

## Exploring the Effect of Structural Modification on the Physical Properties of Various Ionic Liquids

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A few classes of ionic liquids were synthesized and investigated for their physical properties as a function of structural variation. Bis(oxalato)borate (BOB) and bis(trifluoromethylsulfonyl)imide (NTf<sub>2</sub>) ionic liquids (ILs) containing pyridinium, 4-dimethylaminopyridinium (DMAP) and pyrrolidinium cations bearing alkyl, benzyl, hydroxyalkyl and alkoxy substituents, were prepared from the corresponding halide salts. The physical properties of the DMAP based ionic liquids including viscosity, conductivity and thermal profiles were compared to those of their unsubstituted pyridinium analogues. The properties of the BOB and NTf<sub>2</sub> salts bearing similar cations were also compared. It was found that the DMAP salts were easier to synthesize and purify and have higher thermal decomposition points compared to their pyridinium and pyrrolidinium analogues. The BOB salts were found to be higher melting and more viscous than the NTf<sub>2</sub> salts. The synthesis and physical properties of the various ILs are discussed.

### Introduction

Ionic liquids (ILs) have a unique set of tunable properties that have rendered them attractive as alternative solvents in many areas. Their general properties such as low viscosity, high conductivity, negligible volatility, wide liquidus range and the ability to be recycled can be altered or tuned by variation of their chemical structure. This versatility gives researchers a great advantage in designing ILs for diverse and unique applications (1).

Knowledge of the physical properties of structurally unique ILs is what allows researchers to fully utilize them for diverse applications. Although there have been numerous reports of the physical properties of ionic liquids, these studies have been confined to a relatively narrow group of ILs that are commonly used. Two categories of ILs are discussed in this work. The salts bearing the bis(oxalate)borate (BOB<sup>-</sup>) anion were synthesized to assess their physical properties and their potential for the storage and processing of radioactive waste. The second category of ILs containing the functionalized

pyridinium and 4-dimethylaminopyridinium cations coupled with bis(trifluoromethylsulfonyl)imide anions was synthesized to assess the effect of the dimethylamino group on the physical and radiolytic properties of the ionic liquids.

The properties of ILs containing imidazolium and to some extent pyrrolidinium cations with unfunctionalized alkyl substituents have been well documented for several classes of ionic liquids. Pyridinium ILs, which are among the earliest ILs discovered, have been characterized but there is less data available on their physical properties in comparison to imidazolium and tetraalkylammonium ILs. Even less studied are ILs based on dimethylaminopyridinium (DMAP) cations. Pernak and co-workers have investigated 3-DMAP chlorides bearing alkoxyethyl substituents and found that the presence of the dimethylamino group was necessary for high antielectrostatic and antimicrobial activity. (2). They have also reported on the thermal properties of 4-DMAP and 3-DMAP salts and on the properties of trigeminal tricationic 4-DMAP ILs (3,4). Brennecke and co-workers have reported on the physical characterization of several pyridinium bis(trifluoromethylsulfonyl)imide ( $\text{NTf}_2^-$ ) ionic liquids including a few containing the 4-DMAP cation (5). Heat capacities of DMAP  $\text{NTf}_2$  ILs obtained from Merck have also been reported (6).

In terms of anions found in ionic liquids, the physical properties of BOB ILs have not been extensively studied. Angell and co-workers have investigated the fluidity and conductivity of BOB ILs to assess their use as battery electrolytes (7). In recent work, Lall-Ramnarine et al. have examined the physical properties of a few functionalized cations with the BOB anion (8). Comparisons of the properties of these salts with those of pyridinium, 4-dimethylaminopyridinium and pyrrolidinium cations functionalized similarly and bearing the  $\text{NTf}_2^-$  anion are made herein. Structures of the component ions of the ILs being discussed are shown in Figure 1.

## Experimental

### Materials

All chemicals used in this work were commercial grade, and were used without further purification. *N*-methylpyrrolidine, pyridine, 4-dimethylaminopyridine, 3-chloro-1-propanol, benzyl chloride, 1-bromobutane, 2-bromoethyl ethylether, deuterium oxide ( $\text{D}_2\text{O}$ ) and deuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) were obtained from Sigma-Aldrich. Sodium hydroxide, boric acid, and oxalic acid were obtained from Mallinckrodt, Baker, and MCB Reagents respectively. Li $\text{NTf}_2$  was purchased from IoLiTec. For the decolorization of both the halide and BOB salts, activated charcoal (Mallinckrodt) and alumina (MP Biomedicals Neutral Super I Grade, Bodman Industries) were used as they were obtained. 50 mM aqueous silver nitrate was used to test for residual halide in the  $\text{NTf}_2$  salts.

### Synthesis

The quaternary ammonium halide salt precursors were synthesized to bear the desired functional groups as described below.

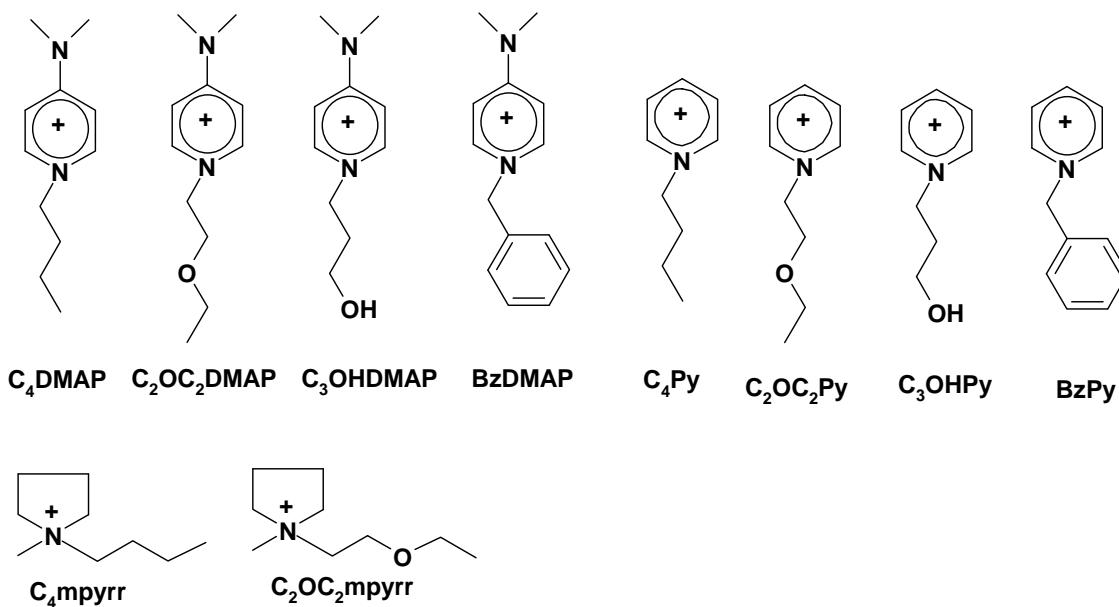
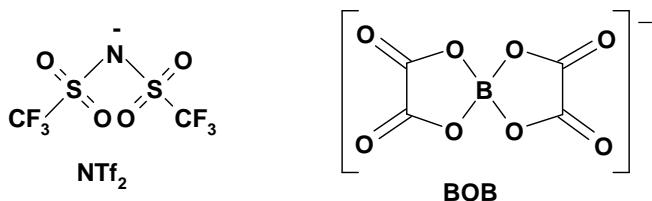
**CATIONS****ANIONS**

Figure 1. Structures of the anions and cations in the ionic liquids used in this study.

### Synthesis: Halide Salts

The quaternary ammonium halide salt precursors were prepared by reaction of the amines (*N*-methylpyrrolidine, pyridine or 4-dimethylaminopyridine) with one equivalent of an alkyl halide bearing the desired functionality in refluxing acetonitrile. The alkyl halides used were 3-chloro-1-propanol, benzyl chloride, 1-bromobutane and 2-bromoethyl ethylether. The syntheses are outlined in related work from this research group (8, 11).

### Synthesis: Ionic Liquids

The halide salts were then converted to the BOB salts by combination with NaBOB using established procedures (7, 8). The NTf<sub>2</sub> salts were also prepared from the quaternary ammonium halide salts and LiNTf<sub>2</sub> by established procedures (9-11).

## Characterization

Nuclear Magnetic Resonance (NMR) spectroscopy was used for structure confirmation of the intermediates and final products.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  spectra were obtained using a Bruker 400 MHz NMR spectrometer. Deuterium oxide ( $\text{D}_2\text{O}$ ) and deuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) were used as solvents with TMS as an internal reference.

A TA Instruments Q100 Differential Scanning Calorimeter (DSC) was used to determine melting points (mp), glass transition onset temperatures ( $T_g$ ), and crystallization temperatures ( $T_c$ ). The reported melting points and crystallization temperatures correspond to the peaks in the DSC scans. A TA Instruments Q500 Thermogravimetric Analyzer (TGA) was used for the determination of thermal decomposition profiles and sample water content on the percent scale. Scan rates were 5 °C/min for DSC and 10 °C/min for TGA. The data were analyzed using TA Universal Analysis 2000 software. A Mettler Toledo DL39 coulometric Karl Fischer titrator connected to a balance was used to determine sample water content at lower levels. Viscosities were measured with a Cambridge Applied Systems ViscoLab 4100 electromagnetic reciprocating piston viscometer that was temperature regulated by a Lauda RM-6 recirculating water bath. Bulk conductivities were measured at 22 °C by complex impedance measurements using a computer-controlled Hewlett-Packard 4129A Impedance Analyzer in the frequency range from 5 Hz to 10 MHz. The samples were placed into a homemade cell consisting of a scintillation vial with electrodes inserted through the cap. The cell constant was determined using an aqueous 0.053% KCl calibration solution (YSI 3167,  $1000 \pm 10 \mu\text{S cm}^{-1}$  at 25 °C, Yellow Springs Instruments).

## Results and Discussion

The effects of dimethylamino-group substitution at the *para* position in pyridinium ionic liquids are assessed across four types of derivatizing functionalities: alkyl (butyl), ether (ethoxyethyl), alcohol (hydroxypropyl) and arylalkyl (benzyl). Table I summarizes the properties of the DMAP and pyridinium ionic liquids. As a further comparison, the properties of ionic liquids containing the corresponding derivatives of the pyrrolidinium cation are also included in the table.

The viscosities of each of the DMAP salts at 25 or 65 °C are higher than their pyridinium congeners, to varying degrees depending on the functionality. C<sub>4</sub>DMAP NTf<sub>2</sub> is only slightly more viscous than C<sub>4</sub>Py NTf<sub>2</sub>, while the other three DMAP derivatives are significantly more viscous than their counterparts. This suggests but in no way proves that the dimethylamino functionality facilitates specific interionic interactions that impede ionic mobility, perhaps in the form of polar interactions (ethoxyethyl), hydrogen bonds (hydroxypropyl) or π-donor-acceptor interactions (benzyl). In future work, Optical Kerr Effect (OKE) or terahertz spectroscopies may shed light on these effects by measuring how interionic vibrational spectra (below 150 cm<sup>-1</sup>) vary with functionalization. Among the three cation classes studied, each functional group has a strong and relatively consistent influence on viscosity. The pyrrolidinium ionic liquids are generally slightly more viscous than the corresponding pyridinium ones but less viscous than the DMAP ILs.

**Table I.** Selected physical properties of 4-dimethylaminopyridinium, pyridinium and pyrrolidinium ionic liquids with bis(triflyl)imide<sup>11</sup> and bis(oxalato)borate<sup>8</sup> anions.

<u>NTf<sub>2</sub><sup>-</sup> Salts</u>	Viscosity <sup>a</sup> cP, 25 °C	Conductivity mS/cm, 25°C	Glass Transition, <sup>b</sup> °C	Melting Point, <sup>b</sup> °C	Degradation Onset, °C
<b>C<sub>4</sub>DMAP</b>	85	2.2	-70	27	444
<b>C<sub>4</sub>Py</b>	60	2.2	-81	26	388
<b>C<sub>4</sub>mpyrr</b>	77	2.7 <sup>c</sup>	-89	-3 <sup>d</sup>	-
<b>C<sub>2</sub>OC<sub>2</sub>DMAP</b>	105	1.8	-67	None	422
<b>C<sub>2</sub>OC<sub>2</sub>Py</b>	57	2.5	-80	-18	380
<b>C<sub>2</sub>OC<sub>2</sub>mpyrr</b>	53	3.4 <sup>c</sup>	-91	None	-
<b>C<sub>3</sub>OHDMAP</b>	198	0.80	-59	None	441
<b>C<sub>3</sub>OHPy</b>	117	1.6	-76	None	355
<b>C<sub>3</sub>OHmpyrr</b>	135	1.5	-79	None	-
<b>BzDMAP</b>	60 (65 °C)	2.1 (63 °C)	-25	62	416
<b>BzPy</b>	23 (65 °C) <sup>141</sup>	1.5	-53	9	313
<b>Bzmpyrr</b>	44 (65 °C) <sup>385</sup>	0.49	-56	None	-
<b>BOB<sup>-</sup> Salts</b>					
<b>C<sub>4</sub>mpyrr</b>	6300 (20 °C) <sup>e</sup>	0.059 (25 °C) <sup>e</sup>	-40	55 <sup>e</sup>	-
<b>C<sub>2</sub>OC<sub>2</sub>mpyrr</b>	1125 (46 °C)	0.099 (32 °C)	-52	None	-
<b>BzPy</b>	-	-	-27	100	-

<sup>a</sup> All viscosity values for the NTf<sub>2</sub><sup>-</sup> salts are calculated from Vogel-Tamman-Fulcher fits of the temperature dependences (Ref. 11). <sup>b</sup> Onset temperature. <sup>c</sup> Ref. 12. <sup>d</sup> Ref. 13. <sup>e</sup> From EMD/Merck literature.

The conductivities, which generally correlate inversely with viscosity, follow a similar trend where the butyl derivatives of the DMAP<sup>+</sup> and Py<sup>+</sup> cations are essentially the same and the other DMAP derivatives have lower conductivities than their Py analogues. Interestingly, the butyl- and ethoxyethyl-pyrrolidinium salts have higher conductivities than the pyridinium salts of similar viscosity but the benzylpyrrolidinium salt's conductivity is substantially lower, mainly due to its higher viscosity.

The DMAP substitution has a substantial effect on the glass transition temperatures as shown in Table I. Addition of the dimethylamino group raises the glass transition by 11

(butyl), 13 (ethoxyethyl), 17 (hydroxypropyl) and 28 °C (benzyl) compared to the regular pyridinium ionic liquids. The upward shift in glass transition temperatures is another indication of stronger interionic interactions in the DMAP series. Benzyl substitution significantly raised the glass transition temperatures in all cases, including the bis(oxalato)borate salt. Glass transition temperatures of the pyrrolidinium series are slightly lower than the pyridinium series.

Many of the ionic liquids prepared for this study do not readily crystallize under DSC conditions, therefore the data on melting points is rather limited. Again, the C<sub>4</sub>DMAP NTf<sub>2</sub> and C<sub>4</sub>Py NTf<sub>2</sub> ionic liquids are virtually identical. The most dramatic effect is seen in the high melting point of BzDMAP NTf<sub>2</sub> (62 °C), suggesting very strong interactions which should be evident if a crystal structure can be determined. Since the inclusion of the dimethylamino group reduces planarity, one would expect a decrease in packing efficiency and a decrease in melting point. The observed increase in melting point supports the argument that there are strong interactions in the DMAP series.

Generally speaking, compared to the Py ILs the DMAP ILs have turned out to have less desirable characteristics among the properties discussed so far, but that situation is reversed when looking at their thermal stability. The degradation onset temperatures are substantially higher for each of the DMAP derivatives than the corresponding pyridinium ones. The contrast is due mostly to the dramatic fall-off of stability in the pyridine series (a difference of 75 °C from C<sub>4</sub>Py NTf<sub>2</sub> to BzPy NTf<sub>2</sub> compared to 28 °C from C<sub>4</sub>DMAP NTf<sub>2</sub> to BzDMAP NTf<sub>2</sub>). Nonetheless, the difference in decomposition onset for the benzyl derivatives is just over 100 °C. The dimethylamino group contributes some electron density to the cationic ring, delocalizing and stabilizing the positive charge and raising the barrier for elimination of the quaternizing functional group (5). Thus, in some applications the substantial gain in thermal stability upon addition of the dimethylamino group could override the less desirable viscosities and conductivities.

A comparison of the BOB and NTf<sub>2</sub> salts in Table I reveals that the BOB salts are higher melting, substantially more viscous and exhibit much lower conductivities and higher glass transition temperatures than the corresponding NTf<sub>2</sub> salts.

## Conclusion

Addition of a *para*-dimethylamino group to pyridinium ionic liquids has a relatively minor effect on IL properties if the quaternizing R-group is a simple alkyl. If the R-group is functionalized, specific interactions accentuate the difference made by the dimethylamino group. The dimethylamino group also substantially increases the thermal stability of the ionic liquids relative to regular pyridinium derivatives, which may prove useful in real-world applications.

## Acknowledgments

The authors thank the Office of Educational Programs at Brookhaven National Laboratory, the Queensborough Bridge NSF STEP Research program and the NSF Louis Stokes Alliance for Minority Participation program for student internship support, and Dr.

Tomasz Szreder for his generous assistance with these studies. This work was supported at BNL by the U. S. DOE Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences under contract # DE-AC02-98CH10886.

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