Mixtures of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride (MEImCl) are liquid electrolytes over the composition range 0.33< mole fraction of CuCl <0.67, with glass transitions at about -50°C. Their densities, electrical conductivities, and viscosities were measured over this composition range and over the temperature range 25 to 50°C. The viscosity \( \eta \) goes through a minimum and the specific conductivity \( K \) a maximum at \( \chi = 0.50 \). The temperature variations of viscosity and conductivity obey the Arrhenius equation. The empirical Frenkel function, \( \eta K (E^{f} / E^{l}_{K}) = \text{constant} \), is obeyed.
Transference numbers were calculated from the results of experiments using a Hittorf cell. Both MEIm\(^+\) cations and chlorocuprate(I) anions were found to play a significant role as charge carriers.

Potentiometric measurements were made on the cells

\[
\text{Cu} \mid 0.50\text{CuCl} + 0.50\text{MEImCl} \parallel \chi\text{CuCl} + (1 - \chi)\text{MEImCl} \parallel \text{Cu and Cu} \\
0.50\text{CuCl} + 0.50\text{MEImCl} \parallel n\text{CuCl}_2 + (0.50 - \frac{n}{2})\text{CuCl} + (0.50 - \frac{n}{2})\text{MEImCl} \parallel \text{Pt}.
\]

The potential of the test Cu(I), Cu(0) half-cell is interpreted in terms of equilibria between a variety of chlorocuprate(I) species. The potential of the Cu(II), Cu(I) couple shows Nernstian behavior over a limited CuCl\(_2\) concentration range.

Electrode kinetic data at the copper-fused salt interface obeyed the Butler-Volmer equation. Symmetry coefficients and exchange current densities were obtained from Tafel plots.

Tests were made of a battery constructed from Al/chloroaluminate and Cu/chlorocuprate(I) half-cells. The cell was rechargeable.

The \(\chi\text{CuCl}/(1 - \chi)\text{MEImCl}\) fused salts react with dioxygen to give black liquid products. The stoichiometry was determined by PVT measurements. The results depend on melt composition and temperature, and are interpreted in terms of oxidation of copper(I) to copper(II) and of the cation to the new compound, 1-methyl-3-ethylimidazolone, which was
characterized. The copper autoxidation products have anomolous paramagnetism and catalyze the oxidative polymerization of 2,6-dimethylphenol.

Weak interaction of carbon monoxide and ethylene with the chlorocuprate(I) melts was observed.
Studies of Low Melting 1-Methyl-3-ethylimidazolium Chlorocuprate(I) Fused Salts

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Steven A. Bolkan

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Studies of Low Melting 1-Methyl-3-ethylimidazolium Chlorocuprate(I) Fused Salts

I. INTRODUCTION

This work concerns the study of a new low melting chlorocuprate(I) fused salt system based on mixtures of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride (MEImCl). These mixtures will be described throughout this dissertation by the formula \( \chi \text{CuCl}/(1-\chi)\text{MEImCl} \), where \( \chi \) is the mole fraction of copper(I) chloride.

Studies of fused salt systems have been motivated by a fundamental interest in their physical, chemical, and electrochemical properties, as well as in their practical application as solvents, reaction media, and as electrolytes. Many industrial processes use fused salts for electrolysis in metal production (Yoshikawa and Numura, 1978). There are numerous examples in the literature of fused salts being used as solvents for a variety of reactions (Kerridge, 1975; Sundermeyer, 1965; Gordon, 1969) and for the purpose of investigating complex ions of transition metal halides dissolved in fused salts (Holt, 1971; Mamantov and Norvell, 1980). Fused salts also have applications in various electrochemical devices, such as batteries (Sudworth, 1980).
Simple molten salt systems commonly exist at temperatures of several hundred degrees Celsius. There are, however, three well known classes of ionic salts that are liquids at and below room temperature. Each of these liquids has bulky organic-substituted ammonium (or phosphonium) cations and complex anions based on aluminum (Hurley and Wier, 1951), copper (Yoke, Weiss, and Tollin, 1963), or boron (Ford, Hauri, and Hart, 1973). Hussey (1984) has recently reviewed these three classes of room temperature fused salts. The room temperature melts offer important advantages over high temperature melts in that they do not have to be heated, corrosion problems are minimized, and solutions can be prepared in them of thermally sensitive solutes.

The preparation of the $\chi\text{CuCl}/(1-\chi)\text{MEImCl}$ fused salts was undertaken after the recent development by Wilkes and co-workers of the 1,3-dialkylimidazolium chloride/aluminum chloride melts (Wilkes, et al., 1982). These have desirable liquid ranges and other physical and electrochemical advantages. The investigation of this new chlorocuprate(I) system is a continuation of a larger study involving the general class of room temperature chlorocuprate(I) fused salts.

The first copper-containing room temperature fused salt, triethylammonium dichlorocuprate(I), was discovered serendip-
itously during studies of the oxidation-reduction reaction between triethylamine and copper(II) chloride (Yoke, Weiss, and Tollin, 1963). Similar liquids containing the triethylchlorophosphonium cation were next discovered (Axtell and Yoke, 1973). Spectroscopic studies, including Raman, IR, NMR, and UV-visible measurements also involved extension of the synthetic work to prepare other room temperature salts with a variety of alkyl-substituted ammonium or phosphonium cations and chlorocuprate(I) anions.

In the Et$_3$NH CuCl$_2$ fused salt, and in related systems, the actual presence of the linear CuCl$_2^-$ ion was demonstrated by observation of its characteristic vibrational frequencies. Conductometric and other types of spectroscopic measurements confirmed the ionic nature of the liquids (Axtell, Good, Porterfield, and Yoke, 1973; Porterfield and Yoke, 1976). One postulate to explain why the chlorocuprates are liquids at room temperature is that low lattice energies result from the steric nature of the bulky cations and consequent poor packing of these with the chlorocuprate(I) anions. Another reason for the liquid nature of the chlorocuprates is the presence of a mixture of chlorocuprate(I) species, causing a mutual melting point depression, arising from such anionic equilibria as

\[ \text{CuCl} + n\text{Cl}^- = \text{CuCl}^{n-1}_n \quad (n=1-3) \]  

(1.1)
\[ \text{CuCl}_2^- + y\text{CuCl} \rightleftharpoons \text{Cu}_{1+y}\text{Cl}_{2+y}^- \quad (y=1, \text{ etc.}) \quad (1.2) \]

\[ 2\text{CuCl}_2^- \rightleftharpoons \text{Cu}_2\text{Cl}_3^- + \text{Cl}^- \quad (1.3) \]

These equations can be thought of in terms of Lewis acid/Lewis base interactions, where a chloride donor is considered a base and a chloride acceptor an acid. Equilibria such as these would be shifted upon the addition of a chloride source or chloride acceptor. Spectroscopic evidence has been presented for species such as \( \text{CuCl}_3^{-2} \) in the chloride-rich (basic) and \( \text{Cu}_2\text{Cl}_3^- \) in the chloride-poor (acidic) \( \text{CuCl} \) room temperature fused salts (Axtell, Good, Porterfield, and Yoke, 1973). The \( \text{CuCl}_3^{-2} \) and \( \text{CuCl}_4^{-3} \) species were also found in \( \text{CuCl} \) solutions in basic \( \text{AlCl}_3/\text{MEImCl} \) melts (Laher and Hussey, 1983) and various polynuclear complexes \( \text{Cu}_m\text{Cl}_n^{-(n-m)} \) have been reported in aqueous \( \text{CuCl} + \text{Cl}^- \) systems (Sukhova, Temkin, and Flid, 1970).

Silkey (1979) measured the density, viscosity and conductivity of triethylammonium dichlorocuprate over a range of temperatures. Potentiometric and spectrophotometric studies were also made of the electrode reactions

\[ \text{CuCl}_2 + e^- \rightleftharpoons \text{CuCl}_2^- \quad (1.4) \]

and
\[ \text{CuCl}_2^- + e^- \rightleftharpoons \text{Cu} + 2 \text{Cl}^- \] (1.5)

on platinum and copper surfaces, respectively, and current density-overpotential measurements permitted calculation of exchange current densities. Preliminary battery studies were carried out using this system as electrolyte (Porterfield and Yoke, 1976; Silkey, 1979), but the results were discouraging because of the excessively high viscosity of this liquid electrolyte and the sluggish kinetics of the electrode reactions.

The purpose of the present work was to study the nature of the \( X \text{CuCl} / (1-X) \text{MEImCl} \) system through a comprehensive survey of its physiochemical and electrochemical properties. These investigations will provide an opportunity for comparison of properties of this new melt with those of previously studied chlorocuprate(I), chloroaluminate, and conventional high temperature melts. They will also provide an opportunity to test fundamental theories of the liquid state as well as theories of electrode kinetics and ionic transport. The areas of study are divided into three separate chapters. Chapter III begins with the examination of the basic physical properties of various CuCl/MEImCl compositions such as liquidus range and transport phenomena. Electrochemical aspects, both thermodynamic and kinetic, are dealt with in Chapter IV. Finally, in Chapter V, a chemical study is given
on the interaction of dioxygen with CuCl/MEImCl compositions and of the interaction of carbon monoxide and ethylene with CuCl/MEImCl and copper(I) chloride/ triethylammonium chloride mixtures.
II. EXPERIMENTAL

A. Materials

1. Solvents

a. Chloroform. Chloroform (Baker reagent) was distilled under nitrogen from P₂O₅. A 25 mL forerun was discarded. The fraction boiling between 59-61°C was collected and stored in an amber bottle over Linde 4A molecular sieves.

b. N,N-Dimethyl Formamide. N,N-Dimethyl formamide (Malinckrodt reagent) was shaken with KOH pellets and then decanted into a still pot and distilled from barium oxide under nitrogen. The fraction boiling at 150-153°C was collected and stored over 4A molecular sieves.

c. Acetonitrile. Acetonitrile (Baker reagent) was shaken with P₂O₅ and allowed to stand for several hours. It was then decanted into a still pot containing fresh P₂O₅ and distilled under nitrogen. The fraction boiling between 80-82°C was collected and stored under nitrogen over 4A molecular sieves.

d. Ethyl Acetate. Ethyl acetate (EM Science) was distilled from P₂O₅ under nitrogen and stored over 4A
molecular sieves. The fraction boiling between 76-78°C was collected.

e. **Diethyl Ether.** Diethyl ether was refluxed over sodium metal and benzophenone for several hours and then slowly distilled under nitrogen.

f. **Other Solvents.** All other solvents used in this work were of a Reagent or Spectral grade and used without further purification.

2. **Metal Halides**

a. **Copper(I) Chloride.** Copper(I) chloride was prepared by the sulfite reduction method of Keller and Wycoff (1946). The product was dried in vacuum at 40-50°C for several hours and then stored in amber bottles under nitrogen until used. Samples which took on a gray discoloration were discarded.

b. **Copper(II) Chloride.** Copper(II) chloride dihydrate (J.T. Baker reagent) was dehydrated by heating to 110°C for 24 hours. It was stored under nitrogen until used.

c. **Aluminum Chloride.** Aluminum chloride (Mallinckrodt reagent) was purified by the method of Howie and MacMillan (1970), and stored under nitrogen until used.
3. **Organic Salts**

   a. **Triethylammonium Chloride.** Triethylammonium chloride was prepared by the reaction of triethylamine with 6M hydrochloric acid. The water was evaporated and the white solid was purified by recrystallization from absolute ethanol. The product was dried at 110°C for 3 hours prior to storage in the nitrogen dry box.

   b. **1-Methyl-3-ethylimidazolium Chloride.** 1-Methylimidazole (Aldrich 99% reagent) and a 2-3 fold molar excess of ethyl chloride (Gebauer Pharmaceutical Preparations) were placed into a chilled monel bomb which had been fitted with a glass sleeve insert. The bomb was then bolted closed and the contents heated to 70-80°C for four days. The excess ethyl chloride was then allowed to boil off and collected in a cold trap for reuse. The 1-methyl-3-ethylimidazolium chloride was then poured as a warm liquid into a flask containing acetonitrile/ethyl acetate from which it was recrystallized at -10°C. The white crystalline solid was dried in vacuo for several hours at 40-50°C before storage under nitrogen in the dry box; m.p. 82-84°C, lit. m.p. 82-87°C (Wilkes, Levisky, Wilson and Hussey, 1982).

   Its density as a solid at 21.5°C was determined by flotation in carbon tetrachloride/hexane using a pycnometer and found to be 1.186 g/mL.
4. Other Materials

a. 2,6-Dimethylphenol. 2,6-Dimethylphenol (Aldrich reagent 99%) was recrystallized from carbon tetrachloride and dried in vacuo before use.

b. Carbon Monoxide. Carbon monoxide (Matheson 99%) was used from the cylinder as received.

c. Dimethyl Ether. Dimethyl ether (Matheson 99%) was used from the cylinder as received.

B. Preparation of Room Temperature Fused Salt Mixtures

All operations involving the preparation and transfer of fused salts were done under an atmosphere of a pre-purified grade of nitrogen in a Forma stainless steel dry box.

1. Copper(I) Chloride and 1-Methyl-3-ethylimidazolium Chloride.

The combination of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride in the molar ratios ranging from 2:1 to 1:2 formed room temperature fused salts. The two solids reacted quickly to form light green to clear pale yellow liquids. A qualitative observation of a small temperature rise when the components were mixed with a thermometer showed that the process was slightly exothermic. The liquids were stored over clean copper foil prior to their
use; this eliminated any additional contribution to the color due to traces of copper(II). Mixtures on each side of the composition range given above were partly or all solid at room temperature. These were prepared by melting the components together on a hot plate in the dry box.

2. Copper(I) Chloride and Triethylammonium Chloride.

Triethylammonium dichlorocuprate(I) was prepared by combining equal molar quantities of copper(I) chloride with triethylammonium chloride.

C. Instrumental Methods

1. Spectroscopic Methods

   a. Infrared Spectra. Infrared spectra were recorded on either a Perkin Elmer Model 727 or Model 621 double beam spectrophotometer. Sodium chloride cells or potassium bromide pellets were used to hold the samples.

   b. Ultraviolet-Visible Spectra. Spectra in the range 800-200 nm were recorded on HP-8451A Diode Array, Bausch and Lomb Spectronic 600 or Cary Model 16 spectrophotometers. Matched quartz cells with 1 cm or 0.1 cm path length were used. Some samples were placed between quartz Suprasil or Infrasil plates.
c. **Nuclear Magnetic Resonance Spectra.** NMR spectra were obtained using a Varian EM 360 spectrometer. Tetramethylsilane in sealed capillary tubes was used as an external standard.

d. **Mass Spectroscopy.** Mass spectra were obtained using a MAT CH-7 mass spectrometer. An EM 360 spectrometer was used to identify hydrogen gas.

e. **Electron Paramagnetic Resonance Spectra.** EPR spectra were obtained on a Varian E-9 spectrometer.

2. **Electrochemical Methods**

   Electrochemical polarization curves and coulometric studies were carried out using a Princeton Applied Research Model 173 Potentiostat/Galvanostat fitted with a Model 179 Digital Coulometer. Current-potential data were recorded directly from a Fluke 8020B Multimeter. Potential measurements of voltaic cells containing fused salt electrolytes were measured either with a Honeywell Digitest 500 or with the Fluke multimeter.

3. **Index of Refraction**

   The index of refraction of liquids was obtained at room temperature with a Bausch and Lomb Abbe-3L refractometer.
D. Analytical Methods

1. Copper Content

   a. Total Copper. The total copper content of a sample was determined after converting it to copper(II) sulfate by oxidative treatment with concentrated nitric acid and subsequent evaporation to fumes with sulfuric acid. After dilution, aliquots were added to an excess of standard Na$_2$H$_2$EDTA, and buffered with ammonium acetate to adjust the pH to 5-6. The solution was heated to boiling, PAN [1-(2-pyridylazo)-2-naphthol] indicator was added, and the excess EDTA was then back-titrated using standard copper(II) sulfate solution.

   b. Copper(II) Content in the Presence of Copper(I). The copper(II) content was determined idiometrically by titration with standard sodium thiosulfate solution. A weighed sample was rinsed into an Erlenmeyer flask with dilute HCl. An excess of KI in 20 mL water was then added to the flask. The liberated iodine was titrated with sodium thiosulfate to a starch endpoint. Before the endpoint was reached approximately 2g KSCN was added to the flask to liberate any absorbed iodine on the surface of precipitated CuCl (Skoog and West, 1976).
2. 1-Methyl-3-ethylimidazolium Chloride Content

1-Methyl-3-ethylimidazolium chloride content was determined by UV spectrophotometry. A sample to be analyzed was dissolved in hydrochloric acid and then diluted. Standard solutions for a calibration curve were prepared from samples of known 1-methyl-3-ethylimidazolium chloride concentration (λ_max = 212 nm, ε = 4700 L/mol cm).
III. PHYSICAL PROPERTIES OF COPPER(I) CHLORIDE 
AND 1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE MIXTURES 

A. Phase Studies 

1. Historical 

Temperature-composition phase diagrams for low melting fused salt mixtures have been reported for the aluminum chloride/N-ethylpyridinium bromide system and for several aluminum chloride/1,3dialkylimidazolium chloride systems (Hurley and Wier, 1951; Fannin, et al., 1984). All of these aluminum chloride based systems show evidence for compound formation at the 1:1 molar mixture corresponding to $\text{R}^+\text{AlCl}_4^-$, where $\text{R}^+$ is the substituted pyridinium or imidazolium cation. The phase diagrams for these systems also show two low melting eutectics occurring at the 1:2 and 2:1 molar mixtures ($40^\circ\text{C}$ and $-40^\circ\text{C}$ for the N-ethylpyridinium chloride and $-80^\circ\text{C}$ and $-100^\circ\text{C}$ for the 1-methyl-3-ethylimidazolium chloride/aluminum chloride melts). Temperature-composition phase diagrams have not been reported for chlorocuprate(I) low melting fused salts.
2. Procedure

Mixtures of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride ranging in the mole fraction of copper(I) chloride from 1 to 0 were sealed in glass capillaries under nitrogen. Measurements below room temperature were made by a visual method which has been shown to be in agreement with the differential scanning calorimetric technique (Fannin et al., 1984). The apparatus is shown in Figure 1. The sample capillary and an iron-constantan thermocouple were immersed in ethanol in a small tube which was suspended from the bottom of a rubber stopper in a 400 ml vessel. This vessel was swept with dry nitrogen which first passed through a copper coil immersed in liquid nitrogen; temperature control was achieved by varying the rate of flow of gas. The vessel was mounted in an insulated jacket with a port permitting illumination and observation with a magnifier. Glass transitions were characterized by a discontinuous increase in viscosity on cooling, with fracturing of the melt. The transition temperatures were actually measured as melting points on slow warming after initial quenching to -100°C. Measurements above room temperature were made using a conventional Mel-Temp melting point apparatus.
Figure 1. Low Temperature Melting Point Apparatus. Nitrogen Cooling Coil (a), Thermocouple Leads (b), Viewing Port (c), Sample Bucket (d), Solid Insulation (e), Loose Insulation (f), Inner Flask (g), and Outer Flask (h).
3. **Results and Discussion**

Mixtures of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride are liquid at room temperature over the composition range $0.33 < \chi < 0.67$. The room temperature liquid range for the CuCl/Et$_3$NHC1 system was more restricted, $0.49 < \chi < 0.67$. Melting points are shown in Figure 2; that for $\chi = 1.0$ is the literature value (Chemical Rubber Handbook, 1981). The vertical dashed lines represent the melting point range of each composition. No attempt was made to separate and analyze co-existing liquid and solid phases and therefore the data in Figure 2 do not represent a true phase diagram.

There is no indication of formation of a solid compound, such as MEIm$^+\text{CuCl}_2^-$, in the broad plateau of glass transition temperatures occurring in the $\chi = 0.3$ to 0.6 range.

Although 1-methyl-3-ethylimidazolium chloride has been reported to decompose thermally into 1-methylimidazole and ethyl chloride at temperatures between 250-260°C (Chan, et al., 1977) there was no evidence of thermal decomposition (such as the evolution of volatile material) when a 0.5 melt sample was heated in vacuo to 257°C. The 0.5CuCl/0.5MEImCl fused salt is thermally stable over a much larger liquid range, (e.g. -50°C to 257°C) than the 0.5CuCl/0.5Et$_3$NHC1 melt. The latter forms a glass on cooling to -10°C and gives off
Figure 2. Melting Point Diagram for CuCl/MEImCL Compositions.
triethylamine at temperatures greater than 100°C (Silkey and Yoke, 1980).

B. Densities and Molar Volumes

1. Historical

The density of triethylammonium dichlorocuprate(I) was measured dilatometrically by Silkey (1979) over the temperature range 25-50°C. The density-temperature relation was linear over this limited range within the experimental error. The molar volume at 25°C was calculated from the molecular weight and density, and found to exceed the sum of the molar volumes of the solid components, triethylammonium chloride and copper(I) chloride, by 10.9%. Such behavior is typical even of simple molten salts; the expansion on fusion is attributed primarily to the formation of holes in the liquid structure rather than to an increase in the inter-ionic distance (Bloom and Bockris, 1959).

2. Procedure

The values of density for liquid mixtures of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride were obtained at 25°, 30°, 40°, and 50°C. Temperature control was maintained to ±0.1°C.
The dilatometer used in density measurements was previously described and calibrated by Joedicke (1976). It is shown in Figure 3. The filled unit was immersed in a constant temperature bath to the initial stem graduation and liquid levels of 0.00 to 1.00 mL were read at the meniscus in the stem. Liquid densities were calculated from the fluid's weight and volume, which is the sum of the bulb and stem volumes.

Figure 3. Dilatometer
3. **Results**

Densities of $\chi CuCl/(1-\chi) MEImCl$ compositions as a function of temperature are shown in Figure 4. The data are well represented by linear functions in this temperature range and numerical values are given in Table I. The dependence of the density on composition at a given temperature is a smooth but non-linear function. The density increases monotonically with mole fraction CuCl, and densities of melts other than those in Figure 4 and Table I were obtained by curvilinear interpolation.

<table>
<thead>
<tr>
<th>Mole Fraction CuCl</th>
<th>a</th>
<th>b</th>
<th>Linear Correlation Coefficient</th>
<th>Coefficient of Expansion deg$^{-1}$</th>
</tr>
</thead>
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<tr>
<td>.332</td>
<td>1.3835</td>
<td>$7.59 \times 10^{-4}$</td>
<td>.9968</td>
<td>$5.92 \times 10^{-4}$</td>
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<td>.9961</td>
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</tr>
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<td>$1.08 \times 10^{-3}$</td>
<td>.9999</td>
<td>$7.34 \times 10^{-4}$</td>
</tr>
<tr>
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<td>1.7162</td>
<td>$1.07 \times 10^{-3}$</td>
<td>.9988</td>
<td>$6.61 \times 10^{-4}$</td>
</tr>
<tr>
<td>.666</td>
<td>1.9042</td>
<td>$1.24 \times 10^{-3}$</td>
<td>.9998</td>
<td>$6.65 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Figure 4. Density Versus Temperature for $\chi \text{CuCl}/(1-\chi)\text{MEImCl}$ Melts.
4. Discussion

The slopes of the density versus temperature curves in Figure 4 describe coefficients of thermal expansion, $\alpha$. Values are given in Table I for $\alpha$ evaluated at 40°C using

$$\alpha = \frac{1}{V} \frac{dV}{dT} = \frac{(d_{400})}{20.0} \left( \frac{1}{d_{500}} - \frac{1}{d_{300}} \right)$$

These values are also plotted in Figure 5 as a function of

---

![Figure 5. Coefficients of Thermal Expansion Versus Melt Composition](image-url)
melt composition. The values pass through a maximum at the composition corresponding to the equimolar mixture. The greater rate of expansion for the melt of this composition may be due to the presence of a larger number of simpler ionic species, such as CuCl\(_2^-\), while in basic or acidic melts fewer but larger ions, such as CuCl\(_3^{2-}\) or Cu\(_2\)Cl\(_3^-\), are present.

Molar volumes of melts of various compositions may be calculated from the melts' density and equivalent weight, \(\bar{W}\). The equivalent weight is given by

\[
\bar{W} = \chi(98.99) + (1- \chi)(146.64)
\]  

(3.2)

Calculated molar volumes at 25°C are plotted in Figure 6 as a function of composition. The molar volume of any particular melt is greater than that which would be predicted from a simple law of additivity, e.g. by 9% for \(\chi = 0.5\). Melt formation upon combining the two dry powders of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride was mildly exothermic, in contrast to the CuCl/Et\(_3\)NCl system where a markedly endothermic process was noted on mixing the solids (Silkey, 1979).
Figure 6. Molar Volumes of CuCl/MEImCl Mixtures.
C. Viscosities and Conductivities

1. Historical and Theoretical

Viscosity depends on the transport of momentum and when measured by the method based on Poiseuille's formula for the flow of fluids through a tube of radius $r$, is given by

$$\eta = b \rho t$$  \hspace{1cm} (3.3)

where $b$ is the viscosimeter constant, $\rho$ the density of the solution, and $t$ the efflux time. Values for viscosity found for high temperature melts are not significantly different from those of common liquids such as water or organic solvents (Sundheim, 1967). Room temperature fused salts have viscosities that are somewhat higher and are comparable to values that might be found for light grades of oil.

The viscosities of fused salts have been found to obey the Arrhenius equation over a fairly wide range of temperatures (Bockris and Reddy, 1970).

$$\eta = B \exp \left( \frac{E^*}{RT} \right)$$  \hspace{1cm} (3.4)

The activation energies for viscous flow of fused salts generally range between 3-11 kcal/mol. The viscosity of
triethylammonium dichlorocuprate showed Arrhenius behavior over the temperature range 25°-50°C, with an activation energy of 9.6 kcal/mol (Silkey, 1979).

Conductivity is the transport of charge and for fused salts it is usually expressed as equivalent conductivity \( \Lambda \) (ohm\(^{-1}\)cm\(^2\)eq\(^{-1}\)), which would be the conductivity of one equivalent of the electrolyte between parallel planar electrodes 1 cm apart. The equivalent conductivity of a fused salt mixture is calculated from the equation

\[
\Lambda = K \frac{\bar{\omega}}{\rho}
\]  

(3.5)

where \( K \) is the specific conductivity (ohm\(^{-1}\)cm\(^{-1}\)), and \( \rho \) is the density. The equivalent weight \( \bar{\omega} \) of a binary mixture is given by

\[
\bar{\omega} = \chi_1 \omega_1 + \chi_2 \omega_2
\]  

(3.6)

where \( \chi_1 \) and \( \chi_2 \) are the mole fractions of the components and \( \omega_1 \) and \( \omega_2 \) are their equivalent weights. Equation (3.2) is the explicit form of equation (3.6) for the CuCl/MEImCl fused salt.
The variation in both specific and equivalent conductivities with temperature has been found to be described approximately by Arrhenius equations of the form (Nachtrieb, 1980)

\[ K = A \exp(-E^*_k /RT) \]  \hspace{1cm} (3.7)

\[ \Lambda = A' \exp(-E^*_\Lambda /RT) \]  \hspace{1cm} (3.8)

Activation energies for fused salts typically fall into the range of 1-4 kcal/mole. The value of \( E^*_\Lambda \) for triethylammonium dichlorocuprate(I) was found to be 7.8 kcal/mol (Silkey, 1979).

The two activation energies for conductivity are theoretically related by

\[ E^*_\Lambda = E^*_k + \alpha RT^2 \]  \hspace{1cm} (3.9)

where \( \alpha \) is the coefficient of thermal expansion. The \( \alpha RT^2 \) term in equation (3.9) takes into account the volume expansion of the liquid between the parallel planar electrodes, which is not accounted for in specific conductivity. The value for \( E^*_\Lambda \) will be greater than \( E^*_k \) since \( \alpha \) is always
positive (Bloom, 1967). The value of $\alpha$ is obtained from the thermal variation of density, and is given by equation (3.1).

A relationship between equivalent conductivity and viscosity is found by combining the Nernst-Einstein equation

$$\Lambda = z^2F^2D/RT$$

(3.10)

and the Stokes-Einstein equation

$$D = kT/6\pi r \eta$$

(3.11)

where $z$ is the ionic charge, $F$ the Faraday, $r$ the ionic radius, $k$ the Boltzmann constant and $D$ the diffusion coefficient. The resulting relationship is known as Walden's rule.

$$\eta \Lambda = \text{constant}$$

(3.12)

This relationship is generally not followed over a temperature range by fused salts. It is more commonly applied to solutions whose viscosity varies with concentration at constant temperature.

By combining the Arrhenius equation for viscosity, equation (3.4), with that for specific conductivity, equation
(3.7), an empirical relationship, known as the Frenkel function, can be derived (Frenkel, 1946). (See Appendix A)

\[ FF = \frac{\eta}{E_4 / E_4^K} = \text{constant} \] (3.13)

This function has been found to describe the behavior of CuCl/Et₃NHCl melts (Silkey and Yoke, 1980) as well as molten alkali halides (Yaffe and Van Artsdalen, 1956) and cadmium halides (Bloom, Harrap and Heymann, 1948). Its apparent validity suggests that the mechanisms for viscous flow and conductivity arise from the same fundamental properties of the constituent ions of the melt (Yaffe and Van Artsdalen, 1956).

2. Procedure

a. Viscosimetry. Values of the viscosity for various mixtures of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride were obtained at 25°C, 30°C, 40°C, and 50°C. Temperature control was maintained to ±0.1°C.

Viscosities were measured with a modified Canon-Fenske type viscometer which was previously calibrated by Silkey (1979) using glycerine-water mixtures. The viscometer is shown in Figure 7. Tygon tubing was used exclusively and the connections were wired to prevent leaks. In practice, the reservoir was filled with the test solution up to the
Figure 7. Viscosimeter; Efflux Marks (a), Fillmark (b).
calibration mark on the lower part of the viscometer. With the three-way stopcock opened to the bulb and lower reservoir, and the two-way stopcock opened to the nitrogen bypass, liquid could be forced to the upper reservoir by application of pressure to the pipet bulb. When the desired amount of liquid had been transferred, the three-way stopcock was opened to all positions allowing flow into the lower reservoir to commence. The two-way stopcock was then closed. Liquid efflux times were measured between two marks at opposite ends of the upper reservoir.

b. **Conductivity Measurements.** Conductivity data for fused salts were obtained with an Industrial Instruments Model RC16B2 conductivity bridge and a dipping cell. The cell constant was 11.65±.07 cm⁻¹ as determined from measurements on a 0.1000M KCl solution at 25.0°C, of equivalent conductance 128.96 ohm⁻¹cm²eq⁻¹ (Conway, 1952). Measurements at 60 and 1000 Hz agreed well and their average was taken. Temperature control was maintained with a Haake constant temperature apparatus to ±0.1°C. The sample solutions were contained in 150 mm x 20 mm test tubes modified to accept the cell with an air tight seal.
3. Results

Isotherms showing the variation in viscosity, $\eta$, and specific conductivity, $\kappa$, with composition are given in Figures 8 and 9 respectively. Pronounced extrema are seen at mole fraction 0.5 corresponding to the nominal MEImCuCl$_2$ composition. Quantitatively, the decrease in viscosity at the composition midpoint is relatively greater than the increase in conductivity, so that the Walden product $\eta\kappa$ passes through a minimum at mole fraction 0.5 at each temperature studied. Although at 25°C the viscosity of the equimolar CuCl/MEImCl melt, 45.9 cp, is significantly less than that of the CuCl/Et$_3$NHCl melt, 123 cp, and the specific conductivity higher, $1.16\times10^{-2}$ vs. $4.30\times10^{-3}$ ohm$^{-1}$cm$^{-1}$, the values of their Walden products are the same within experimental error, 0.532 vs. 0.529 cp ohm$^{-1}$cm$^{-1}$.

Over the temperature range 25° to 50°C, linear plots vs. $1/T$ were obtained of $\ln\kappa$, $\ln\Lambda$, and $\ln\eta$, permitting calculation of energies of activation for specific conductivity $E'_\kappa$, equivalent conductivity $E'_\Lambda$, and viscous flow $E'_\eta$. The viscosity and specific conductivity data are given in Figures 10 and 11 for basic melts and in Figures 12 and 13 for acidic melts.
Figure 8. Viscosity Isotherms for CuCl/MEImCl Melts.
Figure 9. Specific Conductivity Isotherms for CuCl/MEImCl Melts.
Figure 10. Arrhenius Plot Using Viscosity Data Obtained from Basic CuCl/MEImCl Melts.

Figure 11. Arrhenius Plot Using Specific Conductivity Data Obtained From Basic CuCl/MEImCl Melts.
Figure 12. Arrhenius Plot Using Viscosity Data Obtained From Acidic CuCl/MEImCl Melts.

Figure 13. Arrhenius Plot Using Specific Conductivity Data Obtained from Acidic CuCl/MEImCl Melts.
The Frenkel function, equation (3.13), is found to describe the activation energy values for CuCl/MEImCl melts. The data in Table II show that this function is remarkably constant for each composition studied in the CuCl/MEImCl system.

Values of $E_A^*$ calculated by equation (3.9) using the $c_i$ values in Table I are compared in Table III with those obtained from the Arrhenius function for equivalent conductivity, equation (3.8). The agreement between the values calculated by the two methods is excellent.

4. Discussion

Both viscosity and conductivity are markedly dependent on melt composition. In the 1:1 molar mixture the predominant anionic species is certainly the linear CuCl$_2^-$ anion. The isotherms of Figures 9 and 10 show a pronounced minimum in viscosity and maximum in conductivity at this composition, corresponding to the predominance of this simplest of the chlorocuprate(I) anions. In both the MEImCl-enriched basic melts and the CuCl-enriched acidic melts, the lower mobilities of the CuCl$_3^{-2}$ and CuCl$_4^{-3}$ anions or the polynuclear Cu$_m$Cl$_n^-(n-m)$ anions are clearly reflected in the increased viscosity and decreased specific conductivity.
Table II. Activation Energies, Viscosities, Specific Conductivities and Values of the Frenkel Function

<table>
<thead>
<tr>
<th>Mole Fraction CuCl</th>
<th>( F_0 ) kcal/mol</th>
<th>( F_1 ) kcal/mol</th>
<th>( 25.0^\circ )</th>
<th>( 30.0^\circ )</th>
<th>( 40.0^\circ )</th>
<th>( 50.0^\circ )</th>
<th>Mean FF and Std. Dev.</th>
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</thead>
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<td></td>
<td>( n ) ( 10^3 k ) FF</td>
<td>( n ) ( 10^3 k ) FF</td>
<td>( n ) ( 10^3 k ) FF</td>
<td>( n ) ( 10^3 k ) FF</td>
<td>( n ) ( 10^3 k ) FF</td>
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</table>

\( \text{Mean FF and Std. Dev.:} \)  
- 25.0°: \( .361 \pm .009 \)  
- 30.0°: \( .331 \pm .002 \)  
- 40.0°: \( .315 \pm .001 \)  
- 50.0°: \( .298 \pm .002 \)  
- 60.0°: \( .245 \pm .003 \)  
- 66.6°: \( .261 \pm .001 \)  
- 75.0°: \( .250 \pm .001 \)  
- 80.0°: \( .343 \pm .003 \)  
- 90.0°: \( .251 \pm .002 \)  
- 95.0°: \( .386 \pm .007 \)  
- 100.0°: \( .362 \pm .006 \)
TABLE III

Comparison of Activation Energies $E^*_\Lambda$ Calculated From (I)

$E^*_\Lambda = E^*_K + \alpha \gamma RT^2$ and (II) From the Arrhenius Equation

<table>
<thead>
<tr>
<th>Mole Fraction CuCl</th>
<th>$E^*_\Lambda$ (I)</th>
<th>$E^*_\Lambda$ (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.334</td>
<td>12.2</td>
<td>12.2</td>
</tr>
<tr>
<td>.400</td>
<td>9.55</td>
<td>9.53</td>
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</tr>
<tr>
<td>.666</td>
<td>10.9</td>
<td>10.9</td>
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</table>

All past experience with fused salts shows that the energy of activation for viscous flow is greater than that for electrical conductivity, since the transport of momentum requires participation from both cation and anion and is limited by the ion of lower mobility while electrical transport is influenced by the ion with the greater mobility. The $E^*_\gamma/E^*_K$ ratio ranges from 3 to 7 for molten alkali halides, and is about 2 for bivalent metal halides (Bloom, Harrap and Heymann, 1948). The present data on $\chi_{CuCl}/$
(1-χ)MEImCl melts provide quite a contrast with $E^+_\eta / E^-_\kappa$ ratios of 1.1 to 1.2.

D. Transference Numbers

1. Historical and Theoretical

The fraction of current carried by a particular ionic species depends on its transference number, which is a function of concentration and the ionic mobility. The transference number for a species $i$ is defined as

$$t_i = \Lambda_i / \Lambda \quad (3.14)$$

where $\Lambda$ is the total equivalent conductivity of the electrolyte and $\Lambda_i$ the equivalent conductivity due to the species $i$ (Bard and Faulkner, 1980). The sum of the transference number of all the ionic species is unity,

$$\sum_{i} t_i = 1 \quad (3.15)$$

For electrolytes dissolved in a solvent it is not difficult to envision the movement of ions relative to the solvent. For fused salts the concept is more complex. For a
single component fused salt such as potassium chloride, electroneutrality requires that no concentration gradients arise. If the cation and anion transport numbers differ, the passage of current between two electrodes will result in net physical motion of the entire mass of the melt. The situation becomes somewhat less complex when dealing with binary fused salts where concentration gradients can be made to occur through electrolysis. There are several methods available for the measurement of transference numbers in fused salts, such as the Hittorf and moving boundary methods (Sundheim, 1964; Markov and Delimarski, 1961). The most frequently used is the Hittorf method, which is based on measurement of concentration changes in the anolyte and catholyte after passage of a known amount of current. Transference numbers calculated from such experiments may be based on the movement of ions relative to a porous membrane separating the anolyte and catholyte or may be based on motion relative to a particular ion in the melt.

Transference numbers have recently been measured for ions in the acidic and basic AlCl₃/MEImCl room temperature melts (Hussey and Øye, 1984; Hussey, Sander, and Øye, 1985). Here it was found that the major charge carrier was the organic cation, the 1-methyl-3-ethylimidazolium ion. Transference number data for the CuCl/MEImCl system may well differ because of the variety of complex anions in equilibrium in the melt.
The mathematical formalism of Hussey and co-workers is adapted for use in the copper(I) chloride system in the following sections.

2. Equations and Definitions

In calculating the transference numbers for ions in the CuCl/MEImCl fused salt we begin by defining them in terms of the simplest component species: the copper(I) cation Cu\(^+\), the organic cation R\(^+\), and the chloride anion Cl\(^-\) (the actual anionic species include complex ions).

a. Transport Relative to a Membrane (External Transference Number). A diagram for the hypothetical electrolysis of CuCl/MEImCl is given in Figure 14. Taking the cathode compartment and the Cu\(^+\) ion as example, the number of moles of Cu\(^+\) in the cathode compartment after electrolysis, \(n^c_{Cu^+}\), is given by

\[
n^c_{Cu^+} = n^0_{Cu^+} + n^m_{Cu^+} - n^e_{Cu^+} \tag{3.16}
\]

where the superscripts o, m, e refer to original, migration, and electrolysis, respectively. The number of moles of Cu\(^+\) transported to the catholyte is given by rearrangement

\[
n^m_{Cu^+} = n^c_{Cu^+} - n^0_{Cu^+} + n^e_{Cu^+} \tag{3.17}
\]
Since the number of moles of Cu\(^{+}\) transported to the cathode chamber divided by the charged passed, \(n_{Cu^{+}}^M/(Q/nF)\), is by definition the transference number \(t_{Cu^{+}}\), therefore division of equation (3.17) through by \(Q/nF\) and rearrangement gives

\[
(t_{Cu^{+}} - 1) = nF/Q \left[ n_{Cu^{+}}^{C} - n_{Cu^{+}}^{0} \right] \tag{3.18}
\]
where \( t_{\text{Cu}^+} \) is the transference number for the \( \text{Cu}^+ \) ion. A similar equation can be written for \( R^+ \).

\[
t_{R^+} = \frac{nF}{Q} [n^c_{R^+} - n^0_{R^+}] \tag{3.19}
\]

Analogous equations can also be written for the anode compartment.

The number of moles of each species in the anolyte and catholyte is conveniently expressed in terms of the weight fraction of copper(I) chloride, \( W_F \), and the weight of the melt, \( W \), as

\[
n_{\text{Cu}^+} = \frac{W_FW}{M_{\text{CuCl}}} \tag{3.20}
\]

\[
n_{R^+} = \frac{(1-W_F)W}{M_{RCl}} \tag{3.21}
\]

\[
n_{\text{Cl}^-} = n_{R^+} + n_{\text{Cu}^+} = \frac{W[M_{\text{CuCl}}(1-W_F) + M_{RCl}W_F]}{M_{RCl}M_{\text{CuCl}}} \tag{3.22}
\]

where \( M_{\text{CuCl}} \) and \( M_{RCl} \) are the molecular weights of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride, respectively. The transference numbers for \( \text{Cu}^+ \), \( R^+ \), and \( \text{Cl}^- \), given in terms of the above equations are, for the cathode compartment,
\[(t_{Cu^+} - 1) = \frac{nF/Q \left[ W_f^CW_C - W_f^OW_O \right]}{M_{CuCl}} \]  \hspace{1cm} (3.23)

\[t_{R^+} = \frac{nF/Q \left[ (1-W_f^C)W_C - (1-W_f^O)W_O \right]}{M_{RCl}} \]  \hspace{1cm} (3.24)

and for the anode compartment,

\[(t_{Cu^+} - 1) = \frac{nF/Q \left[ W_f^OW_O - W_f^AW_A \right]}{M_{CuCl}} \]  \hspace{1cm} (3.25)

\[t_{R^+} = \frac{nF/Q \left[ (1-W_f^O)W_O - (1-W_f^A)W_A \right]}{M_{RCl}} \]  \hspace{1cm} (3.26)

From equation (3.15) the transference number for Cl⁻ is given by

\[t_{Cl^-} = 1 - t_{R^+} - t_{Cu^+} \]  \hspace{1cm} (3.27)

b. Transport Relative to Chloride (Internal Transference Number). The derivation of an internal transference number \(t'\), referenced against the chloride ion, is based on the
arbitrary definition that the amount of chloride in a compartment is taken as a constant. Using the cathode compartment for an example the following condition must hold:

\[ n_0^{Cl^-} = n_C^{Cl^-} \] \hspace{1cm} (3.28)

Expanding the above expression with equation (3.22) gives

\[ W^0 \left[ \frac{MCuCl(1-W^0_f)+MRC1W^0_f}{MRC1MCuCl} \right] = W_C \left[ \frac{MCuCl(1-W_C^C)+MRC1W_C^C}{MRC1MCuCl} \right] \] \hspace{1cm} (3.29)

Solving this equation for \( W^0 \), insertion into equation (3.24) and replacing \( t_R^+ \) by \( t'_R^+ \) gives

\[ t'_R^+ = \frac{nFW^C/Q}{MCuCl(1-W^0_f) + MRC1W^0_f} \left[ W^0_f(1-W^C_f) - W_C^C(1-W^0_f) \right] \] \hspace{1cm} (3.30)

and

\[ t'_R^+ + t'_Cu^+ = 1 \] \hspace{1cm} (3.31)

for the internal transference numbers for movement of \( R^+ \) and \( Cu^+ \) relative to \( Cl^- \). A similar expression can be written for the anode compartment.
The relationship between the internal and external transference numbers is given in Appendix B.

3. Procedure

The cell used in this experiment is a modified Hittorf cell in which the anode, cathode, and central portions are separated from one another by porous glass membranes. The cell is diagrammed in Figure 15. No leakage through the porous frits due to hydrostatic flow was ever observed. Calibration marks on each of the compartments insured that the

![Diagram of a three-compartment transference cell with labels for silicone rubber seal, copper electrodes, and fine glass frits.](a) (b) (c)

Figure 15. Three Compartment Transference Cell.
levels were the same when the cell was loaded. Each compartment contained about 7 mL of fused salt. The glass joints could be secured by placing rubber bands across glass hooks (not shown in Figure 15). The copper electrodes were fashioned from 0.005 mil 100.0% copper foil and the leads were sealed through holes in the tops of the caps with silicone rubber. In different experiments, electrodes of surface area 60 cm² or 40 cm² were used. The foil electrodes were perforated and rolled loosely; this allowed the flow of liquid to the inside surfaces. The electrodes were pre-treated by dipping them in dilute HNO₃ followed by dilute HCl and H₂O rinses. They were then oven dried at 110°C for 10 minutes and weighed before transfer into the nitrogen glove box.

Before filling the cell with fused salt, it was taken apart, the ground glass joints lightly greased, and then the separate half cells, with their electrodes, weighed empty. With the electrodes removed fused salt was then poured into each half cell up to its calibration mark. The electrodes were inserted once again, and each filled half cell and electrode assembly weighed. The entire cell was then assembled and the central compartment filled with fused salt to its calibration mark.

Electrolysis was accomplished outside of the glove box in a water bath whose temperature was controlled at 30°C. Melts
of initial composition $\chi = 0.450, 0.500, \text{ and } 0.550$ were used in different experiments. A current of 2mA (current density 0.033mA/cm$^2$) was passed for the 0.500 melt and a current of 1.5 mA (current density 0.038mA/cm$^2$) for the 0.450 and 0.550 melts. After the desired amount of charge had been passed the cell was transferred back into the nitrogen glove box and disassembled. Fused salt was wiped free from the inside surfaces of the female joints on half cells A and C. The half cell-electrode assemblies were then weighed. The electrodes were then removed, cleaned, dried and weighed.

The weight fractions of CuCl in the anolyte, catholyte, and central compartments were determined by copper analysis. The average result from triplicate measurements was taken. Analysis of the electrolytes for 1-methyl-3-ethylimidazolium chloride was in fair agreement with copper analysis but found to be of low accuracy and therefore not included in any calculations. It is important to note that no change in the melt composition in the central compartment after electrolysis was observed in any of the experiments.

4. Results

It has been found through these electrolysis experiments that copper metal was stripped or plated in acidic, neutral or basic melts with a current efficiency of 100%. For
calculations, the amount of charge passed was taken as the average based on the weight loss or gain of the electrodes and that determined from the coulometer; these were in good agreement.

The morphology of the copper deposit was dependent on the melt composition at the surface of the copper electrode. A smooth uniform plate of copper was deposited from the melt of neutral composition. In the basic melt a copper sponge was observed while in the acidic melt nodule-like growths with small dendrites of metallic copper were plated out.

The experimental data for the three transport experiments are given in Table IV. The superscripts o and e refer to conditions before and after electrolysis, respectively. The letter a or c following the run number indicates whether the data were calculated for the anode or cathode compartments. The initial weight fractions of the melt compositions were determined from the weights of the components used in preparing the melts. The final weight fraction of a given melt composition is that calculated from the copper analysis.

The external transference numbers relative to the frits in the cell, $t_R^+$, $t_{Cu}^+$, and $t_{Cl}^-$, are given in Table V, which is organized using the run numbers of Table IV. The internal transference numbers relative to the chloride ion held constant, $t'_R^+$ and $t'_{Cu}^+$, are also given in Table V.
Table IV. Experimental Data for Electrolysis of $\chi\text{CuCl}/(1-\chi)$MEImCl Fused Salts.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Mole Fraction CuCl$_2$</th>
<th>Weight Fraction CuCl$_2$</th>
<th>Weight of Fused Salt, g</th>
<th>Coulombs Passed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x^o$</td>
<td>$x^e$</td>
<td>$w_f^o$</td>
<td>$w_f^e$</td>
</tr>
<tr>
<td>1a</td>
<td>.450</td>
<td>.519</td>
<td>0.3359</td>
<td>0.422 ±.001</td>
</tr>
<tr>
<td>1c</td>
<td>.450</td>
<td>.365</td>
<td>0.3359</td>
<td>0.279 ±.002</td>
</tr>
<tr>
<td>2a</td>
<td>.500</td>
<td>.578</td>
<td>0.4030</td>
<td>0.480 ±.004</td>
</tr>
<tr>
<td>2c</td>
<td>.500</td>
<td>.418</td>
<td>0.4030</td>
<td>0.327 ±.004</td>
</tr>
<tr>
<td>3a</td>
<td>.550</td>
<td>.600</td>
<td>0.4521</td>
<td>0.503 ±.002</td>
</tr>
<tr>
<td>3c</td>
<td>.550</td>
<td>.480</td>
<td>0.4521</td>
<td>0.384 ±.001</td>
</tr>
</tbody>
</table>

1. (a) anolyte (c) catholyte
2. (o) before electrolysis (e) after electrolysis
3. (i) from instrument coulometer (w) from weight change (m) mean
Table V. Transference Numbers of $\chi$CuCl/(1-$\chi$)MEImCl Melts.

<table>
<thead>
<tr>
<th>Run No. (1)</th>
<th>$t_R^{+}$ (2)</th>
<th>1a</th>
<th>1c</th>
<th>Mean</th>
<th>2a</th>
<th>2c</th>
<th>Mean</th>
<th>3a</th>
<th>3c</th>
<th>Mean</th>
<th>Overall Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.277</td>
<td>0.308</td>
<td>0.293</td>
<td>0.312</td>
<td>0.260</td>
<td>0.286</td>
<td>0.051</td>
<td>0.204</td>
<td>0.128</td>
<td>0.235</td>
</tr>
<tr>
<td></td>
<td>$t_{Cu}^{+}$ (3)</td>
<td>-0.548</td>
<td>-0.483</td>
<td>-0.516</td>
<td>-0.756</td>
<td>-0.478</td>
<td>-0.617</td>
<td>-0.682</td>
<td>-0.788</td>
<td>-0.735</td>
<td>-0.623</td>
</tr>
<tr>
<td></td>
<td>$t_{Cl}^{-}$ (4)</td>
<td>1.271</td>
<td>1.175</td>
<td>1.223</td>
<td>1.444</td>
<td>1.218</td>
<td>1.331</td>
<td>1.631</td>
<td>1.584</td>
<td>1.608</td>
<td>1.387</td>
</tr>
<tr>
<td></td>
<td>$</td>
<td>t_{Cl}^{-}/t_{Cu}^{+}</td>
<td>$</td>
<td>2.32</td>
<td>2.43</td>
<td>2.37</td>
<td>1.91</td>
<td>2.55</td>
<td>2.16</td>
<td>2.39</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>$t'_R^{+}$ (5)</td>
<td>0.976</td>
<td>0.954</td>
<td>0.965</td>
<td>1.034</td>
<td>0.869</td>
<td>0.952</td>
<td>0.785</td>
<td>0.917</td>
<td>0.851</td>
<td>0.923</td>
</tr>
<tr>
<td></td>
<td>$t'_{Cu}^{+}$ (6)</td>
<td>0.024</td>
<td>0.046</td>
<td>0.035</td>
<td>-0.034</td>
<td>0.131</td>
<td>0.049</td>
<td>0.215</td>
<td>0.084</td>
<td>0.150</td>
<td>0.078</td>
</tr>
</tbody>
</table>

(1) Refer to Table IV for run number
(2) From Eq. 3.24, 3.26
(3) From Eq. 3.23, 3.25
(4) From Eq. 3.27
(5) From Eq. 3.30
(6) From Eq. 3.31
5. Discussion

Examination of Table IV shows that in all cases the melts become more acidic ($\delta$ becomes larger) in the anode compartment after electrolysis, while they become more basic in the cathode compartment. The mass of the anolyte increases, due to migration of electrolyte and to dissolution of the anode, while the mass of the catholyte decreases due to migration out of electrolyte and to plating out of copper on the cathode. In each case the weight gain of the anolyte exceeds the weight loss of the catholyte. Thus the quantity of fused salt in the central compartment diminishes slightly, but without change in composition.

Examination of the external transference numbers, the first three lines of data in Table V, shows that all the ionic constituents in the $\chi$CuCl/$1- \chi$MEImCl melt play a significant role in carrying charge on electrolysis. The 1-methyl-3-ethylimidazolium cation carries about 20% of the charge, more in the more basic melt where it is more abundant and less in the more acidic melt. The negative values of $t_{Cu^+}$ prove that copper(I) migrates as an anion, in agreement with the previous vibrational spectroscopic evidence for CuCl$_2^-$, CuCl$_3^{2-}$, and Cu$_2$Cl$_3^-$ anions in CuCl/Et$_3$NCl melts (Axtell, et al., 1973). The absolute values of the transference number ratio $|t_{Cl^-}/t_{Cu^+}|$ are all about two, in accord with the
supposition that the predominant copper species is CuCl$_2^-$. The highest value of this ratio is found in the most basic melt, where free Cl$^-$ and some CuCl$_3^{2-}$ would be in equilibrium with CuCl$_2^-$. 

The last two lines of data in Table V give the internal transference numbers relative to chloride ion held fixed. These values show that the 1-methyl-3-ethylimidazolium cation can migrate independently of chloride ion, while copper(I) cannot; only in the acidic melt where there is a shortage of chloride ion does $t'_\text{Cu}^+$ exceed 0.05.

Combining equations 3.10 and 3.14 gives an expression for the diffusion coefficient in terms of transference numbers and equivalent conductivity,

$$D = \frac{RT t\Lambda / F^2 |z|^2}{(3.32)}$$

By using equation (3.32) a diffusion coefficient for the linear CuCl$_2^-$ anion can be calculated from the values of the transference number for CuCl$_2^-$, which is taken as $t\text{Cu}^+ + t\text{Cl}^- = 0.764$, and the equivalent conductivity 1.18 ohm$^{-1}$ cm$^2$ eq$^{-1}$ at 30°C for a neutral 1:1 CuCl/MEImCl melt. A melt of this composition is composed predominantly of MEIm$^+$ cations and CuCl$_2^-$ anions. The result of this calculation gives $D_{\text{CuCl}_2^-} =$
2.44 \times 10^{-7} \text{cm}^2/\text{s}. This value can be compared to 2.43 \times 10^{-7} \text{cm}^2/\text{s} which is calculated from the Stokes Einstein equation

\[ D = \frac{K T}{6 \pi \eta r} \] (3.11)

using the viscosity 35.3 cp of a 1:1 melt at 30^\circ\text{C}. The ionic radius for CuCl_2^- was taken as 2.59 \AA, 2.09 \AA for the Cu-Cl distance (Newton, 1970) and 0.50 \AA for the radius of Cl.

The two values of D_{\text{CuCl}_2^{-}} are in good agreement and are of the same order of magnitude found for anionic species in other room temperature melts (Robinson and Osteryoung, 1980; Hussey, King and Carpio, 1979).
IV. ELECTROCHEMICAL STUDIES OF LIQUID COPPER(I) CHLORIDE 1-METHYL-3-ETHYLIMIDAZOLIUM CHLORIDE MIXTURES

The room temperature fused salt mixtures are ionic electrolytes. Their Walden products of conductivity times viscosity, described in Chapter III, are not of a markedly different order of magnitude than the Walden products for more common fused salts such as molten alkali halides. Therefore, a variety of electrochemical measurements can be made on these systems. These include thermodynamic measurements (potentiometry at a reversible electrode with negligible current flow) and kinetic studies (exchange current densities, symmetry coefficients, and Tafel slopes in voltammetric work).

Important variables are melt and electrode composition, temperature, stirring, and applied voltage (or current). Various cells of different designs are used in the various experiments. A goal is that the fundamental information obtained can be applied in the construction of practical batteries.
A. Potentiometry

1. Historical and Theoretical

Potentiometry here involves the measurement of the potential difference between two electrodes of an electrochemical cell under conditions of nearly zero current. This measured potential difference is the sum of the potentials at the interfaces and that of the liquid junction. In the potentiometric experiment one of the two electrodes is the reference electrode and the potential of the test electrode is measured with respect to it. The ideal reference electrode should have a reproducible known potential with a low temperature coefficient, and should be non-polarizable under passage of small currents (Sawyer and Roberts, 1974).

A satisfactory reference electrode for the CuCl/Et$_3$NHCl fused salt was found to be a copper wire immersed in a 0.5CuCl/0.5Et$_3$NHCl melt (Silkey and Yoke, 1980). The electrochemical reaction at the electrode is

$$\text{CuCl}_2^- + e^- \rightleftharpoons \text{Cu}^0 + 2\text{Cl}^- \quad \text{(4.1)}$$

All other potentials in this chlorocuprate(I) fused salt system were measured with respect to this reference. Its
operational potential versus the SCE at 250°C was found to be -0.241 V, but this included an unknown liquid junction potential.

The CuII/CuI couple was studied in the CuCl/Et3NHCl system by potentiometry and by the use of an OTTLE cell. The electrochemical reaction occurring at platinum or gold electrodes was found to be

\[ \text{CuCl}_2 + e^- \rightleftharpoons \text{CuCl}_2^- \]

(4.2)

Reversible (Nernstian) behavior of the CuII/CuI couple was observed only at low concentrations of copper(II) chloride dissolved in the fused salt (less than 0.2 M) (Silkey, 1979).

The CuII/CuI couple at platinum, tungsten and glassy carbon electrodes has been extensively studied through potentiometric techniques using copper(II) chloride solutions in both high and low temperature aluminum chloride fused salt systems. The CuI/Cu0 couple has similarly been studied in these systems (Anders and Plambeck, 1979; Hussey, King and Carpio, 1979; Boxall, Jones and Osteryoung, 1974; Laher and Hussey, 1983; Nanjundiah and Osteryoung, 1983). Nernstian behavior has generally been found.
Potentiometric techniques have been widely used to help solve problems concerning solution equilibria. The complex anionic equilibrium in aluminum chloride fused salts has been extensively studied by a potentiometric method involving concentration cells of the type

<table>
<thead>
<tr>
<th>Cell 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ref)</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>(Test)</td>
</tr>
<tr>
<td>Al</td>
</tr>
</tbody>
</table>

Here RC1 refers to substituted organic ammonium chloride. The composition of the reference half cell is held constant while that of the test half cell is varied. This point by point method has been referred to as a "potentiometric titration" in which the composition in the test side of the cell is changed by successive additions of portions of the powdered solid components to the melt (Robinson and Osteryoung, 1980; Cheek and Osteryoung, 1982). The equilibrium in the aluminum chloride-based fused salts is completely described by the single expression

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

(4.3)
for which an equilibrium constant can be obtained directly from potentiometric data. The value for $K_{eq}$ depends on the particular melt and temperature and ranges from $1 \times 10^{-7}$ for AlCl$_3$/NaCl at 170°C to $2 \times 10^{-19}$ for AlCl$_3$/MEImCl at 25°C. In the 1:1 AlCl$_3$/RC1 melts the major species is the AlCl$_4^-$ ion with only small amounts of Al$_2$Cl$_7^-$ and Cl$^-$ present. Addition of AlCl$_3$ shifts the equilibrium such that in a 2:1 melt the Al is present entirely as Al$_2$Cl$_7^-$. Any extra Cl$^-$ added to the 1:1 melt results in an increase in the Cl$^-$ ion concentration. All of these AlCl$_3$/RC1 systems have characteristic sharp "endpoints" having orders of magnitude change in Cl$^-$ concentration on going from acidic to basic melts.

2. **Procedure**

In the present work it was of interest to study the behavior of both the Cu$^{II}$/Cu$^I$ and Cu$^I$/Cu$^0$ couples in various CuCl/MEImCl melts. The potentiometric experiments were carried out in a two compartment cell constructed from 10/18 joints and a fine glass frit. The cell is shown in Figure 16. Each half cell had a volume of about 4 mL. The reference electrode was a copper wire immersed in a 0.50CuCl/0.50MEImCl melt. Copper and platinum electrodes were pretreated with dilute nitric acid, dilute hydrochloric acid, and then rinsed copiously with water and oven dried at 110°C for 10 minutes.
Figure 16. Cell Used in Potentiometric Studies. Reference Copper Electrode (b) and Test Copper or Platinum Electrode (a).

The cells used to study the redox couples Cu⁺/Cu⁰ and Cu²⁺/Cu⁺ can be represented as

**Cell 2**

(Ref)  (test)

Cu | 0.5CuCl₂,0.5MEImCl | XCuCl₂,(0.50-X/2)MEImCl | Cu

**Cell 3**

(Ref)  (test)

Cu | 0.5CuCl₂,0.5MEImCl | XCuCl₂,(0.50-X/2)CuCl₁,(0.50-X/2)MEImCl | Pt
The composition on the test side was varied by adding increments of solid CuCl or CuCl₂. The solution was stirred magnetically after each addition of solid. After complete dissolution of the solid the stirring was stopped and the cell potential recorded with a millivoltmeter. Measurements were made in the nitrogen dry box at 23°C or 25°C depending on the experiment.

3. Results and Discussion

The potential of Cell 2 at 25°C as the composition of a \( \chi \text{CuCl}/(1-\chi)\text{MEImCl} \) melt is varied is shown in Figure 17. The results show quite a contrast to the behavior of aluminum chloride-based fused salts. While an inflection point does occur at the \( \chi = 0.50 \) melt composition, there is not the orders-of-magnitude change in Cl⁻ concentration which would correspond to a sharp endpoint. These data cannot be interpreted in terms of a single equilibrium expression involving two chlorocuprate(I) anions such as

\[
2\text{CuCl}_2^- \rightleftharpoons \text{Cu}_2\text{Cl}_3^- + \text{Cl}^-
\]  

(4.4)

This is in accord with the abundance of evidence that CuCl₃²⁻, CuCl₄³⁻, and a variety of polynuclear anions play roles in a
Figure 17. Potentiometric Titration of CuCl in the CuCl/MEImCl Fused Salt at 25°C.
series of complex anion equilibria in the copper(I) system. These anions undergo more gradual changes in concentration as a function of the CuCl/MEImCl mole ratio.

The potential of Cell 3, with a platinum electrode immersed in solutions of copper(II) chloride in a melt of composition 0.50CuCl/0.50MEImCl as solvent, is shown in Figure 18. The data were obtained at 23.5°C using the same experimental conditions described above. The [Red]/[Ox] concentration ratios are taken as the ratio of the mole fractions of CuCl (assumed to be in the form of CuCl₂⁻) and of CuCl₂ in the melts. The experimental data are shown as open circles. A linear least squares fit of these points gave a slope of 58.5 mv, in excellent agreement with the theoretical slope of 58.8 mv at this temperature for the Nernst equation applied to

\[ \text{CuCl}_2 + e^- \rightarrow \text{CuCl}_2^- \]  

(4.2)

In other experiments at higher concentrations of copper(II) chloride, deviations from Nernstian behavior were observed. The same result was noted by Silkey for CuCl₂ dissolved in the CuCl/Et₃NHC₁ fused salt (Silkey, 1979).
Figure 18. Potentiometric Titration of CuCl₂ in a 0.50CuCl/0.50MEImCl Melt.

B. Polarization Studies

1. Historical and Theoretical

To study the kinetic characteristics of a half-reaction at an electrode, one observes how the current-voltage behavior responds to perturbations. The result may permit calculation of an exchange current density, \( i_0 \), which is a fundamental property of the system. The exchange current density is the
magnitude of the opposite but equal cathodic and anodic currents which flow when the electrode is at its equilibrium potential and the net current is zero. The exchange current is a quantitative measure of the rate of electron transfer at the electrode-solution interface. The kinetics of the electrode reaction are profoundly affected by the nature of the electrolyte, by the double layer structure, by mass transport, and by the difference between the applied and equilibrium potentials of the electrode (Delahay, 1965; Bockris and Reddy, 1970; Erdey-Gruz, 1972). In the simplest case the rate determining step may be transfer of a single electron. Multi-step mechanisms, pre-equilibria involving the electroactive species, and other complications may make the kinetics more difficult to interpret.

A basic equation relating current and potential is the Butler-Volmer equation, which may be written in simplified form as

\[ i = i_0 \left[ \exp(-\alpha \frac{\eta}{nF/RT}) - \exp((1-\alpha) \frac{\eta}{nF/RT}) \right] \]  \hspace{1cm} (4.5)

Here \( i \) is the current density (current per unit surface area of the electrode) at a given polarization voltage or over-
potential, $\eta$. The convention used in equation (4.5) takes a cathodic or reducing current as positive with an increase in magnitude as the overpotential is made more negative. The first exponential term in equation (4.5) describes the cathodic branch of the $i$ versus $\eta$ relation, and the second term the anodic branch. An important parameter of interest in equation (4.5) is the symmetry coefficient $\alpha$, which gives a qualitative measure of how much an overpotential assists the cathodic reaction relative to the $(1- \alpha)$ coefficient for the anodic branch. For complicated electrode reactions the term $(1- \alpha)$ may be replaced by $\beta$ such that $\alpha + \beta$ may no longer be equal to one (Bard and Faulkner, 1980). The general shape of the $i$ versus $\eta$ curve will be determined largely by the values of the exchange current and the symmetry coefficient, and these may be extracted from the $i$ versus $\eta$ relationship.

There are two well known approximations to the Butler-Volmer equation, one applying in the region of low overpotentials and the other of high overpotentials. At low overpotentials, equation (4.5) can be linearized by using the approximation $\exp(x) \approx 1 + x$ at low $x$. Equation (4.5) then reduces to

$$i = i_0 \eta^n F/RT$$

(4.6)
For systems with high exchange currents this linear approximation is usually satisfactory (Swinkels, 1971). The overpotential range in which the linear approximation is valid has been the subject of numerous papers (Stern and Geary, 1957; LeRoy, 1973 and 1977; Hausler, 1977; Nagy and Land, 1985). The range generally accepted has been ±10 mV, but the actual range will depend on the magnitude of both $i_0$ and $\eta$. When the overpotential is sufficiently large, one of the two exponentials in equation (4.5) becomes insignificant and can be neglected relative to the other. This results in the well known Tafel equation, which when written in logarithmic form is

\begin{align*}
\text{Cathodic} & \quad \ln|i| = \ln i_0 - a \eta nF/RT \quad (4.7) \\
\text{Anodic} & \quad \ln|i| = \ln i_0 - (1-q) \eta nF/RT \quad (4.8)
\end{align*}

Unlike equation (4.6), equations (4.7) and (4.8) allow for calculation of both the exchange current and the symmetry coefficient. In order to observe Tafel behavior, without a significant contribution from the back reaction, the overpotential should be greater than ±100 mV. At such overpotentials the error in their measurement is less than 2% (Delahay, 1965). Deviations from the Tafel relationship will
result if polarization effects other than that of charge transfer contribute to the overpotential. These various effects have been described and include diffusion, concentration, reaction, crystallization, and resistance polarization (Vetter, 1967).

Although the Butler-Volmer equation has usually been used to describe chemical electrode kinetics with solutions in water or similar solvents in mind, the general principles of electrode processes also apply to reactions occurring on metal surfaces in contact with fused salts. Some exchange current measurements previously reported for high temperature fused salt systems have involved a component of the fused salt as the electroactive species, but in the majority of the cases the fused salt served merely as a solvent (Delimarskii and Markov, 1964; Bloom, 1967; Laitinen, et al., 1960). Exchange currents for fused salt systems typically range between $10^{-3}$ and $10^{1}$ A/cm$^2$ for both of the cases mentioned above (Swinkels, 1970; Delahay and Tobias, 1966). The symmetry coefficient is commonly about 0.5 but values have been observed to range between 0.2 and 0.8 (Delahay and Tobias, 1966).

Polarization studies in this work are concerned with the interface which is formed when a copper electrode is immersed in the CuCl/MEImCl fused salt. The oxidation-reduction equation involves the copper electrode and a species in the
fused salt which, for brevity, may be taken as the dichlorocuprate(I) anion.

\[ \text{CuCl}_2^- + e^- \rightleftharpoons \text{Cu}^0 + 2 \text{Cl}^- \] (4.1)

Previous reports of exchange current measurements for this reaction made on low temperature fused salts are limited to those made by Silkey on the CuCl/ET$_3$NHCl system (Silkey and Yoke, 1980).

2. Procedure

A three electrode cell was used to study the behavior at a copper electrode immersed in $X\text{CuCl}/(1-X)\text{MEImCl}$ fused salt mixtures. The cell is shown in Figure 19. The working and counter electrode compartments were separated by a porous glass frit. All copper electrode surfaces were pre-treated before use with dilute nitric acid followed by concentrated hydrochloric acid and finally with distilled water. The back side of the working electrode was masked with a coating of silicone rubber. The electrode was positioned so that the exposed face was orthogonal to the counter electrode. The geometric surface area of the working electrode was 1.0 ± 0.1 cm$^2$. The reference electrode was a copper strip immersed in a
Figure 19. Cell Used for Overpotential Measurements. Working (a), Reference (b) and Counter (c) Electrodes.

0.5 mole fraction CuCl melt in a Luggin capillary. The tip of the Luggin capillary was positioned less than 1 mm from the working electrode. The counter electrode was fashioned from copper foil and had a surface area of about 32 cm².

Polarization current-overpotential data were obtained exclusively by galvanostatic control. Slow scan speeds were employed; these generally ran between 0.2 and 0.5 mA/s for high overpotential measurements and between 1 and 2 mA/s for low overpotential measurements. The solution in the
working electrode compartment was magnetically stirred at the fastest possible rate. At sufficiently low rates of stirring the current required to maintain a given potential was observed to vary with rate. Current-time transients at applied potential steps were obtained by potentiostatic control. The solution was left unstirred for measurements of current-time behavior at the copper-fused salt interface in constant applied potential experiments.

3. Results

a. High Overpotential Measurements. High overpotential data were obtained for melts of composition \( \chi = 0.40, 0.50, \) and 0.60. The values of \( \ln |i| \) as a function of \( \eta \) are shown in Figure 20. The shapes of the curves are typical. There are linear Tafel regions and marked deviations from linearity at the lower overpotentials. The Tafel plot for the 0.60 melt is symmetric about \( \eta = 0 \), while the plots for the 0.50 and 0.40 melts are slightly asymmetric with the cathodic branch lower than the anodic branch. At higher overpotentials than those indicated in Figure 20 non-linearity again became evident. This result had also been observed in the Tafel plots of data obtained in CuCl/Et3NHCl fused salts (Silkey, 1979).

Exchange currents can be obtained from the intercept at \( \eta = 0 \) extrapolated from the linear regions of the anodic and
Figure 20. Tafel Plots for CuCl/MEImCl Melt Compositions at 25.0°C.
cathodic branches of the Tafel plot. The values of $i_0$ are given in Table VI. The values of $\alpha$ and $(1-\alpha)$ determined from the slopes in the linear regions are also given.

Table VI

Exchange Currents and Symmetry Coefficients at 25°C from Tafel Plots and from a Least Squares Computer Program

<table>
<thead>
<tr>
<th>Mole Fraction CuCl</th>
<th>$i_0$ mA/cm²</th>
<th>Symmetry Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exptl (1)</td>
<td>calc (2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.60</td>
<td>2.36</td>
<td>2.42</td>
</tr>
<tr>
<td>0.50</td>
<td>0.87</td>
<td>0.706</td>
</tr>
<tr>
<td>0.40</td>
<td>0.20</td>
<td>0.121</td>
</tr>
</tbody>
</table>

|                    | exptl (1)    | calc (2)              |
|                    | $\alpha$ (1-\alpha) (3) | $\alpha$            |
|                    |              |                        |
| 0.60               | 0.49         | 0.50                  |
| 0.50               | 0.35         | 0.63                  |
| 0.40               | 0.34         | 0.67                  |

(1) From Tafel plot, Figure 20.
(2) From non-linear least squares computer program.
(3) Calculated independently from the slope of the anodic branch in the Tafel region, not from the value of $\alpha$. 
The values for the exchange currents and symmetry coefficients listed in Table VI were adjusted in a least squares computer program optimizing a best fit of the experimental \( i \) versus \( \eta \) data to the Butler-Volmer equation. The computer-generated curves of \( i \) versus \( \eta \) for the three melt compositions, plotted together with the experimental data points, are shown in Figure 21. The experimental values are seen to give an excellent fit to the Butler-Volmer equation. The computer-generated values for the exchange currents and symmetry coefficients for the different melt compositions are shown in Table VI.

Drazic and Vascic (1985) have described a numerical technique which uses the point of inflection in the plot of \( i \) versus \( \eta \) to determine values for the symmetry coefficient. The overpotential at the inflection point is given by

\[
\eta = (2RT/nF)\ln\left[ \frac{\alpha_l}{1-\alpha_l} \right]
\]  

(4.9)

This relation is obtained by setting the second derivative of the Butler-Volmer equation equal to zero and solving for \( \eta \). When \( \alpha_l = 0.50 \) the point of inflection occurs at \( \eta = 0 \). In Figure 21, this is seen to be the case for the \( \chi = 0.60 \) melt. For the \( \chi = 0.50 \) and 0.40 compositions, use of the calculated symmetry coefficients (from Table VI) in equation (4.9)
Figure 21. Current-Voltage Behavior of the Copper-$\chi$CuCl/(1-$\chi$), MEImCl Interface at 25.0°C.
permits calculation of the point of inflection at $\eta = -22.3$ mV and -60 mV, respectively. These values are in agreement with the inflection points observed for these curves in Figure 21.

b. **Low Overpotential Measurements.** As a test of the linear approximation to the Butler-Volmer equation at sufficiently low overpotentials, values of current for the overpotential range $\pm 5$ mV were measured and are shown in Figure 22. Melts of composition $\chi = 0.60$ and 0.40 give data showing good linearity in this range. However, a plot of the data for the melt of composition $\chi = 0.50$ shows significant curvature. New calculations of exchange currents were made from the slopes of the straight lines for the melts of composition $\chi = 0.40$ and 0.60. For the melt of composition $\chi = 0.50$, the slope of the tangent to the curve at $\eta = 0$ was used. The low overpotential data were reproducible and Table VII gives the average value for the exchange current obtained from several different measurements. For comparison, values of the exchange currents from Table VI, determined from high overpotential data, are repeated here.
Figure 22. Low Overpotential Curves for $\chi_{CuCl/(1-\chi)MEImCl}$, Compositions at 25.0°C.
Table VII

Exchange Currents at 25.0°C

<table>
<thead>
<tr>
<th>CuCl Mole Fraction</th>
<th>From Figure 22</th>
<th>From Table VI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(i_0) mA/cm²</td>
<td>(i_0) mA/cm²</td>
</tr>
<tr>
<td>0.60</td>
<td>0.219±9</td>
<td>2.42</td>
</tr>
<tr>
<td>0.50</td>
<td>0.123±15</td>
<td>0.706</td>
</tr>
<tr>
<td>0.40</td>
<td>0.026±2</td>
<td>0.121</td>
</tr>
</tbody>
</table>

The \(i_0\) values obtained from the low overpotential data differ by one order of magnitude from those determined from the intercepts of the Tafel slopes at higher overpotentials. Although the relative error in the low overpotential measurements is inherently larger (due to the lower signal to noise ratio and the uncompensated potential drop in the solution between the reference and working electrodes) the two order-of-magnitude difference between exchange currents determined in the low and high overpotential ranges cannot be accounted for.

Low overpotential measurements obtained over the temperature range 25-40°C on a melt of composition \(X = 0.50\) are shown in Figure 23. Since the exchange current represents
Figure 23. Temperature Variation of the Current-Voltage Behavior of the Cu/(0.50CuCl/0.50MEImCl) Melt at Low Overpotentials.
the rate of electron transfer at the equilibrium potential, its variation with temperature depends on the energy of activation for the electrode process. Exchange currents calculated from the slopes of the tangent to each curve at \( \eta = 0 \) are given in Table VIII. An Arrhenius plot of \( \ln i_0 \) versus \( 1/K \) is shown in Figure 24. The energy of activation for electron flow at the copper electrode in a melt of composition \( \chi = 0.50 \) at low overpotentials is found to be 14.5 kcal/mol. Typical values for the energy of activation for electrode processes generally do not exceed 10 kcal/mol (Sundheim, 1964).

<table>
<thead>
<tr>
<th>T(K)</th>
<th>293.2</th>
<th>298.2</th>
<th>303.2</th>
<th>308.2</th>
<th>313.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( i_0 ) (( \mu A/m^2 ))</td>
<td>65</td>
<td>111</td>
<td>150</td>
<td>215</td>
<td>344</td>
</tr>
</tbody>
</table>

Table VIII

Exchange Currents at Different Temperatures for the 0.5 Melt
c. **Current-Time Transients.** Typical behavior is shown in Figure 25 for current density at a copper electrode in a melt of composition 0.50CuCl/0.50MEImCl following a voltage spike. The electrode potential was stepped cathodically to +50 mV from the initial equilibrium value of zero in an unstirred solution for times up to 60 seconds. The current reaches a maximum value almost instantaneously as the potential is applied, indicating the absence of nucleation effects. It then rapidly decays for the first few seconds. This initial decay is not exponential and therefore not
Figure 25. Current-Time Transient at the Cu/(0.50CuCl/0.50MEImCl) Interface for a 50 mV Cathodic Pulse.
attributed to double layer capacitance effects. The current decay occurs more slowly after this with the current finally reaching a value limited by diffusion.

Current-time behavior under conditions of mass transfer by diffusion at constant potential is described by the Cottrell equation

\[ i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \]  

(4.10)

where \( i \) is the current flowing at the electrode/electrolyte interface at some time \( t \), and \( A, D, \) and \( C \) are the electrode surface area, diffusion coefficient, and concentration of the electroactive species, respectively. The values for \( n \) and \( F \) have their usual significance. For pulse times greater than about 10 seconds the current decay in Figure 25 shows approximate linear dependence on \( t^{-1/2} \). However, CuCl/MEImC1 fused salts do not satisfy the basic criteria for applicability of the Cottrell equation. The melt composition near the electrode is made more basic as reduction of chlorocuprate(I) species occurs. This gives rise to density gradients and local changes in viscosity and conductivity. The electroactive species moving to the electrode from the bulk liquid
then become involved in a dynamic equilibrium with chloride ion and other chlorocuprate(I) species having different mobilities and diffusion coefficients.

4. Discussion

Several factors have been found to influence the current-voltage behavior at the copper/(CuCl/(1-x)MEImCl) interface. The composition of the fused salt is the most important factor. The equilibrium potential at 25°C becomes 0.44 volt more positive as the mole fraction of copper(I) chloride increases from 0.33 to 0.67. The exchange current density at 25°C and at high overpotentials increases from 0.20 to 2.36 mA/cm² as the mole fraction of copper(I) chloride increases from 0.40 to 0.60. There is a large increase in current for a given overpotential as the temperature is raised from 20 to 40°C, corresponding to an unusually high activation energy for the electrode process at low overpotentials. The variation in current at such small overpotentials gives rise to markedly different values of exchange current density than were found from Tafel plots. The assumption that the kinetics and mechanism of the electrode reactions are the same at low and high overpotentials may be invalid.
If electrolyte conductivity and bulk viscosity were the only criteria for choosing which melt composition would have the most facile electrode kinetics, the choice would be the melt of composition $\chi = 0.50$. However, the melt of composition $\chi = 0.60$ proves to have more favorable kinetics at the copper electrode as indicated by its higher exchange current density.

C. Battery Studies

1. Historical

Since the room temperature chlorocuprate(I) melts have desirable physical and electrochemical properties, they might find a practical use as electrolytes in high energy density batteries. A great deal of interest has been given to the room temperature chloroaluminate melts for such an application (Wilkes, et al., 1981).

In previous work with the CuCl/Et$_3$NHCl system (Silkey, 1979) a variety of prototype batteries was investigated for their characteristics on discharge through loads and their ability to be recharged after partial discharge. Because of the high viscosity of that liquid electrolyte, high internal resistance, low voltage (0.8 volt), and very low current density, those cells offered little practical promise.
In this work it was of special interest to combine in a single cell the electropositive aluminum anode in various AlCl$_3$/MEImCl room temperature melts with cathodes in various CuCl/MEImCl melts. The half reactions occurring at the anode of such a battery can be written as

\[ Al + 7 AlCl_4^- - 3e^- \rightleftharpoons 4 Al_2Cl_7^- \]  \hspace{1cm} (4.11)

and

\[ Al + 4 Cl^- - 3e^- \rightleftharpoons AlCl_4^- \]  \hspace{1cm} (4.12)

for acidic and basic AlCl$_3$/MEImCl melts, respectively. For a copper cathode in the basic, neutral and acidic CuCl/MEImCl melts the reactions are, respectively

\[ CuCl_3^- + e^- \rightleftharpoons Cu^0 + 3Cl^- \]  \hspace{1cm} (4.13)

\[ CuCl_2^- + e^- \rightleftharpoons Cu^0 + 2Cl^- \]  \hspace{1cm} (4.1)

\[ Cu_2Cl_3^- + e^- \rightleftharpoons Cu^0 + CuCl_2^- + Cl^- \]  \hspace{1cm} (4.14)

Alternatively, an inert cathode (graphite or noble metal)
could be used in a solution of copper(II) chloride in the 
CuCl/MEImCl melt. In this case the reduction half-reaction 
would be

$$\text{CuCl}_2 + e^- \rightleftharpoons \text{CuCl}_2^-$$  \hspace{1cm} (4.2)

Batteries based on these electrodes and electrolytes can 
formally be written as

**Cell 4**

$$\text{Al} \mid \text{AlCl}_3, (1-X)\text{MEImCl} \parallel \text{yCuCl}, (1-y)\text{MEImCl} \parallel \text{Cu}$$

and

**Cell 5**

$$\text{Al} \mid \text{AlCl}_3, (1-X)\text{MEImCl} \parallel \text{CuCl}_2(M) \text{ in } \text{yCuCl}, (1-y)\text{MEImCl} \parallel \text{Pt,C}$$

where the mole composition of the electrolytes in each half 
cell can be varied.

2. **Procedure**

Electrochemical cells as outlined above were prepared in 
a glass U-tube with a fine porosity glass frit separating the 
anolyte and catholyte (see Figure 16). Copper electrodes were 
pre-treated as described previously. Aluminum electrodes were 
pre-treated with dilute HF solution followed by dilute HNO₃
and then rinsed with water and acetone. The electrodes were then wiped dry and transferred into the nitrogen glove box, where the cells were assembled and the measurements made.

3. Results and Discussion

Two cells were prepared with the initial electrolyte compositions

\[
\text{Cell 6} \quad \text{Al} | 0.4\text{AlCl}_3, 0.6\text{MEImCl}^+ | 0.4\text{CuCl}, 0.6\text{MEImCl} | \text{Cu}
\]

and

\[
\text{Cell 7} \quad \text{Al} | 0.6\text{AlCl}_3, 0.4\ \text{MEImCl} | 0.4\text{CuCl}, 0.6\text{MEImCl} | \text{Cu}
\]

The aluminum and copper(I) based liquids were compatible, in that there was no precipitation or other reaction at the frit. The emf of the two cells was measured in a high impedance circuit as the composition of each right-hand half-cell was varied by adding solid portions of copper(I) chloride. The melt was stirred after each addition of solid. The results of
these measurements are given in Figures 26 and 27 for cells 6 and 7, respectively. The somewhat unsteady potential readings observed in Figure 26 were due to an unknown chemical reaction at the aluminum electrode. This reaction resulted in the formation of gas bubbles at the electrode. Aluminum oxidation has been reported to occur in basic aluminum chloride/N-alkylpyridinium chloride melts with reduction of the organic cation, but this has been said to be much less of a problem in basic AlCl₃/MEImCl melts (Wilkes, Levisky, Wilson, and Hussey, 1982).

![Diagram](image)

**Figure 26. EMF Measurements on the Galvanic Cell**

$$\text{Al} | 0.40\text{AlCl}_3, 0.60\text{MEImCl} || \text{CuCl}, (1- \chi)\text{MEImCl} | \text{Cu}. $$
The data for the 0.40, 0.50, and 0.60 mole fraction CuCl melts are replotted in Figure 28 as a function of the mole fraction of AlCl₃ in cells #6 and #7. Three important conclusions can be drawn from Figure 28: (1) The maximum voltage of a cell based on the aluminum and copper(I) 1-methyl-3-ethylimidazolium chloride fused salts and with
aluminum and copper electrodes is approximately +1.05 V, (2) the cell voltage is significantly more sensitive to AlCl₃/MEImCl composition, (3) the cell reverses polarity at an AlCl₃ composition greater than about $\chi = 0.56$, where the aluminum electrode becomes the cathode. 

The results of Figure 28, obtained under conditions of negligible current flow, were used as a guide to prepare a
test battery. This cell, composed of AlCl$_3$/MEImCl and CuCl/MEImCl fused salts, was used to measure not only open circuit voltage (OCV) but also to study discharge under loads. The cell is diagrammed in Figure 29, which shows the melt compositions used. Each electrode had a surface area of approximately 1 cm$^2$. With the aluminum electrode in the basic AlCl$_3$/MEImCl melt and the platinum electrode in the acidic CuCl/MEImCl melt the OCV was +1.4 volt. After a few hours gas bubbles were evolved at the aluminum electrode at the OCV voltage, but no discoloration was evident in the aluminum melt. The observed instability of the aluminum electrode is

$$\text{Al}(0.44/0.56)\text{AlCl}_3\text{MEImCl}||\text{(0.56/0.44) CuCl, MEImCl}||\text{Pt}$$

OCV 1.44 V

![Diagram of battery](image)

Figure 29. Proof of Concept Battery.
not in accord with the previous report of Wilkes and co-workers. During 4 hours of discharge through a 10.5 kohm resistor, copper metal was deposited onto the platinum electrode so that this became a copper electrode. Pitting at the aluminum electrode due to aluminum dissolution was not apparent. The voltage decreased from 0.89 V to 0.64 V. The discharge curve is shown in Figure 30. The current output decreased from 0.17 mA initially to 0.10 mA at the end.

The final OCV after this partial discharge was 0.84 V in good agreement with the value predicted from Figure 28 for melts of this composition. The cell could be successfully recharged from an external source and the copper removed from the platinum electrode; the OCV then returned to 1.3 volt. The cell held this voltage for 3 days. After the cell was again partially discharged the OCV could be increased by (a) recharging, (b) replacing the copper-coated platinum electrode with a fresh platinum electrode, or (c) by adding cupric chloride to the copper(I) electrolyte with a platinum electrode. After prolonged discharge an orange color was imparted to the AlCl₃/MEImCl electrolyte and internal short circuiting was also apparent as copper metal was observed to plate out onto the aluminum electrode. Such copper plating was expected on the basis of separate experiments in which aluminum metal was immersed directly in CuCl/MEImCl melts. No
Figure 30. Discharge Curve for the AlCl₃/CuCl Battery Through a 10.5 kΩ Resistor.
rapid reaction was apparent in a basic melt of composition \( \chi = 0.4 \), but in an acidic melt, \( \chi = 0.6 \), hydrogen gas (identified by mass spectroscopy) was given off and copper metal plated on the aluminum.

No attempt was made to optimize the battery prepared by the combination of the AlCl\(_3\)/MeImCl and CuCl/MeImCl fused salts in this study. Nevertheless, the results show that current at a useful level can be drawn from such a simple cell and the cell could be recharged after partial discharge.
The use of high temperature molten salts as inorganic reaction media is well known. The field has been extensively reviewed by several authors (Sundermeyer, 1965; Gordon, 1969; Kerridge, 1975). Parshall (1972) has discussed homogeneous catalysis of hydrogenation, isomerization, hydroformylation and carboxylation of olefins using molten salts as solvents. Such solvents facilitate the separation by distillation of the organic product from the catalyst and reaction medium. A recent example of such use is the ruthenium catalyzed preparation of ethylene glycol from CO/H₂ synthesis gas mixtures in molten quarternary phosphonium or ammonium salts (Knifton, 1981).

Salts which are liquid at and below room temperature are of special interest as reaction media when thermally sensitive solutes are involved, as well as from the standpoints of energy conservation and minimization of corrosion. The room temperature AlCl₃/MEImCl melts are miscible with aromatic
hydrocarbons and have been used as solvents and catalysts for Friedel-Crafts alkylation and acylation (Levisky, 1983).

Copper(I) species have long been known to be active in reactions of olefins, carbon monoxide and dioxygen. A recent monograph on homogenous catalysis (Parshall, 1980) gives examples of the involvement of complex copper species in nucleophilic additions of amines and phosphines to coordinated olefins, hydrocyanation, hydrosilation and acetoxylation of olefins, reactions of dioxygen, oxidative coupling, the Ullman reaction, and many other organic reactions. Descriptions have been given of olefin addition of hydrogen, and chlorine addition and elimination, and of skeletal rearrangement reactions using conventional high temperature molten salt media containing copper species (Kerridge, 1975). There has been recent interest in molten salt catalysis using melts composed of ZnX₂ plus CuX or of SbX₃ plus AlCl₃ (X=Cl, I). These are found to be very active catalysts for the hydrocracking of coal (Ida, Nomura, Nakatsuji and Kikkawa, 1979; Buchanan, Dworkin, and Smith, 1983).

This chapter deals with the interaction of dioxygen with various XCuCl/(1-X)MEImCl melts and with the interaction of carbon monoxide and ethylene with both XCuCl/(1-X)MEImCl and with XCuCl/(1-X)Et₃NHC₁ melts. Particular attention is given to reactions with dioxygen. A proton NMR study on neat
$\chi CuCl/(1-\chi)ME\text{ImCl}$ melts is presented first, as it is relevant to understanding the autoxidation reactions. The miscibility of the two chlorocuprate(I) melts with various organic solvents is also reported.

B. $^1$HNMR Studies on $\chi CuCl/(1-\chi)$ Melts

1. Historical

Infrared and NMR studies of $\text{Et}_3\text{NHCuCl}_2$ and $\text{Et}_3\text{PHCuCl}_2$ have been interpreted as showing a degree of hydrogen bonding of the acidic H to the chlorocuprate(I) anion (Axtell, Good, Porterfield and Yoke, 1973). While a dialkylimidazolium cation is formally quarternary, the C-2 proton is relatively acidic as indicated by its facile exchange with solvent $D_2O$ (Chan, Chang, and Grimmett, 1977). Proton NMR studies done on the room temperature $\text{AlCl}_3/\text{MEImCl}$ melt system have shown that the chemical shift of the C-2 proton is extremely sensitive to melt composition. This provides a useful basis for chemical analysis, but only in basic $\text{AlCl}_3/\text{MEICl}$ melts (Wilkes, Levisky, Pfug, Hussey and Scheffer, 1982).

2. Results and Discussion

The $^1$H spectrum of 1-methyl-3-ethylimidazolium chloride with the proton assignments is shown in Figure 31. The
Figure 31. $^1$HNMR Spectrum of 1-Methyl-3-Ethylimidazolium Chloride in CD$_3$CN versus TMS.
protons at the C-4 and C-5 positions could not be resolved at 60 MHz. The $^1$H spectra of CuCl/MEImCl for three different compositions corresponding to acidic, neutral, and basic melts are shown in Figure 32. The resolution of the multiplets for the ethyl CH$_2$ and CH$_3$ protons in the neutral fused salt is markedly degraded from the spectrum of the MEIm$^+$ cation shown in Figure 31. This is probably due to the higher viscosity of the melt. Complete loss of multiplet structure and further broadening of all proton resonances occurs when the melt is made basic or acidic. On going to either basic or acidic melts the chemical shift difference, for any of the proton resonances, did not exceed 0.59 ppm. This result makes NMR analysis for melt composition of little practical use, unlike the case with aluminum melts.

C. Reactions of $\chi$CuCl/(1-$\chi$)MEImCl Melts With Dioxygen

1. Historical

It is well known that the chlorocuprate(I) room temperature fused salts are very air sensitive, quickly developing the visible absorption bands of copper(II), but the actual reaction has not been studied (Axtel and Yoke, 1973; Silkey and Yoke, 1980).
Figure 32. $^1$HNMR Spectra of $\chi$CuCl/(1-$\chi$)MEImCl Fused Salt Composition.
The autoxidation of copper(I) chloride in the presence of water was studied over a century ago (Berthelot, 1880). On the basis of rate studies in the protic solvent acetic acid, the following mechanism has been postulated for the oxidation of CuCl₂⁻ (Henry, 1966)

\[ \text{O}_2 + 2\text{CuCl}_2^- \rightarrow \text{Cl}_2\text{CuOOCuCl}_2^{2-} \xrightarrow{2\text{HOAc}} 2\text{CuCl}_2 + \text{H}_2\text{O}_2 + 2\text{OAc}^- \]  
(5.1)

Another example of a 2e⁻ reduction of dioxygen by copper(I) species to give a peroxide has been reported by Speier and co-workers (Speier, Tyeklar and Rochenbauer, 1982; Balogh-Hergovich and Speir, 1982). The reaction was carried out in the aprotic solvent ether. The reaction was written as

\[ [\text{CuCl}_L]_4 + \text{O}_2 \xrightarrow{\text{Et}_2\text{O}} \text{Cu}_4\text{Cl}_4\text{L}_3\text{O}_2 + \text{L} \]  
(5.2)

where L represents various substituted pyridines. The magnetic moments of such products were lower than expected, presumably due to antiferromagnetic interactions. The products of the reaction were postulated to contain two copper(I) and two copper(II) ions plus a peroxide ion O₂⁻².
However, no real evidence was presented to support this postulate.

The more common four electron reduction to the oxide is reported for the reaction of dioxygen with solutions of CuCl in pyridine (Davies, et al., 1979; Davies and El-Sayed, 1983; Hopf, Rogic and Wolf, 1983). The reaction has been written as

$$4\text{CuCl} + O_2 \xrightleftharpoons{pyridine} 2\text{CuCl}_2 + 2\text{CuO}$$

(5.3)

The species "CuO" stands for growing polymers with a pyridine-stabilized CuO core. Interest in these reactions stems from the catalytic activity of the reaction products in such reactions as the oxidative coupling of acetylenes, aromatic amines and phenols (Bodek and Davies, 1978; Hay, Blanchard, Endres, and Eustance, 1959; Davies, El-Shazly and Rupich, 1981). The oxidative coupling of 2,6-disubstituted phenols gives poly-2,6-dialkylphenylene oxide or 2,2',6,6'-tetra-alkyldiphenquinone depending on the details of the catalyst preparation and the reaction conditions. The oxidation polymerization and coupling reactions are written as
When, in equation (5.3), pyridine is replaced with N,N'-di-ethylnicotinamide, a stable tetranuclear copper complex
[\text{Cu}_4\text{Cl}_4\text{L}_4]_2 \text{O}_2 \text{ is obtained (Churchill and Davies, 1982). Its}

magnetic moment of \( \mu_{\text{eff}} = 1.7 \text{ BM} \) is in the normal range
expected for a copper(II) complex. This compound does not
promote the coupling of 2,6-dimethylphenol according to
equations (5.4a, b). It is proposed to have a cubane-like
structure with two \( \mu_2 \)-oxo bridges. With the pyridine
derivative N-methyl-2-pyrrolidinone as solvent the reaction of
dioxygen with CuCl gives a brown solution, active in catalysis
of oxidative coupling. A material isolated from this gives in
part, and on aging, a complex with the \( \mu_4 \)-oxo - tetrahedral
[\text{Cu}_4\text{OCl}_6] \text{ core. The six chloride ions are above the tetra-
hedron edge centers. There are three pyrrolidinone ligands}
bonded to three corners; a water is hydrogen bonded to the
fourth pyrrolidinone ligand in the remaining corner (Churchill and Rotella, 1979). Air oxidation of $[\text{CuClPEt}_3]_4$ gives, in part, a product with a similar $\mu_4$-oxo-centered structure, $[\text{Cu}_4\text{Cl}_6(\text{OPe}_3)]_4$ (Churchill, DeBoer, and Mendak, 1975). Thus a postulated structure for the catalytically active reaction product in equation (5.3) is such a $\mu_4$-oxo-centered structure (Davies, et al., 1983).

2. **Procedure**

   a. **Gas Absorption Measurements.** Dioxygen uptake in reactions was determined by measuring the decrease in pressure at constant volume. The apparatus consisted of a steel charging tank which was connected to a thick wall Pyrex reaction vessel and a large 100 psi Bourdon gauge through a series of Hoke and Whitey valves and copper tubing. The gas absorption apparatus is shown in Figure 33. Associated valves permitted evacuation of all parts and filling of the tank with compressed oxygen gas. The entire system was enclosed in a constant temperature air bath controlled to ±2°C. The volumes of the charging tank and reaction vessel were determined by water containment while tubing volume was calculated from its length and inside diameter.

   The pressure gauge used in this system was calibrated over the range 23-60 psig by using it to measure the vapor pressure
of dimethyl ether from -1.9 to 20.5°C and comparing with the values of Cardoso and Bruno (1923). A calibration table was constructed giving corrected pressure readings to the nearest 0.1 psi. All gauge readings were corrected using this table.

In the practical use of this system, gas in the charging tank at the initial pressure $p^i$ was allowed to expand into an
evacuated reaction bottle containing the substrate. Calculation of the amount of gas taken up in moles is given by

\[ n = \frac{\Delta PV_f}{RT} \]  

(5.5)

Here \( V_f \) is the total volume of the system (which is the sum of the volume of the reaction bottle \( V_b \) and of the charging tank and tubing \( V_t \)). \( \Delta P \) is the difference between the observed final pressure \( P_f \) and the pressure \( P_c \) calculated for ideal gas expansion. \( P_c \) is determined from the equation

\[ P_c = \frac{V_b P_f}{V_T} \]  

(5.6)

Measured values of \( P_c \) when compressed nitrogen gas was allowed to expand into the empty evacuated reaction bottle agreed to ±0.1 psi with values calculated from the volumes of the parts. The estimated error in reading the gauge is ±0.1 psi. In a typical gas uptake experiment, this would introduce a 2% error into the calculation of the moles of dioxygen consumed.

Many runs were made to determine the stoichiometry of dioxygen uptake by \( \chi \)CuCl/(1-\( \chi \))MeImCl melts of \( \chi = 0.40, 0.50, \) and 0.60 composition. The products of these runs were then
studied further in a variety of ways. In many cases, their paramagnetic susceptibilities were determined. In some cases, various spectrometric measurements, e.g., IR, UV-visible, EPR, etc., were made. In some cases, the catalytic activity of the autoxidation reaction products was investigated. In a number of experiments, the autoxidation reaction products were characterized by analysis and by separation into their components. In the following sections, experimental details are given of magnetic susceptibility measurements and of three typical autoxidation runs, one each at $\gamma = 0.40$, 0.50, and 0.60. The more general results will be summarized and discussed subsequently.

b. Magnetic Susceptibility Measurements. The magnetic susceptibilities of autoxidation products of CuCl/MEImCl fused salts were obtained at room temperature using the Gouy method. Measurements were made at a field strength of about 5k gauss, using an Alpha Model AL 7500 water-cooled magnet with 4-inch pole faces and a 1.5-inch air gap. The strength of the magnetic field was controlled by adjusting the current from a Alpha Model 7500 power supply. Gouy tubes were calibrated with mercury(II) tetrathiocyanatocobaltate(II) as described by Stevens and Yoke (1970).

Gram susceptibilities, $\gamma_g$, were calculated from the equation
\[ \chi_g = \beta \frac{F'}{W} \]  

(5.7)

where \( \beta \) is the tube calibration constant, \( F' \) is the weight change (in mg) of the sample in the magnetic field (corrected for the diamagnetism of the Gouy tube), and \( W \) is the weight of the sample (in g).

The diamagnetic gram susceptibilities of the unoxidized fused salts are shown in Table IX. These values were used as diamagnetic corrections in calculating paramagnetic gram susceptibilities of the autoxidation reaction products (of the same starting composition). Their corrected gram susceptibility is given by

\[ \chi^\text{cor}_g = \chi^\text{para}_g - \chi^\text{dia}_g \]  

(5.8)

A very small part of the weight of a reaction product sample is oxygen, which is neglected in the diamagnetic correction; this introduces only a negligible error.
Table IX

Gram Susceptibilities of Neat Fused Salts

<table>
<thead>
<tr>
<th>Melt Composition</th>
<th>$\chi_{\text{dia}}^\text{g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40CuCl/0.60MEImCl</td>
<td>-(0.688 ±0.025) x 10^{-6} (a)</td>
</tr>
<tr>
<td>0.50CuCl/0.50MEImCl</td>
<td>-(0.518 ±0.015) x 10^{-6} (b)</td>
</tr>
<tr>
<td>0.60CuCl/0.40MEImCl</td>
<td>-(0.545 ±0.023) x 10^{-6} (b)</td>
</tr>
</tbody>
</table>

(a) mean of 7 determinations
(b) mean of 4 determinations

The molar susceptibility per copper, $\chi_{\text{M}}^{\text{cor}}$, was obtained by multiplying the corrected gram susceptibility by the molecular weight calculated to contain one mole of copper in the autoxidation product. Molecular weights of autoxidation products were determined from the equation

$$MW = MW_{\text{CuCl}} + \frac{1-\chi}{\chi}MW_{\text{MEImCl}} + \frac{(\text{mo}1\text{O}_2/\text{molCuCl})MW_{\text{O}_2}}{\chi} \quad (5.9)$$

Here $\chi$ is the mole fraction of copper(I) chloride before dioxygen treatment and the ratio $(\text{mo}1\text{O}_2/\text{molCuCl})$ is determined from the measurement of gas absorption by the sample.
The effective magnetic moment per copper, $\mu_{\text{eff}}$, was then calculated using the equation

$$\mu_{\text{eff}} = 2.828 \left( T \times \chi_{M}^{\text{cor}} \right)^{1/2} \quad (5.10)$$

The major source of experimental error in these measurements was loading the viscous liquids into the Gouy tube.

c. Autoxidation of 0.40CuCl/0.60MEImCl. In a typical experiment, 2.503 g (1.8 mL) of fused salt of composition 0.400 mole fraction CuCl, containing 7.84 mmol of copper(I), was placed in a 51.5 mL bottle. This was evacuated and then opened, with magnetic stirring, to dioxygen in a volume of 276.1 mL at 40.4 psig and 33 ± 2°C. With no reaction, the pressure would drop to 32.0 psig. In fact, when the rate of dioxygen uptake had become negligible the pressure was 26.0 psig, corresponding to a consumption of 5.45 mmol of O$_2$. The final nominal composition based on copper was CuCl·1.5MEImCl·0.694 O$_2$, M.W. 340.5. At 21.5°C, the gram susceptibility (mean of three determinations) $\chi_g^{\text{para}}$ was -(0.319 ±0.024) $\times$ 10$^{-6}$, the corrected gram susceptibility $\chi_g^{\text{cor}}$ was +0.369 $\times$ 10$^{-6}$, and the corrected paramagnetic molar susceptibility $\chi_M^{\text{cor}}$ per copper was +125.6 $\times$ 10$^{-6}$ cgseu, giving a calculated $\mu_{\text{eff}}$ of 0.544 B.M. The IR spectrum of
The black product had intense bands at 1660 cm\(^{-1}\) (C=O), 3400 cm\(^{-1}\) (O-H) and 1240 cm\(^{-1}\) and 1218 cm\(^{-1}\) (C-N), which were not in the spectrum of the starting material.

d. **1-Methyl-3-ethylimidazolone**. The autoxidation product of a 0.40CuCl/0.60MEImCl melt was placed in a continuous extractor with water and extracted with ether. The extract was evaporated and the residue, a light yellow oil, was dried with 4A molecular sieves. The 1-methyl-3-ethylimidazolone, which has not been reported previously, was characterized by mass, IR, and \(^1\)HNMR spectroscopy. The mass spectrum is shown in Figure 34. The parent ion is at mass 126. Intensities at M-15 and M-29 due to loss of CH\(_3\) and C\(_2\)H\(_5\) are also apparent. The IR spectrum of the ketone as a thin film between sodium chloride plates is shown in Figure 35. In addition to the characteristic carbonyl absorption, (C=O, 1660 cm\(^{-1}\)), an olefinic C-H absorption is seen at 3118 cm\(^{-1}\). The bands occurring at 1240 cm\(^{-1}\) and 1218 cm\(^{-1}\) are due to CH\(_3\)-N and C\(_2\)H\(_5\)-N absorption. These peaks do not appear in the IR spectrum of the MEIm\(^+\) cation and provide a particularly good diagnostic estimate for the amount of imidazolone formation in autoxidation reaction products.

The \(^1\)HNMR spectrum of 1-methyl-3-ethylimidazolone in CD\(_3\)CN, with the assigned proton resonances, is shown in Figure 36. The disappearance of the C-2(H) NMR resonance of
1-methyl-3-ethylimidazolium chloride is noted. All proton resonances of the imidazolone have up-field chemical shifts relative to the proton resonances of the imidazolium cation. This is due to the loss of aromaticity of the ring on going from the imidazolium cation to the ketone.
Figure 35. Infrared Spectrum of 1-Methyl-3-ethylimidazolone as a Neat Film Between NaCl Plates.
Figure 36. $^1$HNMR Spectrum of 1-Methyl-3-ethylimidazolone in CD$_3$CN.
e. **Autoxidation of** 0.50CuCl/0.50MEImCl. In the same way, in a typical experiment, 5.358g (3.5 mL) of fused salt of composition 0.500 mole fraction CuCl, containing 21.89 mmol of copper(I), took up 5.69 mmol of O₂. The final nominal composition was CuCl·MEImCl·0.261·O₂, M.W. 253.9, \( \chi_g +2.070 \times 10^{-6}, \)
\( \chi_g^\text{cor} + 2.651 \times 10^{-6}, \)
\( \chi_M^\text{cor} 673.1 \times 10^{-6} \text{ cgsemu}, \mu_{\text{eff}} 1.27 \) B.M. The black liquid had medium intensity absorptions at 1660 and 3400 cm\(^{-1}\) and weak intensity absorptions at 1240 and 1218 cm\(^{-1}\). In a thin film between quartz plates it appeared dark green. It had continuous intense absorption across the visible region with no maximum. Total copper content calculated for CuCl·MEImCl·0.261 O₂ is 25.02%; found, 24.73%. Copper(II) content was found to be 15.15%. The autoxidation product of a similar experiment gave a strong EPR signal at 77K, with \( g_\perp = 2.08, g_\parallel = 2.41. \) After the sample had been heated in vacuo for 2 hours at 140°C, the intensity of the EPR signal at 77K was reduced by a factor of 12. Bulk susceptibility measurements on such heated residues in two experiments led to calculated magnetic moments of 0.19 and 0.31 B.M. respectively. In one case, the sample lost 3.7 wt.% water, which was condensed in a cold trap (\( n_D^{29} 1.331, \text{lit. 1.332}. \)) The absorption at 3400 cm\(^{-1}\) disappeared when the water had been volatilized, but new peaks appeared at 1520 and 610 cm\(^{-1}\).
In another case, the copper(II) content after heating was found to be 4.5%.

**f. Autoxidation of 0.60CuCl/0.40MEImCl.** In the same way, in a typical experiment, 7.241 g (4.3 mL) of fused salt of composition 0.60 mole fraction CuCl, containing 36.81 mmol of copper(I), took up 4.60 mmol of O₂. The final nominal composition was CuCl · 0.667MEImCl · 0.125 O₂, M.W. 200.7, \( \chi_g \) \( 1.178 \times 10^{-6} \), \( \chi_{cor} \) \( 1.723 \times 10^{-6} \), \( \chi_M \) \( 345.9 \times 10^{-6} \) cgsemu, \( \mu_{eff} \) 0.90 B.M. The IR spectrum of the black liquid was virtually identical to that of the starting material, with only slight absorption at 3400 cm\(^{-1}\) and extremely weak absorption at 1660 cm\(^{-1}\).

3. **Results**

a. **UV-Visible Spectra.** The \( \chi_{CuCu/(1-\chi)} \)MEImCl melts vary from colorless to pale yellow to light green with increasing \( \chi \). They darken rapidly in air and become paramagnetic as copper(II) is formed. The UV-visible spectra of CuCl/MEImCl melts of composition \( \chi = 0.04, 0.50, 0.60 \) are shown in Figure 37(a) (versus air in the reference beam). The spectra of these same samples after slight exposure to air are shown in Figure 37(b). Each of the three air-exposed melts absorbs more strongly across the visible region. Absorption maxima are seen in the spectra of the 0.40 and 0.50
Figure 37. UV-Visible Spectra of Neat $\chi = 0.040(1), 0.50(2)$ and $0.60(3)$ CuCl/MEImCl Melts (A) and of the Same Melts After Exposure to Air (B).
air-exposed melts at 408 nm. This same peak was observed in the spectrum of a solution of copper(II) chloride in CuCl/MEImCl as solvent. A solution of copper(II) chloride in CuCl/Et₃NHCl with CuCl/Et₃NHCl in the reference path has an absorption maximum at 402 nm (Silkey, 1979).

b. Reaction Stoichiometry. When the neat $\chi$CuCl/(1-$\chi$) MEImCl fused salt mixtures in small pressure bottles were exposed to dioxygen gas at about four atmospheres pressure and 33°C, they darkened rapidly and in one or a few hours they appeared black and were much more viscous. The rates of dioxygen uptake in different runs cannot be compared. Stirring was not always sufficient to prevent crusts from being formed temporarily, temperature control was only approximate, initial gas pressures were not identical in different runs, and the pressure dropped 10 to 20% during the reactions. At the reaction times indicated in Table X, the rates of pressure drop had become negligible. The final products were very viscous black liquids.
<table>
<thead>
<tr>
<th>$\chi$</th>
<th>Time, days</th>
<th>Mol O$_2$ taken up per mol Cu</th>
<th>$\mu_{\text{eff}}$ per Cu, B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>5</td>
<td>0.125</td>
<td>0.90</td>
</tr>
<tr>
<td>0.60</td>
<td>4</td>
<td>0.129</td>
<td>-</td>
</tr>
<tr>
<td>0.60</td>
<td>1</td>
<td>0.128</td>
<td>0.94</td>
</tr>
<tr>
<td>0.50</td>
<td>6</td>
<td>0.250</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>6.7</td>
<td>0.265</td>
<td>1.22</td>
</tr>
<tr>
<td>0.50</td>
<td>5.9</td>
<td>0.261</td>
<td>1.27</td>
</tr>
<tr>
<td>0.50</td>
<td>0.9</td>
<td>0.253</td>
<td>1.16</td>
</tr>
<tr>
<td>0.50</td>
<td>1.7</td>
<td>0.259</td>
<td>-</td>
</tr>
<tr>
<td>0.40</td>
<td>4</td>
<td>0.694</td>
<td>0.54</td>
</tr>
<tr>
<td>0.40</td>
<td>10</td>
<td>0.646</td>
<td>-</td>
</tr>
</tbody>
</table>

The apparent stoichiometries, shown in Table X as moles of dioxygen taken up per mole of copper, fall into three groups corresponding to the composition of melts. The reaction

$$4 \text{Cu}^+ + \text{O}_2 \rightarrow 4 \text{Cu}^{2+} + 2 \text{O}_2^-$$  \hspace{1cm} (5.11)

would account for 0.250 mole of dioxygen per mole of copper. Autoxidation of melts of composition $\chi = 0.60$ shows a halt at about half this value. The IR spectrum of the product, shown
in Figure 38, is nearly unchanged from that of the starting material at this point (the IR spectra of all neat $\chi$ CuCl/(1-$\chi$)MEImCl melts were essentially identical and only that for the 0.50CuCl/0.5MEImCl is shown in Figure 38). Some ketone is formed in the oxidized 0.60 melt, however, since the characteristic peaks at 1240 cm$^{-1}$ and 1218 cm$^{-1}$ are seen. Although the IR range 900 to 800 cm$^{-1}$ is partially obscured by MEIm$^+$ absorption no IR evidence for $\nu_{\text{O-O}}$ absorptions is observed. Absorptions in this range would be due to formation of a peroxide $\text{O}_2^{-2}$ which is suggested by the observed stoichiometry for autoxidation of this melt. The extremely viscous nature of the oxidized 0.60 melt with some solids formation no doubt contributes to the low stoichiometry.

At the $\chi = 0.40$ composition, dioxygen consumption is far in excess of that required by equation (5.11) and intense C=O and O-H bands appear in the infrared spectrum. The characteristic peaks at 1240 cm$^{-1}$ and 1218 cm$^{-1}$ due to ketone formation are much more apparent than that observed for the 0.60 melt. Both water and the ketone can be isolated from the reaction mixture. One way to represent their formation is by the reaction

$$2\text{MEImCl} + 3\text{CuO} + \text{CuCl}_2 \rightarrow \text{H}_2\text{O} + 4\text{CuCl} + 2\left(\text{CH}_3\text{C} = \text{N} - \text{N-C}_2\text{H}_5\right)$$ (5.12)
Figure 38. Infrared Spectra of $\chi$CuCl/(1-$\chi$)MEImCl Autoxidation Products. Neat MEImCl (a), Neat 0.50CuCl/0.50MEImCl (b). Autoxidation Products $\chi$=0.60 (c), 0.50 (d), and 0.40 (e).
At the $\chi = 0.50$ composition, dioxygen consumption is only slightly in excess of that required by equation (5.11) and the C=O and O-H infrared absorptions are not nearly so intense as at $\chi = 0.40$. However, analysis of the product for total copper and for copper(II) shows that about 40% of the copper remains in the copper(I) form. In addition, the absorption bands at 1240 cm$^{-1}$ and at 1218 cm$^{-1}$ in the IR spectrum of the residue (Figure 38) also show that oxidation of the imidazolium cation is significant. At 70-100°C, autoxidation is rapid and dioxygen consumption is in excess of that required by equation (5.11) even at $\chi = 0.60$. This is also attributed to cation oxidation.

c. Paramagnetism of Reaction Products. The magnetic moments shown in Table X were calculated on a total copper basis and are anomalously low. The values are still low even if for the $\chi = 0.50$ and $\chi = 0.60$ cases the calculations take into account that the copper(II) content is, respectively, 50% or 60% of the total copper. This would increase the calculated moments by $\sqrt{2}$ or $\sqrt{1.7}$ respectively.

In theory the copper(I) fused salts might undergo autoxidation according to the stoichiometry in equation (5.11). If any organic cation were oxidized, additional dioxygen would be taken up, giving a stoichiometric mole ratio $O_2/Cu_{total}$ greater than 0.25. For reaction mixtures
containing much 1-methyl-3-ethylimidazolone, the magnetic data indicate another complicating chemical reaction. That compound contains two aliphatic tertiary amine functions, and it is well known that such amine ligands are oxidized by copper(II) to polymeric amines coordinated to diamagnetic copper(I) (Weiss, Tollin and Yoke, 1964; Lane and Yoke, 1976). If the cation oxidation product, the imidazolone, reduced some copper(II) back to copper(I), the paramagnetism per Cu_{total} in the fused salt autoxidation product would be still further reduced. This would explain the very low apparent paramagnetism of the product at the $\chi = 0.40$ composition.

Moreover, when oxidation products of $\chi = 0.50$ melts are heated in vacuo, water is volatilized and the magnetic moment per copper in the residue drops from 1.2 to about 0.25 B.M. The EPR signal at 77K of the oxidation product becomes very much less intense after the sample has been heated in vacuo. These results are attributed to the formation on heating of additional 1-methyl-3-ethylimidazolone by reaction (5.12) followed by tertiary amine-copper(II) oxidation-reduction to diamagnetic products. Absorption bands that appear at 1520 cm$^{-1}$ and 610 cm$^{-1}$ in the IR spectra of autoxidation products that have been heated are presumably due to these polymeric products. These absorption bands do not appear in the IR spectra of neat fused salt samples or in that of the
imidazolone. Polymeric residue in autoxidation products is also indicated by the observed intractable nature of these materials.

4. Discussion

It has been found through these autoxidation studies that both constituents of the CuCl/MEImCl fused salt undergo oxidation in the presence of dioxygen. Formation of copper(II) chloride is accompanied by darkening of the reaction mixture due to development of intense visible absorption and of paramagnetism and an EPR signal. Oxidation of MEIm$^+$ to the new ketone, 1-methyl-3-ethylimidazolone was demonstrated by its isolation and characterization. Oxidation of the organic cation is more apparent in basic melts or in reaction at higher temperatures.

D. Autoxidation Catalysis

1. Oxidation of 1-Methyl-3-Ethylimidazolium Chloride

An approximately 50% solution of MEImCl in water under 4.4 atmosphere pressure of dioxygen at 35°C showed no reaction in 9 days and the organic salt was recovered unchanged. When a mixture of 1.38g (10.2 mmol) of anhydrous copper(II) chloride, 2.45g (30.8 mmol) of copper(II) oxide, and 3.00g
(20.5 mmol) of MEImCl was heated to 110°C in vacuo a black-green liquid was formed. The water evolved over 2 hr. was condensed in a cold trap, 0.155g (8.60 mmol), yield 84% based on equation (5.12). In another case, for a heated mixture of MEImCl/CuCl₂/CuO of molar ratio 2:1:1, analysis of the product residue gave for total copper: found, 25.4%; calculated 25.5%; for copper(II): found, 2.2%; hence by difference copper(I), 23.2%. Water was also collected from this mixture (nD₃₀ 1.3309; Lit. nD₃₀ 1.3319). The IR spectra of these residues show evidence for the formation of 1-methyl-3-ethylimidazolone (C=O, 1660 cm⁻¹ and C-N, 1218 cm⁻¹). In addition, absorption peaks at 1520 cm⁻¹ and 610 cm⁻¹ due to ketone oxidation products were observed.

2. Reaction With 2,6-Dimethylphenol

Approximately 4g each of various fused salt autoxidation products and of 2,6-dimethylphenol were stirred under nitrogen at various temperatures in the range 32 - 45°C for 1 hr. The reaction mixture was added to 50 mL methanol plus 1 mL conc. HCl, the solution was cooled in an ice/salt bath, 75 mL of water was added in portions, and the mixture was filtered. The precipitate from reactions using X = 0.40 autoxidation products was poly(2,6-dimethylphenylene oxide). Its discoloration due to copper salts could be removed by washing with
dilute HCl, to give a yellow-white polymer which darkened on standing in air. Reactions using the $\chi = 0.60$ autoxidation products at the higher temperatures gave the red crystalline 2,2',6,6'-tetramethyldiphenoquinone, m.p. 208°C; lit. 214°C (Hay, Blanchard, Endres, and Eustance, 1959), while mixtures of polymer and the quinone were obtained under intermediate conditions.

3. Discussion

The salt 1-methyl-3-ethylimidazolium chloride does not react with dioxygen at 35°C and 4.4 atm. pressure, yet the C-2 position in the ring is readily oxidized to the ketone under such conditions in the presence of copper(I) chloride. The same imidazolone was identified when 1-methyl-3-ethylimidazolium chloride was heated with a mixture of copper(II) oxide and copper(II) chloride. The formation of a large amount of water, with reduction of most of the copper(II) to copper(I), is attributed to the reaction described in equation (5.12). Thus, copper(I) chloride can catalyze the autoxidation of 1-methyl-3-ethylimidazolium chloride. In addition, the $\chi_{CuCl/(1-\chi)MEImCl}$ autoxidation products bring about the oxidative polymerization or coupling of 2,6-dimethylphenol, according to equations (5.4a,b). At $\chi = 0.40$ the yellow-white polyphenylene oxide was the major product, while as the mole
fraction of copper(I) chloride and the reaction temperature were increased, the major product became the crystalline red quinone.

Although the oxidized copper species in reaction (5.12) are written as CuCl\(_2\) and CuO, the actual state of the copper(II) is of interest from the standpoint of its catalytic activity in organic autoxidation. As noted in Section V-B,1, a number of clusters have been described with four copper(II) ions at the corners of a tetrahedron, with four or six chloride ligands on the face centers or edge centers, and often with four exo-ligands on the corners. These may have a \(\mu^4\)-oxo ligand in the center, \(\mu^2\)-oxo bridges, or corner oxo-donor atom ligands. Some of these do, and some do not, cause the oxidative polymerization of 2,6-dimethylphenol or other organic oxidations. One possibility for a component of the \(\chi\text{CuCl}/(1-\chi)\text{MEImCl}\) autoxidation product would be such a cluster, partly copper(I) and partly copper(II). Intervalence interactions might account for the black color and anomalous paramagnetism.
E. Interaction of Carbon Monoxide and Ethylene with $\chi \text{CuCl}/(1-\chi)\text{MEImCl}$ and $\chi \text{CuCl}/(1-\chi)\text{Et}_3\text{NCl}$ Melts

1. Historical

Solid copper(I) carbonyl chloride, Cu(CO)Cl, has a dissociation pressure of carbon monoxide of three atmospheres at 24°C (Wagner, 1931). A relatively more stable carbonyl halide is formed in aqueous systems at one atmosphere of carbon monoxide giving the Cu(CO)Cl$_2^-$ ion and the [Cu(CO)Cl]$_2$ solid dimer (Busch and Franklin, 1979). Copper(I) chloride as a suspension in methanol will take up a stoichiometric amount of carbon monoxide at 1 atmosphere to give a "CuCOC1" adduct. Loss of carbon monoxide, even under an atmosphere of carbon monoxide, occurs when the solid is isolated from solution (Pasquali, Floriani, and Gaetani-Manfredotti, 1981). The C=O infrared stretch in solution occurs at 2070 cm$^{-1}$. Similar formation of carbonyl adducts of amine-containing copper(I) complexes and of binuclear copper(I) complexes is of current interest (Pasquali, et al., 1981; Kitagawa and Munakata, 1981, Clark, et al., 1981).

The interaction of ethylene with CuCl$_2^-$ (and with other chlorocuprate(I) species formed in solutions of CuCl in aqueous HCl) is one of the classic examples of metal-olefin coordination (Sidgewick, 1950). The solid copper(I)
chloride-ethylene 1:1 complex has a dissociation pressure of 8 atmospheres at 24°C (Gilliland, Seebold, Fitzhugh and Morgan, 1939). Quite stable complexes are obtained when the salt contains the poorly coordinating trifluoromethanesulfonate anion (Salomon and Kochi, 1973). The solid copper(I) perchlorate complex with ethylene is explosive but the olefin complexes in solution are stable (Ogura, 1976; Manahan, 1966; Harvelchuck, Aikens and Murry, 1969). A stable copper(I)-ethylene complex is also obtained when copper(I) is coordinated by the tris(3,5-dimethyl-1-pyrazolyl)borate ligand (Thompson, Harlow, and Whitney, 1983).

2. **Procedure**

The stoichiometries of interaction between chlorocuprate(I) fused salts and carbon monoxide and ethylene were determined in the same manner described in the preceding section on dioxygen reactions. Some of these measurements involved the use of methanol as a solvent. In those cases corrections for the vapor pressure of the solvent and for gas solubility in methanol were incorporated into the calculated pressure drop \(P_C\).
3. Results

a. Carbon Monoxide Absorption by CuCl. Suspensions of CuCl in methanol containing triethylammonium chloride were treated with carbon monoxide at pressures in the range 3.7 to 4.1 atmospheres and at 25°C. The carbon monoxide-copper(I) mole ratios measured for these mixtures are given in Table XI along with the CuCl/Et₃NHCl mole ratio and the chloride concentration based on the amount of added Et₃NHCl.

<table>
<thead>
<tr>
<th>CuCl/Et₃NHCl</th>
<th>[Cl⁻]</th>
<th>CO/CuCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.708</td>
<td>1.561</td>
<td>0.44</td>
</tr>
<tr>
<td>1.000</td>
<td>1.029</td>
<td>0.52</td>
</tr>
<tr>
<td>1.633</td>
<td>0.986</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Higher CO/CuCl mole ratios were obtained at the lower concentrations of triethylammonium chloride. The suspended copper(I) chloride in these mixtures was brought into solution when they were first exposed to the carbon monoxide, and a
transient homogenous liquid phase was formed. Within three to five minutes, clear colorless crystals of "CuCOCl" precipitated. The IR spectrum of the supernatant methanol solution showed $\nu_{\text{CO}}$ at 2070 cm$^{-1}$.

b. Carbon monoxide and 0.50CuCl/0.50Et$_3$NHCl. When the 1:1 CuCl/Et$_3$NHCl fused salt was exposed to carbon monoxide at a pressure of 4.1 atmosphere at 25°C, it became more viscous and in about one hour it solidified. The amount of gas actually consumed was very small ($\text{CO/CuCl} \approx 0.1$). The solid reliquified when the carbon monoxide pressure was relieved.

c. Carbon Monoxide and $x$CuCl($1-x$)MEImCl Melts. For the neutral and acidic melts of composition $x = 0.50$ and 0.60 under a carbon monoxide pressure of about 4 atmosphere and at 30°C, the carbon monoxide/copper(I) mole ratios were found to be 0.26 and 0.25, respectively. Carbon monoxide was not taken up in the chloride-rich (basic) melt of composition $x = 0.40$ under similar conditions.

The initially pale yellow to light green neutral and acidic melts took on a deep golden color when exposed to the carbon monoxide gas, with no obvious change in viscosity or precipitation of solids. The infrared spectrum of a 50% vol/vol solution of a $x = 0.50$ melt in methanol showed the $\nu_{\text{CO}}$ absorption at 2100 cm$^{-1}$. 
d. Ethylene and CuCl/Et₃NCl. Only small amounts of ethylene were taken up by the neat 0.50CuCl/0.50Et₃NCl fused salt at 4.0 atmospheres pressure and at 25.0°C. (No interaction between ethylene and CuCl/MEImCl melts was observed under similar conditions.) The ethylene/copper mole ratios in several experiments never exceeded 0.1. When ethylene was added to suspensions of CuCl in methanol containing triethylammonium chloride the solid dissolved, but the amount of ethylene taken up was only about 10% of the stoichiometric amount for a 1:1 CuCl-ethylene complex. A green precipitate was observed to form in these mixtures when they were allowed to stand for several minutes. The $^1$HNMR spectrum of 1.25M Et₃NCl solution in methanol-d₄ containing suspended CuCl and under 1 atmosphere of ethylene is shown in Figure 39. The ethylene proton resonance at $\delta=5.0$ has been shifted up-field slightly; a value of $\delta=5.41$ is observed for ethylene under identical conditions but in the absence of CuCl. The small peak occurring at $\delta=4.8$ in Figure 39 is due to solvent proton exchange with Et₃NCl. Up-field chemical shifts for the ethylene proton resonance are usually larger for transition metal-ethylene complexes than that observed here. For example, in Zeise's salt K[C₁₃PtC₂H₄] the ethylene proton resonance occurs at $\delta=4.41$ (Kaplan and Orchin, 1965).
4. Discussion

The objective of this study was to investigate the coordination chemistry of possible carbonyl or ethylene complexes with the chlorocuprate(I) fused salts. Although there was not a stoichiometric reaction between the melts and either carbon monoxide or ethylene, the results do show weak interaction. Competition between chloride ion and carbon monoxide or ethylene for ligand sites on copper(I) is seen to be an important factor in determining the amount of these gases absorbed by the fused salts. Even though there is only weak interaction between carbon monoxide or ethylene with the
chlorocuprate(I) melts these gases may be sensitized enough by the melts to undergo further chemical reactions with other added substrates.

F. Miscibility of CuCl/MEImCl and CuCl/Et₃NHC₁ Fused Salts With Organic Solvents

1. Historical

The Et₃NHC₁CuCl₂ melt was found to be miscible with acetonitrile. Electrolyte solutions with lower viscosities could be prepared by mixing these two solutions (Silkey, 1979). The AlCl₃/RCl room temperature ionic melts have the remarkable property of being miscible with such non-polar liquids as benzene and toluene (Koch, Miller and Osteryoung, 1976; Robinson, et al., 1979). Lower viscosities and higher conductivities are observed for these fused salt-organic solvent solutions.

2. Results and Discussion

In this work it has been found that the 0.50CuCl/0.50MEImCl fused salt is miscible with polar liquids such as water, methanol, ethanol, tetrahydrofuran, N,N-di-methylformamide, chloroform, acetonitrile and nitrobenzene at least to the 50% vol/vol mixture. The 0.50CuCl/0.50Et₃NHC₁...
melt was found to be miscible with these solvents and to about the same vol/vol concentration. For the CuCl/MEImCl melt, solutions lower in viscosity by 3 to 7 cp and higher in specific conductivity by 0.0227 to 0.0748 ohm⁻¹ cm⁻¹ result in these solvent mixtures. These results may be important not only from the standpoint of electrochemistry but also from the standpoint of the use of such solutions as media for various chemical reactions. For example, the organic co-solvents may enhance the solubility of various solutes.
VI. SUMMARY

This research has shown that the CuCl/MEImCl fused salt system has more desirable physical and electrochemical properties than the previously studied CuCl/Et₃NHCl system. These new chlorocuprate(I) melts are less viscous and more conductive. They are liquid over wider ranges both of composition and temperature. Exchange current densities at the copper/fused salt interface are larger, indicating more facile electrode kinetics. These results make the CuCl/MEImCl melts promising for application in batteries.

The model for the copper(I) melts is that various chlorocuprate(I) anions are in equilibrium. The isothermal variations in conductivity and viscosity are in agreement with this model, as are results of the variation of potential of a Cu electrode as a function of composition of the melt.

Physical properties of CuCl/MEImCl melts resemble those of AlCl₃/MEImCl melts. Diffusion constants of the complex anions in the two melts are similar. The two melts are compatible at the liquid junction of a cell, and a rechargeable cell based on the two liquid systems has been demonstrated.
It was previously known that copper(I) species in low-melting fused salts were oxidized by dioxygen. The reaction was found to be surprisingly complicated, also involving copper-catalyzed oxidation of the imidazolium cation to the new compound, 1-methyl-3-ethylimidazolone, with additional subsequent reactions. It would be interesting to try an imidazolium cation substituted in the C-2 position to see if this complication could be avoided. Another example of copper catalysis, oxidative polymerization of a phenol, was demonstrated.

Interaction of the chlorocuprate(I) fused salts with carbon monoxide and ethylene was disappointingly minor in extent. Competition between these compounds and the chloride ion as ligands for copper was shown.
VII. BIBLIOGRAPHY


Hausler, R.H. (1977), Corrosion, 33, 117.


Appendix A

**Derivation of the Empirical Frenkel Function**

The activation energies for specific conductivity and viscosity were given in Chapter III as

\[ K = A \exp \left( -\frac{E^*_K}{RT} \right) \]  \hspace{1cm} (3.7)

\[ \eta = B \exp \left( \frac{E^*_\eta}{RT} \right) \]  \hspace{1cm} (3.4)

Raising equation (3.7) to an arbitrary power of \( n \) and multiplying by equation (3.4) gives

\[ \eta K^n = A^n B \exp \left[ \left( -\frac{E^*_K n + E^*_\eta}{RT} \right) \right] \]

In order for the product \( \eta K^n \) to be constant

\[ -nE^*_K + E^*_\eta = 0 \]

therefore

\[ n = \frac{E^*_\eta}{E^*_K} \]

which gives the empirical Frenkel function equation (3.13) as

\[ \eta K \left( \frac{E^*_\eta}{E^*_K} \right) = \text{constant} \]
Appendix B

Relationship Between External and Internal Transference Numbers

In the calculation of internal transference numbers, any constituent ion in the melt can be used as reference for the relative movement of the other ions. The derivation of internal transference numbers in this study relies on movement of Cu⁺ and R⁺ relative to Cl⁻. See pages 44-48 for the definition of symbols.

It can be seen from Figure 14 that movement of the cations Cu⁺ and R⁺ to the right requires simultaneous movement of Cl⁻ to the left, since the composition of melt in the central compartment remains unchanged. The movement of chloride can be divided between the movement of R⁺ and Cu⁺ according to the stoichiometry of their equivalent weight fractions. The internal and external transference numbers are then related by the following equations

\[ t'_{\text{Cu}^+} = t_{\text{Cu}^+} + t_{\text{Cl}^-} - \frac{n_{\text{Cu}^+}}{n_{\text{Cu}^+} + n_{\text{R}^+}} \]  \hspace{1cm} (1B)

\[ t'_{\text{R}^+} = t_{\text{R}^+} + t_{\text{Cl}^-} - \frac{n_{\text{R}^+}}{n_{\text{Cu}^+} + n_{\text{R}^+}} \]  \hspace{1cm} (2B)
Substitution of equations (3.20), (3.21), and (3.27) into equations (1B) and (2B) gives

\[
\begin{align*}
t'_{\text{Cu}^+} &= t_{\text{Cu}^+} + (1-t_{\text{R}^+} - t_{\text{Cu}^+}) \frac{W_f^0 M_{\text{RC}1}}{W_f^0 M_{\text{RC}1} + (1-W_f^0) M_{\text{CuCl}}} \\
t'_{\text{R}^+} &= t_{\text{R}^+} + (1-t_{\text{R}^+} - t_{\text{Cu}^+}) \frac{(1-W_f^0) M_{\text{RC}1}}{W_f^0 M_{\text{RC}1} + (1-W_f^0) M_{\text{CuCl}}} 
\end{align*}
\]

(3B) \hspace{1cm} (4B)

The consistency of these equations is shown when equations (3.23) and (3.24) are substituted into equation (4B). The result is equation (3.30) giving the internal transference number \(t'_{\text{R}^+}\) which was previously derived by setting \(n^0_{\text{Cl}^-}\) equal to \(n^c_{\text{Cl}^-}\):

\[
t'_{\text{R}^+} = \frac{n F W^c / Q [W_f^0 (1-W_f^c) - W_f^c (1-W_f^0)]}{W_f^0 M_{\text{RC}1} + (1-W_f^0) M_{\text{CuCl}}} 
\]

(3.30)