Development of Low Melting Ionic Liquid Compositions using Mixtures of Imidazolium and Pyrazolium Ionic Liquids

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Development and applications of room temperature ionic liquids have largely focused on those based on 1,3-dialkylimidazolium cation. In order to achieve low melting points the imidazolium cation was made asymmetric by the introduction of a large alkyl group on one nitrogen, while keeping a small alkyl group (e.g. methyl) on the other nitrogen. In the case of 1,3-dialkylimidazolium tetrachloroaluminate ionic liquids the melting point decreased from 75 ^{o}C for 1,3-dimethylimidazolium tetrachloroaluminate, to 7 ^{o}C for 1-ethyl-3-methylimidazolium tetrachloroaluminate (1). For the corresponding tetrafluoroborate ionic liquids the melting point decreased from 103.4 ^{o}C for 1,3-dimethylimidazolium tetrafluoroborate (2) to about 13 ^{o}C for 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$). One of the commonly used ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate, m. pt. 10 ^{o}C) contains a four carbon n-butyl group on one of the nitrogens. However, the presence of a long chain alkyl group on the cation increases the viscosity and decreases the density of the ionic liquid. Further, the ionic liquid undergoes oxidation at lower potentials and becomes less thermally stable.

Electrochemical Systems Inc., has developed pyrazolium cation based ionic liquids for application in lithium and lithium-ion batteries (3). The melting points of the 1,2-dialkylpyrazolium ionic liquids also decreased with increase of asymmetry of the cation (Table I). During the development of these high voltage, high energy batteries, attempts were made to develop low melting pyrazolium cation based ionic liquids by the use of mixtures of 1,2-dialkylpyrazolium tetrafluoroborate ionic liquids. In high temperature molten salt chemistry, eutectic mixtures are routinely used to obtain lower melting points. Mixtures of ionic liquids have also been used in an attempt to decrease the melting points of several ionic liquids (4,5).

During these studies to develop low melting ionic liquids using mixtures of pyrazolium ionic liquids, it was observed that when there was only a small difference in the structures of the cations of two single salts having the common anion (BF_4^-), the melting point decreased only slightly. For example a mixture consisting of 33.3 mole % 1,2-dimethylpyrazolium tetrafluoroborate ($DMPBF_4$)-66.7 mole % 1-ethyl-2-methylpyrazolium tetrafluoroborate ($EMPBF_4$) melted in the temperature range 42 to 49 ^{o}C. However, an increase in the structural difference between the two cations, by substituting a fluorine to the 4-position of $DMPBF_4$ caused a significant decrease in melting point with a eutectic (15.5 to 16.5 ^{o}C) at about 60 mole % 1,2-dimethyl-4-fluoropyrazolium tetrafluoroborate ($DMFPBF_4$)-40 mole % $EMPBF_4$.

Structural differences between the two cations can also be introduced by the use of 1,3-dialkylimidazolium and 1,2-dialkylpyrazolium ionic liquids. The melting point of 50 mole % $EMIBF_4$-50 mole % $EMPBF_4$ mixture, where the two heterocyclic rings also cause different spatial distribution of the ethyl and methyl groups, was observed to be -18 to -14 ^{o}C. Further the 70%-30% mixture did not crystallize, but showed glass transition at about -90 ^{o}C These results show that, while the melting points of single salts can be decreased by the increase of asymmetry of the cation, ionic liquid compositions with very low melting points can also be obtained by the use of mixtures of ionic liquids where the cations have significant differences in their structures.

Table I
Melting Points of Imidazolium and Pyrazolium Ionic Liquids and Their Mixtures

Ionic Liquid/Ionic Liquid Mixture*	Melting Point (^{o}C)
$DMPBF_4$	80.5 to 82.0
$EMPBF_4$	47.5 to 49.0
$DMFPBF_4$	54.0 to 55.5
$EMIBF_4$	12.3 to 13.1
33.3% $DMPBF_4$-66.7% $EMPBF_4$	42 to 49
60% $DMFPBF_4$-40% $EMPBF_4$	15.5 to 16.5
50% $EMIBF_4$-50% $EMPBF_4$	-18 to -14
70% $EMIBF_4$-30% $EMPBF_4$	-90**

*composition in mole % **glass transition

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