Room Temperature Ionic Liquids

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Room temperature ionic liquids are salts with melting points as low as -96°C.[1] Inefficient packing, caused principally by the use of bulky, asymmetrical cations, leads to their low melting points. They can be divided into three general categories: salts with chloroaluminate anions,[2] weakly coordinating anions,[3] and transition metal-bipyridine cations.[4] Potential applications of these liquids include uses as reaction solvents, catalysts,[1] electrolytes,[5] and separation solvents.[6]

Chloroaluminate salts that melt below room temperature, the most studied class of ionic liquids, have been known since the 1950's. However, they were rarely studied until 1982, when 1-ethyl-3-methylimidazolium ([emim]$^+$) was first used as a cation in a chloroaluminate melt.[2] Several other organic cations can also be used, such as 1-butylpyridinium and 1-butyl-3-methylimidazolium. The chloroaluminate [emim]$^+$ melt has attracted interest due to its wide liquid temperature range (-96°C to ~200°C)[1] and electrochemical window (4.7 V).[5]

The chloroaluminate melt of [emim]$^+$ is prepared by adding $AlCl_3$ to [emim]Cl while stirring under a dry atmosphere.[2] If equal amounts of the two reactants are added, the resulting ionic liquid can be regarded as [emim]$^+$[$AlCl_4^-$], since $AlCl_4^-$ is the principal anion present in the melt. However, non-stoichiometric ratios of $AlCl_3$ and [emim]Cl can also be combined to form ionic liquids. By varying the ratio of moles of $AlCl_3$ to total moles of reactants, one can control the acidity of the melt. When the molar ratio of $AlCl_3$ is less than 0.5, both $AlCl_4^-$ and Cl^- are present as anions and the liquid is basic. When the molar ratio of $AlCl_3$ is above 0.5, the dimeric and trimeric ions $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ will form, and the melt is acidic.[7] Melting point also varies with the molar ratio of $AlCl_3$; the low melting point of -96°C is attained when the molar ratio of $AlCl_3$ is 0.65.[1]

Chloroaluminate ionic liquids have properties which make them attractive alternatives to conventional solvents for some systems. They have been used as the reaction solvent and catalyst in reactions such as Friedel-Crafts alkylations and acylations,[8] isomerisation of alkanes,[9] and the alkylation of isobutane with butene.[10] It can be advantageous to use ionic liquids as solvents from an environmental perspective, since ionic liquids have no measurable vapor pressure. Also, some reactants and catalysts are more soluble in ionic liquids than in conventional solvents, which can make process intensification possible, leading to a reduction of reactor volumes.[11] The ability of ionic liquids to dissolve many metal compounds without forming complexes makes them useful not only for dissolving catalysts, but for dissolving metal complexes for spectroscopic or electrochemical analysis.[12] In addition, the acidity of a melt can be easily adjusted to suit a particular reaction.

Chloroaluminate salts must be protected from moisture, since they will react with water. In an effort to make room temperature ionic liquids that are not sensitive to water, salts with weakly coordinating anions, such as BF_4^-, PF_6^-, and SbF_6^-, have been synthesized.[3] Common cations in chloroaluminate melts (such as [emim]$^+$) are also used in weakly coordinating anion melts. These melts are neutral stoichiometric compounds, so they lack the tunable acidity of the chloroaluminate systems.[13] Such melts have already demonstrated their utility as solvents in reactions such as butadiene dimerization[14] and Rh-catalyzed hydrogenation.[15] They have also been used as separation solvents in liquid-liquid extraction.[6]

A third class of room temperature ionic liquids are salts with cations that are transition metal-bipyridine complexes, such as $[Ru(bpy)_2(bpy(CO_2MePEG\text{-}350)_2)][ClO_4]_2$ (Figure 1). The MePEG350 moieties are short poly(ethylene glycol)-mono(methyl ether) chains with molecular weights of 350.[4] Work with these liquids is still in its early stages, but the potential for useful applications includes use in electrochromic and electroluminescent displays, molecular electronic devices, and polymer electrolytes and batteries.[16]

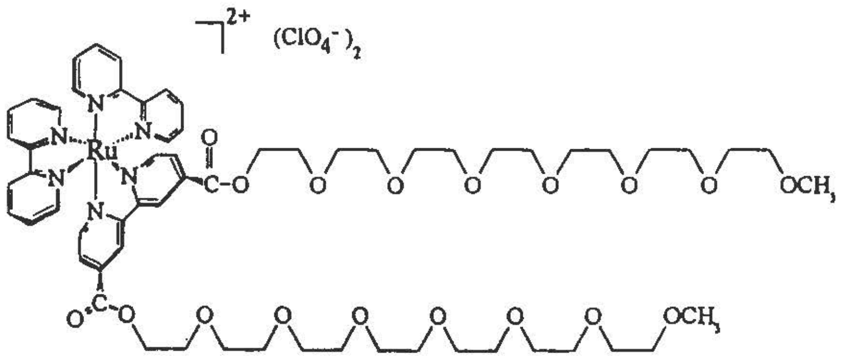

Figure 1

It has already been demonstrated that ionic liquids, when used as solvents, can offer distinct advantages over conventional solvents for some systems. Improvements in selectivity, reaction rate, and catalytic activity for specific reactions have all been reported.[13] More work needs to be done to develop the possible uses of ionic liquids as battery electrolytes[17] and, in some cases, electroactive materials.[16]

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