Energetic Ionic Liquids

The AMPAC-GaTech Partnership fosters research aimed at opening and developing new avenues and compounds that fit the American Pacific Corporation (AMPAC)'s potential market. Under this umbrella, we are exploring advanced propellants technologies (ionic liquids, energetic polymers), azide chemistry, and applied polymers (agriculture, biomedical). The energetic ionic liquids is one example to illustrate the collaborative research that Ampac and Georgia Tech have carried on for more than five years.

a. Introduction & Background

The tetrazole ring is a mimic of the azide moiety and releases a comparable amount of energy upon combustion. However, the tetrazole group is more stable and versatile than the azide group, and can be manipulated to produce a wide range of materials. In our research, the tetrazole moiety has been used to develop novel energetic ionic liquids.

Heterocyclic five member-rings are critical building blocks for innumerable applications. Interestingly, systems like imidazoles have found themselves in the center of the emerging ionic liquid technology. Although ionic liquids have been used in electrochemistry since the mid-fifties, they also have been the subject of significant attention during the last decade. In theory they can dissolve both organic and inorganic chemicals, possess relatively low vapor pressure, and offer multiple opportunities for recycling expensive and/or toxic catalysts. These last two characteristics have categorized them as "green solvents". They are a great asset for developing sustainable technologies and their full potential has yet to be discovered. The quest for alternative ionic liquids that will overcome the current shortcomings has already begun. For example, non-fluorinated anions have been proposed. There is a growing interest in discovering novel ionic liquids that can complement those already on the market.

Ionic liquids were not initially intended to be used as solvents for organic syntheses but rather as electrochemical media. In the propulsion field, ionic liquids have been developed, not for their unique solvent properties but for their reduced sensitivity to impact, and other more general safety concerns. For example, Drake and Hawkins have reported energetic ionic liquids using triazole substituted rings. Energetic ionic liquids based on the tetrazolium cation have also been reported. Though these appear attractive, they still are unfortunately prepared only via laborious syntheses.

Ionic liquids based upon a tetrazolide ring (negatively charged tetrazole) have been largely neglected, despite their simple synthesis and the considerable flexibility (**Figure 1**).

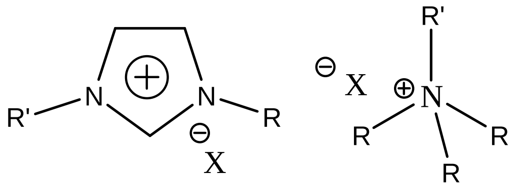

Figure 1. Imidazolium based Ionic Liquids (Left) and Ammonium Based Ionic Liquids (Right).

Over the years, the tetrazole moiety has become a strategic group in many areas like gas generants, propellants, and pharmaceuticals. Tetrazoles are well established in the gas-generant and propulsion arenas as azide mimics. Tetrazoles generate two molecules of nitrogen per ring upon decomposition. Although the tetrazole ring is (theoretically) energetically similar to an azide group, it is more stable and benign. It is a common functional group in pharmaceutically active compounds, and from a pharmaceutical prospective, the tetrazole moiety is often considered an attractive substitute for the carboxylic acid group.

The melting points of organic salts are influenced by the symmetry of the molecule, the flexibility of the alkyl or aryl substituents, and the accessibility of the charges. An interesting graph in the ionic liquids literature, **Figure 2**, is the plot of the melting point of an ionic liquid as a function of structure modification. This graph shows the tremendous effect of modest structural changes on the ionic liquid's physical properties. A similar trend is observed when the melting point is plotted versus the counter anion structure. This illustrates one of the greatest advantages of ionic liquids, their tunable physical properties.

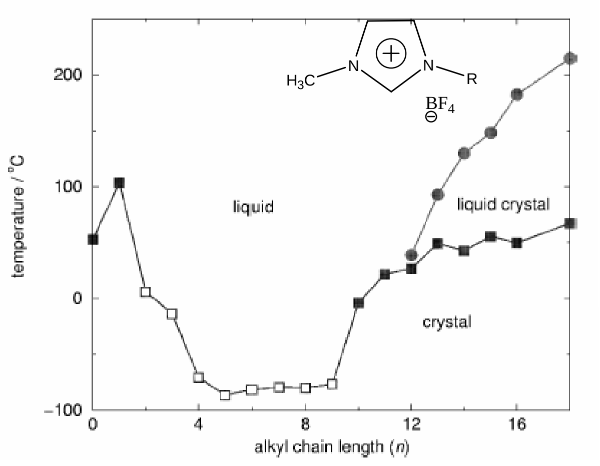

Figure 2. Melting point versus alkyl chain length of 1-Alkyl-3-methyl imidazolium tetrafluoroborate

b. Results: 5-methyltetrazolide-alkylammonium salts

The tetrazole ring is an excellent candidate for the preparation of ionic liquids. Interestingly, the proton in the 1-position exhibits acidic character; for example, the pKa of the 5-methyl-*1H*-tetrazole is 4.8. Our first aim was to develop tetrazole-based ionic liquids for gas-generant and propulsion applications by analogy with the well known imidazolium ionic liquids, while taking advantage of the acidic character of the 5-subsituted tetrazoles. Since they are basic enough to undergo acid-base reactions with tetrazoles, organic amines were especially attractive as basic counter ions. Also, they are available with an almost limitless substitution patterns and alkyl chain lengths. Since 5-methyl-*1H*-tetrazole is commercially available, inexpensive, and has a high nitrogen to carbon ratio, it was chosen for further study (**Figure 3**).

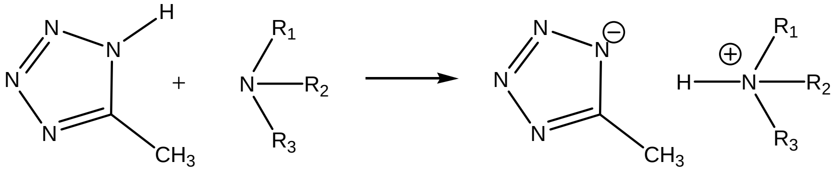

Figure 3. Reaction between 5-methyl-1H-tetrazole and amines to yield ionic liquids and/or salts.

The definition of ionic liquids (IL), or molten salts remains quite controversial; the community tends however to agree that a salt that melts below 100°C is considered an "ionic liquid". According to this definition, when 1-butylamine, 1-pentyl amine, and 1-hexylamine reacted with 5-methyl-*1H*-tetrazole, molten salts were formed. Indeed, the melting point range for the [1-butylammonium][5-methyl-1-tetrazolide] (BMT), [1-pentylammonium][5-methyl-1-tetrazolide] (PMT), and [1-hexylammonium][5-methyl-1-tetrazolide] (HMT) are remarkably low, -38 to -34, -35 to -30, and -38 to -32°C, respectively. The melting point ranges were measured on glass like materials; we have not attempted to crystallize the IL salts. When we plot the melting point versus the alkyl chain length of the primary amines, as seen in **Figure 4**, the shape of the plot is noticeably similar to that demonstrated for imidazolium based ILs. The wide range of temperatures at which the BMT, PMT and HMT are liquids is particularly attractive for propulsion under varied atmospheric conditions as well as for storage considerations.

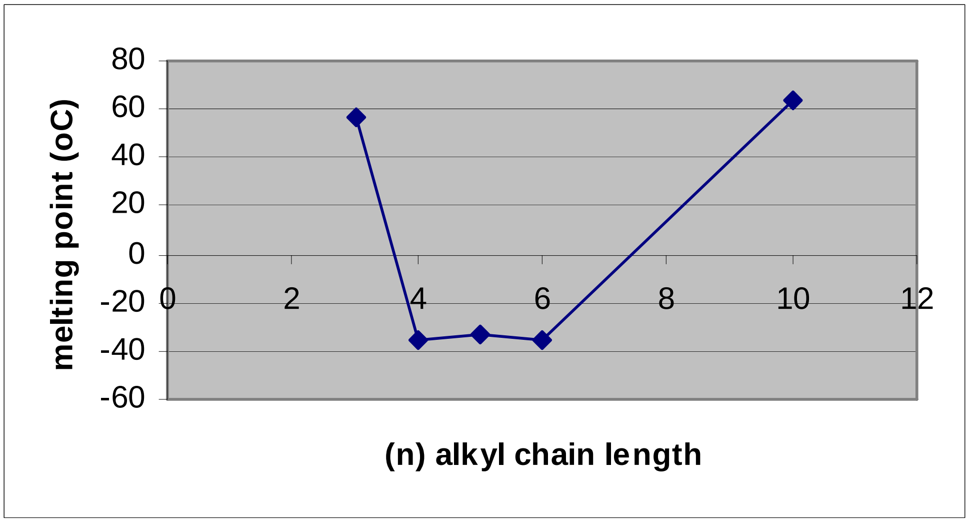

Figure 4. Melting point of [5-methyl-1H-tetrazolide][alkylammonium] as a function of alkyl chain length (n).

Differential Scanning Calorimetry (DSC) is a useful tool to study thermal stability. The DSC profiles for both BMT and PMT ionic liquids (**Figure 5**) have been studied. The onset temperature occurs at about 250°C, showing the relative thermal stability of these materials. They also can be stored for months without decomposition. For propellant applications, we are particularly interested in predicting the experimental material's density impulse (D*Imp). This calculation requires information regarding the material density and it heat of formation. The densities of both BMT and PMT have been determined experimentally to be 1.0 +/-0.2 g/cm^3. To calculate the heat of formation, knowledge of the ground state energy of the equilibrium geometry of the molecules must be determined. This was done using a density functional model.

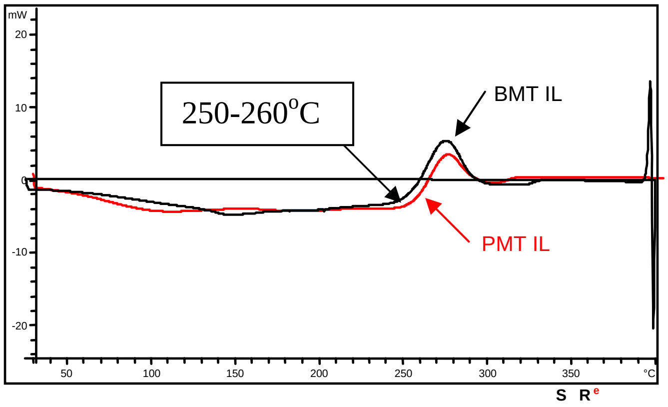

Figure 5. DSC for BMT and PMT Ionic Liquids.

Using calculated enthalpies of formation and experimental densities, the propellant performance was calculated using the NASA Lewis Research Center's

Chemical Equilibrium with Applications (CEA) computer program. In these calculations, the ionic liquid was the fuel, and inhibited fuming red nitric acid (IRFNA) was the oxidant. Since BMT and PMT are denser than the hydrazines, their performance compared to known propellant fuels were comparable, under similar conditions. In **Figure 6**, the predicted performances of the ionic liquids (yellow and turquoise) are compared to the performances of well known propellants or energetic candidates - monomethyhydrazine (MMH, red), N,N-dimethylaminoethylazide (DMAZ, pink).

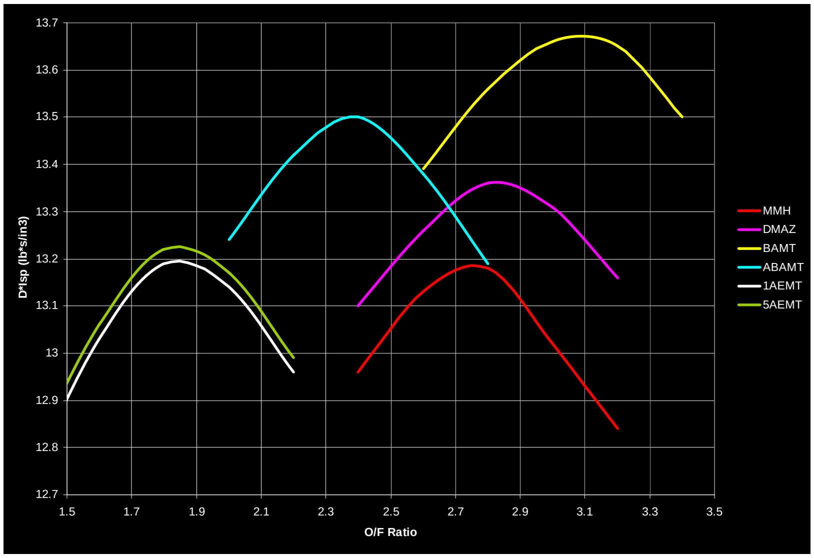

Figure 6. D*Imp of various energetic materials vs O/F ratio. IRFNA is the oxidant.

c. Conclusion

If tetrazole derivatives have already proved their great potential to mimic azide and carboxylic acid moieties, they appear as attractive for ionic liquid applications. By analogy with their imidazolium analogs, this nitrogen-rich ring system has the ability to form ionic liquids that exhibit comparable physical properties. The counter-cation—ammonium or other—can be tuned to provide the properties sought. Although they maintain basic ionic liquid's characters: low vapor pressure, low melting point, solvent abilities; they are prepared by simple acid-base reaction, which appears as a great strength. For the propulsion standpoint, they are highly competitive.