

INTRODUCTION

- Investigations into the thermophysical properties and extent of nano-structuring of ionic liquids using photochromic responsive dyes have yielded hydrated IL systems for polarity analysis and created environments suitable for effective enzyme activity.^{1,2}
- In this study we investigate hydrated ILs containing hydrophilic and hydrophobic regions through Raman spectroscopy and thermal analysis.
- The ILs investigated were Trihexyltetradecylphosphonium Chloride [P_{6,6,6,14}][Cl] Tributyltetradecylphosphonium Chloride, [P_{4,4,4,14}][Cl], 1-Ethyl-methyl-3-imidazolium-ethyl Sulfate [C₂mIm][EtSO₄] and Trihexyltetradecylphosphonium Dicyanamide [P_{6,6,6,14}][DCA].

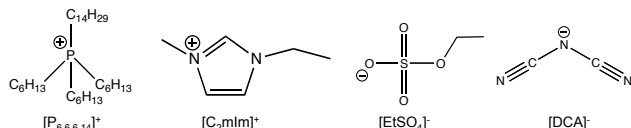


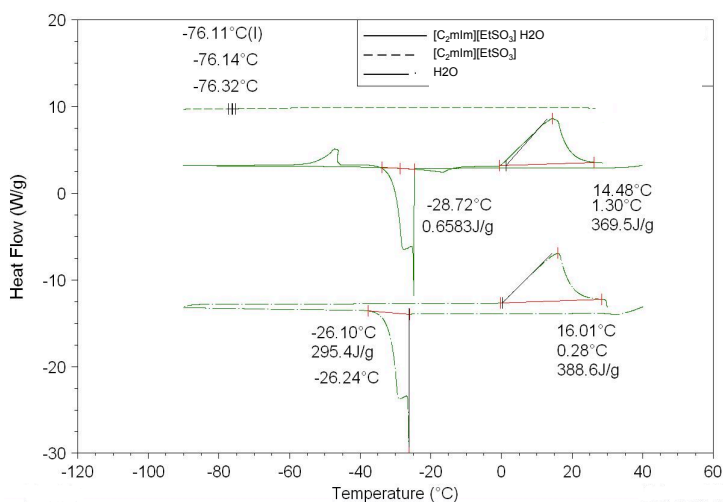
Figure 1. Cations and Anions used in this study

- The aim of this investigation was to analyze the changes in peak intensities and peak positions of the cation and anion of the ILs after the addition of water. Looking at hydrogen interactions between water and the anion of the ILs. And to see if these interactions manifest a change in the melting point of these systems.

EXPERIMENTAL

- All of the ILs studied were commercially available (CYTEC, Sigma-aldrich)³. The IL/water systems were prepared using a weight ratio of 1:1. Regarding impurities the ILs were purified using previously published techniques⁴, in order to prevent acidic impurities protonating the phenolate ion of the Reichardt's dye.
- The Raman spectra was measured in the spectra range 600-3200 cm⁻¹ at a resolution of 1 cm⁻¹. This accounted for all the characteristic peaks of the ILs, displaying any changes of the system after the addition of water.
- UV-Vis spectroscopy was performed between the range of 400-900 nm at a resolution of 2 cm⁻¹. The concentration of Reichardt's dye used was 10⁻⁴ M. The dye was used to locate specific domains that had been formed as a result of specific interactions between the water and the IL.
- Thermal scans were measured between the temperature range -50 °C to +30 °C at increments of 1,10 and 20 °C/min. The thermal characteristics of the ILs were analyzed to monitor any change after the addition of bulk water.

Results and Discussion



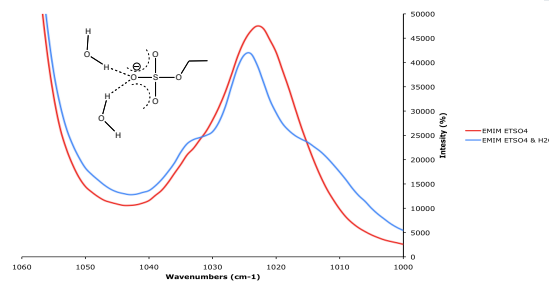
- After the addition of H₂O to [C₂mIm][EtSO₄], the above graph clearly shows that there is a shift of the ILs melting point.
- This shows that the interactions occurring at a molecular level between the IL and the solvent are manifested physically in the shifting of the ILs melting point and change of transition enthalpy.

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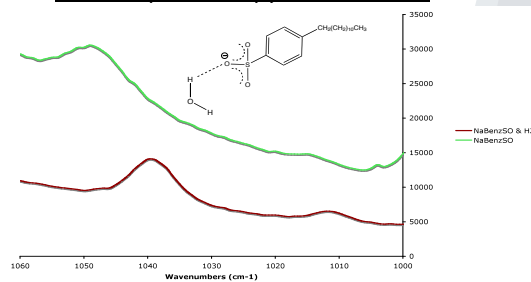
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Raman Spectroscopy [C₂mIm][EtSO₄]



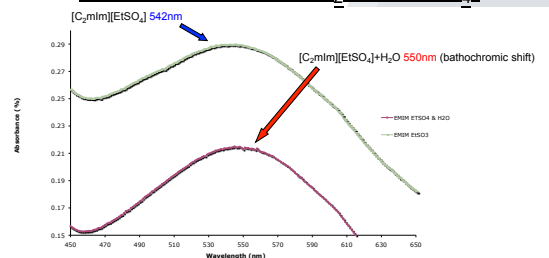
- Symmetrical stretch of sulphate occurs in narrow region
- When mixed with H₂O the symmetry is distorted due to interactions

Raman Spectroscopy Sodium DBSA



- NaDBSA used as a derivative to compare with sulphate stretch of [C₂mIm][EtSO₄], shows more symmetrical peak when mixed with H₂O, due to more structured solvation.
- Na⁺ is more hydrophilic than C₂mIm⁺ so forms a more structured solvation shell than [C₂mIm][EtSO₄]

UV-VIS Spectroscopy [C₂mIm][EtSO₄]



- Bathochromic shift of IL/ H₂O mix shows specific solvation.
- The IL head groups coordinates with H₂O creating specific regions.
- Shows a reduction in the interaction between Reichardt's dye and the IL (Fig 1).

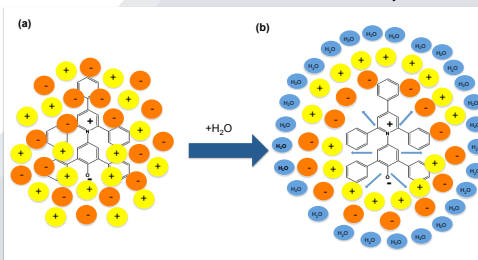


Figure 1. (a) IL anions (orange) and cations (yellow) interacting with Reichardt's dye. (b) Addition of H₂O and formation of solvation shell to mediate dissolution of probe dye an IL interaction with water. Reduced interaction with dye results in bathochromic shift in dye λ_{max}.

Conclusion

- UV-VIS:** Using Reichardt's Dye, [C₂mIm][EtSO₄] is seen to experience a bathochromic shift when mixed with water. Polar H₂O coordinating with head-groups of IL, forming specific solvation shells, leading to reduction of the stabilization ground state of Reichardt's dye.⁵
- Raman:** Sulphate symmetrical stretch of [C₂mIm][EtSO₄] becomes unsymmetrical when mixed with H₂O, showing interactions at head-group of IL

DSC: Coordinating of ionic head-groups with H₂O shows structural changes by shifting of melting points of [C₂mIm][EtSO₄].