We have observed that it is possible to buffer 1-ethyl-3-methylimidazolium chloride (EMIC) – AlCl₃ melts to neutrality using MgCl₂ or CaCl₂. CaCl₂ acts as a base, buffering acidic (AlCl₃-rich) melts, while MgCl₂ acts as an acid, buffering basic (EMIC-rich) melts. The electrochemical window of both buffered melts is about 4.4V, the same as that of a neutral (equimolar) melt and wider than that of an acidic or basic melt.

CaCl₂ buffers melts by forming the Ca²⁺ ion. CaCl₂-buffered melts have greater ‘residual’ acidity than melts buffered with alkali metal chlorides, as shown by potentiometric analysis with an Ag/AgCl electrode, and studies of the relative solubility products of LiCl and CaCl₂.

MgCl₂ buffers basic melts by taking up chloride ions to form the MgCl₄²⁻ ion. MgCl₂ is a weaker acid than CdCl₂ but a stronger acid than NiCl₂.
INTRODUCTION

1-ethyl-3-methylimidazolium chloride/aluminum chloride (EMIC/AlCl₃) room-temperature melts have attracted considerable interest due to their interesting acid-base properties, their low freezing point and wide liquid composition range at room temperatures, and their wide electrochemical window (up to 4.4V for an equimolar mixture).

The acidity of the melts may be defined using the mole ratio R = n_{AlCl₃}/n_{EMIC}. Melts containing an excess of EMIC (R<1) contain the anions AlCl₄⁻ and Cl⁻; since chloride is a Lewis base, these melts are referred to as basic. Melts containing an excess of AlCl₃ (R>1) contain the anions AlCl₄⁻ and Al₂Cl₇⁻; since the Al₂Cl₇⁻ ion is a strong Lewis acid, these melts are referred to as 'acidic'. Melts containing equal amounts of the two components (R=1) contain only the AlCl₄⁻ ion, and are referred to as 'neutral'. The acid-base chemistry of the melts may be described by the following reactions;

\[ \text{EMIC} + \text{AlCl}_3 \rightarrow \text{EMI}^+ + \text{AlCl}_4^- \quad (1) \]

\[ \text{AlCl}_4^- + \text{AlCl}_3 \rightarrow \text{Al}_2\text{Cl}_7^- \quad (2) \]

\[ 2\text{AlCl}_4^- \leftrightarrow \text{Cl}^- + \text{Al}_2\text{Cl}_7^- \quad (3) \]

Reaction (3) is the 'solvolysis' reaction for the melts. The electrochemical window of the melts is defined by the melt acidity. In basic melts, the anodic limit (relative to Al/Al(III) in a 1.5:1 melt, the standard reference electrode for these systems) is at about +1V, due to the oxidation of chloride. The cathodic limit is at about -1.9V, due to the reduction of the EMI⁺ ion. In acidic melts, the anodic limit is at about +2.5V, due to the oxidation of the AlCl₄⁻ to give chlorine, while the cathodic limit is at about -0.5V due to the deposition of aluminum metal from the Al₂Cl₇⁻ ion. In a neutral melt, where neither Cl⁻ nor Al₂Cl₇⁻ is present in significant amounts, the voltage window is about 4.4V, limited by the reduction of EMI⁺ and the oxidation of AlCl₄⁻. However, it is difficult to work with neutral melts as they are not buffered, and the addition of even small amounts of acidic or basic species destroys the condition of neutrality.

Melton et al(2) reported that it is possible to buffer acidic melts to neutrality using alkali metal chlorides. The buffering reaction is;

\[ \text{Al}_2\text{Cl}_7^- + \text{MCl(s)} \leftrightarrow \text{M}^+ + 2\text{AlCl}_4^- \quad (4) \]

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The alkali metal chloride is sparingly soluble in the neutral melt, so once all the $\text{Al}_2\text{Cl}_7^-$ has reacted, no more chloride goes into solution. This gives a neutral buffered melt with a 4.5V electrochemical window. Noel and Osteryoung(3) reported that $\text{CdCl}_2$ will buffer basic melts to neutrality. The reaction is

$$\text{CdCl}_2(\text{s}) + 2\text{Cl}^- \rightarrow \text{CdCl}_4^{2-} \quad (5)$$

Once all the chloride has reacted with the $\text{CdCl}_2$, the melt is neutral. If more chloride is added, it reacts with more $\text{CdCl}_2$ to give $\text{CdCl}_4^{2-}$, while if an acid (a chloride acceptor) is added, it will take up chloride from the $\text{CdCl}_4^{2-}$, precipitating $\text{CdCl}_2$. The electrochemical window of these melts is limited by the deposition of Cd metal at about -1V.

We have observed that it is possible to buffer acidic melts to neutrality using $\text{CaCl}_2$, while it is also possible to buffer basic melts using $\text{MgCl}_2$.

**BUFFERING WITH $\text{CaCl}_2$**

Calcium chloride buffers acidic melts to neutrality, according to the reaction;

$$\text{CaCl}_2 + 2\text{Al}_2\text{Cl}_7^- \rightarrow \text{Ca}^{2+} + 4\text{AlCl}_4^- \quad (6)$$

Calcium chloride is sparingly soluble in the basic melt, so once all the $\text{Al}_2\text{Cl}_7^-$ has reacted, no further chloride is introduced into the melt. A cyclic voltammogram of a R=1.1:1 melt buffered with $\text{CaCl}_2$ is shown in figure 1. The electrochemical window of the melts is the same as that of a neutral melt, though a small deposition/stripping peak is sometimes visible at $\approx -0.5$V; this is probably due to the deposition of Al or an Al/Ca alloy. The concentration of $\text{Al}_2\text{Cl}_7^-$ is low enough, however, that this peak is very small.

In order to determine the limit of the buffering capacity of $\text{CaCl}_2$, a series of melts with mole ratios $1.05 \leq R \leq 1.4:1$ were prepared, and were stirred with excess $\text{CaCl}_2$ for three days. After this time, the melts were filtered, hydrolyzed and the resulting solutions analyzed for calcium by atomic absorption. The results are shown in figure 2. The concentration of $\text{Ca}^{2+}$ increases with initial melt acidity up to a mole ratio of about $R=1.25:1$, in keeping with equation (6), and above this initial mole ratio the concentration of $\text{Ca}^{2+}$ is seen to reach an approximately constant value (about 0.35molkg$^{-1}$).

We have previously(4) determined the residual acidity of LiCl-buffered melts from the potential of an Al electrode in the melts. However, the potential of these
electrodes is not reproducible in the CaCl$_2$-buffered melts. We attempted to use the Ag/AgCl electrode as a chloride-sensitive electrode in these melts. The electrode reaction is:

$$\text{AgCl(s)} + e^- \leftrightarrow \text{Ag(s)} + \text{Cl}^-$$  \hspace{1cm} (7)

Since this is a one-electron, one-chloride reaction, the Nernstian potential would be:

$$E = E^o - RT/F \ln [\text{Cl}^-]$$  \hspace{1cm} (8)

giving a slope of 25.67mV per log unit at 25°C. As $E^o$ is not known, and to determine whether the electrode behaves ideally, it was necessary to calibrate the electrodes.

The electrodes were prepared by anodizing an Ag wire (Goodfellow, 99.99%) in a 50mM aqueous solution of NaCl, rinsing in water and drying. The electrodes were calibrated by dipping into a series of melts of known composition (0.85≤R≤1.10:1). The electrodes were stable in the melts with 0.92≤R≤1.05:1. In the other melts, the electrodes were stable for about 10min, after which time the potential began to drift. When these electrodes were removed from these melts after several hours standing, the (black) coating of AgCl on the electrode had been stripped off. The reaction may be

$$\text{AgCl(s)} + \text{Al}_2\text{Cl}_7^- \rightarrow \text{Ag}^+ + 2\text{AlCl}_4^-$$  \hspace{1cm} (9)

$$\text{AgCl(s)} + \text{Cl}^- \rightarrow \text{AgCl}_2^-$$  \hspace{1cm} (10)

The calibration data points were fitted to the following function:

$$E = a + b \ln[\text{Cl}^-]$$  \hspace{1cm} (11)

giving $a=-97\pm14$ mV and $b=-24.9\pm0.2$ mV. In calculating the chloride concentration of the melts used for calibration, it was necessary to assume a value for the equilibrium constant of reaction (3). The value used was $K_{solv}=10^{-17}$. There is some uncertainty as to the value of $K_{solv}$, with published values(1,5-7) ranging between $10^{-16.3}$ and $10^{-16.7}$. For the slope to be equal to the reversible one-electron value of -25.67mV, it would be necessary for $K_{solv}$ to be about $2.7\times10^{-17}$ ($10^{-16.8}$).
It was necessary to determine the liquid junction potential between an acidic melt and a CaCl₂-buffered melt. To determine this, the potential of an aluminum electrode was measured in a partly-buffered melt (with known concentrations of AlCl₄⁻, Al₂Cl₇⁻ and Ca²⁺). The difference between the expected potential of the electrode (from the concentration of AlCl₄⁻ and Al₂Cl₇⁻) and the measured potential gave the liquid junction potential as. The full procedure has been described previously(4).

After this, the electrode was used to determine the chloride concentration in CaCl₂-buffered melts. The results are shown in figure 3. The Al₂Cl₇⁻ concentration is in the range 2-25mM. In fitting a ‘best fit’ line to the data, it was assumed that the ‘solubility product’ for CaCl₂ is third-order $K_{sp} = [Ca^{2+}][Cl^-]^2$. The work with the relative solubility products of CaCl₂ and LiCl (vide infra) indicates that the solubility product is probably third-order, so the data was fitted to a ‘constant third-order solubility product’ function, giving a best-fit value of

$$K_{sp} (CaCl_2) = (1.3±0.9) \times 10^{-28} M^3$$ (12)

The results indicate that the CaCl₂-buffered melts have a much higher residual concentration of Al₂Cl₇⁻ than do LiCl-buffered melts, where the concentration(4) is in the range 30-800µM. Experiments were also carried out to determine the relative values of the solubility products of LiCl and CaCl₂. If the solubility products are defined as;

$$K_{sp} (CaCl_2) = [Ca^{2+}][Cl^-]^2$$ (13)

$$K_{sp} (LiCl) = [Li^+][Cl^-]$$ (14)

Then,

$$K_{sp}^2(LiCl) = [Li^+]^2[Cl^-]^2$$ (15)

Then, eliminating $[Cl^-]^2$ from equations (13) and (15) gives

$$\frac{K_{sp}^2(LiCl)}{K_{sp}(CaCl_2)} = \frac{[Li^+]^2}{[Ca^{2+}]}$$ (16)

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Therefore, the concentration of Ca\(^{2+}\) should be proportional to the square of the lithium concentration. Melts with a known (acidic) mole ratio were prepared, and buffered by stirring with both LiCl and CaCl\(_2\). After about three weeks, the melts were filtered (to remove solid chlorides), hydrolyzed and the resulting solutions were analyzed for Li\(^+\) and Ca\(^{2+}\) by atomic emission spectroscopy and atomic absorption spectroscopy. The results are shown in figure 4. The concentration of Ca\(^{2+}\) is approximately proportional to the square of the Li\(^+\) concentration, and the best-fit ratio is \([\text{Li}^+]^2/[\text{Ca}^{2+}] = 14\text{M}\). Again, these results show that a CaCl\(_2\)-buffered melt is more acidic than a LiCl-buffered melt with the same mole ratio prior to buffering.

**BUFFERING WITH MgCl\(_2\)**

Magnesium chloride reacts with basic melts\(^{(8)}\) according to the following reaction:

\[
\text{MgCl}_2(s) + 2\text{Cl}^- \rightarrow \text{MgCl}_4^{2-} \tag{17}
\]

Once all the free chloride has reacted, the melt is neutral. A cyclic voltammogram of an R=0.95:1 melt buffered with MgCl\(_2\) is shown in figure 5. The electrochemical window of the melts is about 4.4V, running from EMI\(^+\) reduction at -1.9V to AlCl\(_4^-\) oxidation at +2.5V. In some cases, a peak at about +1.9V was observed, usually if the (glassy carbon) electrode had been in the glove-box for a while. The peak appears to be due to the reaction of some impurity on the glassy carbon electrode surface with the Mg-containing melt; it was not observed in other melts at a glass carbon electrode, nor in Mg-containing melts at a Pt electrode.

In order to determine the limit of the buffering capacity of MgCl\(_2\), basic melts with mole ratios of 0.55 - 0.97:1 were stirred with excess MgCl\(_2\) for two days. Each melt was filtered, weighed and hydrolyzed, and analyzed for magnesium using atomic absorption spectroscopy. Melts with R\(\geq 0.65\) contained the amount of Mg which would be expected if all the chloride was used to form MgCl\(_4^{2-}\) complex ions, while the more basic melts (R\(< 0.60\)) contained less Mg than expected. The results of these measurements are shown in figure 6. The maximum concentration of magnesium in the melts is about 0.75mol/kg. From the data obtained, it is possible to calculate the number of chlorines per magnesium ion (x in MgCl\(_{x}^{(x-2)}\)), as 4.0±0.2, corresponding to the ion MgCl\(_{4}^{2-}\).

Experiments were carried out to compare the behavior of the transition metal species, NiCl\(_2\) and CdCl\(_2\), in the MgCl\(_2\) buffered melts to the behaviour which is observed in basic or acidic melts. In the AlCl\(_3\)-NBPC (N-butylpyridinium chloride) melts, NiCl\(_2\) exists as the NiCl\(_2^{2-}\) complex in basic melts with absorption peaks at 658 and 705 nm\(^{(9)}\). In acidic melts, it exists as NiCl\(_2\) which has a weak and uncharacteristic
Two basic melts were prepared, both with a mole ratio of $R=0.91:1$ and containing 12 mM of NiCl$_2$. One melt was stirred with excess MgCl$_2$ for one week. The melt without MgCl$_2$ showed a standard NiCl$_4^{2-}$ spectrum, with peaks at 656 and 706 nm. The melt that had been stirred with MgCl$_2$ showed almost no absorbance in the 400-800 nm range. From the spectrum, it appears that NiCl$_4^{2-}$ is not present in the MgCl$_2$ buffered melts. This can be explained if NiCl$_2$ is a weaker acid than MgCl$_2$, so that the reaction below goes to the right

$$\text{NiCl}_4^{2-} + \text{MgCl}_2 \rightleftharpoons \text{NiCl}_2 + \text{MgCl}_4^{2-} \quad (18)$$

CdCl$_2$ was also used as an acid-base probe. It has previously been shown$^2$ that CdCl$_2$ will buffer basic melts to neutrality, and that the melt window is limited by cadmium deposition, at $\approx -1V$. When a melt was stirred with both MgCl$_2$ and CdCl$_2$, the peak at $\approx -1V$ was observed to be very similar to that in a melt buffered with CdCl$_2$. Therefore, the reaction below does not proceed

$$\text{MgCl}_2 (s) + \text{CdCl}_4^{2-} \rightleftharpoons \text{MgCl}_4^{2-} + \text{CdCl}_2 (s) \quad (19)$$

and thus melts buffered with both chlorides contain a large amount of CdCl$_4^{2-}$. A sample of the melt was filtered, hydrolyzed and analyzed for magnesium by atomic absorption spectroscopy; the magnesium concentration was about 1% of that expected if the melt were buffered with MgCl$_2$.

Also, the chloride concentration in the MgCl$_2$-buffered melts was determined using the Ag/AgCl electrode. Preliminary results indicate that the liquid junction potentials between MgCl$_2$-buffered melts and acidic melts are less than 25mV. Therefore, in these admittedly preliminary results, the liquid junction potential between an acidic melt and a melt containing the MgCl$_4^{2-}$ ion was ignored. A liquid junction potential of 25mV would lead to approximately a factor of 2 error in the chloride concentration. The results are shown in figure 7, indicating that the chloride concentration is in the range 40-200$\mu$M, depending on the initial mole ratio.

**EXPERIMENTAL**

The preparation of EMIC, by reaction of ethyl chloride with 1-methylimidazole, followed by recrystallisation from acetonitrile/ethyl acetate, has been described previously($1,10$) Aluminum chloride (Fluka, puriss.$>99\%$) was distilled in a sealed, high-pressure glass tube. Basic (EMIC-rich) melts were prepared by mixing the appropriate amounts of EMIC and AlCl$_3$, and then protons and oxide were removed by
the application of a high vacuum and by treatment with phosgene, respectively (11,12). More AlCl₃ was then added to bring the melt to the required mole ratio. All work was carried out in a glove-box filled with dry nitrogen.

The buffered melts were prepared by either stirring a basic melt with excess MgCl₂ overnight, or by stirring an acidic melt with excess CaCl₂ for 2-3 days. At the end of these times, the melts were tested voltametrically to check that they were now neutral.

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Figure 1: Cyclic staircase voltammogram of a R=1.1:1 acidic melt buffered with CaCl$_2$. Sweep rate 100mV/s. Reference electrode: Al/Al(III) in a R=1.5:1 acidic melt. Working electrode: glassy carbon, 3mm$^2$. Counter electrode: Al

Mole ratio prior to buffering: 

Figure 2: Observed (data points) and theoretical (line) concentrations of Ca$^{2+}$ in acidic melts buffered with CaCl$_2$, vs initial mole fraction prior to buffering. Theoretical concentrations calculated using the reaction:

CaCl$_2$ + 2Al$_2$Cl$_7^- \rightarrow$ Ca$^{2+}$ + 4AlCl$_4^-$

Figure 3: Al$_2$Cl$_7^-$ concentration in CaCl$_2$-buffered melts vs. initial mole ratio prior to buffering. Concentrations determined using the Ag/AgCl electrode.

Figure 4: Concentration of Ca$^{2+}$ vs concentration of Li$^+$, in acidic melts buffered with both LiCl and CaCl$_2$. Line is best-fit line to equation (16)
Figure 5: Cyclic staircase voltammogram of a R=0.9:1 basic melt buffered with MgCl₂. Sweep rate 500mV/s. Reference electrode; Al/Al(III) in a R=1.5:1 acidic melt, working electrode; Glassy carbon, 3mm², counter electrode; Al.

Figure 6: Observed (data points) and theoretical (line) concentration of Mg²⁺ in basic melts buffered with MgCl₂, vs initial mole fraction prior to buffering. Theoretical concentrations calculated using the reaction:

\[ \text{MgCl}_2(s) + 2\text{Cl}^- \rightarrow \text{MgCl}_4^{2-} \]

Figure 7: Chloride concentration in MgCl₂ - buffered melts, vs. initial mole ratio prior to buffering. Concentrations determined using the Ag/AgCl electrode.

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