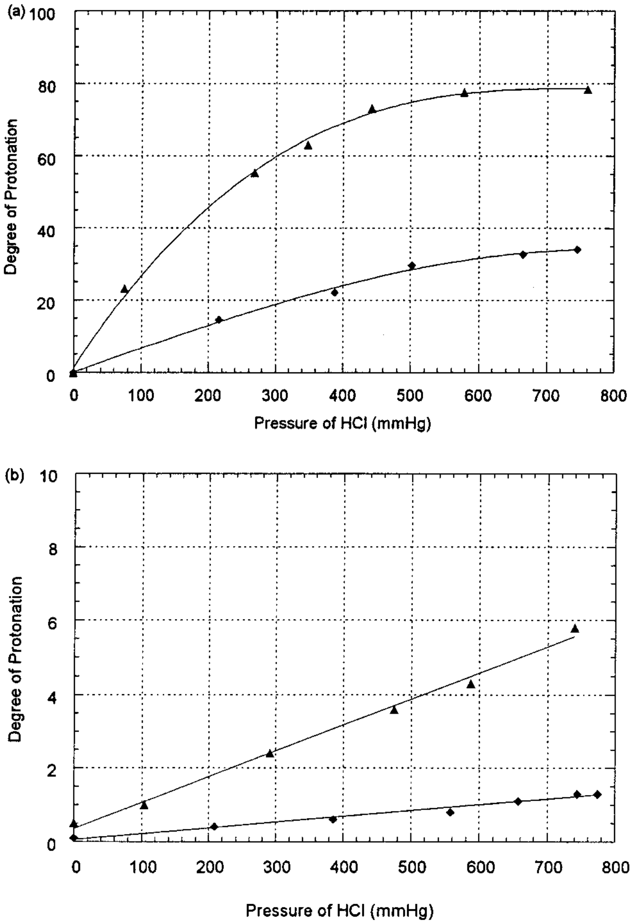

Figure 5. Degree of protonation of hexamethylbenzene versus pressure of HCl (mmHg) for various neutral buffered melt systems: (a) LiCl buffered melts, (b) NaCl buffered melts (55 mol % $AlCl_3$, ◆; 60 mol % $AlCl_3$, ▲).

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[14] Mantz, R. A.; Trulove, P. C.; Carlin, R. T.; Osteryoung, R. A. *Tenth International Symposium on Molten Salts/1996*; The Electrochemical Society Proceedings Series; The Electrochemical Society: Pennington, NJ, 1996.

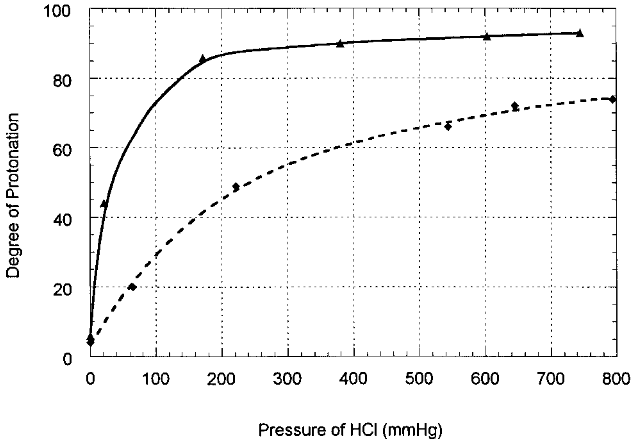

Figure 6. Degree of protonation of 9,10-dimethylanthracene versus pressure of HCl (mmHg) for various NaCl buffered melt systems (55 mol % $AlCl_3$, ◆; 60 mol % $AlCl_3$, ▲).

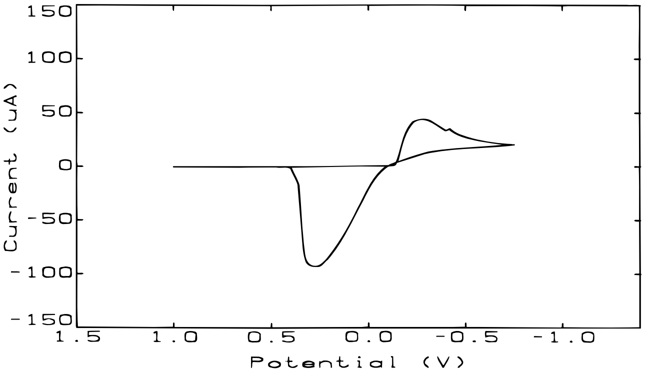

Figure 7. Cyclic staircase voltammogram (working electrode, Tungsten; scan rate, 500 mV/s) of an acidic 60 mol % $AlCl_3$ melt with KCl added.

The curvature in the line observed in the LiCl buffered melts is absent in the NaCl buffered melts. The linearity seen in the NaCl buffered melt can be attributed to the fact that the concentration of the unprotonated base is so large in comparison to the protonated base that we are essentially plotting the ionization ratio ($[BH^+]/[B]$) versus pressure of HCl rather than the degree of protonation, as seen in eq 9.

When $[B] \gg [BH^+]$, then

$$\frac{[BH^+]}{[B] + [BH^+]} \approx \frac{[BH^+]}{[B]} \tag{9}$$

[B] is defined as the concentration of the unprotonated base and $[BH^+]$ as the concentration of the protonated base (see eq 8). If a stronger base is used in the NaCl buffered melts, the data once again is curved because the condition of $[B] \gg [BH^+]$ no longer holds. This can be seen in Figure 6 where 9,10-dimethylanthracene is used as the indicator base in the NaCl buffered melts.

An analogous comparison could not be made in the KCl buffered melts. An electrochemical experiment was conducted, and it was discovered that an acidic melt (60 mol % $AlCl_3$) with KCl added was not completely buffered after 2 weeks of stirring at room temperature. As a melt is buffered, the aluminum wave disappears allowing the electrochemical window to "open." For the KCl (60 mol % $AlCl_3$) buffered melt, the aluminum reduction wave decreased, but did not disappear (see Figure 7). Therefore, a comparison in the acidity of HCl between a KCl (55 mol % $AlCl_3$) and a KCl (60 mol % $AlCl_3$) melt could not be made.

Table 1. Degree of Protonation of Indicator Base (ca. 760 mmHg)

	9,10-dimethylanthracene ($\log K_B = 6.4$)[a]	hexamethylbenzene ($\log K_B = 1.4$)[a]
basic melt	0	0
KCl buffered (55 mol % $AlCl_3$)	≈2	0
NaCl buffered (55 mol % $AlCl_3$)	74−85	<2
NaCl buffered (60 mol % $AlCl_3$)	93	6−10
LiCl buffered (55 mol % $AlCl_3$)	>98	34
LiCl buffered (60 mol % $AlCl_3$)	>98	78
55 mol % $AlCl_3$ acidic melt[b]	100	98+

[a] $\log K_B$ in HF, values taken from *Carbonium Ions*; Olah, G. A., Schleyer, P. von R., Eds.; Wiley-Interscience: New York, 1970; Vol II. [b] Values taken from *J. Am. Chem. Soc.* **1989**, *111*, 525−530.

The maximum buffering possible in a melt is dictated by the solubility of the alkali metal tetrachloroaluminate in the melt.

$$AlCl_4^- + M^+ \rightleftharpoons MAlCl_4(s) \tag{10}$$

The solubility limit can be determined by preparing the initial melts with increasing mole ratios of $AlCl_3$:EMIC and buffering with the alkali metal chlorides. The concentration of alkali metal cation in the melt will plateau as the solubility limit is reached. The maximum buffering possible was found to be approximately 1.2:1.0 for KCl, 1.5:1.0 for NaCl, and no limit was reached for LiCl even at a mole ratio of 1.9:1.0.[15] For example, if a 1.3:1.0 melt was prepared and then buffered with KCl, the melt would eventually buffer, but it would be the same as an initial melt with a mole ratio of 1.2:1.0. The excess KCl that reacted with $Al_2Cl_7^-$ would have precipitated from the solution as $KAlCl_4(s)$.

Considering both the specific type of metal cation as well as the concentration of the metal cation, the relative acidity of HCl in neutral buffered melts can be compared to the acidity of HCl in the acidic (55 mol % $AlCl_3$) melt on the basis of degree of protonation (Table 1). Basic melts exhibit no latent acidity and therefore show no degree of protonation for any of the bases we used at any pressure of HCl(g). The order of acidity for the neutral buffered melts are as previously described—LiCl buffered > NaCl buffered ≫ KCl buffered—and within each buffered melt system, the greater the M^+ concentration, the greater the relative acidity. The Brønsted acidity of HCl is the strongest in the acidic melts.

Using eq 7, an equilibrium expression can be written using the pressure of HCl;

$$K' = \frac{[BH^+]}{[B][M^+][P_{HCl}]} \tag{11}$$

Plotting the ionization ratio ($[BH^+]/[B]$) versus the pressure of HCl (Figure 8), yields a line whose slope will be equal to $K'[M^+]$. Using the appropriate M^+ concentration, $[M^+] = 0.948$ M for an originally 55 mol % $AlCl_3$ buffered melt and $[M^+] = 1.946$ M for an originally 60 mol % $AlCl_3$ buffered melt, K' values were calculated for bases in the various melts (Table 2). The calculation for K' is based on the assumption that a linear variation of HCl solubility exists with pressure in the neutral buffered melts. This relationship has been shown

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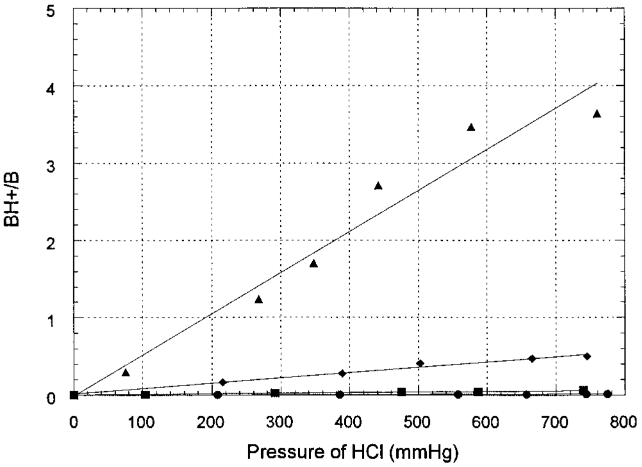

Figure 8. Ionization ratio of hexamethylbenzene versus pressure of HCl (mmHg) for various neutral buffered melt systems. LiCl buffered melts: 60 mol % $AlCl_3$, ▲; 55 mol % $AlCl_3$, ◆. NaCl buffered melts: 60 mol % $AlCl_3$ ■; 55 mol % $AlCl_3$, ●.

Table 2. Equilibrium Constants ($M^{-1}\ P_{HCl}{}^{-1}$)

	hexamethylbenzene	9,10-dimethylanthracene
LiCl buffered melts	$(1.7 \pm 0.2) \times 10^{-3}$	$(1.1 \pm 0.3) \times 10^{-1}$
NaCl buffered melts	$(4.2 \pm 0.4) \times 10^{-5}$	$(8.9 \pm 1.3) \times 10^{-3}$

to hold true in both acidic and slightly basic melts.[16] This assumption has proven to be valid for the NaCl buffered melts.[13] As expected, bases in the LiCl buffered melts have a larger equilibrium constant than the bases in the NaCl buffered melts. The difference in the equilibrium values between bases is due to the strength of the base. Thus, 9,10-dimethylanthracene ($pK_B = 6.4$ in HF) has a larger equilibrium constant than hexamethylbenzene ($pK_B = 1.4$ in HF). The important point to note is that the order of magnitude of the difference in K' between the LiCl and NaCl buffered melts remains constant.

Quantification of Acidity. In order to study solutions of greater ionic strength the Hammett acidity function H_o was proposed in the early 1930s by L. P. Hammett and A. J. Deyrup.[17] The Hammett acidity function provides a quantitative scale to express the acidity for more concentrated and non-aqueous solutions. Determination of the Hammett acidity function involves the use of the spectrophotometric indicator method. As discussed earlier, this method provides a simple and reliable means of determining the ionization ratio for the protonation of a base.

$$B + H^+ \rightleftharpoons BH^+ \tag{12}$$

$$H_o = -pK_B + \log \frac{[B]}{[BH^+]} \tag{13}$$

[B] = concentration of unprotonated base and $[BH^+]$ = concentration of protonated base.

In order to compare the acidity of HCl in a neutral buffered melt to an acidic melt, it was necessary to first determine H_o for an acidic melt. Although Smith and co-workers concluded that HCl(g) (1 atm) in an acidic (55 mol % $AlCl_3$) melt is a Brønsted superacid on the same order of acidity as 100% HF ($H_o = -15.1$),[2] the exact H_o value has never been determined because the concentration of HCl in the melt was unknown. The [HCl] is necessary in order to calculate pK_B in the Hammett equation.

If the protonation reaction shown in eq 12 is conducted in an acidic melt,

$$Al_2Cl_7^- + HCl + B \rightleftharpoons 2AlCl_4^- + BH^+ \tag{14}$$

the corresponding pK_B can be calculated. The equation above is comprised of two equilibria:

$$Al_2Cl_7^- + Cl^- \rightleftharpoons 2AlCl_4^- \tag{15}$$

and

$$B + HCl \rightleftharpoons BH^+ + Cl^- \tag{16}$$

The equilibrium constant for eq 15 is 10^{-16}.[4] Solving the equilibrium expression (eq 15) for $[Cl^-]$ results in

$$[Cl^-] = \frac{[AlCl_4^-]^2}{[Al_2Cl_7^-](10^{16})} \tag{17}$$

Substituting the result into the equilibrium expression for the equilibria in eq 16, gives

$$K_B = \frac{[BH^+]\left[\dfrac{[AlCl_4^-]^2}{[Al_2Cl_7^-](10^{16})}\right]}{[B][HCl]} \tag{18}$$

Concentrations of the chloroaluminate anionic species were calculated using an in-house melt program. In an acidic (55 mol % $AlCl_3$) melt, $[Al_2Cl_7^-] = 0.948$ M and $[AlCl_4^-] = 3.32$ M. This past year, solubility studies were conducted in the binary melts by Campbell and Johnson.[16] Using their equations for HCl solubility in the binary melts, the [HCl] in an acidic (55 mol % $AlCl_3$) melt equals 523 mM at 760 mmHg. Using the ionization ratio ($[BH^+]/[B]$) for hexamethylbenzene in an acidic (55 mol % $AlCl_3$) melt ([0.98]/[0.02] from Table 1), the pK_B was calculated.

$$pK_B = -\log \frac{[0.98][3.32\ M]^2}{[0.02][523\ mM][0.948\ M](10^{16})} = 12.96 \tag{19}$$

Using the Hammett acidity function, (eq 13) the pK_B value calculated in eq 19, and the ionization ratio for hexamethylbenzene in an acidic (55 mol % $AlCl_3$) melt, we obtain eq 20.

$$H_o = -(12.96) + \log \frac{[0.02]}{[0.98]} \tag{20}$$

Therefore, $H_o = -14.6$ for an acidic (55 mol % $AlCl_3$) melt under ca. 1 atm of HCl pressure. This is in very close agreement with the approximations made by Smith and co-workers.

The calculation of the Hammett acidity function for a neutral buffered melt is based on the assumption that pK_B does not change between the neutral buffered melts and the acidic melts. Although, pK_B values are traditionally not transferable from one solvent to another, many indicators have shown nearly the same pK_B values in similar solvents. For example, *p*-nitrotoluene has a $pK_B = 11.35$ in HF[18] and a $pK_B = 11.35$ in an $H_2O{-}H_2SO_4{-}SO_4$ solvent system.[19]

Therefore, using the calculated pK_B value for hexamethylbenzene in an acidic (55 mol % $AlCl_3$) melt and the ionization ratio for hexamethylbenzene in a NaCl (originally 55 mol %

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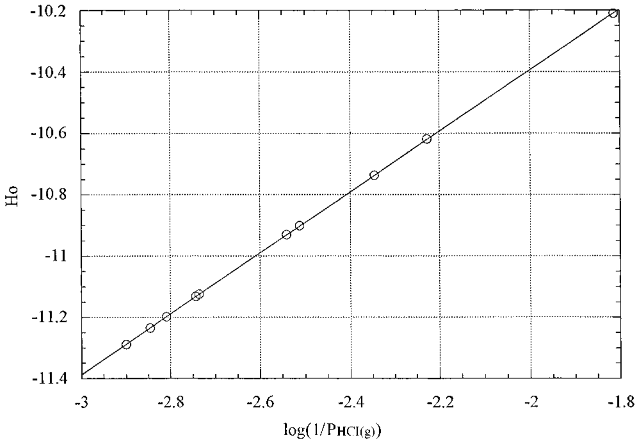

Figure 9. H_o values for a HCl/NaCl (originally 55 mol % $AlCl_3$) buffered melt versus the log($1/P_{HCl(g)}$) in mmHg.

$AlCl_3$) buffered melt under ca. 1 atm of HCl(g) pressure,

$$H_o = -(12.96) + \log \frac{[0.98]}{[0.02]} \qquad (21)$$

Therefore, $H_o = -11.3$ for a NaCl (55 mol % $AlCl_3$) buffered melt under ca. 1 atm HCl pressure.

The H_o for a NaCl (55 mol % $AlCl_3$) can be altered by varying the pressure of HCl(g) over the melt. Utilizing ionization ratio data at various pressures of HCl(g) for hexamethylbenzene in a NaCl (55 mol % $AlCl_3$) buffered melt, a H_o value can be calculated and is plotted versus the log ($1/P_{HCl(g)}$) in mmHg in Figure 9. As the pressure of HCl increases, the H_o value also increases. The relation is linear as per eqs 11 and 13.

An analogous calculation can be done using the calculated pK_B value for hexamethylbenzene in an acidic (55 mol % $AlCl_3$) melt and the ionization ratio for hexamethylbenzene in a LiCl (originally 55 mol % $AlCl_3$) buffered melt under ca. 1 atm of HCl(g) pressure.

$$H_o = -(12.96) + \log \frac{[0.66]}{[0.34]} \qquad (22)$$

Therefore, $H_o = -12.67$ for a LiCl (55 mol % $AlCl_3$) buffered melt under 1 atm HCl pressure.

Summary

This work was done in an effort to compare the Brønsted acidity of HCl in the neutral buffered melts to the Brønsted acidity of HCl in the binary melts. The Brønsted acidity of HCl in the neutral buffered melts is enhanced relative to the neutral unbuffered and basic melts. However, the increase in acidity is not to the same extent as that in an acidic (55 mol % $AlCl_3$) melt. The enhancement in acidity observed in the netural buffered melts has been attributed to the chemical behavior termed “latent acidity”. The acidity of HCl in the neutral buffered melts was found to be dependent on (1) the specific type of alkali metal cation and (2) the concentration of the alkali metal cation in solution. Using the degreee of protonation as an indicator for the acidity of HCl in the various neutral buffered melts, the effect of the alkali metal cation on the acidity can be ranked: LiCl buffered > NaCl buffered ≫ KCl buffered. Within each neutral buffered melt system, the greater the alkali metal cation concentration, the greater the relative acidity.

Combining the data collected for the degree of protonation for an indicator base and the solubility data from Campbell and Johnson, a Hammett acidity function was determined for an acidic (55 mol % $AlCl_3$) melt. For an acidic (55 mol % $AlCl_3$) melt, $H_o = -14.6$, which would be considered a Brønsted superacid. Using the pK_B value for hexamethylbenzene in the acidic (55 mol % $AlCl_3$) melt, H_o values were calculated for a NaCl (originally 55 mol % $AlCl_3$) buffered melt and a LiCl (originally 55 mol % $AlCl_3$) buffered melt. For a HCl (1 atm)/$AlCl_3$:EMIC (55 mol % $AlCl_3$) NaCl buffered melt, $H_o = -11.3$. For a HCl (1 atm)/$AlCl_3$:EMIC (55 mol % $AlCl_3$) LiCl buffered melt, $H_o = -12.67$. On the basis of these values, a HCl (1 atm)/NaCl (55 mol % $AlCl_3$) buffered melt would be very close to being considered a Brønsted superacid and a HCl-(1 atm)/LiCl (55 mol % $AlCl_3$) buffered melt would be considered a Brønsted superacid.

In conclusion, it has been shown that the Brønsted acidity of HCl in chloroaluminate melts can be varied by changing numerous melt parameters. Adjustment of the pressure of HCl over the melt combined with altering the buffering agent and the metal cation concentration in solution allow the experimentalist to choose a specific HCl acidity. This tunable solvent system could provide unique opportunities in both complexation and reaction chemistry.

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