

Introduction

Ionic liquids (ILs) are defined as salts that have a melting point at or below 100°C.¹ They are composed of anions and cations of a bulky, charge delocalized, often asymmetric nature. The choice of IL cation or anion can affect their physicochemical properties, including mutually water solubility.

In an effort to evaluate the suitability of ionic liquids (ILs) as solvents for the extraction of fission products from acidic media, two series of hydrophobic, room-temperature ILs, one comprising a dialkylimidazolium cation and the other an analogous (1-hydroxyalkyl)-functionalized imidazolium cation, have been prepared and characterized as their bis[(trifluoromethyl)sulfonyl]imide salts. The extraction of Sr(II) from aqueous nitric acid solutions by dicyclohexano-18-crown-6 into these ILs has been measured. Under certain conditions (i.e., adequate IL cation hydrophobicity and nitrate concentration), a linear correlation has been observed between the extent of Sr(II) extraction and the equilibrium water content of the IL phases.² Although a precedent has been established for a similar correlation with *n*-alcohols,³ the relationship in extraction systems employing IL diluents has yet to be adequately studied. That is, the role of water in the partitioning of the metal ion complexes remains largely unexplored.

Infrared and Raman spectroscopy has been utilized to elucidate the states of dissolved water and its interactions with the IL.^{4,5} This study was designed to explore the feasibility of using IR techniques to gain a better understanding of the role water may play in the extraction system described above.

Methods

Synthesis of dialkylimidazolium IL

Microwave-assisted synthesis of 1-methyl-3-decylimidazolium bromide (C₁₀mimBr) was achieved by microwave-assisted reaction of 1-bromodecane (in 1% excess) and 1-methylimidazole (Figure 1). The resulting IL was washed with ethyl acetate to remove unreacted precursors. Ethyl acetate was removed by distillation using rotatory evaporation and then at 80°C *in vacuo*. Purity was estimated by ¹H NMR. For the conversion to the bis(trifluoromethylsulfonyl)imide (Tf₂N) salt, LiTf₂N was added in excess and left to stir overnight. The resulting C₁₀mimTf₂N was washed with deionized water until the aqueous wash showed no precipitate with silver nitrate. The percent yield after drying was found to be 77%.

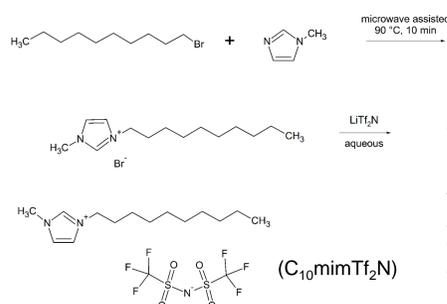


Figure 1: Nucleophilic substitution of 1-bromodecane with 1-methylimidazole to form C₁₀mimBr. Step 2: Metathesis to C₁₀mimTf₂N in aqueous solution.

Methods

Synthesis of hydroxylated IL

A similar method for synthesis was followed for the 1-(12-hydroxydodecyl)butylimidazolium bromide, a more hydrophobic IL. 12-bromododecanol (in 1% excess) and butylimidazole were microwaved at 70°C for thirty minutes to yield the desired IL (Figure 2). Several washings with ethyl acetate followed by distillation and drying prepared the IL for conversion to the Tf₂N salt. Once it was allowed to react overnight, the IL was washed with water. The aqueous layer was tested with silver nitrate to ensure the bromide was no longer present. After drying, the percent yield was calculated to be 63%.

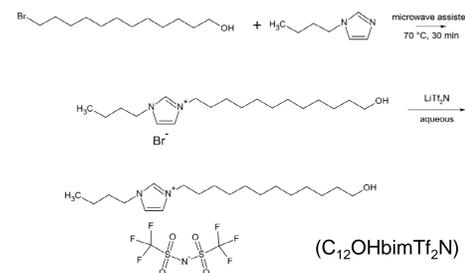


Figure 2: Nucleophilic substitution of 12-bromododecanol and butyl imidazolium to make 1-(12-hydroxydodecyl) butylimidazolium bromide. Step 2: Metathesis to bis(trifluoromethylsulfonyl)imide salt in aqueous solution.



Figure 3. A dry sample of the slightly yellow C₁₀mimTf₂N.

Sample Preparation & Analysis

Aliquots of the ILs were contacted with either deionized water ("wet") or 1.2 M HNO₃ to simulate a liquid-liquid extraction system without extractant. The phases were disengaged by centrifugation and the IL phase was removed for analysis. To ensure the dryness of the "dry", a small aliquot was placed in a vacuum oven at around 80°C for three hours.

FTIR spectra of the IL phases at the three conditions ("dry", "wet", 1.2 M HNO₃) were acquired using a Perkin Elmer Spectrum Two FTIR spectrometer with UATR Two (diamond) attachment. Raman spectra were acquired using a BW Spec i-Raman spectrometer with a fiber-coupled cuvette holder.

Results

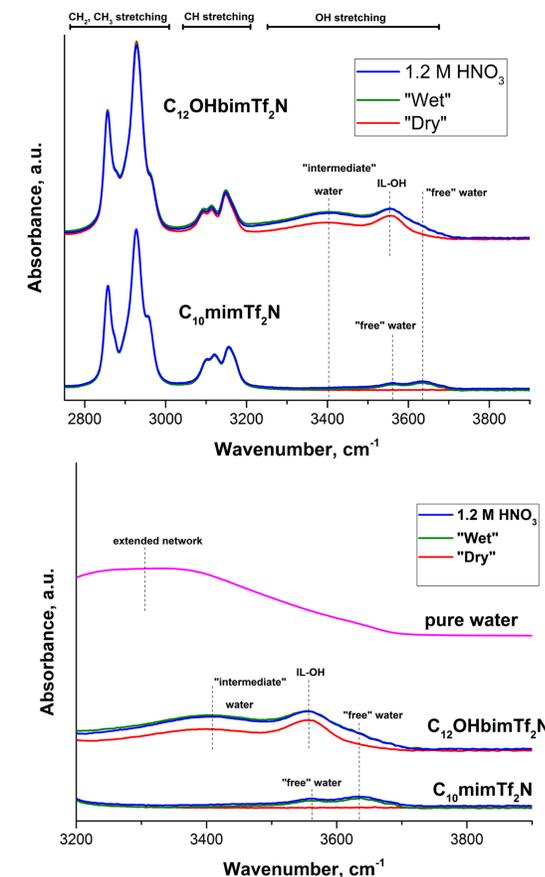


Figure 4. Top: Infrared spectra of IL samples showing the CH- and OH-stretching regions; Bottom: Infrared spectra of IL samples in OH-stretching region with a water spectrum for reference.

Assignment	C ₁₀ mimTf ₂ N	C ₁₂ OHC ₄ bimTf ₂ N
ν_s CH ₂	2875	2875
ν_{as} CH ₂	2928	2928
ν_s CH ₃	2870	2876
ν_{as} CH ₃	2956	2958
ν C ² H	3103	3095
ν_{as} C ⁴ HC ⁵ H	3121	3114
ν_s C ⁴ HC ⁵ H	3156	3149
ν H ₂ O	3568, 3635	3401
ν IL-OH	----	3556

Table 1. Selected vibrational bands and their assigned modes (ref. 4) for ILs under all three conditions

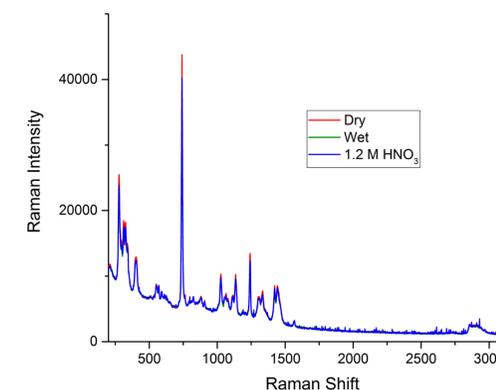


Figure 5: Overlapped Raman spectrum of all three samples of C₁₂OHC₄bimTf₂N

Conclusion

Raman

No distinguishing characteristics were found in the observable range of Raman shifts (Figure 5). The water shifts that may be observed are at a higher frequency than the laser source and detector can achieve.

FTIR

For either IL the vibrational bands do not shift with changing conditions. However, the water bands indicate that the dissolved water is in distinct states. Those states have been categorized into three different groups, based on the shift. Pure water exhibits very broad series of overlapping states, consistent with a large hydrogen bond network. At high frequency, the bands are indicative of molecules that are more isolated ("free"), like those in the wet and acidified C₁₀mimTf₂N. Water bands that are red-shifted (lower frequencies) are consistent with states that are "intermediate", between bulk, networked molecules and "free" molecules. This indicates that some of the water in C₁₂OHbimTf₂N is in clusters of some unknown size and some may be isolated as distinct molecules.

How these states pertain to the crown ether, metal ion extraction system remains to be explored.

Future Work

- Measure water contents by Karl Fischer titration
- NMR spectroscopy may yield data about the non-covalent interactions between water and the ILs or other constituents
- Seek a Raman spectrometer capable of resolving the water shifts
- Analyze IL phases that are more like the extraction system being investigated (e.g., add crown ether)

References/Acknowledgements

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