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Brønsted Superacidity of HCl in a Liquid Chloroaluminate. $AlCl_3$–1-Ethyl-3-methyl-1*H*-imidazolium Chloride

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Abstract: The system HCl (0.1–1 atm)/$AlCl_3$–EMIC (55.0 mol % $AlCl_3$) (EMIC = 1-ethyl-3-methyl-1*H*-imidazolium chloride) at 23 °C is a Brønsted superacid capable of protonating arenes to a degree similar to that of liquid HF at 0 °C ($H_0 = -15.1$). Arenes used in this investigation were biphenyl (I), naphthalene (II), 9*H*-fluorene (III), chrysene (IV), 2-methylnaphthalene (V), mesitylene (VI), pentamethylbenzene (VII), hexamethylbenzene (VIII), anthracene (IX), and 9,10-dimethylanthracene (X). In both the chloroaluminate melt and HF I is a weak base while VIII–X are strong bases. In between these extremes the order of basicities in both media is II < III and IV < V < VI < VII < VIII. A study of the effect of HCl partial pressure showed, for example, that V is 50% protonated at 0.3 atm of HCl. The overall reaction is arene + HCl + $Al_2Cl_7^-$ $\rightleftarrows$ arene·H^+ + $2AlCl_4^-$ and is reversible. The degree of protonation was measured by optical absorption spectrophotometry. The arenes are stable in the liquid chloroaluminate for many hours, and their protonated forms (arenium ions) are stable for 1 h or more. A new procedure for the preparation of EMIC was developed that yields exceptionally clean $AlCl_3$–EMIC melts with very low concentrations of protic and oxidizing impurities.

We have found that HCl dissolved in a chloroaluminate molten salt containing excess $AlCl_3$ is a Brønsted superacid at ordinary temperatures and pressures. Brønsted superacids are generally considered to be those acids more acidic than 100% sulfuric acid,[2] which has a Hammett acidity function (H_0) of −12.3. Examples are fluorosulfonic acid (FSO_3H) and trifluoromethanesulfonic acid (CF_3SO_3H), which have H_0 values of −15.1 and −14.1,[3] respectively. When a strong Lewis acid is added to a Brønsted acid, the acidity of the medium usually increases, sometimes dramatically. For example, 100% HF has $H_0 = -15.1$,[4] whereas a medium consisting of equimolar amounts of HF and SbF_5 has an H_0 value in excess of −30.[3] Thus, a medium formed by combining a Brønsted acid with a strong Lewis acid is a potential superacid.

Mixtures of HCl and $AlCl_3$, as well as HBr and $AlBr_3$, both of which have been implicated in Friedel–Crafts chemistry, may be superacids. Experiments by Farcasiu and co-workers on the protonation of benzene[5] and by Kramer on the kinetics of the isomerization and hydrogen isotope exchange of alkanes[6] suggest that HBr/$AlBr_3$ is one of the most powerful superacids known, although this has been disputed.[3] HCl/$AlCl_3$ is also a very strong acid by Kramer's criterion.[6] However, mixtures containing only HBr and $AlBr_3$ or HCl and $AlCl_3$ are experimentally difficult to handle because these compounds and their mixtures are liquid only at temperature–pressure combinations well removed from ambient. Probably for this reason, additional studies related to the acidity of these two systems have not been attempted. Fortunately, it is now possible to overcome these experimental difficulties because of the recent development of molten salt systems that are liquid at ambient temperatures and in which the aluminum chloride activity can be varied over an exceedingly wide range.[7,8] These media are formed by mixing $AlCl_3$ with organic chloride salts. Two such systems have been investigated much more thoroughly than others. These employ *N*-1-butylpyridinium chloride (BPC) and 1-ethyl-3-methyl-1*H*-imidazolium chloride[9] (EMIC), respectively, as the organic salt component. The former was developed by Osteryoung and co-workers[7] while the latter was developed by Wilkes and co-workers.[8] In the present investigation we chose to work with the $AlCl_3$–EMIC system for reasons given below. $AlCl_3$ and EMIC react to form ionic liquids with organic cations and a mixture of chloro anions. Over much of the liquid range, the anions present in significant quantities are Cl^-, $AlCl_4^-$ and $Al_2Cl_7^-$, and their relative amounts are controlled by the reaction in eq 1. The equilibrium constant for this

$$Al_2Cl_7^- + Cl^- \rightleftarrows 2AlCl_4^- \qquad (1)$$

reaction is on the order of 10^{16} at ambient temperatures[8f] so that, in melts containing more than a slight excess of $AlCl_3$, the Cl^- concentration is very small. Thus, the $Al_2Cl_7^-$ anions are powerful Cl^- acceptors and are the source of a high Lewis acidity. When the melt composition approaches or exceeds ca. 67 mol % $AlCl_3$, other, even more strongly acidic chloroaluminate species, such as $Al_3Cl_{10}^-$ and Al_2Cl_6 must be taken into account.[8g] However, in the investigation to be described here, the melt composition is fixed at 55.0 mol % $AlCl_3$ for which the anionic constituents are adequately represented by eq 1.

There has been no previous study of the acidity of HCl in any chloroaluminate melt, but it is known that small amounts of adventitious protons in $AlCl_3$–BPC (67 mol % $AlCl_3$) readily protonate anthracene to yield the moderately stable 9*H*-anthracenium ion[7d] so that there is clearly the possibility that HCl might behave as a very strong Brønsted acid in such media. However, the role of the melt in enhancing the protic strength of HCl is almost certainly indirect. It arises through the ability

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of a melt containing excess $AlCl_3$ to maintain an exceedingly low Cl^- concentration rather than through the formation of a covalent bond between HCl and a chloroaluminate species. Over 35 years ago Brown and Pearsall demonstrated that HCl and $AlCl_3$ do not react to form species such as $HAlCl_4$.[10] Furthermore, recent NMR studies suggest that HCl exists in its molecular form in $AlCl_3$–EMIC mixtures containing excess $AlCl_3$.[8h] Thus, the equilibrium between HCl and a generic base (B) in these media is simply that given by eq 2. Since the equilibrium constant for

$$HCl + B \rightleftarrows BH^+ + Cl^- \qquad (2)$$

eq 1 in $AlCl_3$–EMIC mixtures is very large, eq 2 should be driven far to the right in the presence of excess $AlCl_3$ to yield an overall reaction represented by eq 3.

$$HCl + B + Al_2Cl_7^- \rightleftarrows BH^+ + 2AlCl_4^- \qquad (3)$$

The purpose of the present investigation is to relate the Brønsted acidity of HCl at ordinary pressures in $AlCl_3$–EMIC (55.0 mol % $AlCl_3$) to that of Brønsted superacids. We do this by the spectrometric indicator method using arenes as the indicator bases. Although arenes are not often used as indicator bases, we anticipate that they interact only weakly with acidic chloroaluminate species, as Robinson et al.[7f] demonstrated in the case of benzene, whereas the more common indicator bases contain atoms with lone-pair electrons that should be susceptible to such interaction. Fortunately, the basicities of a wide variety of arenes have been carefully measured by Mackor et al.[11] in liquid HF at 0 °C, and, as we shall see, the protonating power of HF with respect to arenes is similar to that of HCl/$AlCl_3$–EMIC (55.0 mol % $AlCl_3$) at ordinary HCl pressures.

Results and Discussion

$AlCl_3$–EMIC Mixtures. In order to study arene protonation in $AlCl_3$–EMIC mixtures, it was necessary to develop a new procedure for the preparation of EMIC that yielded a cleaner product and overcame other disadvantages of the literature preparation.[8a] These disadvantages include small batches, elevated pressures, and the use of ethyl acetate as a cosolvent for crystallization.[12] Acidic $AlCl_3$–EMIC mixtures prepared by our new procedure (see below) contained no more than a trace (ca. 0.03 mM) of oxidizing impurities (which otherwise yield intensely absorbing arene radical cations) and only small amounts of protic impurities (typically 0.3 mM), substantially below the concentration level of the added arenes (7–15 mM).[13] These melts also had a much wider UV window (down to 250 nm) than that previously achieved by others for these melts.[8a] This wide window allowed us to measure the spectra of the unprotonated arenes as well as those of their protonated forms (arenium ions). This UV window was an important reason for choosing the $AlCl_3$–EMIC system rather than the $AlCl_3$–BPC system for the present study since absorption by the *N*-1-butylpyridinium ion in the near-UV obliterates the spectra of many of the indicator arenes used in this investigation.

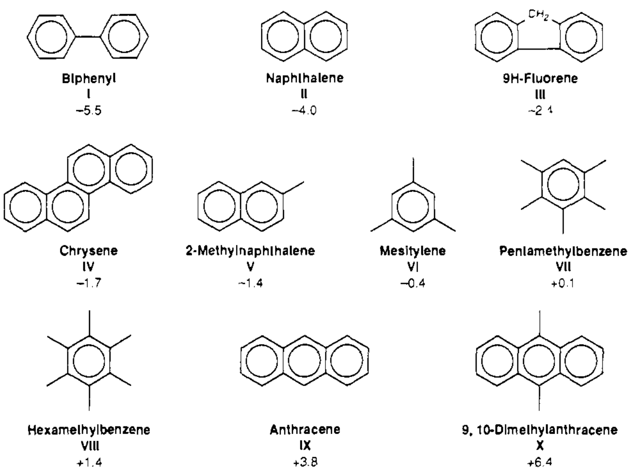

Figure 1. Indicator arenes used in this study. The numerical value below each arene is log K_B in HF.

Our failure to observe spectroscopically detectable amounts of radical cations, even for the more oxidizable arenes, is noteworthy in view of the many reports of radical-cation formation in the presence of $AlCl_3$.[14] It has been known for a long time that the addition of $AlCl_3$ to solutions of oxidizable aromatics in many solvents (nitromethane, carbon disulfide, chloroform, benzene, etc.) commonly results in radical-cation formation. $AlCl_3$–nitromethane, for example, is reported to be a much more effective oxidizing medium for generating these reactive intermediates than is sulfuric acid.[14c] Similar oxidations are reported to occur upon contact of arenes with solid $AlCl_3$ without a solvent.[14d,e] In the case of highly acidic $AlCl_3$–BPC melts,[7e] some workers have reported arene radical-cation formation while others could find no evidence of such reactions.[7d] Although $AlCl_3$ has sometimes been assumed to be the oxidant in these reactions,[14d] the reduced products have never been identified. Because of this history, we made a deliberate search for radical-cation formation in our $AlCl_3$–EMIC melts by using the indicator arenes and also 10*H*-phenoxazine (POZ) and 10*H*-phenothiazine (PTZ), both of which can be oxidized coulometrically in acidic $AlCl_3$–EMIC melts to form extremely persistent radical cations with intense absorption bands in the visible region.[15] We used not only mixtures containing 55.0 mol % $AlCl_3$ but also melts saturated with $AlCl_3$ (ca. 67 mol %) in which solid $AlCl_3$ was present. The solutions showed no observable radical-cation formation at the path lengths used for the protonation research. Solutions of POZ and PTZ were examined at long path lengths, and a trace (ca. 0.03 mM) of radical cations was found.

It is obvious from these experiments that $AlCl_3$, as such, is not an oxidant. It may, however, substantially enhance the oxidizing power of other substances, for example, by complexing with a reduced product. In the various observations of radical-cation formation in the presence of $AlCl_3$ or an acidic chloroaluminate, it is plausible to suppose that a solvent, e.g., nitromethane, or an impurity served as the oxidant.

Indicator Arenes. The 10 arenes displayed in Figure 1 served as indicators. The protonation of these arenes in liquid HF is schematically represented by eq 4, where B is an arene base, and

$$B + HF \rightleftarrows BH^+ + F^- \qquad (4)$$

$$K_B = \frac{\gamma_\pm^2}{\gamma_B}\frac{C_{BH}C_F}{C_B} \qquad (5)$$

the basicity constant for B is conventionally defined in eq 5, where $\gamma_\pm$ and γ_B are activity coefficients while C_{BH}, C_F, and C_B are the concentrations of BH^+, F^-, and B, respectively. Values of log K_B at 0 °C from Brouwer et al.[11a] are given in Figure 1 beneath each arene. Although these values are based on molal concentration units, the density of liquid HF is close to unity so that the use

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[10] Brown, H. C.; Pearsall, H. *J. Am. Chem. Soc.* **1951**, *73*, 4681.

[11] (a) Brouwer, D. M.; Mackor, E. L.; MacLean, C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. von R., Eds.; Wiley-Interscience: New York, 1970; Vol. II, Chapter 20. (b) Mackor E. L.; Hofstra, A.; van der Waals, J. H. *Trans. Faraday Soc.* **1958**, *54*, 66, 186.

[12] Residual ethyl acetate in acidic chloroaluminate melts undergoes Friedel–Crafts reactions that interfere with the study of dilute solutions of arenes as demonstrated in ref 7d.

[13] It has recently been shown that protic impurities in acidic $AlCl_3$–EMIC melts can be scavenged with diethylaluminum chloride.[8h] However, routine procedures have not as yet been developed for removing trace protic impurities without leaving residual amounts of this very reactive reagent.

[14] See, for example: (a) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155. (b) Kaim, W.; Bock, P. *Chem. Ber.* **1978**, *111*, 3585. (c) Forbes, W. F.; Sullivan, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 2862. (d) Rooney, J. J.; Pink, R. C. *Proc. Chem. Soc.* **1961**, 142. (e) Sato, H.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 631.

[15] We are currently investigating the electrochemical oxidation of POZ, PTZ, and various arenes and the characterization of their radical cations in $AlCl_3$–EMIC melts. These radical-cation spectra are similar to those for the same species in a $SbCl_3$-based melt as reported in: Chapman, D. M.; Buchanan, A. C., III; Smith, G. P.; Mamantov, G. *J. Am. Chem. Soc.* **1986**, *108*, 654.

Table I. Electronic Spectra of Arenes in $AlCl_3$–EMIC (55:45 mol %) at 23 °C

arene	λ_{max}, nm [$\epsilon \times 10^{-3}$, M^{-1} cm^{-1}][a]
I	252 [17.1]
II	248 (s) [~2.0], 260 [3.29], 269 [4.70], 278 [5.14], 286 [3.60], 301 (s) [0.38], 311 [0.25]
III	258 [16.4], 262 [18.2], 265 [19.7], 273 (s) [14.6], 277 (s) [~11.2], 290 [6.7], 301 [9.2]
IV	243 [17.2], 266 [very large], 285 (s) [~12.6], 297 [11.2], 310 [11.9], 324 [11.9], 345 [0.80], 362 [0.74]
V	272 (s) [~4.7], 278 [4.79], 306 [0.60], 314 [0.41], 320 [0.56]
VI	258 [0.2–0.3], 263 [0.2–0.3], 267 [0.2–0.3], 273 [0.24]
VII	270 [0.37], 275 [0.30], 280 [0.29]
VIII	272 [0.24]
IX	328 [2.56], 342 [4.75], 360 [6.98], 380 [6.36]
X	342 [2.45], 360 [5.47], 380 [9.21], 402 [9.21]

[a] s = shoulder.

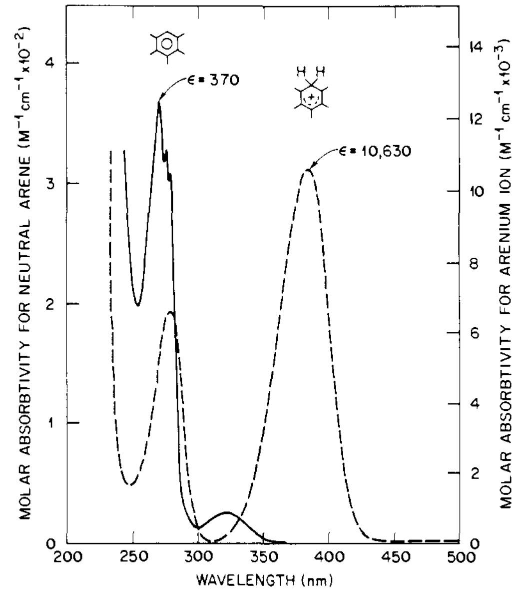

Figure 2. Absorption spectra of VII, solid line, and its protonated form (1*H*-pentamethylbenzenium cation), dashed line, in $AlCl_3$–EMIC (55.0 mol % $AlCl_3$) at 23 °C.

of molar concentration units introduces only a small error.

The UV–vis spectra of dilute solutions of the 10 indicator arenes in $AlCl_3$–EMIC (55.0 mol % $AlCl_3$) under argon at 23 °C showed that they were present as neutral arene molecules and that their solutions were stable for several hours. Band maxima for these spectra are listed in Table I. Wavelengths for these bands are, in nearly all instances, quite close to their values in organic solvents such as methanol. Values of the molar absorptivity (ϵ) tend to run a little higher than in organic solvents. An example of one of these spectra is displayed in Figure 2. Spectra of the five less basic arenes (I–V) contained no bands attributable to other substances and showed no perceptible changes after 18 h, while spectra of the five more basic arenes (VI–X) initially showed the presence of small amounts of arenium ions attributable to protic impurities. After extended periods of time (1–4 days), these spectra generally indicated a small (typically 2%) loss of arene. IX showed the greatest loss, a trace after 1 h and 10% after 24 h. These slow changes with time are attributed to chemical reactions, such as those reported for IX in $AlCl_3$–BPC (67 mol % $AlCl_3$).[7d]

When freshly prepared, dilute solutions of the above 10 arenes at 23 °C were equilibrated with HCl at ca. 1 atm, the following results were obtained: Spectra of I and II were virtually unchanged by the presence of HCl except that a very weak absorption occurred in the spectrum of II at the position expected for the arenium ion. Hence, I was not protonated while II may have been slightly protonated. Spectra of III and IV showed bands of both the protonated and unprotonated forms in significant amounts.

Table II. Electronic Spectra of Protonated Arenes in $AlCl_3$–EMIC (55:45 mol %) at 23 °C and in Other Media

starting arene	λ_{max}, nm [$\epsilon \times 10^{-3}$, M^{-1} cm^{-1}]	
	$AlCl_3$–EMIC (55:45)	other media
I	ion not formed	240 [22.9], 285 [22.9], 440 [8.5] in HF/BF_3[a]
II	390 (?)	254 [12.9], 280 [14.8], 390 [11.0] in HF/BF_3[a]
III	382	283 [6], 372 [17.4] in HF/BF_3[a]
IV	520	
V	271 [4.7 ± 0.9], 400 [16.1 ± 2.5]	
VI	262 [10.2], 360 [10.7]	254 [8.7], 355 [11.0] in HF/BF_3[a] 358 [9.2] in CF_3SO_3H[b]
VII	279 [6.60], 384 [10.6]	272 [4.3], 377 [9.8] in HF[a]
VIII	285 [6.70], 396 [9.88]	283 [7.24], 395 [~10] in 97% H_2SO_4[c]
IX	250 [8.17], 257 [9.74], 280–300 [2.20], 420 [37.1]	408 [37.2] in HF[a,d,e] 424 [34.5] in $SbCl_3$–$AlCl_3$–BPC (60:22:18 mol %)[f]
X	252 [9.57], 300 [6.48], 415 [30.3]	

[a] Dallinga, G.; Mackor, E. L.; Verrijn Stuart, A. A. *Mol. Phys.* **1958**, *1*, 123. [b] Bokoss, H. J.; Ranson, R. J.; Roberts, R. M. G.; Sadri, A. R. *Tetrahedron* **1982**, *38*, 623. [c] Deno, N. C.; Groves, P. J.; Jaruzelski, J. J.; Lugasch, M. N. *J. Am. Chem. Soc.* **1960**, *82*, 4719. [d] Reference 11b. [e] Verrijn Stuart, A. A.; Mackor, E. L. *J. Phys. Chem.* **1957**, *27*, 826. [f] Reference 7d.

From the absorbances of bands for the unprotonated arenes and their ϵ values (see Table I), we estimate that these arenes were, roughly, 10–20% protonated. The spectrum of V indicated 75–90% protonation. Although the spectra of VI–VIII showed no discernible absorption due to unprotonated arene and, hence, were mostly, if not completely, protonated, the ϵ values for their protonated forms were found to be very much greater than those of the neutral arenes (see below) so that in these cases we cannot exclude the possibility of a few percent of unprotonated material. The spectra of IX and X indicated complete protonation.

Band maxima for the arenium ions are listed in Table II, and an example of one of these spectra is given in Figure 2. Molar absorptivities for the arenium ions of VI–X were calculated under the assumption that protonation was complete under HCl at 1 atm. The molar absorptivities of the bands of protonated V were extrapolated from a study of the effect of pressure on the degree of protonation that is described below. In Table I and Figure 2 the spectra of VI–X have been corrected for absorption due to protic impurities by scaling and subtracting the spectra of the arenium ions.

An additional discrimination among the relative basicities of some of the arenes was obtained by first equilibrating with ca. 1 atm of HCl and then reducing the pressure to a low value by pumping off the HCl until bubbling ceased, a process which left a small residual of HCl in solution. The spectrum of IV indicated essentially complete deprotonation while V was largely but not entirely deprotonated. On the basis of the study of the effect of HCl pressure on the protonation of V (see below), we estimate that in this case the amount of HCl left in solution after evacuation correspond to an equilibrium pressure of ca. 4×10^{-3} atm. The spectra of VI and VII showed a partial deprotonation, which was greater for VI than for VII, while VIII–X showed no appreciable deprotonation.

The above experiments show that I and II are the least basic arenes in HCl/$AlCl_3$–EMIC (55.0 mol % $AlCl_3$) while VIII–X are the most basic. In between these extremes the order of basicity is II < III and IV < V < VI < VII < VIII. This order is the same as that in liquid HF as determined by the K_B values. Not only is the relative order of basicities the same for both these media but the degree of protonation in the 55.0 mol % $AlCl_3$ melt under ca. 1 atm of HCl is similar to that in neat HF. That is, in both media I behaves as a weak base (virtually unprotonated), and IX and X behave as strong bases (highly protonated), while V is a base of intermediate strength.

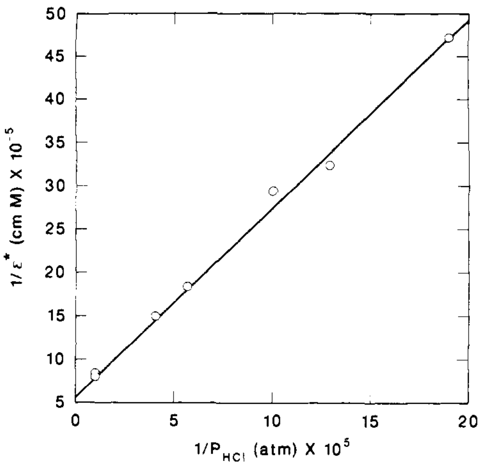

Figure 3. Effect of HCl partial pressure on the formal absorptivity of protonated V (1*H*-2-methylnaphthalenium cation) in $AlCl_3$–EMIC (55.0 mol % $AlCl_3$) at 23 °C.

Effect of HCl Pressure on the Protonation of V. We chose V as being well suited for a quantitative study of the effect of HCl partial pressure (P_{HCl}) on the degree of protonation. The protonated form of V (denoted BH) has an intense absorption band at 400 nm where the unprotonated arene (B) has no appreciable absorption. In experiments carried out at various P_{HCl} values, b, the cell path length, and C_o, the concentration of the arene before adding HCl, were varied so as to keep the absorbance at 400 nm (A_{BH}) large enough to measure accurately but not so large as to exceed the range of the spectrophotometer. Therefore, it proved useful to express A_{BH} in terms of a quantity ϵ_{BH}^*, defined by eq 6, which has the units of molar absorptivity.

$$\epsilon_{BH}^* = A_{BH}/(bC_o) \qquad (6)$$

Figure 3 displays the results of eight experiments conducted at 23 °C. These data approximate a straight line to within experimental uncertainty, and the least-squares fit is given by eq 7 with a standard deviation of 0.88×10^{-5} (correlation coefficient

$$1/\epsilon_{BH}^* = 6.20 \times 10^{-5} + (2.15 \times 10^{-5})/P_{HCl} \qquad (7)$$

0.9981). The units of P_{HCl} are atmospheres. In one of the spectra measured at ca. 1 atm of HCl and also in some preliminary experiments, weak bands due presumably to products of side reactions were observed at 335 and ca. 550 nm, but these were not detected in other spectra upon which eq 7 and Figure 3 are based.

The interpretation of eq 7 in terms of chemical reactions is straightforward. The protonation equilibrium is given by eq 2 with a stoichiometric equilibrium constant (K') given by eq 8,

$$K' = C_{BH}C_{Cl}/(C_B P_{HCl}) \qquad (8)$$

where C_B, C_{Cl}, and C_{BH} are, respectively, the molar concentrations of B, Cl^-, and BH^+. Although C_{Cl} is very small, it is under the control of reaction 1 and changes relatively slowly with changes in melt composition near 55 mol % $AlCl_3$. In our experiments C_o is negligible compared with the concentrations of $AlCl_4^-$ and $Al_2Cl_7^-$ so that changes in C_{Cl} due to reaction 2 are negligible. Furthermore, the melt has a high and virtually constant ionic strength so that the activity coefficients implicitly contained in K' should change little. For these reasons, C_{Cl} and K' are plausibly treated as fixed quantities in our experiments. Noting that $C_o = C_{BH} + C_B$, we can rewrite eq 8 in terms of the fraction protonated $\alpha = C_{BH}/C_o$. The result is eq 9. The Bouguer–Beer law

$$K'/C_{Cl} = \alpha/[(1 - \alpha)P_{HCl}] \qquad (9)$$

$$1/\epsilon_{BH}^* = 1/\epsilon_{BH} + [C_{Cl}/(K'\epsilon_{BH})]/P_{HCl} \qquad (10)$$

provides an accurate relation between A_{BH} and C_{BH} or α, viz., $A_{BH} = \epsilon_{BH}bC_o\alpha$, which, when combined with eq 6 and 9, yields eq 10. Since the quantity in square brackets is a constant in our experiments, eq 10 is identical with eq 7. Equating terms gives $\epsilon_{BH} = (16.1 \pm 2.5) \times 10^3\ M^{-1}\ cm^{-1}$ and $C_{Cl}/K' = 0.3$ atm. It also follows that $\alpha = \epsilon_{BH}^*/\epsilon_{BH}$. Therefore, $\alpha = 0.5$ when $P_{HCl} = C_{Cl}/K' = 0.3$ atm, and $\alpha \approx 0.77$ when $P_{HCl} = 1$ atm. The fact that eq 7 is valid for independent experiments covering a wide range of $1/P_{HCl}$ values establishes the reversibility of the protonation reaction with respect to variations in P_{HCl} and verifies to within experimental error that the absorption at 400 nm is due exclusively to the arenium ion.

The arenes used in our investigation cover a K_B range in HF of 10^{12} so that, for purposes of making comparisons between their protonation in 100% HF and in $HCl/AlCl_3$–EMIC (55 mol % $AlCl_3$), it is adequate to approximate the activity coefficient ratio in eq 5 by unity and useful to rewrite the result in the form given in eq 11.

$$K_B = \alpha^2 C_o/(1 - \alpha) \qquad (11)$$

When we substitute K_B values into eq 11, we find that, in HF at 0 °C, X, IX, and VIII are highly protonated up to large values of C_o, just as in $HCl/AlCl_3$–EMIC (55.0 mol % $AlCl_3$) they are highly protonated down to low values of P_{HCl}. At the opposite extreme, I is not appreciably protonated in HF until C_o begins to approach the impurity level, while in $HCl/AlCl_3$–EMIC (55.0 mol % $AlCl_3$) I is not appreciably protonated at 1 atm of HCl. The remaining arenes (except, possibly, for II) are partially protonated at ordinary C_o values in HF and at ordinary P_{HCl} values in $HCl/AlCl_3$–EMIC (55.0 mol % $AlCl_3$). For example, V is 50% protonated in HF at C_o on the order of 80 mM and 50% protonated in the chloroaluminate melt when $P_{HCl} = 0.3$ atm. The value of C_{Cl} and, hence, the value of K' can be estimated from the thermodynamic data reported by Hussey et al.[8f] together with the density data reported by Fannin et al.[8d] At 23 °C the value of log C_{Cl} in $AlCl_3$–EMIC (55.0 mol % $AlCl_3$) is −15.1. Hence, log $K' = -14.6$ where the units of K' are molar/atmosphere.

These results establish the fact that HCl (0.1–1 atm)/$AlCl_3$–EMIC (55 mol % $AlCl_3$) at 23 °C is a Brønsted superacid comparable in strength with liquid HF at 0 °C. It is interesting to note that although the solubility of HCl in this chloroaluminate melt has not been measured, it is certainly very much less than the concentration of HF in liquid HF (ca. 50 M). If one were to scale the acid strength of these two media on the basis of the molar concentration of protons, HCl in the chloroaluminate melt would be much stronger than HF. Dymek et al.[8g] recently developed a thermodynamic model of $AlCl_3$–EMIC that includes, in addition to $Al_2Cl_7^-$, the chloride acceptors that become important at high $AlCl_3$ contents, namely, $Al_3Cl_{10}^-$ and Al_2Cl_6. According to their model C_{Cl} decreases by a factor of nearly 5×10^2 when the $AlCl_3$ content of the melt increases from 55 to 67 mol % the solubility limit of $AlCl_3$ at ambient temperatures. It is reasonable to suppose that this decrease in C_{Cl} will be accomplished by a substantial increase in the Brønsted acidity of HCl in these media.

Experimental Section

General Procedures. All weighing and material transfers involving $AlCl_3$, EMIC, and their mixtures were carried out in an Ar-atmosphere glovebox in which the Ar was continuously circulated through a purification train that maintained the H_2O and O_2 levels at <1 ppm, each. $AlCl_3$–EMIC mixtures were prepared by slowly adding weighed amounts of $AlCl_3$ to weighed amounts of EMIC with continuous stirring.

Cyclic voltammetric measurements were carried out in the above glovebox with both tungsten and glassy-carbon disk electrodes. The reference electrode consisted of a 1-mm Al wire (Alfa, puratronic, 4N8) immersed in a $AlCl_3$–EMIC mixture saturated with $AlCl_3$ and separated from the main compartment by a fine-quartz frit. The counterelectrode, made from the same Al wire, was separated from the main compartment by a coarse-quartz frit. Instrumentation consisted of an EG&G PAR Model 173 potentiostat/galvanostat and a Model 175 waveform generator. Data were recorded on a Hewlett-Packard Model 7045A X-Y recorder.

UV–vis absorption spectra were measured on a Cary Model 14 spectrophotometer. The absorption cells consisted of 1-cm square silica cuvettes with vacuum-tight closures previously described.[7d] Precision

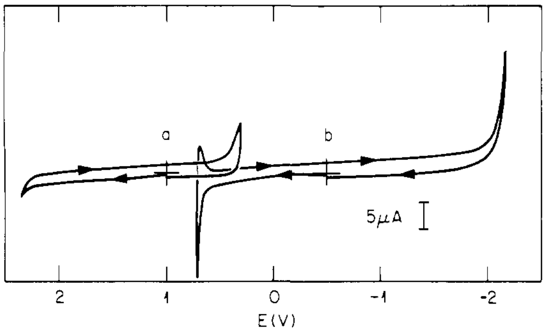

Figure 4. Cyclic voltammograms for $AlCl_3$–EMIC mixtures at a tungsten electrode (d = 4 mm) with ν = 0.1 V s^{-1}. Referenced to Al/$AlCl_3$–EMIC saturated with $AlCl_3$: (a) 67 mol % $AlCl_3$; (b) 45 mol % $AlCl_3$.

silica inserts were used to obtain short path lengths (50–100 μm). These short path lengths were calibrated with K_2CrO_4 in 0.05 N aqueous KOH (ϵ = 4842 M^{-1} cm^{-1} at 370.0 nm[16]).

Chemicals. $AlCl_3$ (Fluka, puriss) and IX (Eastman, scintillation grade) were purified as previously described.[7d] Ethyl chloride (Matheson) was used as received.

Acetonitrile (Burdick and Jackson) was predried overnight with 4-Å molecular sieves. Then, it was decanted into another flask and calcium hydride was added until gas no longer evolved. The CH_3CN was refluxed overnight and then distilled from CaH_2 onto 4-Å molecular sieves. The purified solvent was stored and transferred under argon.

1-Methylimidazole (Chemical Dynamics Corp.) was purified by standing overnight over KOH, then decanting onto fresh KOH and 3-Å Linde molecular sieves, then refluxing overnight, and, finally, fractionally distilling (bp 94° [15]) onto 3-Å Linde molecular sieves. The purified liquid was stored and transferred under argon.

The following arenes were purified before use by recrystallization from a suitable solvent [arene (source), recrystallization solvent, corrected mp (°C)]: I (Eastman), cyclohexane/methylene chloride, 68.5–69.0; IV (Eastman), acetone, 252.0–252.5; V (Eastman), low boiling (35–36 °C) petroleum ether, 34.5; VII (Aldrich, 99%), cyclohexane/methylene chloride, 50.5–51.0; VIII (Aldrich, 99%), cyclohexane/methylene chloride, 165.0–166.0; and X (Aldrich, 99%), hexane/methylene chloride, 183.0–183.5.

VI (Aldrich, Gold Label) was distilled under argon at atmospheric pressure (bp 162–163 °C), degassed by four freeze–pump–thaw cycles, and stored in an inert atmosphere glovebox over molecular sieves.

III [mp 115–115.5 °C (cor)] was prepared by the Wolff–Kishner reduction of fluorenone, recrystallized from ethanol, and sublimed. Purity was checked by capillary GC.

Preparation of EMIC. The reaction vessel was a 3-L, three-neck round-bottomed flask with stirring bar. Attached to the three 24/40 ₸ necks were a condensor and bubbler, a glass tube with frit, and a pressure-equalizing addition funnel. Teflon sleeves were used on all ₸ joints and grease was rigorously excluded from the system. The glass tube at its nonfrit end was connected by Teflon tubing and Swageloks to a three-way, oblique-bore stopcock with a Teflon plug, which in turn was attached to tanks of argon and ethyl chloride (EtCl). After sweeping the apparatus with argon, 460 g (447 mL, 5.61 mol) of distilled, dry 1-methylimidazole and 225 mL of distilled, dry acetonitrile were added to the reaction vessel by cannula through a white rubber septum at the top of the addition funnel. When addition was completed, the funnel was replaced by a thermometer whose tip was below the surface of the liquid. The stopcock was then turned to allow the EtCl to bubble very slowly through the solution. Since a small amount of EtCl was vented into the atmosphere, the reaction was performed in a hood. Once bubbling commenced, the vessel was heated to an internal temperature of 70 °C and bubbling was continued at this temperature for 1 week at which time the volume of liquid had been greatly increased. The resulting liquid was clear but slightly yellow. The EtCl atmosphere was then replaced by an Ar atmosphere and the solution cooled to room temperature. EMIC crystallized slowly from the cooled solution. This often required 24 h. After crystallization was complete, the supernatant liquid was removed by cannula and replaced by 160 mL of dry acetonitrile. Recrystallization from this solvent under Ar afforded very large colorless crystals, which were collected, ground to a powder in an Ar-atmosphere glovebox, and dried in an evacuated Abderhalden drying apparatus (Aldrich Z10, 318-7) over refluxing CCl_4. This generated 290 g of EMIC, mp 87.0 87.8 °C (cor) (lit.[8a] mp 82–87 °C), whose ^1H NMR spectrum showed no trace of impurity. From the combined mother liquors it was possible to get three additional crops of products. This gave a total yield of 583 g of EMIC (71% yield).

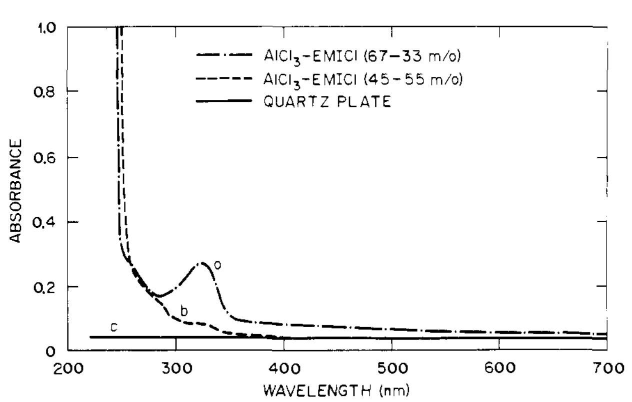

Figure 5. Spectra of $AlCl_3$–EMIC mixtures (silica cuvette, 1.0-cm path length; air reference, 25 °C): (a) 67 mol % $AlCl_3$; (b) 45 mol % $AlCl_3$; (c) silica plate. Note that reflective losses at melt/window interfaces are negligible so that (c) represents the total loss at the cell windows.

UV–Visible Spectral and Cyclic Voltammetric Characterization of Basic and Acid Melts. Background cyclic voltammograms (CV's) for $AlCl_3$–EMIC mixtures containing 45 and 67 mol % $AlCl_3$ at 25 °C were measured at a tungsten (d = 4 mm) disk electrode with results shown in Figure 4. The widths of the observed electrochemical windows were similar to those reported by Wilkes et al.[8a] and Karpinski et al.[8i] CV's previously reported[8a] for $AlCl_3$–EMIC mixtures showed the presence of large amounts of impurities, whereas background CV's on melts prepared in this laboratory showed no evidence of these impurities.

Figure 5 shows the UV–visible spectra for $AlCl_3$–EMIC mixtures in a 1-cm path length cell at 25 °C. An exceedingly weak band occurs at 324 nm for the basic (45 mol % $AlCl_3$) composition and a somewhat stronger band occurs at 320 nm for the acidic (67 mol % $AlCl_3$) composition. Additional weak shoulders between 260 and 270 nm are observed in both spectra. (Note that these absorptions are very small at the short path lengths used to measure the spectra of arenes and arenium ions.) The rapidly rising UV cutoff reaches an absorbance of unity at 244 nm for the 67 mol % mixture and 249 nm for the 45 mol % mixture. Exposure of either of these mixtures to moist air or gaseous HCl increased the absorbance in the 260–270-nm region but had no other effect on the spectra. Thus, the shoulders found in this region may be due to protic impurities.

Protic impurities in $AlCl_3$–EMIC (67 mol % $AlCl_3$) were quantified by the spectrophotometric determination of the 9*H*-anthracenium ion formed in dilute solutions of IX.[17] In five separate determinations using 10–21 mM IX, the concentration of the anthracenium ion was found to be 0.2–0.6 mM with an average of 0.3 mM. The 420-nm band of the 9*H*-anthracenium ion was used for these determinations. It has a high molar absorptivity (Table I), and correction can be made for a small absorption at 420 nm due to unprotonated IX.

Further evidence for the low content of oxidizing impurities in these melts is the fact that dilute solutions of POZ and PTZ in $AlCl_3$–EMIC (67 mol % $AlCl_3$) mixtures at 25 °C were found to be stable with no more than a trace (ca. 0.03 mM) of radical cations. The latter have band maxima at 270 nm (6.37 × 10^3 M^{-1} cm^{-1}) for $POZ^{\cdot +}$ and 257 nm (39.0 × 10^3 M^{-1} cm^{-1}) for $PTZ^{\cdot +}$.[15]

Electronic Spectra of Arenes in 55 mol % $AlCl_3$. Solutions of arenes in the $AlCl_3$–EMIC (55 mol % $AlCl_3$) molten salt were prepared by stirring a weighed amount of arene in a weighed amount of molten salt. The molar concentration of arene was deduced from the density of the melt.[8d]

Preparation and Electronic Spectra of Protonated Arenes in 55.0 mol % $AlCl_3$ under HCl Gas. Solutions of arenes were prepared as described above and transferred by pipette to the side arm of the hydrochlorination cell shown in Figure 6. The silica insert and its holder were then lowered into the cell and the vacuum stopcock closed to the outside. The cell was then removed from the glovebox and attached to a glass/Teflon apparatus by which HCl and Ar could be introduced into and removed from the cell. The gases were manipulated and pressures measured by standard manometric techniques. HCl (Matheson, electronic grade, minimum purity 99.995%) was further treated by passing through a train

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(16) Smith, G. P.; Boston, C. R. *J. Chem. Phys.* **1961**, *34*, 1396.

(17) The same method was used to determine protic impurities in acidic $AlCl_3$–BPC melts.[7d]

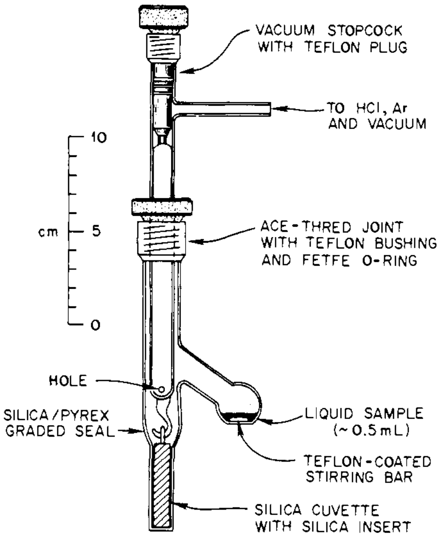

Figure 6. Protonation cell.

consisting first of anhydrous $CaSO_4$, then reduced copper oxide wire at 270 °C, and finally anhydrous $Mg(ClO_4)_2$. High-purity Ar was further treated by passing through a train consisting first of anhydrous $Mg(ClO_4)_2$ and then reduced copper oxide wire at 315 °C. Once the cell was fastened to the manometric apparatus, the connecting arm was evacuated and the cell slowly opened to a vacuum. Care had to be taken here because the stirred molten salt solution tended to froth. Once the frothing had subsided and the pressure at the pump reduced to less than 10^{-5} atm, the cell was isolated from the vacuum and HCl introduced at a pressure equal to the external atmospheric pressure. The virtually instantaneous color change indicated the protonation reaction to be rapid. Thorough mixing was achieved by stirring for several minutes. Then the vacuum stopcock was closed and the hydrochlorination cell disconnected from the manometric apparatus. The solution was then carefully poured into the cuvette by tipping the cell so that the solution filled all the space between the walls of the cuvette and the insert. The electronic spectrum was then recorded. In several experiments, the arene solution was first equilibrated with HCl at ca. 1 atm and then, with the solution still in the side arm, the cell was evacuated (care, frothing) until gas bubbles no longer formed. Then the cell was back-filled with Ar, disconnected from the manometric apparatus, and tilted so as to fill the cuvette with solution, after which the spectrum was recorded. In experiments on the effect of P_{HCl} on the protonation of V, the cell was filled with HCl to a predetermined pressure. After the mixture was stirred for several minutes, the HCl pressure was measured. Then the cell was closed and disconnected, the cuvette was filled, and the spectrum was recorded.

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Structure and Optical Properties of CdS Superclusters in Zeolite Hosts

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Abstract: Direct synthesis of CdS within the pore structure of zeolites leads to a novel supercluster with a structural geometry superimposed by the host framework. Detailed X-ray powder diffraction and EXAFS analysis together with optical absorption data reveal discrete $(CdS, O)_4$ cubes located within the small sodalite units of the structure which begin to interconnect as the loading density within the zeolite rises. The discrete cube building blocks consist of interlocking tetrahedra of Cd and S with a CdS bond length of 2.47 Å. At higher loadings these cubes begin to occupy adjacent sodalite units where the Cd atoms point toward each other through the double six-rings linking the sodalite moieties with a Cd–Cd distance of ~6 Å. As this three-dimensional interconnection proceeds, the corresponding changes in optical properties indicate a progression toward a semiconductor supercluster with behavior intermediate between that of the discrete CdS cubes and bulk semiconductor. Semiconductor superclusters of this type represent a novel class of materials where the three-dimensional structure and electronic properties can be controlled by using different zeolites as the template. The unique stability of the semiconductor clusters inside the sodalite units is due to the coordination of Cd atoms with the framework oxygen atoms of the double six-ring windows. The stability of the supercluster comes from the interaction between clusters in the adjacent sodalite units. We suggest that through-bond coupling is responsible for the interaction between clusters.

I. Introduction

Small metal and semiconductor clusters, having hybrid molecular and bulk properties, represent a new class of materials and are under intensive investigation. Many approaches exist for preparing these small clusters. Well-defined, mass-selected clusters up to hundreds of atoms can be generated in the gas phase with supersonic jet expansion techniques.[1-3] Many interesting properties of these "bare" clusters, including chemical reactivities, have been studied, although direct structure determination of these

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