

Physico-chemical properties of Ionic- Liquid/Water Mixtures

Simon Gallagher

Contents

- Introduction
- Ionic Liquid based Poly(N-Isopropylacrylamide) Gels
- Experimental
 - *Raman Spectroscopy of Ionic Liquid/Water Interactions*
- Conclusions
- Acknowledgements

Introduction

IL Polymer Gels

Raman of IL/H₂O

Conclusions

Acknowledgments

National Centre for Sensor Research

Over 260 f/t researchers and support staff

23 affiliated faculty

Investments and income since 1999 now approaching €100 million

1500 m² well-equipped specialist lab space and offices

Phase II expansion completed 2008 (1300 m²)



CLARITY
The Centre for Sensor Web Technologies



Introduction

IL Polymer Gels

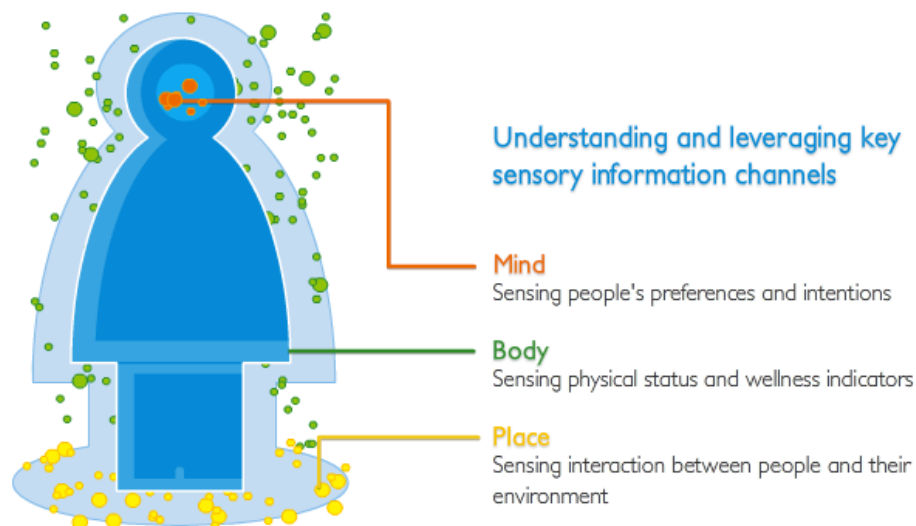
Raman of IL/H₂O

Conclusions

Acknowledgments

CLARITY – SFI CSET

Vision: Sensing Mind, Body & Place



- 5-year, €16.4 million research program to develop next generation Sensor Web Technologies with significant environmental focus
- Brings together fundamental materials science, functional polymers, device prototyping, energy management, adaptive middleware, wearable sensors, distributed environmental monitoring.

www.clarity-centre.org

Introduction

IL Polymer Gels

Raman of IL/H₂O

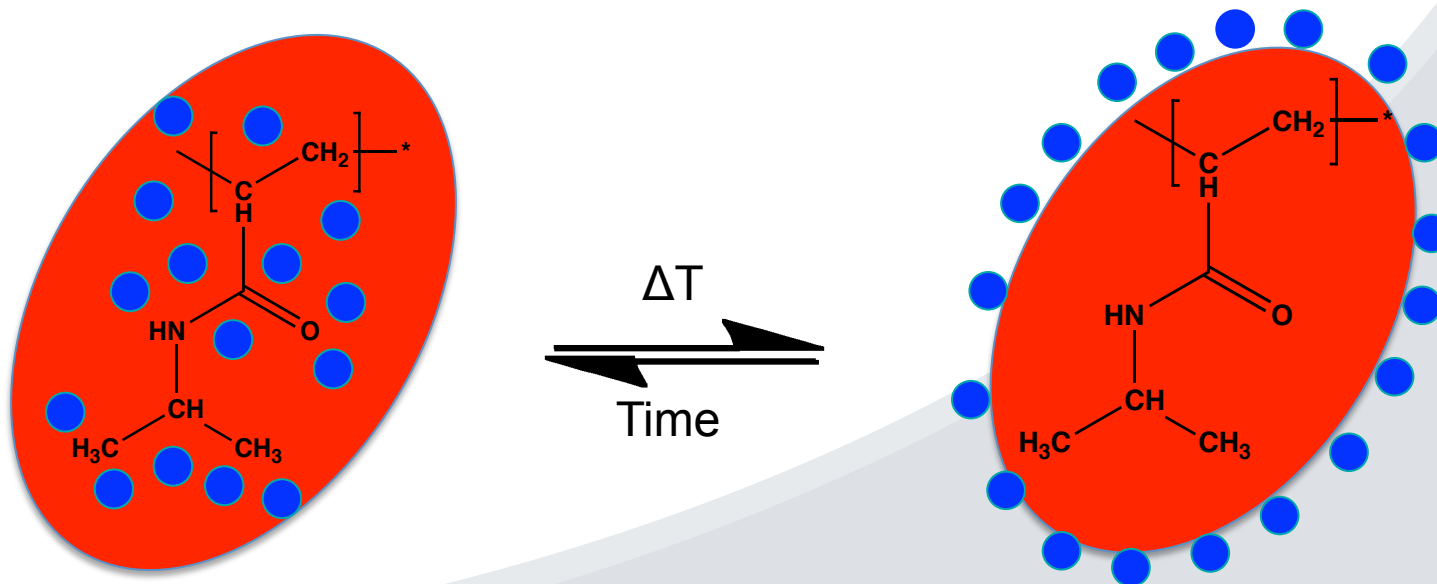
Conclusions

Acknowledgments

- Poly(N-Isopropylacrylamide) or “PNIPAAm”, display inverse solubility upon heating.
- Hydrophilic to Hydrophobic transition occurs at lower critical solution temperature (LCST), 30-35°C.
- **Below LCST**, gel swells by intake of water molecules through hydration of aliphatic groups and hydrogen bonding with amide group.
- **Above LCST**, gel collapses along backbone before water molecules are expelled, process is driven by the conversion from polymer-solvent bonds to polymer-polymer and solvent-solvent bonding.¹

Hydrophilic (below LCST)

Hydrophobic (above LCST)



Introduction

IL Polymer Gels

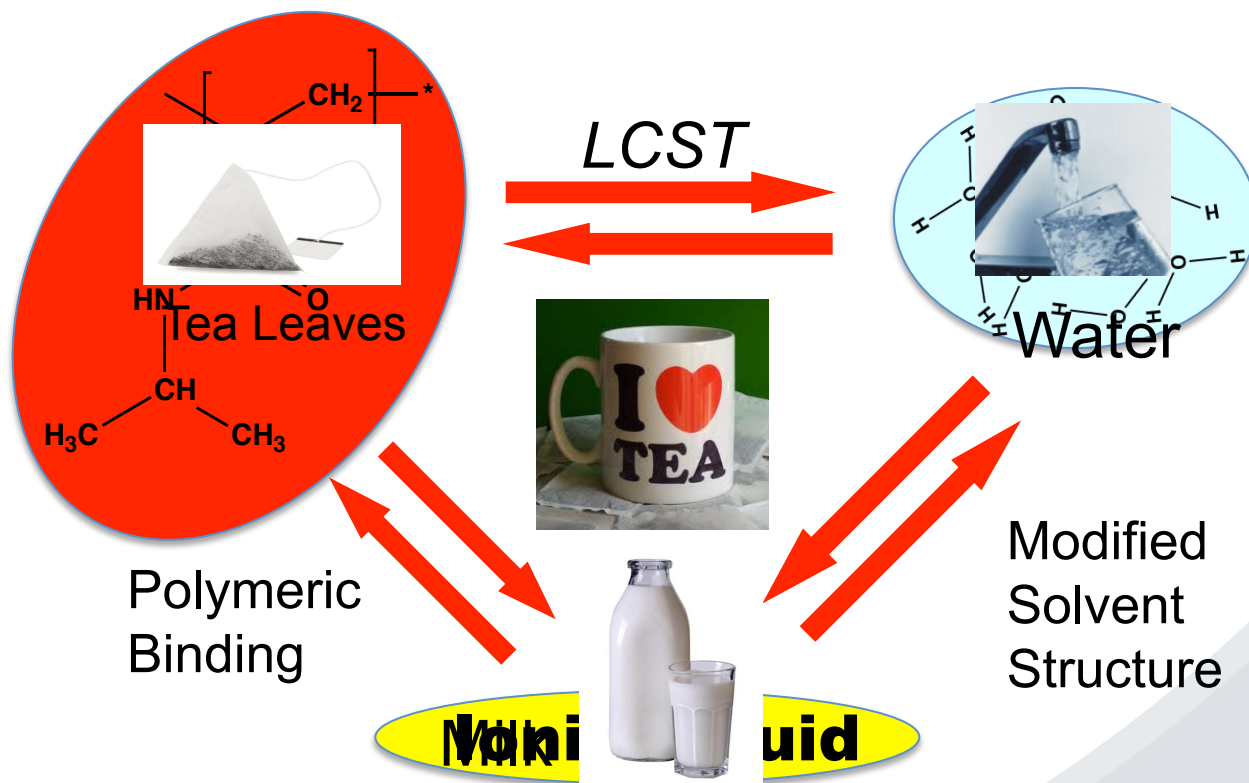
Raman of IL/H₂O

Conclusions

Acknowledgments

1. H.G Shild, Prog. Polym. Sci., Vol. 17, 163-249, 1992

Triphasic PNIPAAm System



- Ionic Liquids incorporated into the polymer forms a modified triphasic system.
- With certain Ionic Liquids, rate of contraction can be manipulated.
- When placed in water, the IL can tune the LCST temperature, employing plasticizer effect.
- Also improve the mechanical stability of the gel.

Introduction

IL Polymer Gels

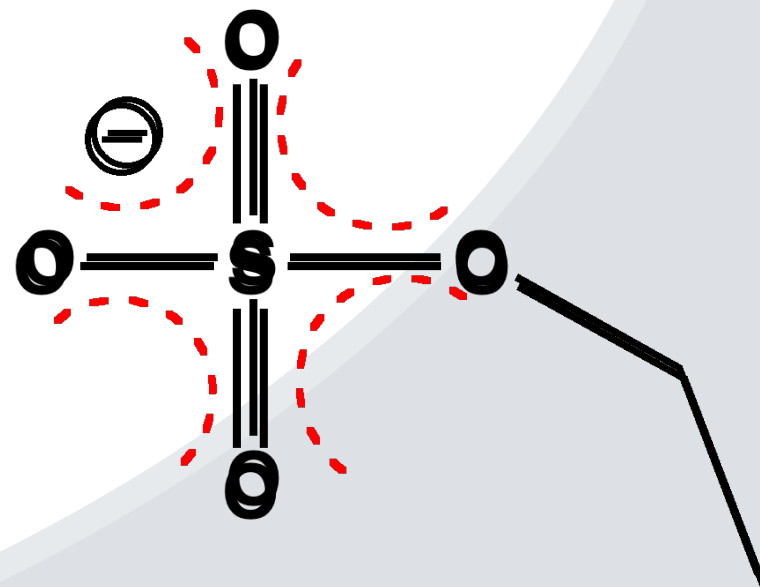
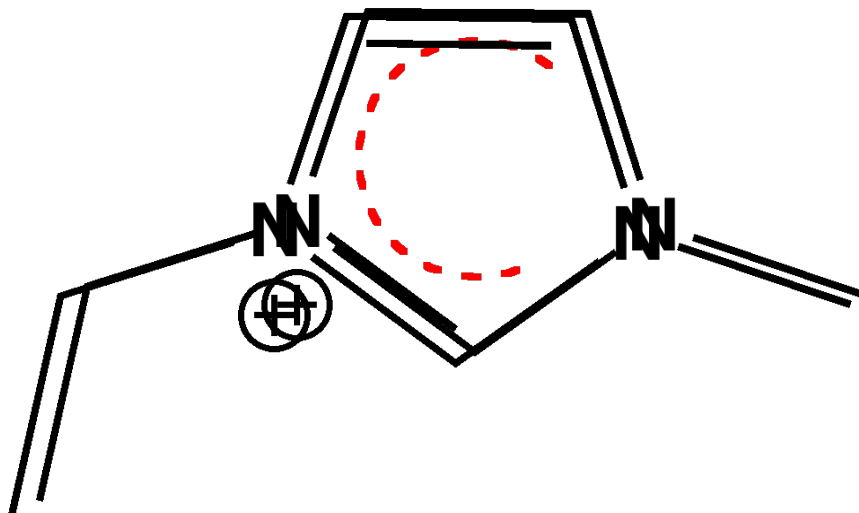
Raman of IL/H₂O

Conclusions

Acknowledgments

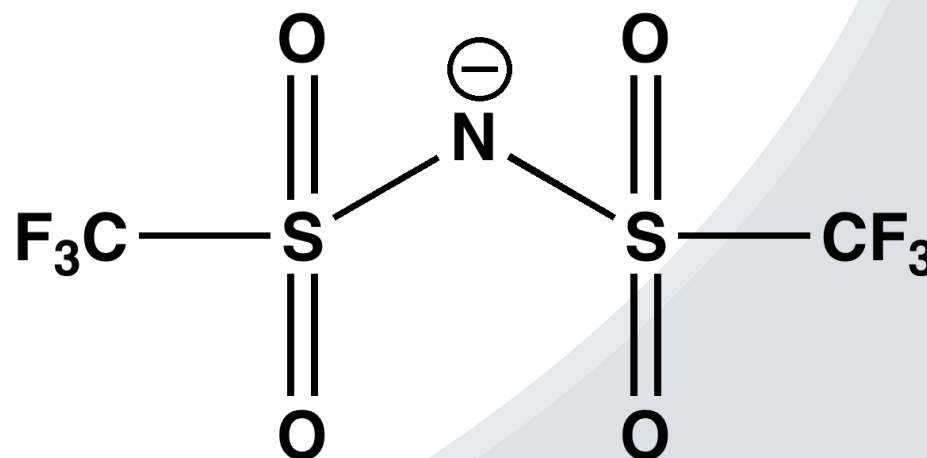
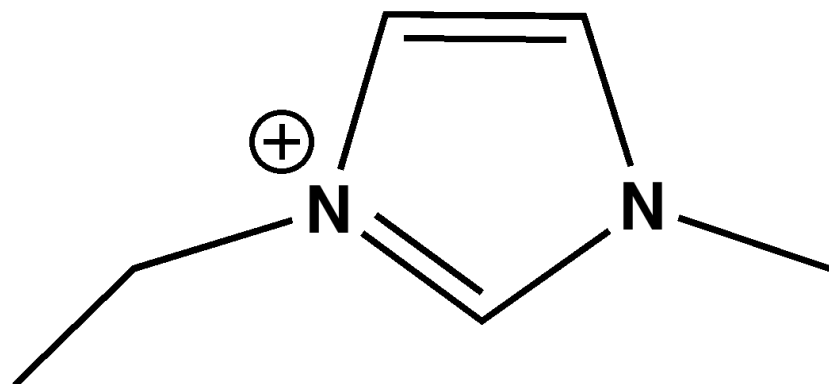
Ionic Liquids crosslinked w/ PNIPAAm

- 1-Ethyl-methyl-3-imidazolium-ethyl sulfate; [C₂mim EtSO₄]



Variation of Anion for Comparison

- 1-Ethyl-methyl-3-imidazolium Bis(trifluoromethylsulfonyl)imide; [C₂mim NTf₂]



Introduction

IL Polymer Gels

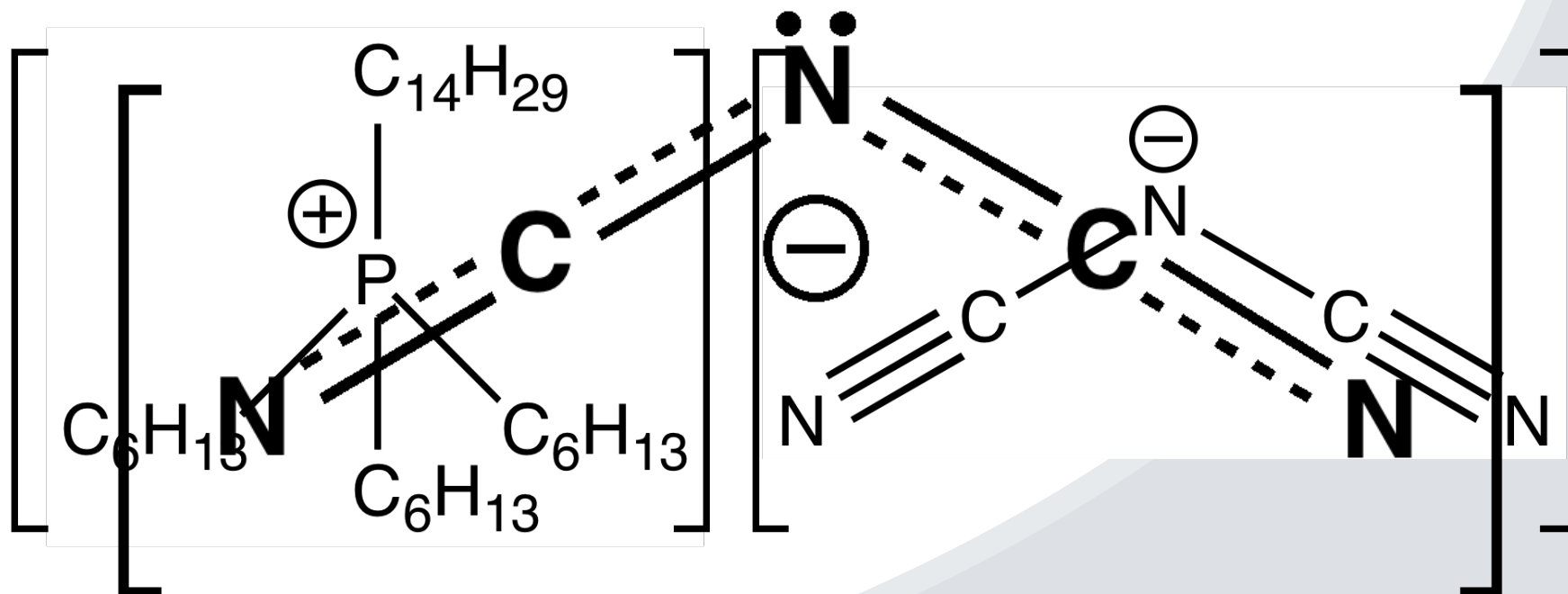
Raman of IL/H₂O

Conclusions

Acknowledgments

Ionic Liquids crosslinked w/ PNIPAAm

- Trihexyltetradecylphosphonium Dicyanamide; $[P_{66614}][DCA]$



Introduction

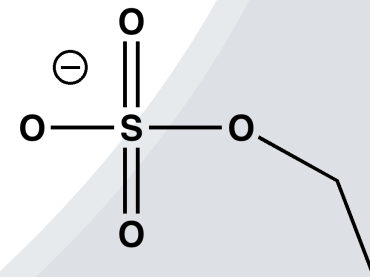
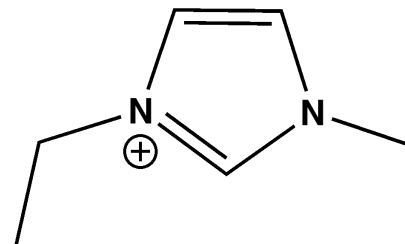
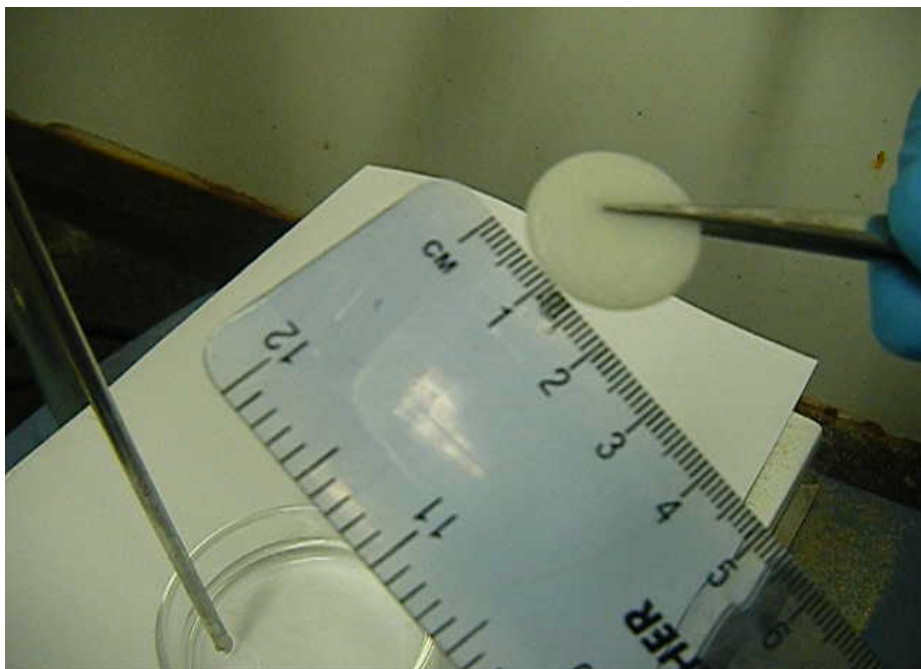
IL Polymer Gels

Raman of IL/H₂O

Conclusions

Acknowledgments

PNIPAAm (g)	Ionic Liquid (g)	% Vol change after ~10secs	Flexibility	
			(~20°C)	(~40°C)
0.5	1	56	*****	*****



- [C₂mim][EtSO₄] crosslinked with PNIPAAm monomer submerged in water above LCST

Introduction

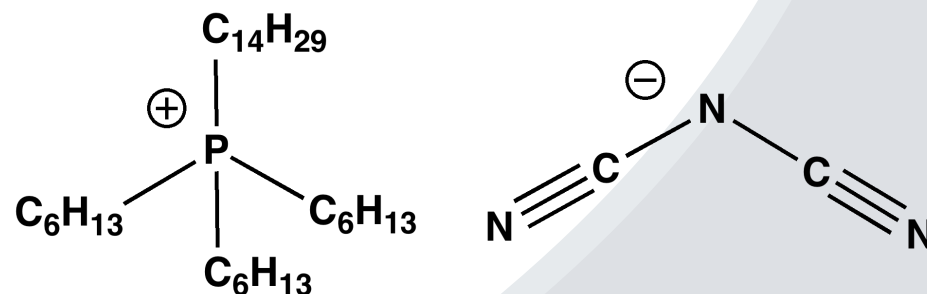
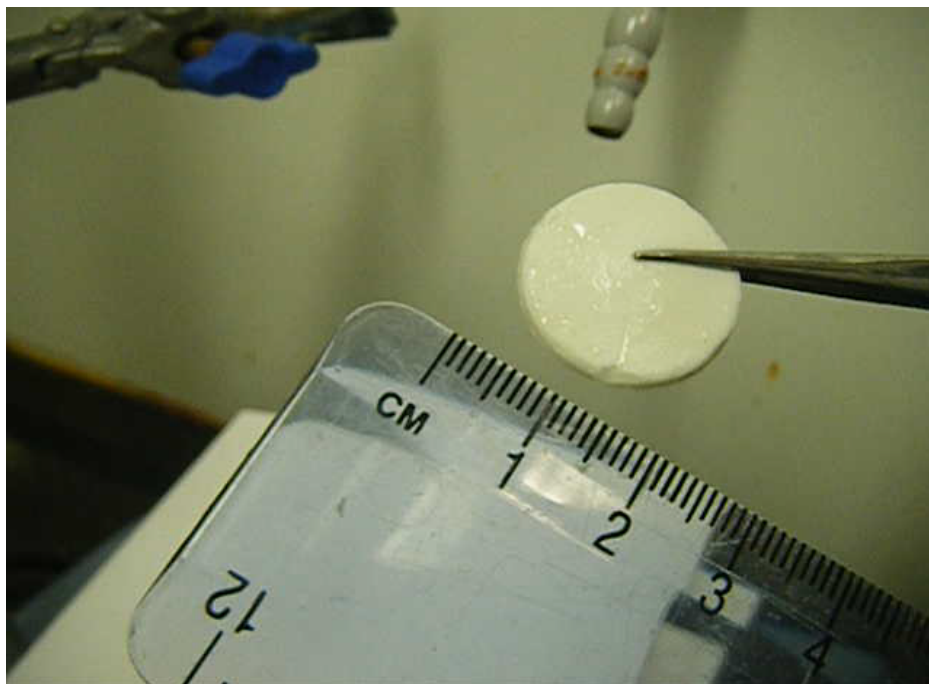
IL Polymer Gels

Raman of IL/H₂O

Conclusions

Acknowledgments

PNIPAAM (g)	Ionic Liquid (g)	% Vol change after ~10secs	Flexibility	
			(~20°C)	(~40°C)
0.5	1	17	*****	**



- $[\text{P}_{66614}][\text{DCA}]$ crosslinked with PNIPAAM monomer submerged in water above LCST

Introduction

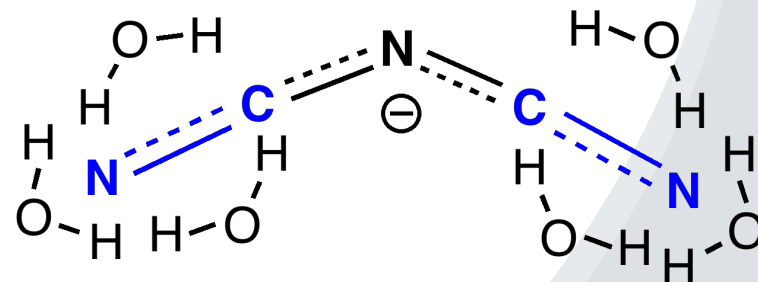
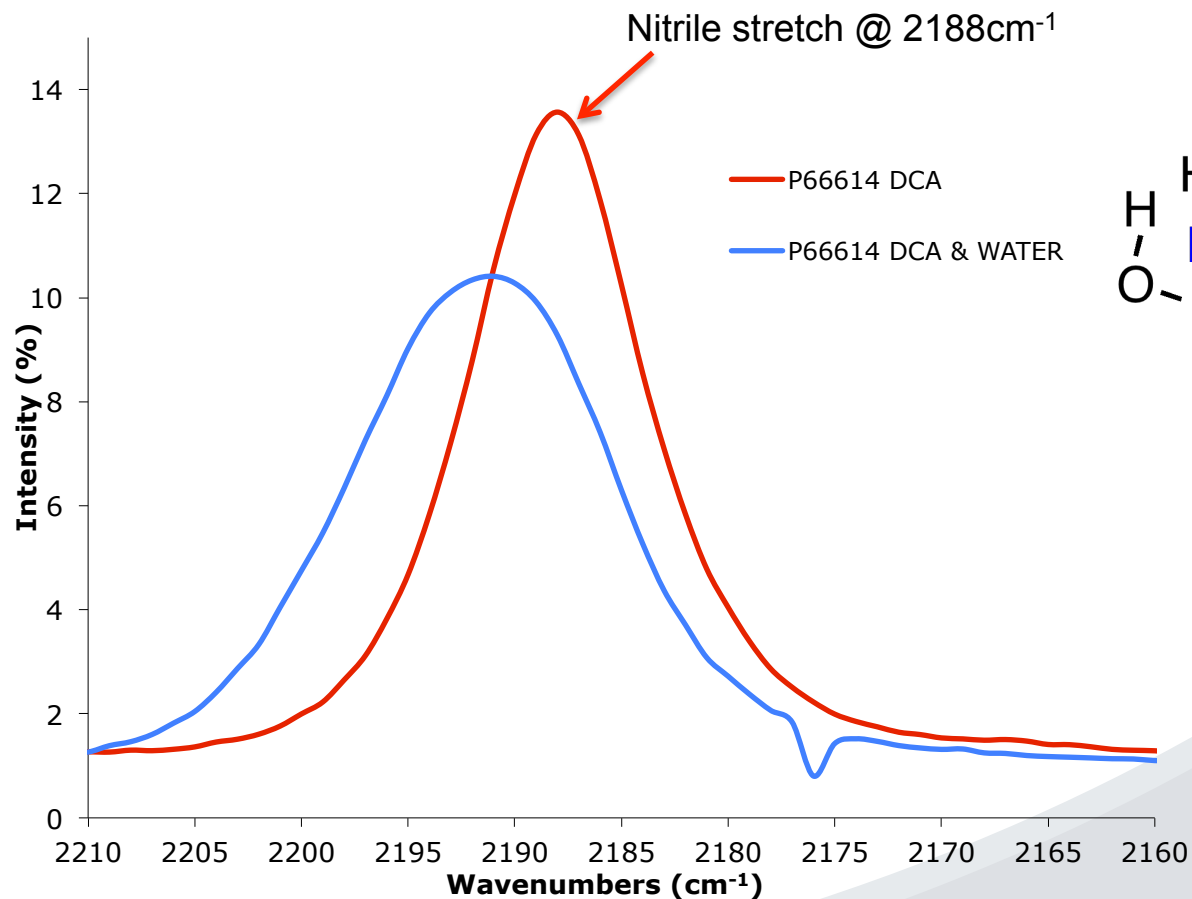
IL Polymer Gels

Raman of IL/H₂O

Conclusions

Acknowledgments

Raman Spectroscopy of $[P_{6,6,6,14}][DCA]$ & H_2O Mixture



- Nitrile stretch at **2188cm⁻¹** shifts upfield to **2191cm⁻¹**, increasing in energy

Introduction

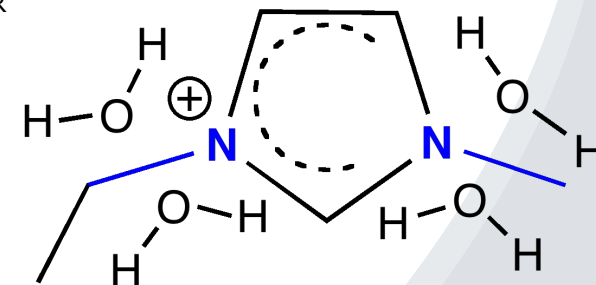
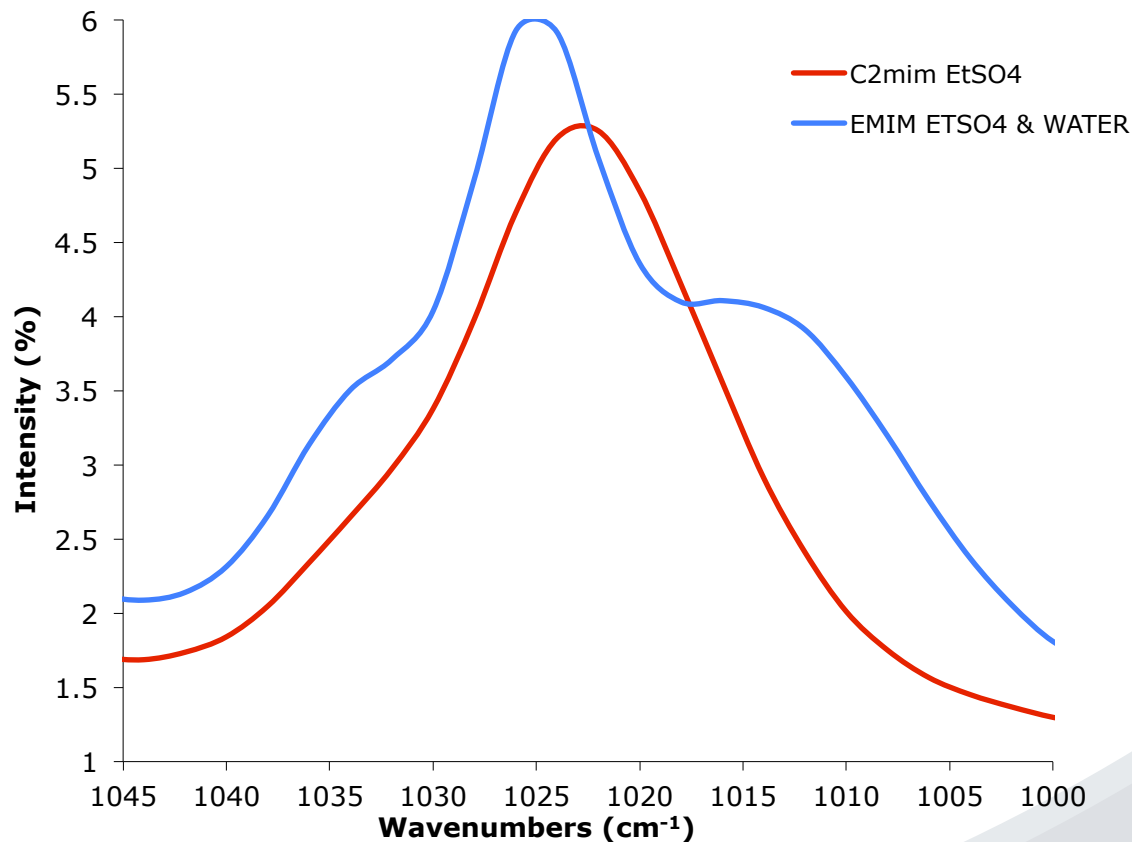
IL Polymer Gels

Raman of IL/H₂O

Conclusions

Acknowledgments

Raman Spectroscopy of [C₂mim][EtSO₄] & H₂O Mixture



- CH₃(N) and CH₂(N) stretch at 1022cm⁻¹ increases in energy with the addition of bulk water
- Also a broadening of the peak indicates more solvation

Introduction

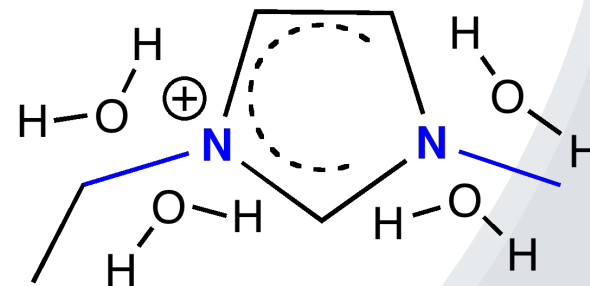
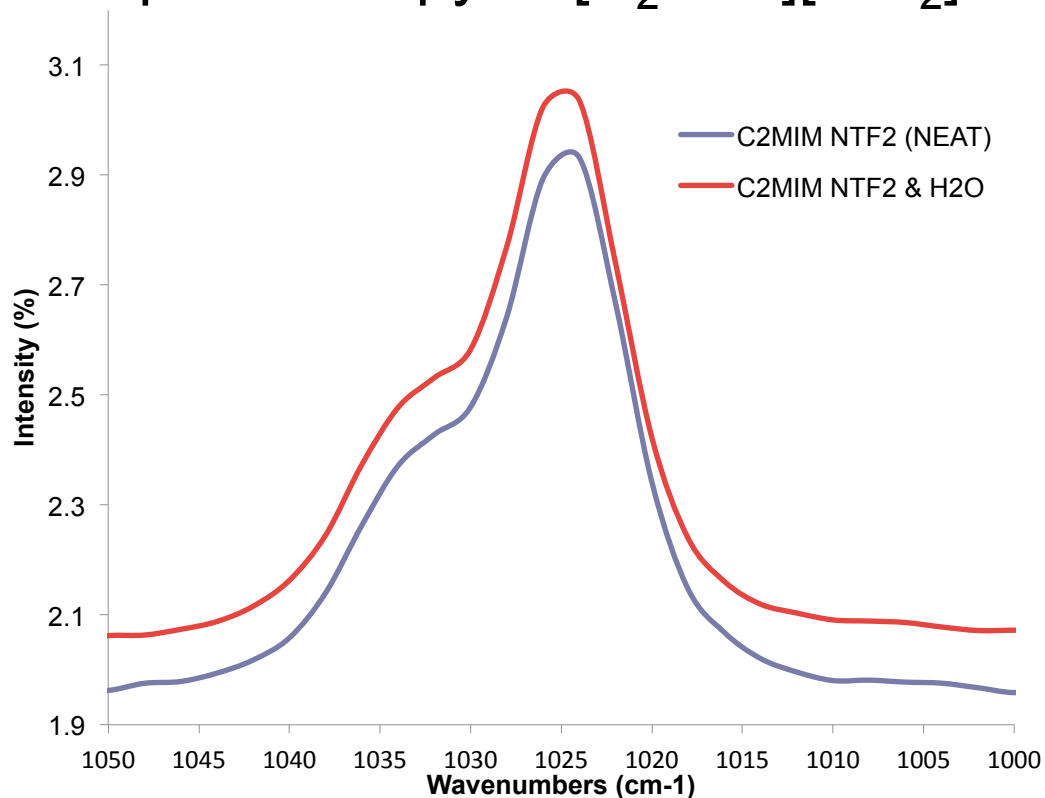
IL Polymer Gels

Raman of IL/H₂O

Conclusions

Acknowledgments

Raman Spectroscopy of [C₂mim][NTf₂] & H₂O Mixtures



- The anion is changed to the more hydrophobic [NTf₂]
- The less significant change shown, displays the effect that bulk water interaction is more apparent in the IL containing the more hydrophilic EtSO₄ anion

Introduction

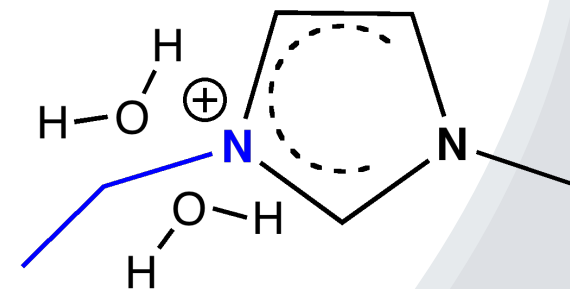
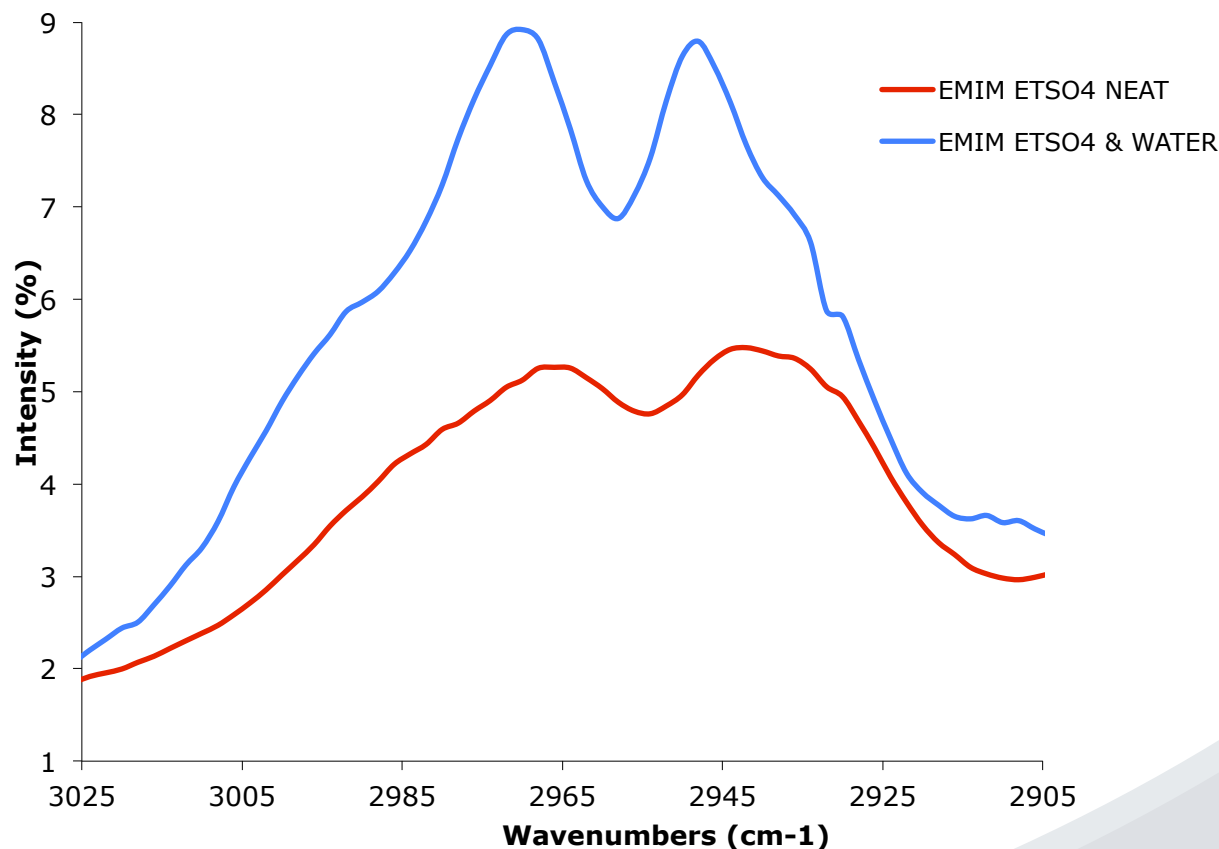
IL Polymer Gels

Raman of IL/H₂O

Conclusions

Acknowledgments

Raman Spectroscopy of [C₂mim][EtSO₄] & H₂O



- Ethyl HCH stretch at 2944cm⁻¹ and 2966cm⁻¹ broadens and shifts in energy due to solvation by bulk water.

Introduction

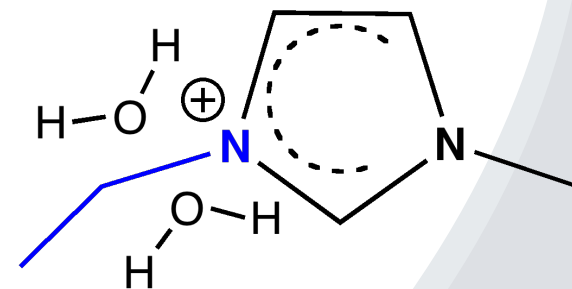
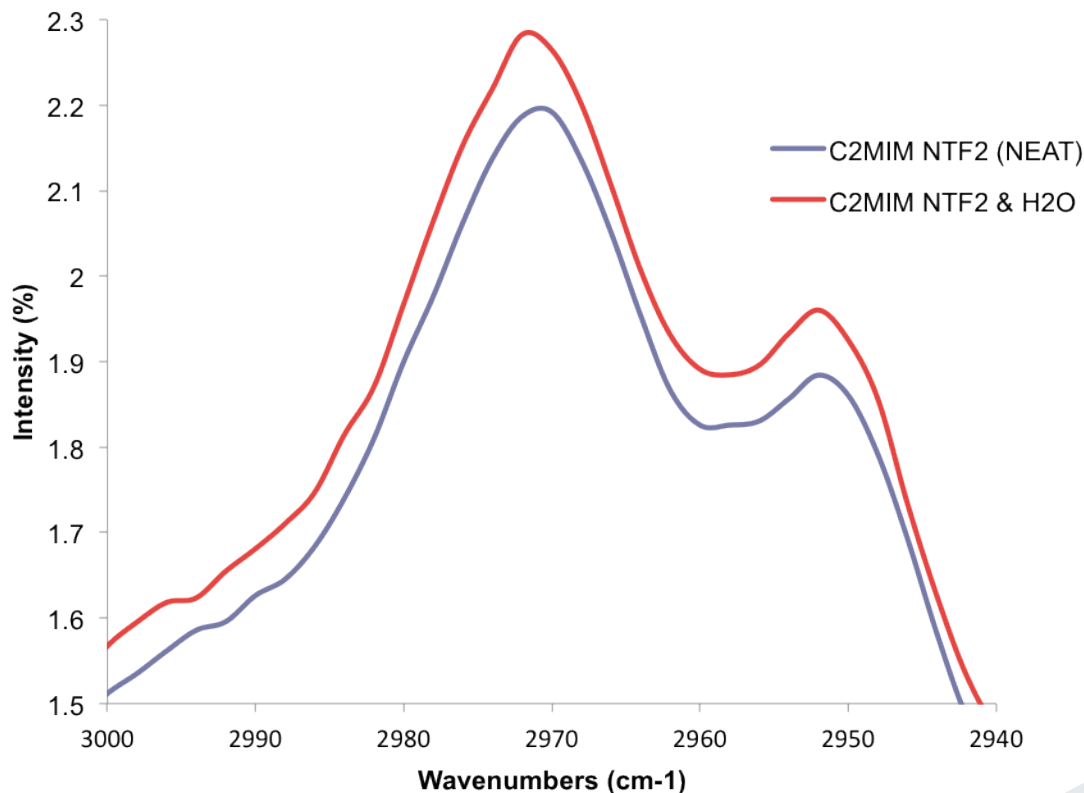
IL Polymer Gels

Raman of IL/H₂O

Conclusions

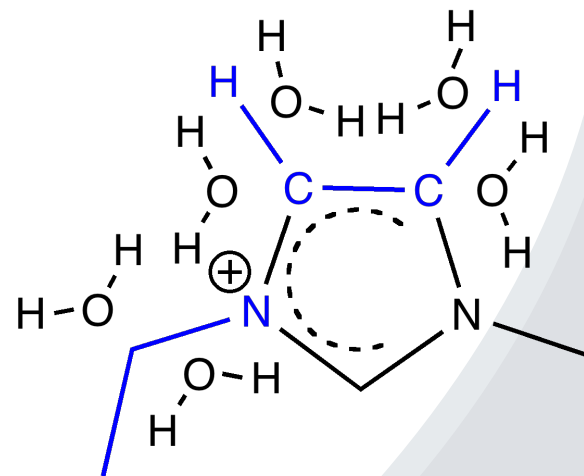
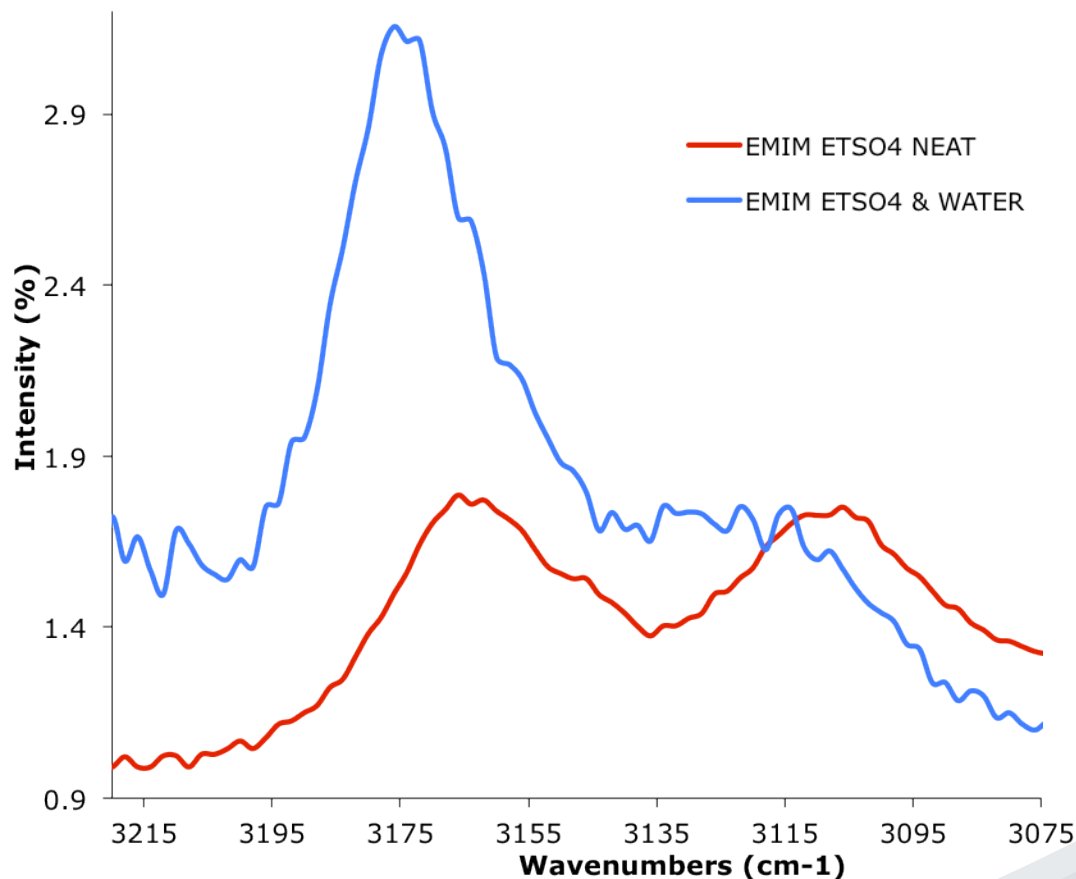
Acknowledgments

Raman Spectroscopy of [C₂mim][NTf₂] & H₂O Mixtures



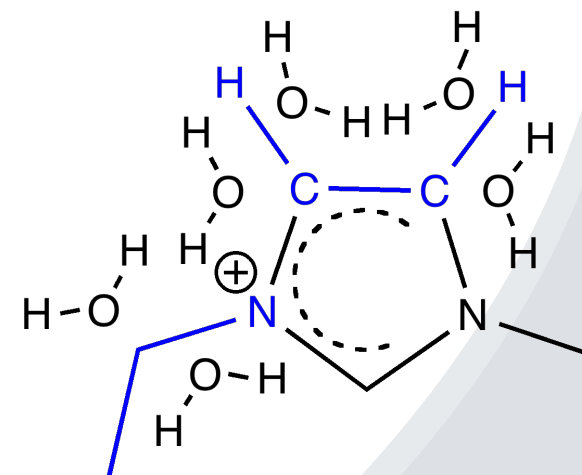
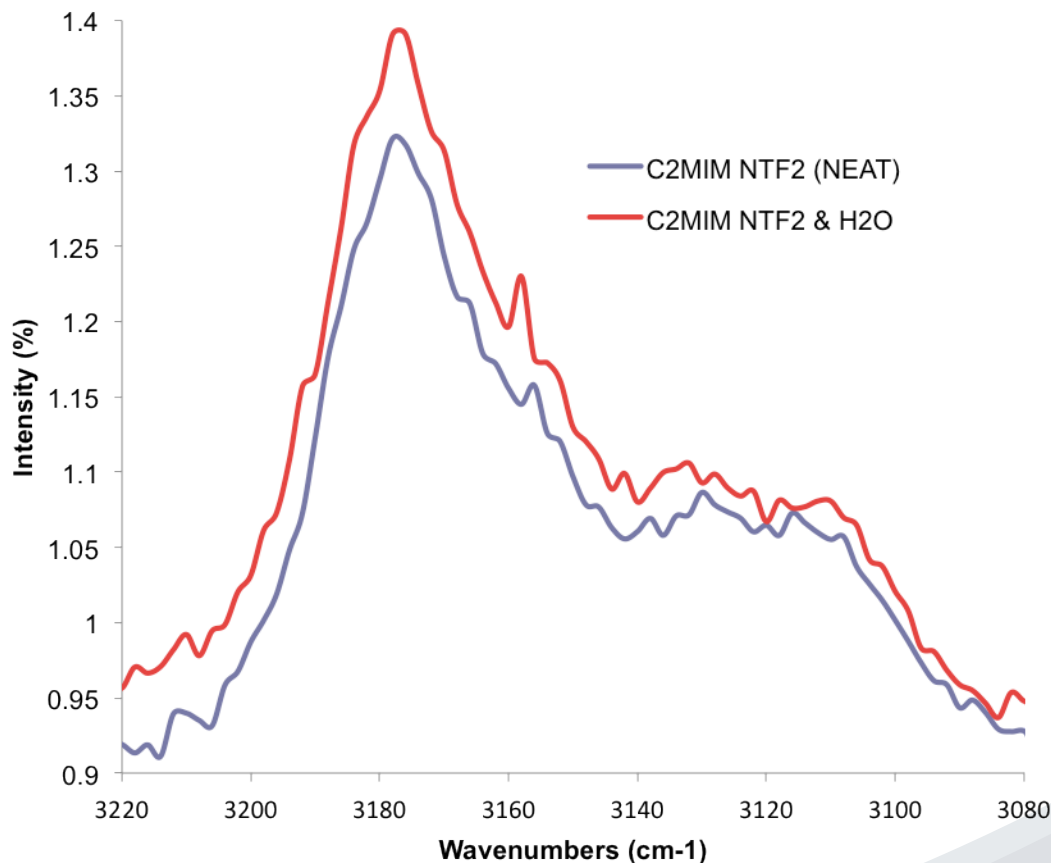
- The anion is changed to the more hydrophobic [NTf₂]
- Shown that water has interacted more significantly with the IL containing the more hydrophilic [EtSO₄] than the IL containing the hydrophobic [NTf₂]

Raman Spectroscopy [C₂mim][EtSO₄] & H₂O Mixtures



- CH₃(N)HCH stretch at 3110cm⁻¹ and ring HCCH stretch at 3166cm⁻¹
- After addition of bulk water, ratio between peaks increases substantially

Raman Spectroscopy of [C₂mim][NTf₂] & H₂O Mixtures



- Changing to the hydrophobic [NTf₂] leads to no change in ratio between peaks.
- Showing again water interaction favours the hydrophilic [EtSO₄]

Introduction

IL Polymer Gels

Raman of IL/H₂O

Conclusions

Acknowledgments

Conclusions

[P₆₆₆₁₄][DCA]

- Nitrile group of [P₆₆₆₁₄][DCA] was found to be affected by bulk water interaction, showing a shift to increase in energy.

[C₂mim][EtSO₄]

- IL containing hydrophilic [EtSO₄] shows interactions specifically with imidazole ring
- Varying of anion to more hydrophobic [NTF₂] shows IL undergoes less change when interacting with water
- Result shows that the anions in both ILs play a prominent role in Ionic Liquid crosslinked PNIPAAm gel.

Acknowledgments



Prof. Dermot Diamond

Dr. Kevin Fraser

Dr. Robert Byrne

Thanks for Listening!