Phase Equilibria and Structures in the Sodium Chloride + 1-Methyl-3-ethylimidazolium Chloride + Aluminum Chloride System

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ABSTRACT

The melting points of the aluminum chloride + sodium chloride + 1-methyl-3-ethylimidazolium chloride system were determined by differential scanning calorimetry and by visual observation in a capillary tube. Also, the melting points of the sodium chloride + 1-methyl-3-ethylimidazolium chloride binary system were measured to establish the third side of the ternary diagram. A large portion of the ternary phase diagram has the solid-liquid transition below room temperature. The compositions with AlCl₃ mole fraction of 1/2 is particularly interesting, because they are Lewis neutral mixtures. One composition along that line is a syntectic point, where the compound Na(MEI)(AlCl₄)₂ is indicated. The salt was crystallized and the structure determined by x-ray diffraction. The packing of the ions is composed of a sodium tetrachloroaluminate anionic network separated by layers of 1-methyl-3-ethylimidazolium cations.

INTRODUCTION

Room-temperature chloroaluminate molten salts composed of 1-methyl-3-ethylimidazolium chloride (MEIC) and aluminum chloride have proven to be versatile solvents for electrochemistry, spectroscopy, and reaction chemistry (1). More recently, ternary melts produced by adding an alkali metal chloride (MCl) to melts with N > 0.5 (termed an acidic melts), where N is the mole fraction of AlCl₃, are being evaluated for battery applications (2-7). In the preparation of these ternary melts, the alkali metal chloride neutralizes the Lewis-acidic Al₂Cl₇⁻ ions to form AlCl₄⁻ ions and, at the same
time, introduces alkali metal cations into the melt. Because MCI is not soluble in the resulting neutralized melt, the addition of excess MCI to the binary acidic melt produces a neutral ternary melt of composition AlCl₃-MEIC-MCI where the moles of AlCl₃ equal the total moles of MEIC and MCI. Tetrachloroaluminate is the predominant anion in the neutral melts, and only negligible quantities of Al₂Cl₇⁻ and Cl⁻ ions are produced by the reaction

\[ 2 \text{AlCl}_4^- = \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \quad K_{eq} = 6 \times 10^{-18} \text{ at } 40 \, ^\circ\text{C}. \] (1)

When chloride ions are introduced into the melt by physical, chemical, or electrochemical means, solid alkali metal chloride precipitates from the neutral ternary melt. Also, when excess MCI is present as a solid phase, Al₂Cl₇⁻ ions introduced into the melt are removed by conversion to AlCl₄⁻. Thus, the melt is maintained at a neutral composition and is termed a buffered neutral melt (7).

The physical properties of the binary AlCl₃-MEIC ionic liquids have been thoroughly investigated (8), and the local ion-ion interactions, in particular hydrogen-bonding, have been used to explain trends in conductivities and viscosities (9-13). Although a number of AlCl₃-MEIC-NaCl ternary melt physical properties have been determined (14), the phase diagram of the ternary melt system has not been reported.

We present here the phase diagram of the AlCl₃-MEIC-NaCl ternary system. The compositions of that ternary having \( N = 0.5 \) are the neutral buffered melts. At the 0.5:0.25:0.25 composition in the AlCl₃-MEIC-NaCl phase diagram, the congruently melting compound (MEI)(Na)(AlCl₄)₂ is found. We have grown crystals of this compound and report here a single crystal structure analysis of this unusual mixed organic-inorganic tetrachloroaluminate salt.

**EXPERIMENTAL**

The preparation of MEIC is reported elsewhere (15). High purity, anhydrous NaCl was obtained from Aldrich and used without further purification. Salts used for determining the phase diagram were made by preparing the binary mixtures A, C, E, G, I, K, W, X, Y, and Z shown in Figure 1. Additions of the appropriate third component were added to attain the desired ternary composition. The mixtures were fused, cooled to room temperature, and the solid samples were ground in a mortar and pestle. All operations were conducted under anhydrous helium gas atmosphere in a glove box.

Melting points were determined using a Perkin Elmer Model 7 DSC with stainless steel sample pans, or visually in sealed glass capillary tubes.
Crystals of Na(MEI)(AlCl₄)₂ were grown by a seed method using slow rotation of a seed touching the surface of the melt (16, 17). The melt for crystal growth was prepared by mixing AlCl₃ and MEIC to \( N = 0.667 \) and then adding NaCl in a stoichiometric amount corresponding to the amount of Al₂Cl₇⁻. The crystalline product obtained was colorless and formed crystals suitable for single crystal X-ray diffraction analysis. The sample was placed in a glass capsule and sealed under He and sent to Molecular Structure Corporation for single crystal analysis. All handling and preparation of the crystals was performed inside a glove box under a dry helium atmosphere.

For structural analysis, a colorless irregularly cut crystal of Na(MEI)(AlCl₄)₂ having approximate dimensions of 0.700 x 0.450 x 0.350 mm was mounted on a glass fiber. Data collection was performed at -120 ±1°C on a Rigaku AFC6R Diffractometer with a graphite monochromated MoKα radiation and a 12 kw rotating anode generator. All calculations were performed with the TEXSCAN crystallographic software package from Molecular Structure Corporation. Final cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of 25 carefully centered reflections in the range 21.94 < \( 2\theta < 26.73^\circ \). The crystal was found to have a triclinic cell with the dimensions given in Table I. Based on statistical analysis of the intensity distribution, the space group was determined to be \( P\bar{1} \). The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The three hydrogen atoms on the ring carbons were located and refined with isotropic thermal parameters. Space limitations prevent the listing of final positional and isotropic parameters for all atoms and the anisotropic thermal parameters for non-hydrogen atoms. The position of the hydrogen atoms on the methyl and ethyl groups were calculated and are given in the supplemental material. Final full-matrix least-squares refinement on 185 parameters using 2713 observed reflections (I > 3.00 \( \sigma(I) \)) yielded residuals of \( R = 0.037 \) and \( R_w = 0.045 \). Additional details of the structure solution and refinement will be published at later date.

RESULTS AND DISCUSSION

Phase Diagram.

The melting points of the AlCl₃-MEIC-NaCl salts are depicted in Figure 2 as contours on a ternary composition diagram. A large area of the diagram has relatively low melting points. The cross-hatched region was not investigated, since there was evidence of thermal decomposition during preparation of samples having those compositions. The compositions at \( N = 0.5 \) (line M-N in Fig. 1) are particularly interesting since those are the buffered neutral melts. At the 0.5:0.25:0.25 AlCl₃-MEIC-NaCl composition there is a syntectic point that melts congruently at 36.7 °C. This indicates a compound of formula Na(MEI)(AlCl₄)₂.
Na(MEI)(AlCl\textsubscript{4})\textsubscript{2} Structure.

The formula unit is shown in Figure 3 and exhibits no unusual structural features. Table I contains the crystallographic properties of the compound.

Table I. Crystal Data for Na(MEI)(AlCl\textsubscript{4})\textsubscript{2}

| Property          | Value                                         |
|-------------------|-----------------------------------------------|
| Formula           | C\textsubscript{6}H\textsubscript{11}Al\textsubscript{2}Cl\textsubscript{8}N\textsubscript{2}Na |
| f.w.              | 471.74                                        |
| a/Å               | 10.321(4)                                     |
| b/Å               | 10.895(3)                                     |
| c/Å               | 9.284(4)                                      |
| V/Å\textsuperscript{3} | 984.7(6)                                     |
| α/°               | 98.31(2)                                      |
| β/°               | 100.83(4)                                     |
| γ/°               | 101.95(3)                                     |
| Z                 | 2                                             |
| t/°C              | -120±1                                        |
| d\textsubscript{cal}/(g cm\textsuperscript{-3}) | 1.591                                         |
| space group       | P\textbar\textbar                           |
| µ(MoKα)/cm\textsuperscript{-1} | 25.00                                         |
| R                 | 0.037                                         |
| R\textsubscript{w} | 0.045                                         |

The crystal packing shown in Figure 4, reveals that sodium ions form a chain along the \(a\)-axis which resides in a channel created by the AlCl\textsubscript{4}\textsuperscript{-} ions. This is more clearly seen in Figure 5 where only the sodium and chlorine atoms are drawn; the chlorines have been connected to each other, forming empty tetrahedra, and to the sodium ions. The sodium atoms form a zig-zag chain with an average Na-Cl distance of 3.04 Å and standard deviation of 0.19 Å. The organic cations fill the regions between the [(Na)(AlCl\textsubscript{4})\textsubscript{2}]\textsuperscript{+}\textsuperscript{n-} columns. A detailed analysis of sodium-chlorine and sodium-aluminum distances and
geometries showed that Na\(^+\) is closer to the tetrachloroaluminate anions than in the structure of NaAlCl\(_4\). Apparently the large organic imidazolium cations relax the structure and allow more efficient packing of the inorganic part of the compound.

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Figure 1. Compositions used in experimental procedure.

Figure 2. Melting point contours.
Figure 3. Crystal structure of Na(MEI)(AlCl₄)₂.
Figure 4. Crystal packing of Na(MEI)(AlCl$_4$)$_2$.

Figure 5. Inorganic portion of the packing of Na(MEI)(AlCl$_4$)$_2$. 