Asymmetric Quaternary Ammonium Ionic Liquids and Their Properties

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Imidazolium ions are known to form ionic liquids (ILs) with chloroaluminate ions. They have been used as the electrolyte for electroplatings[1~4] and energy conversion devices[5,6]. Also, many fundamental studies have been performed with imimdazolium-based ILs[7,8]. The imidazolium ion is useful in forming ionic liquids because it has moderate size giving the IL adequate conductivity, modest viscosity, and high solubility for other species. Recently, a variety of quaternary ammonium based ILs have been reported[9,10]. Quaternary ammonium salts (Quats) are attractive for use in ILs because they are easy to synthesize, relatively safe, and can have very low molecular weights, possibly leading to lower viscosity and higher conductivity.

In this work, a new series of quaternary ammonium chloride salts are introduced as the cationic part of room temperature ILs. Figure 1 shows a series of Quats investigated in this study. They are composed of a benzyl group, and three alkyl groups (methyl, ethyl, and/ or propyl groups). The melting point and conductivity were investigated as a function of the asymmetry of the cation. The Quats were mixed with $AlCl_3$ in the ratio of 55 mole % $AlCl_3$ and 45 mole % Quat, N=0.55. (N represents the mole fraction of acid in the melt.) The lewis acid, $AlCl_3$, forms $AlCl_4^-$ (Lewis neutral) and $Al_2Cl_7^-$(Lewis acid) when mixed with the quaternary ammonium chloride, as shown in Equation 1 and 2. Neutralization of the $Al_2Cl_7^-$ occurs by reacting the $Al_2Cl_7^-$ with a lewis base (e.g. Cl^-, such as from NaCl[11]), to produce neutral $AlCl_4^-$ ions (Equation 3).

$$Quat^+Cl^- + AlCl_3 \rightarrow Quat^+ + AlCl_4^- \quad (1)$$

$$AlCl_4^- + AlCl_3 \rightarrow Al_2Cl_7^- \quad (2)$$

$$Al_2Cl_7^- + NaCl \rightarrow NaAlCl_4 + AlCl_4^- \quad (3)$$

Blomgren et al. reported that 67 mole % $AlCl_3$ (acidic melts) with Quats were usable for aluminum plating[12].

The conductivity (κ), density (ρ), melting point (MP), and viscosity (η) of the ILs will be discussed for acidic (55 mole % $AlCl_3$) melts. Also, properties for the neutral (neutralized by NaCl) will be compared. Three of the Quats shown in Fig.1 are structural isomers, and the molecular weight of the non-isomer (Fig 1A) is close to the others. The density for each acidic IL is nearly the same. However, the viscosity and conductivity of the Quats are quite different. It appears that the packing density around the nitrogen is important. For example, the isopropyl substituent on Quat C is more compact than the n-propyl on Quat B leading to a higher viscosity for Quat C.

Previously, we reported the MPs of several benzyltrialkylammonium chloroaluninates[13]. MPs of ILs with benzyltrimethylammonium chloride (BTMACl) and benzyltriethylammonium chloride (BTEACl) were 55.6°C and 66.4°C, respectively. Figure 2 compares the structures of Quats and their MPs. The three Quats in Figure 2 have similar structure and molecular weights. However, the asymmetric nature of benzyldimethylethylammoniuim chloride (BDMEACl) (mixture of the methyl and ethyl groups from the other two) has a dramatic effect on its melting point compared to BTMACl and BTEACl. It is believed that the higher symmetry of the Quat permits easier crystallization resulting in a higher MP. We also will introduce the smaller asymmetric Quats to show how the conductivity and viscosity are improved for electrochemical applications. The values are approaching closer to the properties of imidazolium melts.

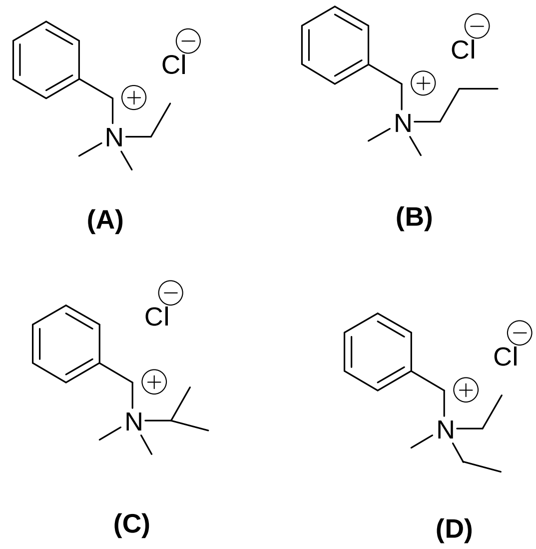

Figure 1. Quats with a benzyl substituent.
Quat A: benzylethyldimethylammonium chloride, Quat B: benzyl- propyldimethylammonium chloride, Quat C: benzylisopropyldimethylammonium chloride, Quat D: benzylmethyldiethylammonium chloride.

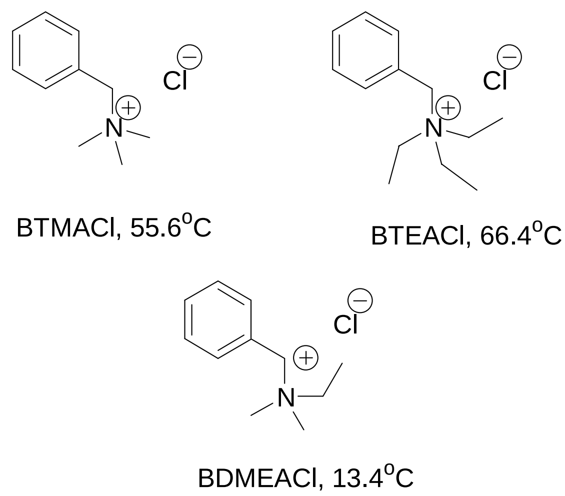

Figure 2. Structural comparison of Quats and MPs of their ionic liquids (N= 0.55). Quats are; benzyltrimethylammonium chloride (BTMACl), benzyltriethylammonium chloride (BTEACl), and benzyldimethylethylammonium chloride (BDMEACl).

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