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Latent Acidity in Buffered Chloroaluminate Ionic Liquids

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Chloroaluminate ionic liquids, or molten salts, formed from $AlCl_3$ and an organic chloride, typically 1-ethyl-3-methylimidazolium chloride (ImCl) or *N*-butylpyridinium chloride (BuPyCl), are liquid at room temperature.[1,2] These molten salts exhibit Lewis acid–base chemistry governed by the equilibrium

$$2\mathrm{AlCl_4^-(l)} \rightleftharpoons \mathrm{Cl^-(l)} + \mathrm{Al_2Cl_7^-(l)} \qquad K = 1 \times 10^{-17} \quad (1)$$

The melts are termed acidic or basic if the mole ratio of $AlCl_3$ to the organic chloride is greater than or less than 1.00. When exactly equimolar amounts of $AlCl_3$ and the organic chloride are mixed, a "neutral" melt is obtained in which the principal anionic species is $AlCl_4^-$; neutral melts obtained in this manner are not buffered but have an electrochemical window of 4.4 V.[3]

A method of producing and maintaining buffered neutral melts, which are of considerable interest as potential battery electrolytes, is to add NaCl(s) or LiCl(s) to an acidic melt.[4,5] The reaction

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

takes place, where M^+ is an alkali metal cation.

The addition of MCl to an acidic melt results in the dissolution of MCl equivalent to the number of moles of $Al_2Cl_7^-$ initially present and buffers the melt. If $Al_2Cl_7^-$ is generated, neutrality is maintained by dissolution of excess MCl(s); if chloride is generated, neutrality is maintained by precipitation of MCl(s). Recent work in our laboratory, however, has revealed an unexpected consequence of these buffered melts. These melts show a chemical behavior that we term "latent acidity". We report on the use of acetylferrocene as a probe of this behavior in nonbuffered and NaCl-buffered melts.

The chemistry of acetylferrocene in nonbuffered melts was reported by Slocum *et al.*[6] In basic melts, only free acetylferrocene was observed. In acidic melts, an $AlCl_3$ adduct was formed at the carbonyl group:

$$\mathrm{Fc(COMe)} + \mathrm{Al_2Cl_7^-} \rightleftharpoons \mathrm{Fc(C(O{:}AlCl_3)Me)} + \mathrm{AlCl_4^-} \quad (3)$$

where Fc = $(C_5H_5)Fe(C_5H_4\text{-})$. Formation of such adducts has been reported for carbonyl, cyanide, and ferrocyanide groups in acidic melts.[7–9] The adduct undergoes a 1-electron oxidation at a potential 400 mV positive of acetylferrocene itself.

In unbuffered neutral melts, we have found that a mixture of adduct and free acetylferrocene is formed (Figure 1), although the ratio of species varied from batch to batch of melt. However, the concentration of adduct was always less than 2 mM, and occasionally only free acetylferrocene was observed. We believe that the formation of the adduct in unbuffered neutral melts arises from the presence of a small amount of $Al_2Cl_7^-$, which is present simply as a result of the difficulty of preparing an "exactly" neutral melt.[3] The conventional method of preparing neutral melts is to add either ImCl to a slightly acidic melt or $AlCl_3$ to a slightly basic melt until no voltammetric waves indicative of $Al_2Cl_7^-$ reduction or Cl^- oxidation are observed. Previous work has shown that low concentrations of $Al_2Cl_7^-$ and Cl^- cannot be detected electrochemically.[10] Thus "neutral" melts may, in fact, be several millimolar in Cl^- or $Al_2Cl_7^-$, which cannot easily be detected.

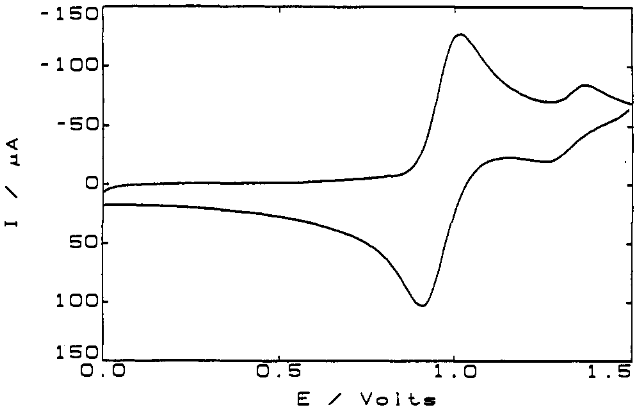

Figure 1. Acetylferrocene, 8.2 mM, on a glassy carbon disk electrode in an unbuffered "neutral" melt, 2 V/s. The potential is shifted 150 mV positive due to a reference electrode problem.

In contrast, addition of acetylferrocene to a neutral buffered melt, $[Na^+] = 0.36$ M, prepared by the addition of NaCl(s) to an initially acidic melt, i.e., one containing excess $AlCl_3$, resulted solely in the formation of the acetylferrocene–$AlCl_3$ adduct (Figure 2a), even at high concentrations of acetylferrocene (20 mM). Reverse-pulse voltammetric experiments on the oxidized adduct cation indicate that it suffers a loss of $AlCl_3$ to yield free acetylferrocene at the electrode surface (Figure 2b). In a melt containing high concentrations of sodium ions, a mixture of the adduct cation and acetylferrocene cation is observed. Intuitively, this is as expected as the electron density on the carbonyl group is decreased in the adduct cation and thus the interaction with the Lewis acid is weakened.

The behavior of acetylferrocene in a buffered melt clearly suggests that there is a source of $AlCl_3$ present which is not obviously present in the buffered melt itself. No aluminum deposition wave was observed in the buffered neutral melt at either platinum or glassy carbon electrodes, which implies that the concentration of $Al_2Cl_7^-$ is very low; however, recent work in a NaCl-buffered melt using a platinum electrode suggests that Al, at least to a small extent, may be deposited from the neutral buffered melt.[11] A possible source of $AlCl_3$, however, is $AlCl_4^-$, a very weak Lewis acid. In an unbuffered neutral melt, the equilibrium

$$\mathrm{Fc(COMe)} + \mathrm{AlCl_4^-} \rightleftharpoons \mathrm{Fc(C(O{:}AlCl_3)Me)} + \mathrm{Cl^-} \quad (4)$$

lies far to the left. The $AlCl_4^-$ is not a sufficiently strong Lewis acid for the reaction to occur. In a buffered melt, however, the reaction

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(1) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263.

(2) Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 323.

(3) Lipsztajn, M.; Osteryoung, R. A. *J. Electrochem. Soc.* **1983**, *130*, 1968.

(4) Melton, T. J.; Joyce, J.; Maloy, J. T.; Boon, J. A.; Wilkes, J. S. *J. Electrochem. Soc.* **1990**, *137*, 3865.

(5) Scordilis-Kelley, C.; Fuller, J.; Carlin, R. T.; Wilkes, J. S. *J. Electrochem. Soc.* **1992**, *139*, 694.

(6) Slocum, D. W.; Edgecombe, A. L.; Fowler, J. S.; Gibbard, H. F.; Phillips, J. *Organometallics* **1990**, *9*, 307.

(7) Cheek, G.; Osteryoung, R. A. *J. Electrochem. Soc.* **1982**, *129*, 2488 and 2739.

(8) Woodcock, C.; Shriver, D. F. *Inorg. Chem.* **1986**, *25*, 2137.

(9) Das, B.; Carlin, R. T.; Osteryoung, R. A. *Inorg. Chem.* **1989**, *28*, 421.

(10) Karpinski, Z. J., Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 4561.

(11) Riechel, T. L.; Wilkes, J. S. *J. Electrochem. Soc.* **1993**, *140*, 3104.

0002-7863/94/1516-2649$04.50/0

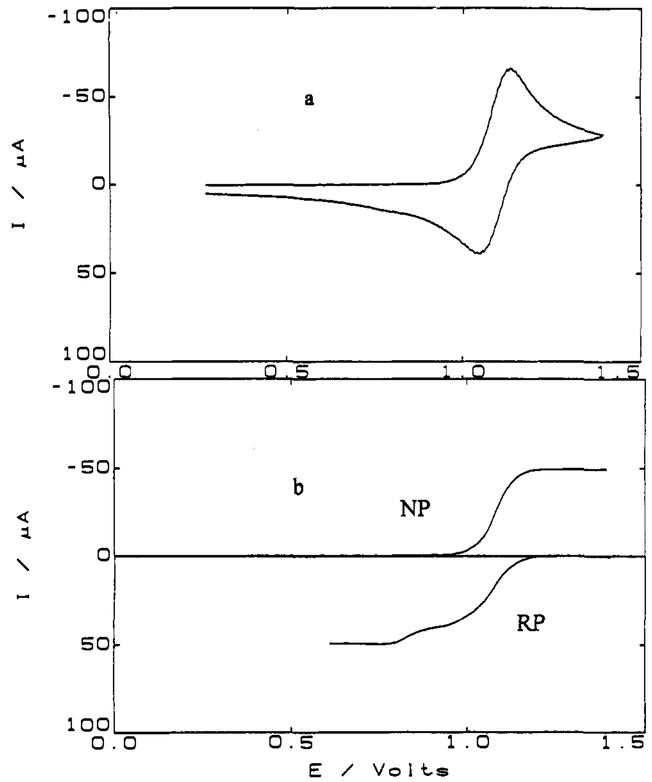

Figure 2. Acetylferrocene, 20 mM, in a buffered melt, $[Na^+] = 0.36$ M: (a) cyclic staircase, 200 mV/s; (b) normal pulse voltammetry ($t_p = 0.2$ s, $t_w = 2$ s, $E_i = 0.6$ V); reverse-pulse voltammetry ($t_p = 0.2$ s, $t_w = 2$ s, $E_i = 1.4$ V).

$$Fc(COMe) + AlCl_4^- + Na^+(l) \rightleftharpoons Fc(C(O{:}AlCl_3)Me) + NaCl(s) \quad (5)$$

can take place; the generation of chloride ion results in the precipitation of Na^+ to yield NaCl(s), thus providing a driving force to pull the equilibrium to the right.

To test this hypothesis, we prepared an acidic melt which was ~40 mM in $AlCl_3$ (Al deposition evident) and added NaCl(s). A neutral melt electrochemical window was observed. Acetylferrocene was then added to the neutral buffered melt and its electrochemistry examined. The adduct was the only species present in a 35 mM solution of acetylferrocene, Figure 3a. As the concentration of acetylferrocene was increased to 61 mM, a second wave, due to uncomplexed acetylferrocene, appeared, Figure 3b, as predicted by eq 5. That is, once all the sodium ions precipitated, no adduct could form (eq 4).

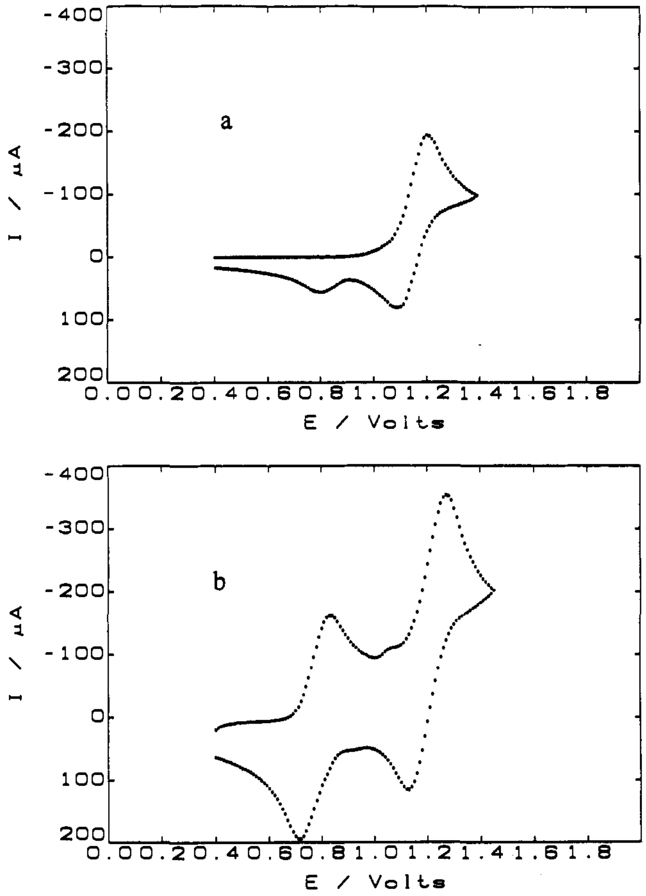

Figure 3. Cyclic staircase voltammogram of acetylferrocene in a buffered melt, ~40 mM Na^+; 500 mV/s; [acetylferrocene], (a) 35 mM, (b) 61 mM.

In conclusion, MCl-buffered melts exhibit latent acidity in the presence of a weak Lewis base. These melts are an excellent medium in which to study $AlCl_3$ complexation, allowing precise control of the amount of $AlCl_3$ available for complexation and possessing a very large electrochemical window in which to observe complexed species.

A more detailed spectroscopic and electrochemical investigation of the acid–base equilibria in buffered melts is in progress.[12]

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(12) Quarmby, I. C.; Mantz, R. A.; Goldenberg, L. M.; Osteryoung, R. A., work in progress.