Molecular Insight into the Lower Critical Solution Temperature Transition of Ionic Liquids

Hyungmook Kang,[1,2] David E. Suich,[3] Robert Kostecki,[3] Jeffrey J. Urban [1,*]

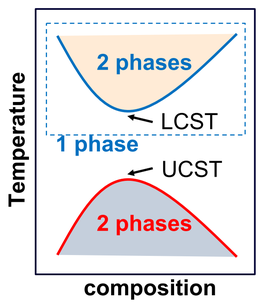
[1] The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA
[2] Department of Mechanical Engineering, University of California, Berkeley, CA
[3] Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, CA

email: hmkang@berkeley.edu (H.Kang) jjurban@lbl.gov (J.J.Urban)

Introduction

LCST behavior

A thermo-responsive spontaneous phase-separation behavior

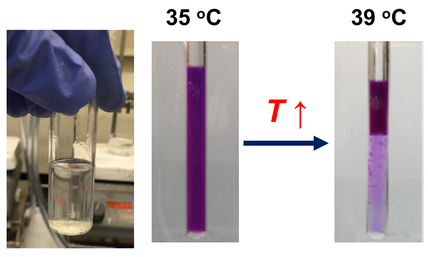


with the critical temperature, called the **Lower Critical Solution Temperature**

At temperatures below LCST, the system is completely miscible in all proportions, whereas above LCST partial liquid miscibility occurs.

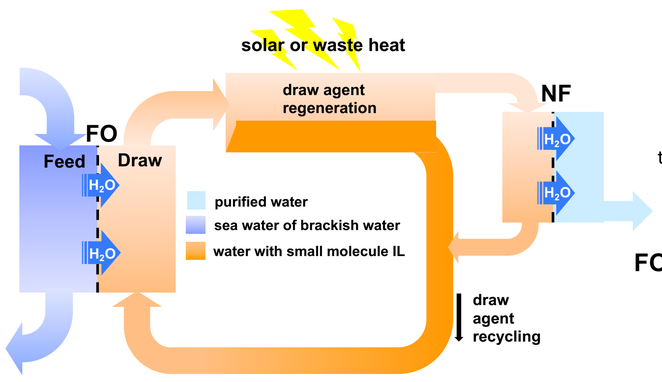
Visualization

Nile Red dye dissolved by IL



Target Application

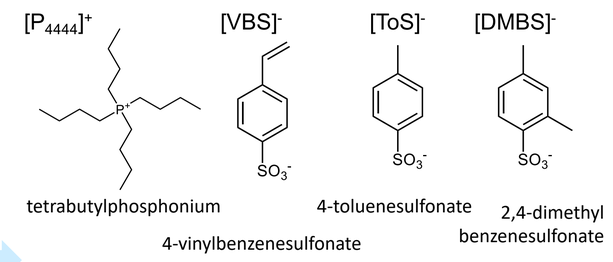
Forward Osmosis desalination process based on Ionic Liquids with LCST behavior



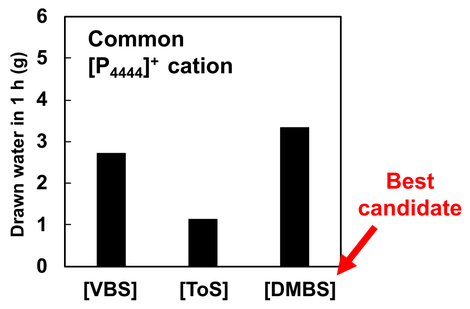
Ideal draw agents should possess

- high osmotic pressure
- being easily regenerated with only low grade heat
- low reverse diffusion, viscosity
- good chemical and thermal stability
- low toxicity

Draw Agents: Ionic Liquids with LCST behavior



FO performance using 10 wt.% ILs as draw solutions

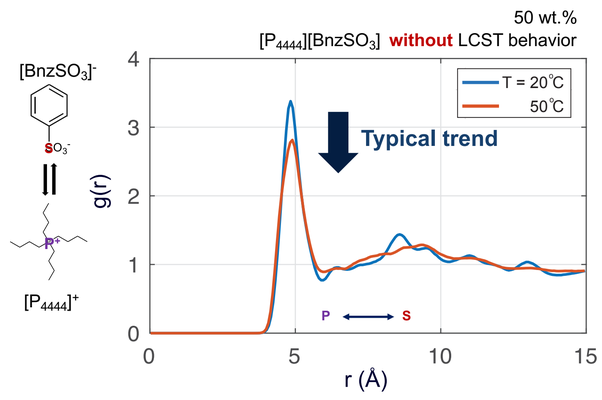


Validation of MD results

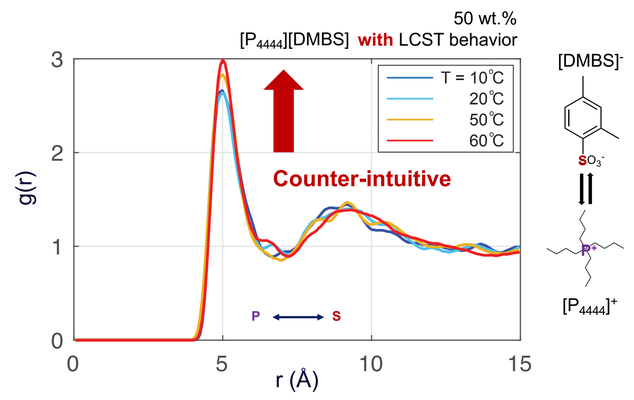
Radial Distribution Functions

between P cation – S anion

The mostly charged atom represents the position of each ion.
i.e. P atoms for the cations, S atoms for the anions

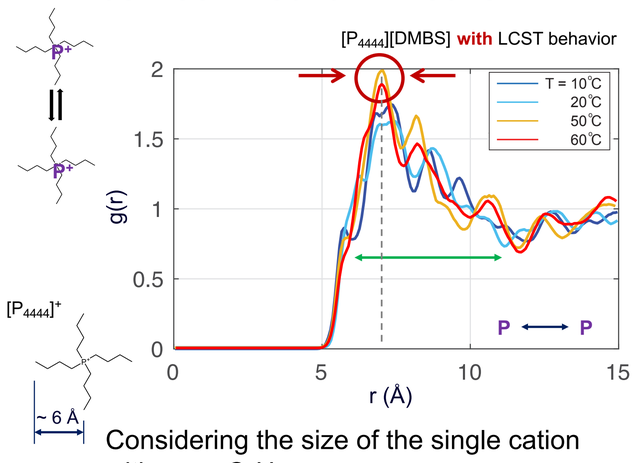


The more thermal motion at higher temperature



At above T_c range, **a stronger attractive interaction** was observed between the cations and anions.

between P cation – P cation



Since the RDF is averaged data, **the multiple peaks** come from different orientations so thus mean the ions **are loosely tied**.

The peaks are merged at elevated temperatures and **a major peak** is observed **at above T_c range**.

- The ions are compactly tied to each other by the strong electrostatic forces
- The ion-pair aggregation is in the dense form of multiple layers of cation-anion shells.

Evidence of clustering at above T_c range

Considering the size of the single cation with even C_4H_9 group,

the peaks **between 5 and 12 Å** can be interpreted as all located **in the first coordination shell**.

but, what drives this phenomena?

Motivation

Scientific Questions

1. How does **the molecular environment** depend on temperature and LCST phase transition ?

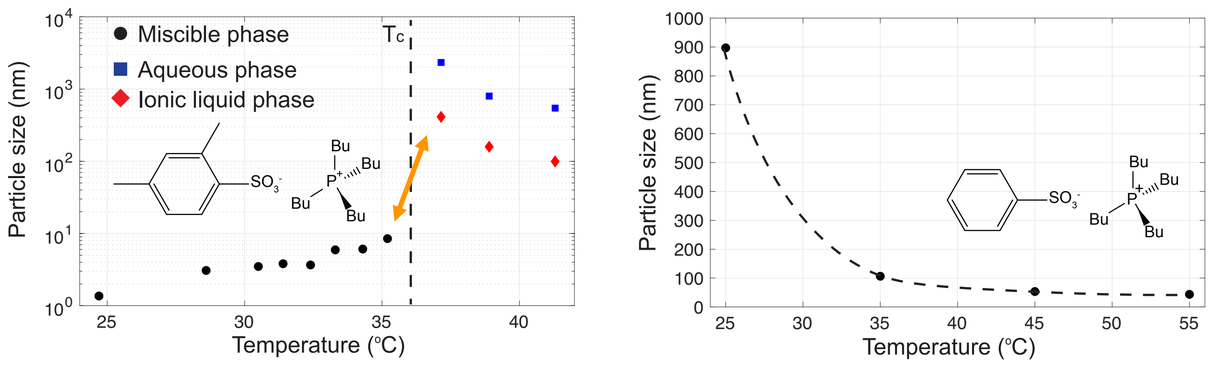
2. Why can **a minor chemical change** induce markedly different phenomena ?

$[P_{4444}][DMBS]$ — **with** LCST behavior

$[P_{4444}][BnzSO_3]$ — **without** LCST behavior

Particle size by Dynamic Light Scattering (DLS)

50 wt.% $[P_{4444}][DMBS]$ **vs.** **50 wt.% $[P_{4444}][BnzSO_3]$**

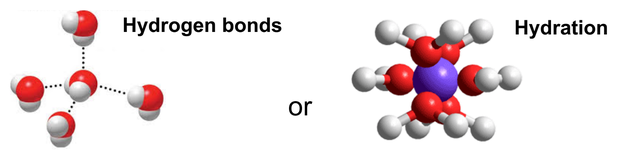


Discussion

Hydrogen bonds [G.D. Smith et. al., Phys Rev Lett, 2000]

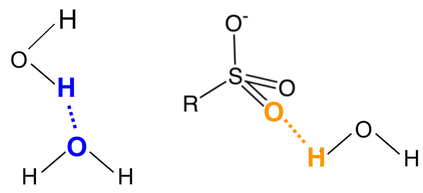
The **gain or loss of the directional bonding** has been used to explain the behavior of small molecules

Water molecules in these systems essentially contribute to



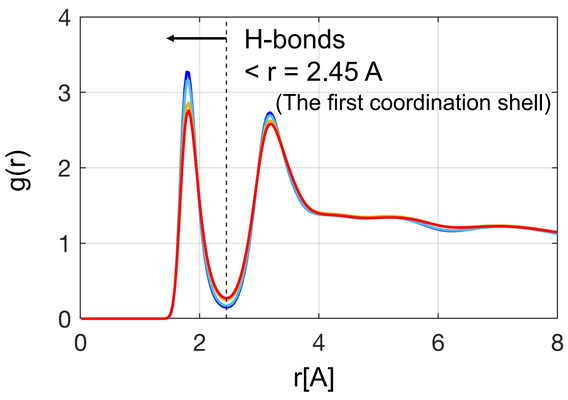
(there is essentially no free water for solutions > 50 wt.%)

Main H-bonds in these systems

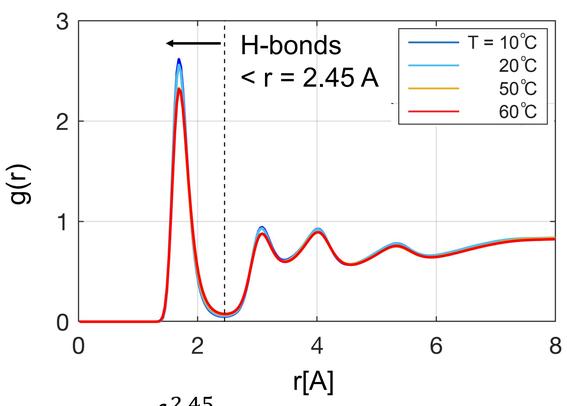


Counting Hydrogen bonds in MD simulation

RDF between O and H in water

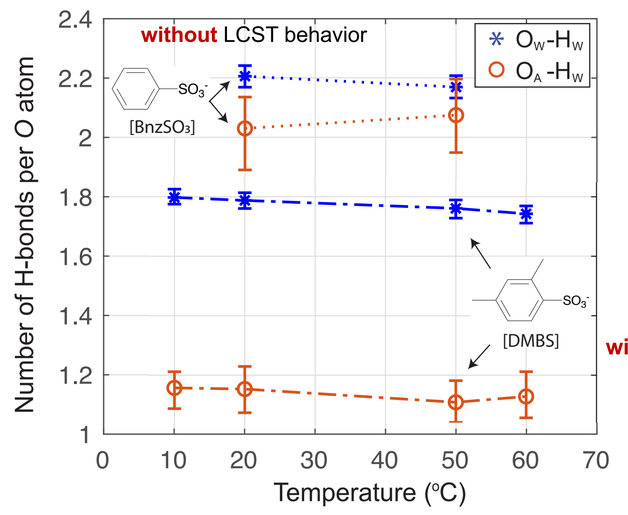


RDF between O in anions and H in water



$$g(r) = \frac{dn(r)}{\rho_n 4\pi r^2 dr} \longrightarrow N_{H-bonding} = \int_0^{2.45} 4\pi r^2 g(r) \rho_H dr$$

Number of Hydrogen bonds per O atom



More water molecules participate in perfecting the hydration shell of ILs

The hydration shell of ILs is the necessary requirement for the LCST

LAMMPS set up

Initial placement

- $[P_{4444}][DMBS]$: 80 pairs of ILs & 1920 water molecules (= 50.8 wt.%) **with** LCST behavior
- $[P_{4444}][BnzSO_3]$: 80 pairs of ILs & 1440 water molecules (= 49.6 wt.%) **without** LCST behavior

Potentials

- pair style : lj/cut/tip4p/long, cutoff distance 15 A (LJ),13 A (charge) + *pppm* algorithm
- bond, angle style : harmonic
- dihedral style : charmm
- special style : amber

Parameters from
[*G. Zhou et. al., J Phys Chem B, 2007*]
[*X. He et. al., J Phys Chem B, 2010*]

MD Running

Isothermal-Isobaric ensemble (NPT)

- Below T_c: 10 °C, 20 °C
- Above T_c: 50 °C, 60 °C

Ref. critical T = 36 °C at 50 wt.%

Timestep : **1.0 fs**

Total timesteps : **10 M timesteps** = **10 ns** for every T cases (after pre-running for equilibration)

Acknowledgement

Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Depart ment of Energy under Contract No. DE-AC02-05CH11231.

Published as [*H. Kang et. al., Comms Chem, 2 (51) 2019*]