Understanding Lower Critical Solution Temperature (LCST) Ionic Liquid (IL) Behavior via Molecular Simulation

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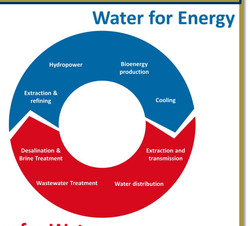
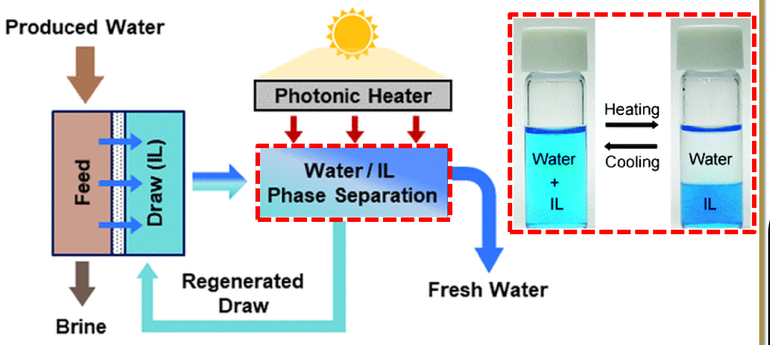
Motivation

- Advancement in water desalination technologies require…
  - Energy-efficient separation (cf. ΔH_{vap}~630 kWh_{th}/m^3 for evaporative desalination)
  - Minimal operational cost
  - Low carbon footprint



Panagopoulos, A. Water-energy nexus: desalination technologies and renewable energy sources. *Environ Sci Pollut Res* **28**, 21009–21022 (2021).

Thermally Responsive ILs:



A. Haddad, et al. *Environmental Science & Technology* 2021 55 (5), 3260-3269

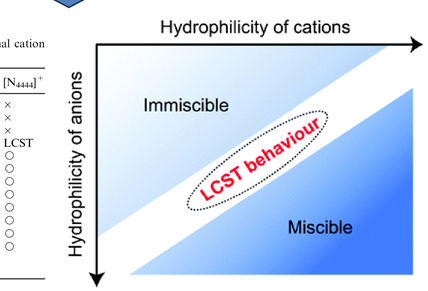


Table 1 Phase behaviour of ILs composed of the individual cation and anion after mixing with equal weight of water

	$[P_{5555}]^+$	$[P_{4448}]^+$	$[P_{4444}]^+$	$[N_{4444}]^+$
$[Tf_2N]^-$	×	×	×	×
BF_4^-	×	×	×	×
$CF_3SO_3^-$	×	×	×	×
$[TMBS]^-$	×	×	LCST	LCST
CF_3COO^-	×	×	LCST	○
$[DMBS]^-$	×	×	LCST	○
$[TsO]^-$	×	×	LCST	○
$[BzSO_3]^-$	×	×	○	○
NO_3^-	×	×	○	○
Br^-	×	LCST	○	○
Cl^-	×	○	○	○
$CH_3SO_3^-$	○	○	○	○

○: hydrophilic IL, ×: hydrophobic IL.

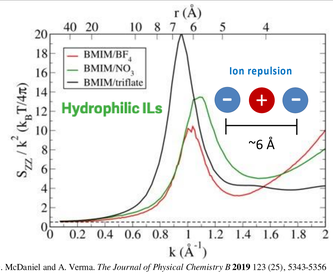
Phys. Chem. Chem. Phys., 2012,**14**, 5063-5070

Universal design principles of LCST ILs are unknown.

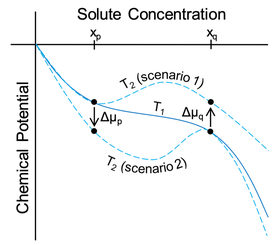
Hypothesis and Approach

$$\Delta G_{mix} \propto \chi_{IL} \cdot \chi_{H_2O} \left(E_{IL/H_2O} - \frac{(E_{IL}+E_{H_2O})}{2} \right) + (\chi_{IL} \ln \chi_{IL} + \chi_{H_2O} \ln \chi_{H_2O})$$

$$\Delta\mu = RT\ ln(a)$$

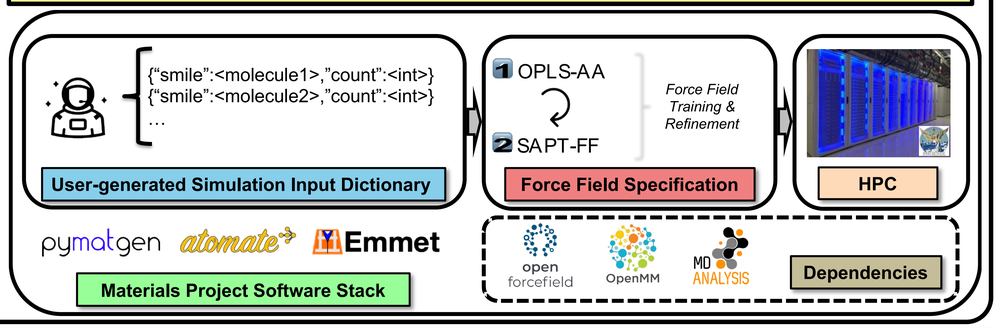


J. G. McDaniel and A. Verma. *The Journal of Physical Chemistry B* **2019** 123 (25), 5343-5356



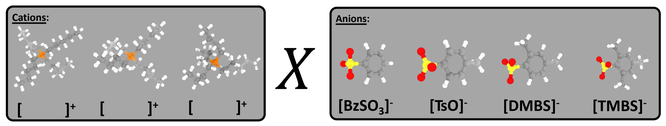
LCST behavior is driven by structural and thermodynamic properties:
1. cross-interaction energy term, $\mathbf{E_{IL/H_2O}}$ ($\propto \mathbf{S_{zz}/k^2}$)
2. excess chemical potential, $\boldsymbol{\Delta\mu_{excess}(T)}$

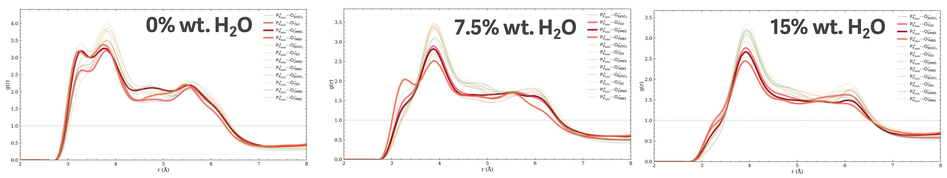
High-throughput molecular dynamics (HTMD) workflow enables ~1000s of IL simulations.

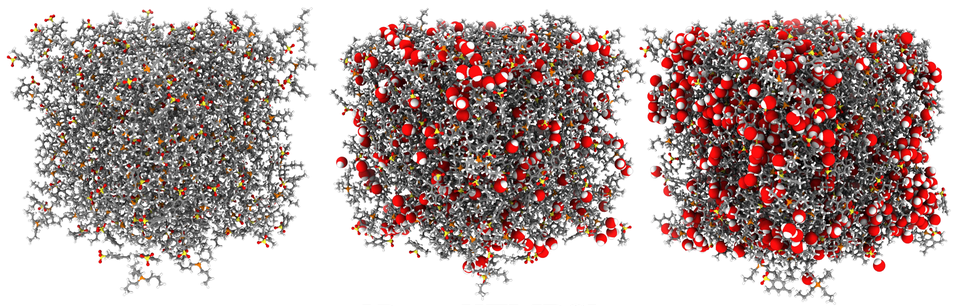


Results

12 ionic liquids, 10 concentrations, 4 temperatures



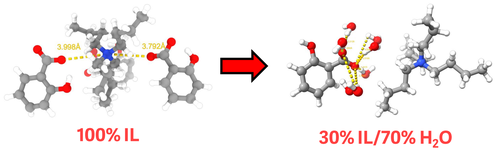




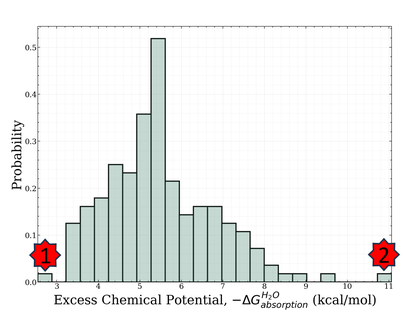
$[P_{4444}][TMBS]$

Cation-anion RDFs indicate that at increased H_2O concentrations, water hydrogen bonding dominates in **LCST systems**.

ΔH_{mix}(T=300 K)	ΔH_{mix}(T=350 K)
-8.43 kJ/mol	-7.56 kJ/mol



Enthalpic contributions are negative.



$\Delta\mu_{ex}$ distribution generated via thermodynamic integration indicates **microenvironment structure governs phase separation**.

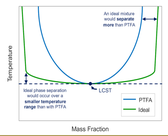
Objective

Understand fundamental mechanisms that drive LCST behavior in IL/H_2O mixtures.

Future Work

(1) Investigate entropic contributions via **thermodynamic integration**.

(2) Use graph neural networks for **inverse design optimization** space.



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