Here we discuss the concept of latent acidity in neutral buffered chloroaluminate ionic liquids. Latent acidity involves a reaction between a weak organic base and a Lewis or Bronsted acid in a buffered chloroaluminate melt. The reactions are

\[ B: + AlCl_4^- + M^+ = B:AlCl_3 + MCl(s) \]
\[ HC1 + B: + M^+ \rightarrow B:H^+ + MCl(s) \]

where \( B: \) is an organic base that can form an aluminum chloride or protonated adduct, and \( M^+ \) is an alkali metal (or alkaline earth) cation. Neither of these reactions will take place in basic or neutral, but unbuffered, melts. Both reactions are driven by the precipitation of the \( MCl(s) \), and the acidity depends on the alkali metal cation used, with the acidity increasing \( Li^+ > Na^+ > K^+ \).

INTRODUCTION

As is well known, the fundamental solvolysis equation of ambient temperature chloroaluminate ionic liquids composed of either \( N,N'- \text{butylpyridinium chloride} \) \( \text{(BuPyCl)} \) or \( 1 \)-ethyl-3-methylimidazolium chloride \( \text{(ImCl)} \), and aluminum chloride, is:

\[ 2 \text{AlCl}_4^- \rightleftharpoons \text{Al}_2\text{Cl}_7^+ + \text{Cl}^- \]  

[1]

Melts containing an excess of the organic chloride are referred to as basic, as they contain chloride ion, a Lewis base. Those containing an excess of \( \text{AlCl}_3 \) are acidic, and contain the strongly Lewis acidic heptachlorodialuminate, \( \text{Al}_2\text{Cl}_7^- \), ion. Those melts where the mole ratio of the organic chloride to the aluminum chloride is unity are “neutral”.3 “Neutral” melts were of much initial interest, in large part the result of their very large – about 4.5V – electrochemical window. However, they were difficult to prepare, and difficult to maintain neutral. This is because the neutrality condition,

\[ [R^+] = [\text{AlCl}_4^-] \]  

[2]
where \( R^+ \) is the organic cation, is easily upset by addition of very small amounts of acid or base.

**NEUTRAL BUFFERED MELTS**

The discovery of “neutral buffered” chloroaluminate ambient temperature ionic liquids generated renewed interest in these systems, since it generated melts with the wide electrochemical window of the “neutral” melts, but which were simple to both prepare and maintain neutral.\(^4\) In addition, it proved possible to deposit Li and Na from LiCl and NaCl neutral buffered melts.\(^5\)

Neutral buffered melts were initially prepared by adding an alkali chloride, MCl, to an acidic melt, resulting in the reaction:

\[
\text{Al}_2\text{Cl}_7^+ + \text{MCl(s)} \rightarrow 2 \text{AlCl}_4^- + \text{M}^+ \tag{3}
\]

The neutrality condition is:

\[
[R^+] + [M^+] = [\text{AlCl}_4^-] \tag{4}
\]

and MCl is insoluble in the now neutral melt. It was subsequently found that melts could be buffered from both the acidic and basic side; in the latter case, for example, MgCl\(_2\) reacts as follows:\(^6\)

\[
\text{MgCl}_2 + 2 \text{Cl}^- \rightarrow \text{MgCl}_4^{2-} \tag{5}
\]

In this instance, MgCl\(_2\) is insoluble in the neutral melt, and the neutrality condition is:

\[
2 [\text{MgCl}_4^{2-}] + [\text{AlCl}_4^-] \approx [R^+] \tag{6}
\]

CaCl\(_2\), perhaps surprisingly, buffers the melt from the acidic side.\(^7\)

**LATENT ACIDITY**

Serendipity played a part in the discovery of what we have termed “latent acidity”. We were investigating the electrochemistry of acetylferrocene, Fc(COME), where Fc = (C\(_5\)H\(_5\))Fe(C\(_5\)H\(_4\)). This had been reported to form an AlCl\(_3\) adduct:
which underwent a 1-electron oxidation at -400 mV positive of the uncomplexed acetyl ferrocene. In a basic or neutral, but unbuffered melt, no AlCl₃ adduct was formed; in an acidic melt, only the adduct oxidation was seen. We found that in a neutral melt buffered with NaCl, where the concentration of Na⁺ exceeded the concentration of acetylferrocene in solution, only the complex oxidation wave was seen. If the concentration of the alkali ion in the melt was, for example, some portion of the concentration of acetylferrocene, both the uncomplexed and complexed acetylferrocene oxidation waves were observed. We then confirmed that, quantitatively, the reaction that took place was:

\[
\text{Fc(COME)} + \text{AlCl}_4^- + \text{Na}^+ = \text{Fc(C(O:AlCl₃)Me)} + \text{NaCl(s)} \tag{8}
\]

The driving force for this reaction, which does not take place in the absence of the buffering alkali halide, is provided by the precipitation of the NaCl. Both electrochemical (rotating disc) and spectroscopic measurements verified the quantitative aspects (stoichiometry) of this equation.

The use of other bases, such as dimethylaniline, DMA, which also form an AlCl₃ adduct, was investigated. In this case, NMR was used to follow the chemical reaction, postulated to be:

\[
\text{DMA} + \text{AlCl}_4^- + \text{Na}^+ \rightarrow \text{DMA:AlCl₃} + \text{NaCl(s)} \tag{9}
\]

The \(^1\)H NMR spectrum of the methyl hydrogen shows a single line. The chemical shift is proportional to the population weighted average of the spectrum of the AlCl₃:DMA adduct and the free DMA, since there is a fast exchange between the DMA and the DMA:AlCl₃ adduct. The chemical shift of the DMA methyl protons were followed as a melt containing a given concentration of sodium ion was titrated with DMA. When the amount of DMA added to the melt was less than the amount of sodium ion, the chemical shift was that of the adduct. When the concentration of DMA added to the melt started to exceed the amount of sodium ion in the initial solution, the chemical shift decreased linearly with the amounts of DMA in excess of the sodium ion.

We were also able to show that in the case of a melt buffered with CaCl₂ that the reaction:

\[
2 \text{Fc(COME)} + 2 \text{AlCl}_4^- + \text{Ca}^{++} \rightarrow 2 \text{Fc(C(O:AlCl₃)Me)} + \text{CaCl}_2(s) \tag{10}
\]
probably takes place. Again, the voltammetry of the acetylferrocene was followed during a titration of a CaCl\(_2\) buffered melt. The experimental stoichiometric value for the ratio of Fc(COMe)/Ca\(^{2+}\) was about 2.2; the reason for this considerable discrepancy, compared to the results for melts buffered with NaCl is not known.

It had been known for some time that the proton, in an acidic melt, behaved as a superacid\(^{11,12}\). We were curious to see if the proton in a buffered neutral melt would also show the latent acidity effect. That is, would the following reaction, where M\(^+\) is an alkali or alkaline earth cation, take place?

\[
\text{HCl} + \text{B}: + \text{M}^+ \rightarrow \text{B}:\text{H}^+ + \text{MCl}(s) \tag{11}
\]

B: is a weak base, an organic arene, such as 9, 10 – dimethylanthracene, DMAn. Arenes were used by Smith et al in their studies of superacidity, and we have investigated the chemistry and electrochemistry of anthracene in acidic melts containing protons\(^{11,12,13}\). Figure 1 shows the electrochemical behavior of DMAn in a buffered melt, with and without the addition of HCl(g)\(^{14}\). In 1-a, the typical voltammogram of DMAn is seen; similarly to anthracene, it forms a radical cation and then a dication on oxidation. When protonated, upon addition of HCl(g), the oxidation wave decreases in magnitude, and a cathodic peak from the reduction of the protonated DMAn is seen at ca +0.3V; this is very similar to the behavior we had observed for anthracene in an acidic melt containing proton\(^{13}\). It clearly indicated that the neutral buffered melt possessed latent acidity, since DMAn is not protonated in a neutral unbuffered, or basic, melt containing HCl.

Figure 1. Cyclic staircase voltammogram (working electrode: glassy carbon electrode, scan rate: 500mV/sec) of 9,10-dimethylanthracene in a NaCl (originally 55 mole% AlCl\(_3\)) buffered melt. (a.) Before adding HCl(g) to the melt, (b.) after adding ca 1 atm HCl(g) to the melt.
Equation 11 above would have an equilibrium constant:

\[ K = \frac{[B : H^+]}{[B : ] [M^+] P_{HCl}} \]  \[12\]

and, rearranging:

\[ \frac{[B : H^+]}{[B : ]} = K [M^+] P_{HCl} \]  \[13\]

The ratio of B:H\(^+\) to B: for the arene bases used was determined spectrophotometrically. A plot of the protonation ratio, \([B:H^+]/[B:H^+][B:]\), is shown in Figure 2. If the data shown are plotted against \(P_{HCl}\) as per equation 13, straight lines result.\(^{15}\) It was also found that for melts of a given initial acidity – the same mole ratio of AlCl\(_3\) to ImCl prior to buffering – there was a large difference in the extent to which equation 11 proceeded to the right which depended on the alkali halide used as the buffering agent.\(^{15,16}\) We found that the acidity of the buffering agent increased in the order Li\(^+\) > Na\(^+\) > K\(^+\).\(^{16}\) This is in accord with Gutmann acceptor studies on the buffered melt which showed the same order of the alkali metal cation acidities.\(^{17}\)

![Figure 2. Degree of protonation of 9,10-dimethylantracene versus pressure of HCl (mmHg) for various NaCl buffered melt systems.](image)

Figure 2. Degree of protonation of 9,10-dimethylantracene versus pressure of HCl (mmHg) for various NaCl buffered melt systems. (initially 55 mole% AlCl\(_3\) ———

♦ ——, initially 60 mole% AlCl\(_3\) ——▲—).
One possible explanation for this is that the solubility of HCl(g) in the buffered melts might differ depending on the alkali metal cation used. This was not the case; the solubility of HCl as a function of the partial pressure of HCl(g) was linear with $P_{HCl}$ and within experimental error, was the same for melts buffered with LiCl, NaCl, KCl, or unbuffered at the same initial acidity.\textsuperscript{16}

This behavior was examined further by measuring the relative solubility of the alkali metal chlorides. That is, we assume solubility product relationships:

$$K_{sp}(M) = [M^+][Cl^-]$$ \hspace{1cm} [14]

For melts buffered with both LiCl and NaCl:

$$K_{sp}(Na)/K_{sp}(Li) = [Na^+)/[Li^+]$$ \hspace{1cm} [15]

It was found that LiCl is less soluble than NaCl which is less soluble than KCl. For instance, the mole ratio of $[Na^+)/[Li^+]$ was ~ 80/1, independent of the mole ratio of AlCl$_3$ to ImCl prior to buffering. This solubility order would tend to force equation 11 to the right in the order found, $Li^+ > Na^+ > K^+$.

Similar experiments were performed to ascertain the relative solubility product of CaCl$_2$ with respect to LiCl.\textsuperscript{16} That is we used the relationship:

$$K_{sp}^2(LiCl)/K_{sp}(CaCl_2) = [Li^+]^2/[Ca^{2+}]$$ \hspace{1cm} [16]

and buffered a melt with both CaCl$_2$ and LiCl. A plot of the experimentally determined ratio is shown in Figure 3 below. Note that the X-axis in this figure essentially is the initial acidity -- i.e., the initial concentration of AlCl$_3$ in the acidic melt -- since the $[Li^+] >> [Ca^{2+}]$. The average ratio, $K_{sp}^2(LiCl)/K_{sp}(CaCl_2)$, was found to be ~2000 M. This means that CaCl$_2$ is more acidic than LiCl, the most acidic of the alkali metal cations.
Figure 3. Concentration of calcium vs concentration of lithium in melts buffered with both CaCl₂ and LiCl. Line is best-fit to data assuming \([\text{Li}^+]^2/[\text{Ca}^2+]\) is constant, as per equation 16.

As far as we know, there is one report on the use of the buffered melt/latent acidity concept in synthesis.\(^{18}\) This work examined the linear dimerisation of but-1-ene, using a Ni-catalyst. It was found necessary to remove the excess LiCl, the buffering agent, from the 1-butyl-4-methylpyridinium chloroaluminate buffered melt, for the catalyst to function. These authors also partially buffered a melt with organic bases, pyridine derivatives, to inactivate proton.

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