REACTION OF CHLORINE WITH AMBIENT TEMPERATURE CHLOROALUMINATE MOLTEN SALTS

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ABSTRACT

Chlorine is a potentially useful cathode in electrochemical cells using low melting chloroaluminate molten salts as the electrolyte. Chlorine generated electrochemically in 1-methyl-3-ethylimidazolium chloride – aluminum chloride melts or bubbled in the melt reacts with the imidazolium cation. The melt may be converted quantitatively to one where the cation is 4,5-dichloro-1-methyl-3-ethylimidazolium. Both basic and acidic melts are chlorinated, but the basic melts react at a much slower rate. Once the cation has been fully chlorinated, the melts appear to be resistant to further attack by chlorine. The chlorinated melts have higher melting points, higher viscosities and lower electric conductivities than the unchlorinated melts.

INTRODUCTION

The behavior of chlorine has been studied in chloroaluminate molten salts composed of alkali chloride – aluminum chloride mixtures (1,2), but little is known about the reactions of chlorine in the related organic chloride – aluminum chloride melts. Mixtures of 1-methyl-3-ethylimidazolium chloride (MeEtImCl) and aluminum chloride are salts that are liquid at room temperature and below (3). The anodic limit of this and other chloroaluminate melts is the oxidation of chloride. A chlorine electrode would have the greatest possible potential as a cathode in a battery utilizing the chloroaluminate melts. The cell where chlorine is the cathode and aluminum is the anode (i.e. an AlCl₃ formation cell) would have a cell voltage of 2.2 V and a theoretical energy density of 1315 Wh/kg (based on

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If chlorine is to be a useful electrode in the low temperature chloroaluminate molten salts, its physical and chemical behavior in the melts must be studied. We report here some details about the reactivity of chlorine in the MeEtIm chloroaluminate melts and some physical properties of melts that have reacted with chlorine.

In basic melts, the anodic oxidation of chloride produces tri-chloride (Cl$_3^-$) ion (4). Chloride oxidation at the anodic limit of acidic MeEtIm and the similar 1-(1-butyl)pyridinium chloroaluminate melts produces dissolved Cl$_2$ (5). The apparent lack of any interfering processes suggested to the authors that the equilibrium chloride electrode potentials could be used in potentiometric experiments to determine accurately the equilibrium constant for the tetrachloroaluminate dissociation. Lipsztajn and Osteryoung did note that approximately 3 hours after anodic oxidation of Cl$^-$ in basic melt, the chlorine reduction wave disappeared and the expected increase in the chloride oxidation wave was not observed. There may, in fact, be a chemical interference with the Cl$^-$/Cl$_2$ couple in both acidic and basic MeEtIm chloroaluminate melts.

EXPERIMENTAL

The preparation of the melts was as reported earlier (1). The melting points, electric conductivities and viscosities were measured as reported for the unchlorinated melts (5). NMR spectra were recorded on a JEOL FX90Q spectrometer.

Completely chlorinated melt could be prepared by slowly bubbling chlorine gas through a stirred sample of the melt at approximately 90°C. The time necessary to completely convert the imidazolium cation depended on the melt composition. The progress of the reaction could be monitored using NMR spectroscopy by observing the disappearance of the protons at the 4 and 5 positions of the imidazolium ring.

RESULTS AND DISCUSSION

When 1 atmosphere of chlorine was introduced over a sample of basic MeEtImCl-AlCl$_3$ melt, the melt rapidly took up the chlorine and became yellow-green in color. This is consistent with the dissolution of Cl$_2$ followed by the rapid reaction with free Cl$^-$ to form Cl$_3^-$. Surprisingly, after several hours the melt returned to colorless, indicating some chemical reaction of Cl$_3^-$ with the melt. The process of chlorine introduction followed by slow reaction could be repeated many times with the same melt. A similar experiment done on an acidic melt gave similar results with two notable exceptions. The color produced when chlorine was dissolved
was light yellow, indicating that \( \text{Cl}_3^- \) was not formed, and the disappearance of the color from the dissolved chlorine was much more rapid. The weight gain of a sample that was exhaustively treated with chlorine, then degassed \textit{in vacuo} corresponded to one mole of chlorine (\( \text{Cl}_2 \)) gained per mole of melt.

The consumption of very large amounts of chlorine implies that the reaction is not solely with impurities in the melt, but with a component of the melt itself. Figures 1 and 2 show \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectra taken regularly over several hours while chlorine was bubbled into an acidic MeEtIm melt. The resonances for the 4 and 5 protons at 7.9 ppm decrease in intensity and eventually disappear. The \( ^{13}\text{C} \) NMR spectra show that at the end of the reaction there are still five carbons in the organic cation, but during the chlorination process two intermediates are present. The spectra clearly show that chlorine reacts with the MeEtIm cation, and that the cation is quantitatively converted to the 4,5-dichloro-1-methyl-3-ethylimidazolium ion, as shown in equation 1.

\[
\begin{align*}
\text{Me} &+ \text{Cl}_2 \\
\text{Et} & \\
\text{N} & \\
\text{N} & \\
\text{H} & \\
\text{H} & \\
\end{align*}
\]

\[\text{Cl} \quad \text{Cl}\]

The same conversion occurs in basic melts, but at a much slower rate.

Once all of the MeEtIm had reacted, the melts were apparently resistant to further reaction with chlorine. An acidic melt completely reacted with chlorine retained the yellow color of dissolved chlorine indefinitely, unless a vacuum was applied to it. This suggests that while the MeEtIm chloroaluminate melts are not suitable for use with chlorine electrodes, the dichloro-MeEtIm chloroaluminate melts might be. The dichloro-MeEtIm melts are new materials and are likely to have physical properties different from the parent melts. We measured the electrical conductivities and viscosities of the dichloro-MeEtIm melts as a function of melt composition. We also determined a rough phase diagram for the new melts.

Figure 3 shows that the phase diagram for the dichloro-MeEtIm melts is qualitatively similar to the MeEtIm melts (6), but the melting points are about 50° higher than the parent melts. Interestingly, the dichloro-MeEtIm melts have normal melting points in the regions of the phase diagram where the MeEtIm melts only undergo glass transitions.

The electrical conductivities of the dichloro-MeEtIm melts are significantly lower than for the parent melts, as seen in Figure 4.
They also do not show the strong composition dependence that the parent melts have.

Reduced electrical conductivities are often caused by elevated viscosities, and this is born out by the comparison shown in Figure 4. Only a few compositions were measured, but the trend toward higher viscosities in basic compositions is present in the chlorinated samples as in the unchlorinated ones.

The reduced electrical conductivities of the chlorinated melts and the higher melting points make them less attractive as electrolytes. A cation that is resistant to attack by chlorine would be welcome, but not at the expense of the desirable thermal properties of the MeEtIm chloroaluminate melts or if there is a substantial conductivity penalty. The electrochemical properties of the 4,5-dichloroimidazolium melts were not examined in detail, but the electrochemical window is probably shorter on the cathodic end. Work on low temperature chloroaluminate melts having cations resistant to attack by chlorine is in progress.

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Fig. 1. $^1$H NMR spectrum of 0.60 AlCl$_3$ mole fraction MeEtImCl-AlCl$_3$ melt at 90°C. External reference is hexamethyldisiloxane.

Fig. 2. $^{13}$C NMR spectrum of 0.60 AlCl$_3$ mole fraction MeEtImCl-AlCl$_3$ melt at 90°C. External reference is hexamethyldisiloxane.
Fig. 3. Phase diagram.

Fig. 4. Specific conductivities as function of melt composition.

Fig. 5. Kinematic viscosities as function of melt composition.