Inorganic Chemistry in Room Temperature Molten Salts

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The first room temperature molten salt was reported by Hurley and Wier in 1951 [1]. Mixing $AlCl_3$ and ethylpyridinium bromide in a 2:1 mole ratio causes a spontaneous and exothermic reaction. The resulting liquid is a light gold color if the starting materials are carefully purified. Upon electrolysis for two to three weeks, the solution becomes colorless [2]. The resulting liquid is hygroscopic and is oxidized by air. It was found that this liquid is miscible with benzene in all proportions up to a 50% volume ratio. In 1979, Robinson and Osteryoung reported a new system based on $AlCl_3$ and n-butylpyridinium chloride (BPC) [3]. Since that time, several new ambient temperature molten salts based on $AlCl_3$ and various organic salts have been reported.

The acid-base properties of these salts can be described by the following equilibrium:

$$2\ AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$$

For the $AlCl_3$-BPC system, the best value for the equilibrium constant appears to be 1.2×10^{-13} at 40°C [4]. An excess of $AlCl_3$ promotes formation of $Al_2Cl_7^-$ and results in an acidic solution. Solutions with less than 50 mole % $AlCl_3$ are basic and a 1:1 mixture is neutral.

Another class of room temperature molten salts was reported in 1963 by Yoke and co-workers [5]. Equimolar quantities of copper(I) chloride and triethylammonium chloride combine to give a light yellow oil of formal composition $(C_2H_5)_3NH^+(CuCl_2^-)$. The color is a result of an ultraviolet charge transfer band and is not due to contamination [6]. Other molten salts based on copper(I) and either trialkylammonium or trialkylphosphonium salts have been prepared. These liquid salts are extremely oxygen sensitive and darken rapidly if exposed to air.

Vibrational spectroscopy suggests that several copper chloride species are present in these solutions [6]. Porterfield and Yoke used visible spectroscopy to study metal chloride complexes in these Cu(I) liquid salts [7]. The results obtained were very similar to the results obtained by other workers in high temperature molten salt systems.

Although the Cu(I) liquid salts are not suitable for electrochemical studies [8], there have been several studies of inorganic compounds in $AlCl_3$ based molten salts. These molten salts have several advantages over other solvent systems:

(a) Radical species are stabilized. The decamethyl ferrocene dication can be prepared electrolytically in $AlCl_3$/BPC and is stable for days under argon. However, addition of dried, redistilled acetonitrile destroys the compound [9].

(b) Certain compounds can be spontaneously oxidized simply by adjusting the melt to an acidic composition. Decamethylferrocene [9] and nickelocene [10] can both be oxidized to their corresponding cations in this manner.

(c) Uncommon oxidation states are found for some compounds. Molybdenum(III) and molybdenum(IV) are both stable in these salts [11].

(d) Due to the variable acidity, chloro complex formation can be studied. In basic melts, tetrahedral metal chlorides are found for Co(II), Ni(II), Fe(II), Fe(III), Ag(I), and Cu(I) [12]. In acidic melts the nature of coordination is not as well understood. Co(II) and other related dipositive 3d ions are believed to be octahedrally coordinated, but the nature of the ligand is not known [13].

Photochemical reactions can also be done in these molten salts. It has been shown that several iron(II) diimines can be photochemically oxidized to the corresponding iron(III) diimines with low intensity visible light [14]. For most of the complexes studied, almost 100% of the ferrous complex was converted to the ferric form.

One of the most recent applications of molten salts is in the area of photoelectrochemistry at semiconductor electrodes. Liquid salts offer advantages over both aqueous and aprotic solvents. The conductivity of these salts is fairly high and the semiconductors appear to be stable to corrosion for months. Cells have been tested using n-GaAs, n-InP, and n-TiO_2 [15]. Overall efficiencies of close to 2% have been obtained if the liquid salt is diluted with benzene (50% by volume). In a closely related development, it was found that oxidation of several species can be sustained on illuminated semiconductors at potentials much smaller than in the dark [16].

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