Novel Ambient Temperature Ionic Liquids
Formulated from 1-Methyl-3-ethylimidazolium
Chloride and Anhydrous Metal Chloride Salts
other than Aluminum Chloride
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ABSTRACT
The reactions of several anhydrous metal chlorides
with 1-methyl-3-ethylimidazolium chloride were stu­
died. In most cases, low temperature (< 90 °C)
molten salts were formed according to: MCln + mCl⁻ $\rightarrow$ MCln⁺m⁻. Generally, the metal chloro complexes
formed were of lowest stoichiometry. Ionic inter­
actions occurring in chlorolithate molten salts were
studied by multinuclear NMR techniques.

Introduction - True ionic liquids that are molten at or below
room temperature were first reported nearly forty years ago
(1). Since then, a large number of reports appeared,
detailing these unique materials (2). The chloroaluminates
are the most widely studied and best understood example. These are typically a mixture of a quaternary ammonium salt,
such as 1-methyl-3-ethylimidazolium chloride, and an anhy­
drous metal chloride salt, such as aluminum chloride (2).
However, there are a number of closely related melts that are
much less studied, but no less interesting or potentially
useful. Recently, reports appeared detailing the use of
other metal chlorides in place of aluminum chloride (3,4).
The present study details some of our investigations of ionic
liquids formulated from AgCl, CuCl, LiCl, CdCl₂, CuCl₂, SnCl₂,
ZnCl₂, LaCl₃, YCl₃, SnCl₄, and TiCl₄, used with 1-methyl-3-
ethylimidazolium chloride (MEIC). Nearly all of these mix­
tures produced ionic liquids at or near room temperature, at
least at some compositions.

Experimental - All experimental manipulations were performed
inside a Kawaunee Scientific Equipment Corp. dry box, which
recirculated a dry nitrogen atmosphere containing < 5 ppm H₂O
and O₂. The metal salts used were of at least reagent grade
purity, and dried at 110 °C for several days. Some were
obtained as hydrated salts; these were dried by refluxing in
thionyl chloride. All NMR spectra were obtained on a JEOL
FX90Q spectrometer equipped with a multinuclear, variable temperature probe. Spectra were recorded at 30 and 90 °C, as indicated. The NMR reference materials were hexamethyldisiloxane for all proton studies, and aqueous lithium chloride at 0.5 or 2.0 mol/dm³. In all cases, external references were used. Melting points were obtained with a Meltemp apparatus that was modified to allow cooling with LN₂-cooled dry nitrogen. Melting points were spot verified with a DuPont model 910 differential scanning calorimeter.

Results and Discussion — Figures 1 and 2 are compilations of H NMR data obtained for a variety of melts at 30 (AlCl₃, CuCl, CdCl₂, and ZnCl₂-based mixtures) or 90 °C (all others). From these figures, several different behaviors were indicated: 1) melts which saturated or underwent compound formation at the 1:1 mole fraction (AgCl and LiCl); 2) melts which appeared to saturate at the 2:1 RCl/MCl₃ composition (CdCl₂ and ZnCl₂); and the familiar Lewis acid-base melts based on CuCl and AlCl₃ (2). Of special note is the behavior of SnCl₂/MEIC mixtures. This formulation appeared to undergo compound formation at both the 2:1 and 1:1 RCl/MCl₃ compositions.

Chlorocuprates — Chlorocuprate melts were first obtained during studies of the reactions of copper(I) and copper(II) chlorides with triethylamine (5). An equimolar mixture of CuCl and triethylammonium chloride results in triethylammonium dichlorocuprate:

\[
(C₂H₅)₃NHCl + CuCl \rightleftharpoons [(C₂H₅)₃NH⁺][CuCl₂⁻]
\] (1)

which is liquid at room temperature. Recently, studies were made of the CuCl/MEIC system, with similar results (6). Figures 1 and 2 contain comparisons of the C-2 proton chemical shift of the imidazolium ring observed in chloroaluminate and chlorocuprate melts. The chlorocuprates, also display Lewis acid base behavior similar to the chloroaluminates, however, the appropriate autosolvolyis is not as large. Qualitatively, the systems are quite similar, although comparison of the dependencies of their respective physical properties on composition reveal marked differences (6,7). Unlike the chloroaluminates, the exact anionic nature of the chlorocuprates is unknown. Due to the extremely broad NMR resonances observed for ⁶⁵Cu complex ions, multinuclear magnetic resonance studies of this system were not performed.

Chloroargentates — Mixtures of silver(I) chloride and MEIC also formed room temperature melts. Figure 1 shows proton chemical shift data over the 0.0 to 0.45 AgCl mole fraction composition range. Of
particular interest in both the chlorocuprate and chloroargentate system is the discrepancy of behavior of these salts as one half of a binary system and as a solute in the chloroaluminate system. Laher and Hussey reported that very stable chloro complexes are formed by these salts in the AlCl₃/MEIC system, i.e., CuCl₄³⁻ and AgCl₄³⁻ (8,9). Formation of these ions would result in compound formation at the 3:1 or 0.25 mol% composition. Clearly, this was not the case and these formulations require further study.

Chlorocadmiates and chlorozincates
Anhydrous CdCl₂ and ZnCl₂ each formed binary ambient temperature fused salts when mixed with 1-methyl-3-ethylimidazolium chloride. Figure 1, again contains ¹H chemical shift data for these systems. These melts were clear, colorless liquids, with relatively low viscosities, comparable to the chloroaluminates. Little physical data has been tabulated for these systems, however, these melts appeared to saturate at ca. 0.333 mol% metal chloride composition indicating that the principal anionic species in these melts were CdCl₄²⁻ and ZnCl₄²⁻. Of particular note is the fact that these data were obtained at room temperature over a limited (0.2 - 0.3 MClₙ mole fraction) composition range.

Chlorostannates and chlorotitanates
Anhydrous tin(IV) chloride and titanium(IV) chloride, which are liquids at room temperature, did not make ambient temperature fused salts until at or just beyond the 0.50 mole fraction composition. We have only preliminary data on these systems, having synthesized melts from ca. 0.0 to ca. 100 mol% metal chloride. Their melting points appeared to go through a maximum near the 0.333 mol% point to another maximum just before the 0.5 mol% composition, indicating two distinct regions of differing behavior, giving rise to the speculation of two melts systems comprised of SnCl₆²⁻ or TiCl₆²⁻ before the 0.333 mole fraction composition and SnCl₅⁻ or TiCl₅⁻ between mole fractions 0.333 and 0.50. Most surprisingly, these systems saturated at or just beyond the 0.50 mol% point, forming ambient temperature melts at that point, with very low liquidus temperature (< 0 °C). Beyond the 0.50 composition, a bi-phasic system was formed, with the lighter, undissolved metal chloride salt above the saturated melt. These saturated melts had low viscosities, comparable to the pure anhydrous metal salt. Both of these melts required careful synthesis, as they were the only other examples, other than the chlorocuprates and chloroaluminates, wherein the reaction between the quaternary ammonium salt and the metal chloride was exothermic. Charring of these melts occurred very easily. Additionally, the titanate melts were a deep, pure orange, while the stannate melts had little or no native color.
Chlorolithates

As the behavior of lithium salts as solutes in the chloride ion-rich chloroaluminate fused salt was well studied via NMR and other means (10), LiCl/MEIC mixtures were chosen for detailed study. Figure 3 is a phase diagram obtained in this melt over the 0.0 to 0.55 mol% composition range. Compositions between ca. 0.28 and 0.45 mol% LiCl were liquid below room temperature. Also of note is the fact that these compositions did not crystallize on cooling, they underwent glass transitions (as shown by the open circles in the figure.) In fact, at any composition beyond ca. 0.30 mole-%, the melts could be caused to form glasses, if cooled slowly enough.

Figure 4 is the composition dependent chemical shift (at 90 °C) of the C-2 proton of the imidazolium ring. The solid line is a calculated fit using the stacked trimer ion association model proposed by Wilkes (11). Though this model has caused some controversy, it appears to be an adequate representation of these melts. The dashed line is a linear least squares fit, included for comparison.

Figures 5, 6, and 7 are the results of 7Li NMR studies performed using aqueous Li+ as an external reference. Figure 5 shows a typical response obtained for a mole fraction = 0.250 melt. Of note here are the large positive chemical shift and the relatively broad resonance. These observations indicated the presence of a large amount of negative character associated with the lithium nucleus, as well as suggested that the lithium center was in fast exchange.

Figure 6 is the composition dependent chemical shift of the lithium resonance. This dependence was obviously linear, which was in contrast to other reports (10) of lithium ion in similar melts, wherein the lithium resonance showed a marked curvature with composition, which was interpreted in terms of a dinuclear lithium species. We found no evidence to support dinuclear lithium complexes or higher chloride coordination of the lithium nucleus (vide infra).

Figure 7 is a plot of the observed relaxation time (T1) of the lithium center as a function of melt composition. For a system in fast exchange, the relaxation time of the exchanging nucleus was shown to be inversely proportional to the maximum probability of encounter of the exchanging moieties (12). For a melt which displays compound formation at the equimolar composition, such as AlCl3/MEIC or LiCl/MEIC, the maximum probability of encounter occurs at the 0.333 mole fraction, that is, when the anion fractions of the metal chloro complex and free chloride ion are equal, as indicated with the solid and dashed lines in the figure, which are proposed anion

284
distribution curves for Cl\(^-\) and a lithium chloro complex, such as the dichlorolithate ion, LiCl\(_2\)^{2-}, respectively.

Taken together, these data indicated that LiCl reacted with MEIC according to:

\[ \text{LiCl} + \text{MEIC} \rightarrow \text{LiCl}_2^{2-} + \text{MEI}^+, K_r > 1 \]  

However, \( K_r \) in the chlorolithate system was apparently smaller than that observed for the aluminum chloride-based melts. Therefore, it was most likely that the ionic species present in chlorolithate melts at less than the 1:1 composition were the imidazolium cation, free chloride ion, and a lithium chloro complex, such as LiCl\(_2\)^{2-}. The minimum in relaxation time near the 0.333 mole fraction composition is strong evidence for the preponderence of a lithium chloro complex, such as LiCl\(_2\)^{2-}. We are presently performing electrochemical and vibrational spectroscopic studies to confirm the presence of the dichlorolithate ion LiCl\(_2\)^{2-} in these melts, and are attempting to extract information on the magnitude of \( K_r \) from the chemical shift and relaxation time data.

**Other systems**

Several other systems were given cursory examination. Barium chloride, copper(II) chloride, lanthanum chloride, and yttrium chloride did not readily form low melting fused salts over an appreciable composition range, either because the melts did not form or because their liquidus temperatures are above room temperature. However, all of these salts did form melts at elevated temperature (60 - 100 °C), though the barium, ytterium, and lanthanum systems formed fused salts over a very restricted composition range (< 0.20 mol% metal chloride). Of these systems, the barium chloride melts are the most interesting, as barium is known to form complex ions only with some difficulty, and the nature of the ionic species present in these melts may be interesting.

**Summary**

Many anhydrous metal chlorides react with 1-methyl-3-ethylimidazolium chloride to form fused salts, some of which were liquid at room temperature. The probable formation reaction was:

\[ \text{MCl}_n + m\text{Cl}^- \rightarrow \text{MCl}_{n+m}^{m-} \]  

The exact nature of the metal chloride complexes in such melts is unknown, however available evidence indicated that complex ion of the lowest coordination was commonly formed.

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Figure 1 - $^1$H chemical shift of the C-2 proton of the imidazolium ring (hexamethyldisiloxane external reference) for a variety of melts of the type MCl$_n$/MEIC. MCl$_n$ = (□), AlCl$_3$, 30°C; (+), CuCl, 30°C; (◇), LiCl, 90°C; (◇) AgCl, 90°C.

Figure 2 - $^1$H chemical shift of the C-2 proton of the imidazolium ring (hexamethyldisiloxane external reference) for a variety of melts of the type MCl$_n$/MEIC. MCl$_n$ = (□), AlCl$_3$, 30°C; (+), CuCl, 30°C; (X), SnCl$_2$, 90°C; (◇) CdCl$_2$, 90°C; (◇), ZnCl$_2$, 90°C.
Figure 3 - Phase diagram for LiCl/MEIC melts. The open circles are glass transitions. For data points without error bars, the observed variance for replicate measurements was smaller than the symbol size.

Figure 4 - Chemical shift of C-2 proton as a function of the apparent mole fraction LiCl. The solid line is a fit to the ion-trimer associative model of Wilkes. The dashed line is a linear fit, included for comparison.

Figure 5 - $^7$Li resonance line for a melt of mole fraction 0.2503 obtained at 90 °C. The reference was LiCl, 0.5 mol/dm$^3$ in $D_2O$. 

288
Figure 6 - $^7$Li chemical shifts as a function of the apparent mole fraction LiCl at 90 °C, using an aqueous Li$^+$ external reference. The straight line is a linear least squares fit to this data.

Figure 7 - $^7$Li relaxation time ($T_1$) as a function of the apparent mole fraction LiCl at 90 °C, compared with the proposed anion fraction of chloride ion (---) and dichlorolithate ion (----), based on eqn. (2).