Thermophysiochemical Properties of pure and water-saturated Ionic Liquids

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INTRODUCTION

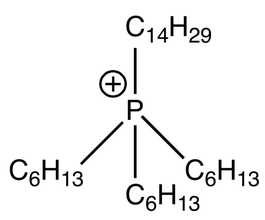
- Poly-(N-isopropylacrylamide) (pNIPAAM) is a thermo responsive polymer gel that displays an inverse solubility of aqueous solutions upon heating above its Lower Critical Solution Temperature (LCST).
- Below the LCST, the gel becomes solvated by water molecules through hydration of aliphatic groups and hydrogen bonding with the amide group.
- Above the LCST, the gel collapses along the polymer backbone before water molecules are expelled.
- This process is driven by the conversion from polymer-solvent bonds to polymer-polymer and solvent-solvent bonding.[1]
- Here at CLARITY, we have crosslinked these particular gels with ionic liquids (ILs), which have shown different rates of contraction and mechanical stability when placed in water above its LCST 30-35 °C.[2]
- These gels are now touted as possible next generation actuators in microfluidic platforms.

AIMS

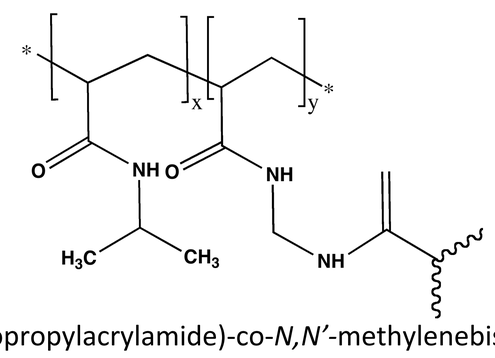
- To investigate the physicochemical interactions that occur between A) IL B) Water C) Polymer as a result in a change in temperature .
- Examine the macro actuator effect as a result of these interactions

EXPERIMENTAL

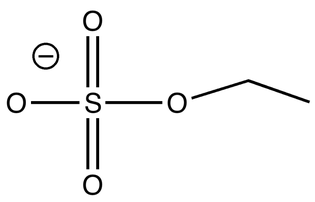
- ILs of interest in this study are; 1-ethyl-3-methylimidazolium ethyl sulfate $[C_2mIm][EtSO_4]$ and trihexyltetradecylphosphonium dicyanamide $[P_{6,6,6,14}][DCA]$ (Figure 1).



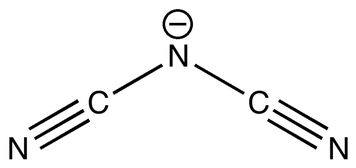
$[P_{6,6,6,14}]^+$



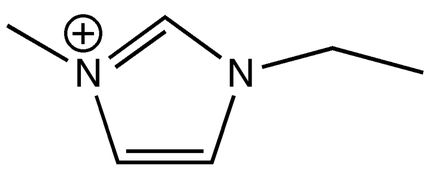
Poly(*N*-isopropylacrylamide)-co-*N,N'*-methylenebisacrylamide



$[EtSO_4]^-$



$[DCA]^-$



$[C_2mIm]^+$

Fig 1: *Ionic Liquids of interest and repeating unit of the polymer.*

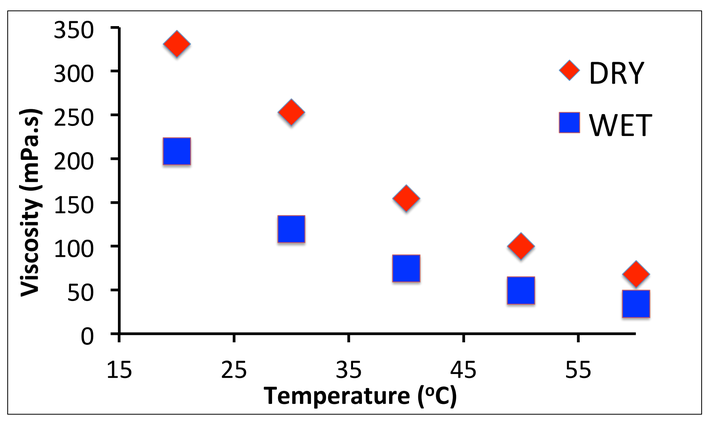
- The thermo-physical properties of these pure water-saturated ILs were investigated using density, viscometry, and rheometry.
- The IL / water systems were prepared by vigorous shaking in the presence of water, where after 48 hrs the the IL rich phase was extracted.
- All measurements were performed from temperatures 20 - 60 °C in 10 °C increments.

RESULTS AND DISCUSSION

- Viscosity values were found to decrease substantially after water saturation for $[C_2mim][EtSO_4]$ compared to $[P_{6,6,6,14}][DCA]$.

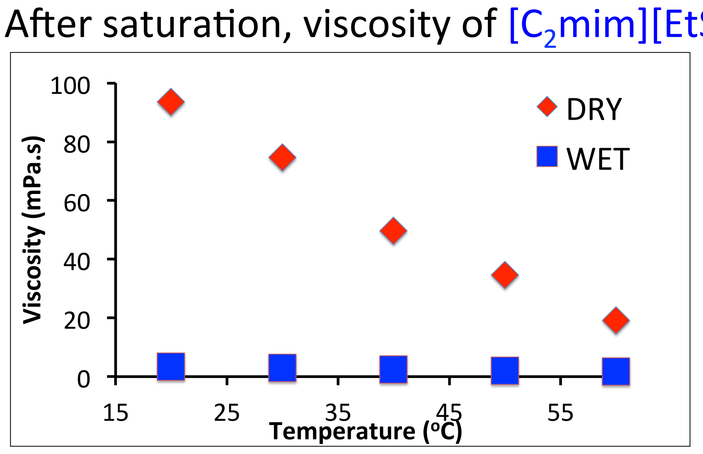
Viscosity

- After saturation, viscosity of $[P_{6,6,6,14}][DCA]$ changes by 36.91%



$[P_{66614}][DCA]$	20 °C (mPa.s)	60 °C (mPa.s)	% Change
DRY (mPa.s)	330.65	67.63	79.54
Wet (mPa.s)	208.6	34.19	83.6

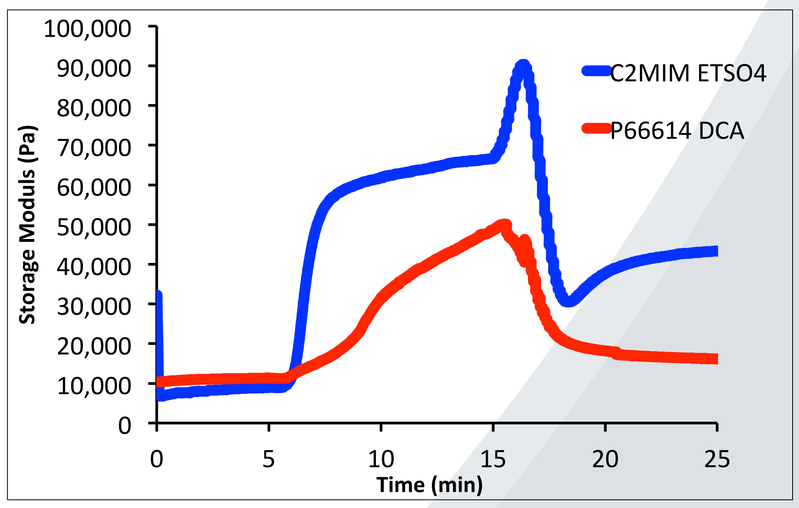
- After saturation, viscosity of $[C_2mim][EtSO_4]$ changes by 96.33%



$[C_2mim][EtSO_4]$	20 °C (mPa.s)	60 °C (mPa.s)	% Change
DRY (mPa.s)	93.6	19.23	79.77
Wet (mPa.s)	3.43	1.73	49.57

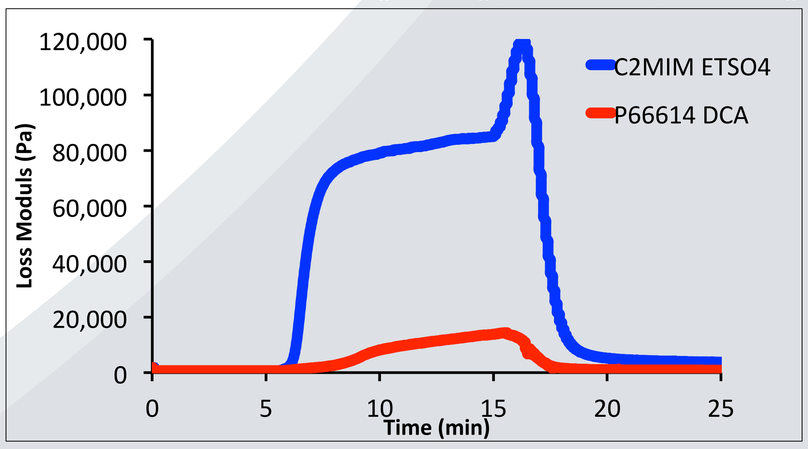
Rheometry

- Storage modulus, measuring the elastic energy of the hydrated gel



- Gels swelled with H_2O overnight and then modulus change measured above 45 °C
- Clear difference observed between $[C_2mim][EtSO_4]$ and $[P_{6,6,6,14}][DCA]$
- Stiffer $[P_{6,6,6,14}][DCA]$ shown to retain more energy when pressure is applied at 45°C

- Loss Modulus, measuring energy loss of hydrated gel when pressure is applied



- $[C_2mim][EtSO_4]$ shown to lose more energy than the stiffer, mechanically stronger $[P_{6,6,6,14}][DCA]$

Conclusions

- The more hydrophobic $[P_{6,6,6,14}][DCA]$ gel shows stronger mechanical stability, while the hydrophilic $[C_2mim][EtSO_4]$ gel shows improvement in the rate of contraction.
- Viscosity value of $[C_2mim][EtSO_4]$ changed by 96.33% when saturated with water, while $[P_{6,6,6,14}][DCA]$ changes value by 36.91%
- Storage and Loss modulus results show that the stiffer $[P_{6,6,6,14}][DCA]$ retains more energy than the mechanically weaker $[C_2mim][EtSO_4]$ when pressure is applied on the gel above the LCST

References

1. *H.G Shild, Prog. Polym. Sci., Vol. 17, 163-249, 1992*
2. Benito-Lopez, Fernando and Byrne, Robert and Raduta, Ana Maria and Vrana, Nihal Engin and McGuinness Garrett and Diamond Dermot (2010) Lab on a Chip, 10 (2). pp. 195-201.

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