EuroHPC
Summit Week 2022

# THERMORESPONSIVE IONIC LIQUID/WATER MIXTURES

Nancy C. Forero-Martinez, R. Cortes-Huerto and P. Ballone

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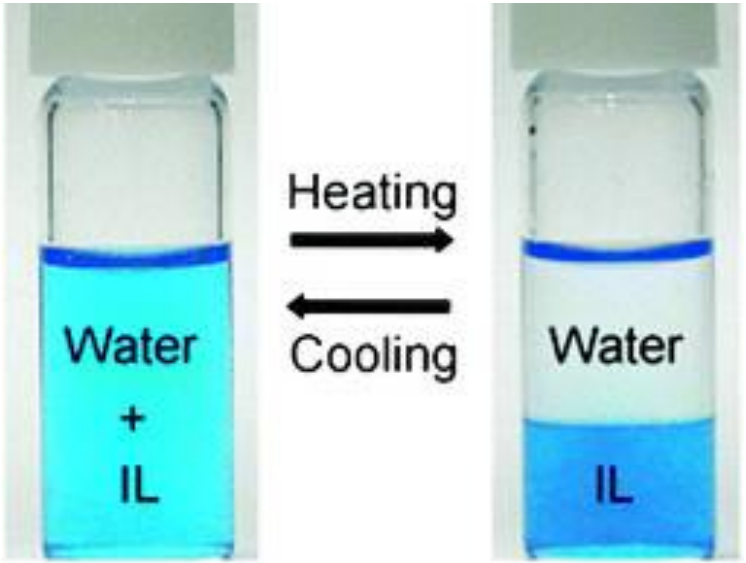
#EHPCSW #PRACEdays

# Thermoresponsive Ionic Liquid / Water Solutions and their applications

- Selected room-temperature ionic liquids (RTILs) present a temperature-dependent solubility gap.
- Demixing can take place with decreasing (UCST) or increasing (LCST) temperature.
- Goal: investigating demixing mechanism, and exploring energy and environmental applications.

Figure adapted from
Kohno and Ohno, Phys. Chem. Chem. Phys. 2012, 14, 5063-5070

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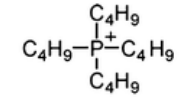
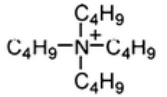
## Systems, models and method

- Systems: RTILs $[P_{4444}][DMBS]$, $[P_{4444}][TsO]$, $[P_{4444}][TMBS]$, $[P_{4444}][TFA]$, $[N_{4444}][TMBS]$
- IL / Water solutions at 50-50 wt% composition
- Samples of $10^6$ – 1.2 x $10^6$ atoms
- NPT molecular dynamics over $\mu$s times
- Gromos-type force field
- Analysis in terms of Kirkwood-Buff integrals and partial structure factors



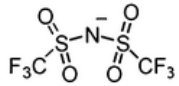

tetrabutylphosphonium
$[P_{4444}]^+$



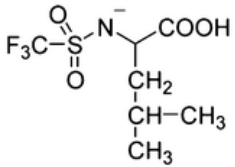

tetrabutylammonium
$[N_{4444}]^+$


nitrate

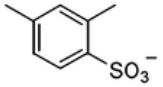

trifluoroacetate



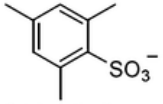

bis(trifluoromethane-sulfonyl)imide
$[Tf_2N]^-$




*N*-trifluoromethanesulfonyl leucine
$[Tf\text{-}Leu]^-$




2,4-dimethylbenzene-sulfonate
$[DMBS]^-$




2,4,6-trimethylbenzene-sulfonate
$[TMBS]^-$

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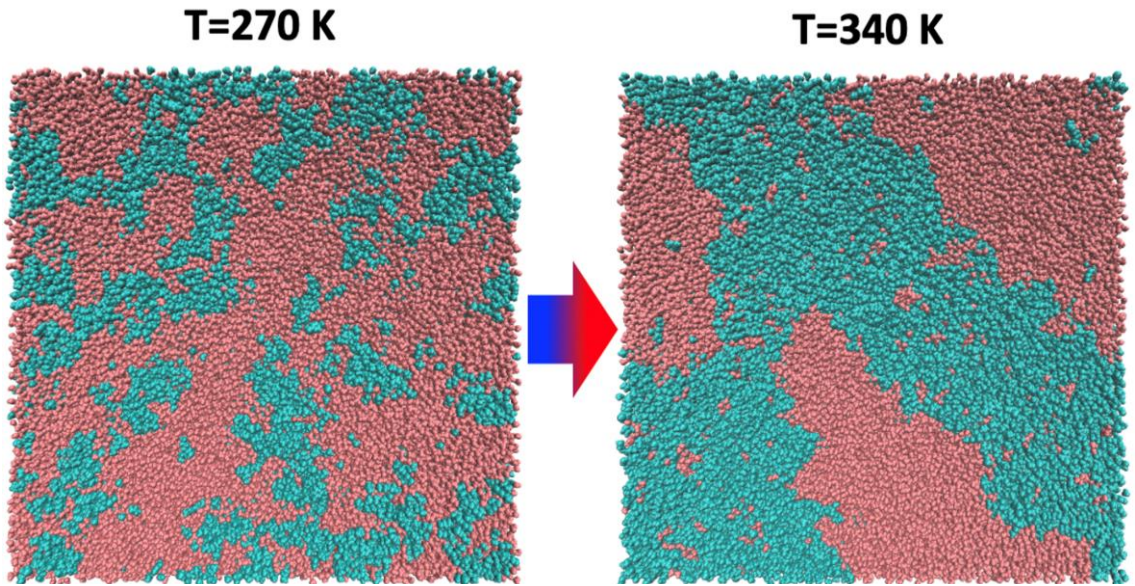
# Entropy-driven demixing of $[P_{4444}][DMBS]$ / Water solutions




- Demixing anticipated by nanostructuring of increasing length scale.
- Slow separation into a nearly pure water phase and a water-contaminated (~10%) IL phase
- Demixing driven by entropy release due to the breaking of water-anion hydrogen bonds (See next).

Forero-Martinez, Cortes-Huerto, Benedetto and Ballone, Molecules 27, 1647 (2022)

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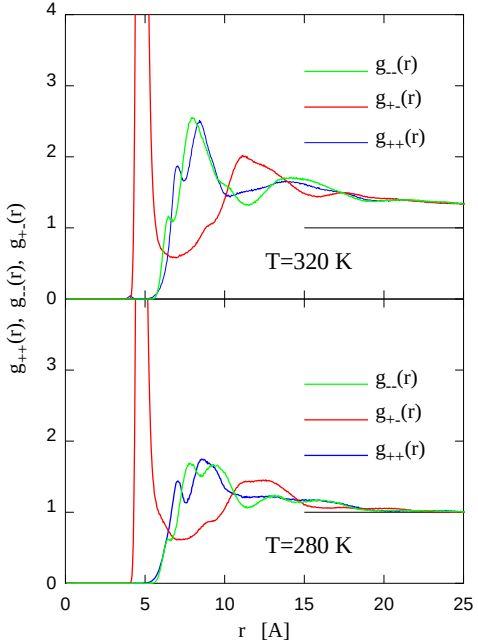
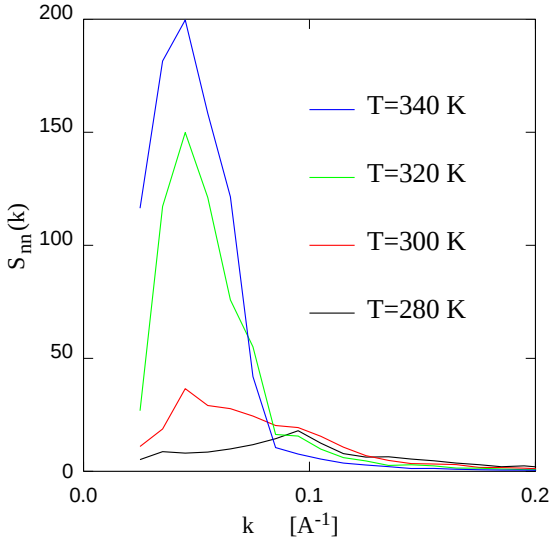
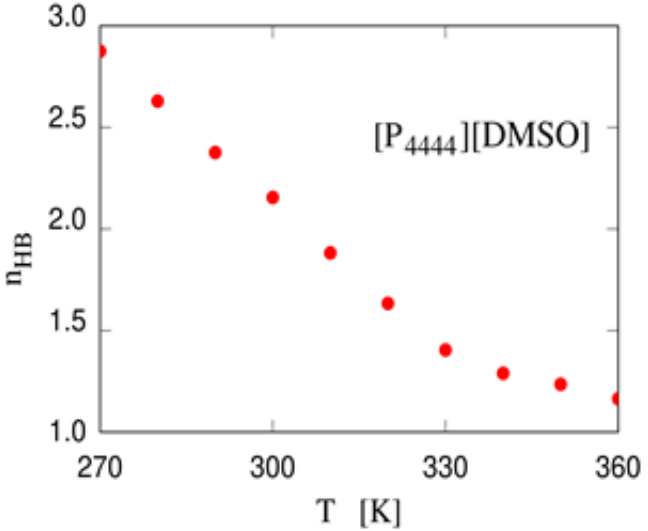
# Structural and binding properties of $[P_{4444}][DMBS]$




## Temperature dependence of the number of hydrogen bonds $n_{HB}$

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# Energy and environmental applications: Desalination by forward osmosis

- Water absorbed by a dry organic salt driven by osmotic pressure and giving a thermoresponsive solution.
- Water separation and draw-solvent regeneration by UCST or LCST demixing.
- Upon a change of ~40 $^{0}$C. This stage only requires low-grade heat.
- Further water purification using low-pressure backward osmosis.

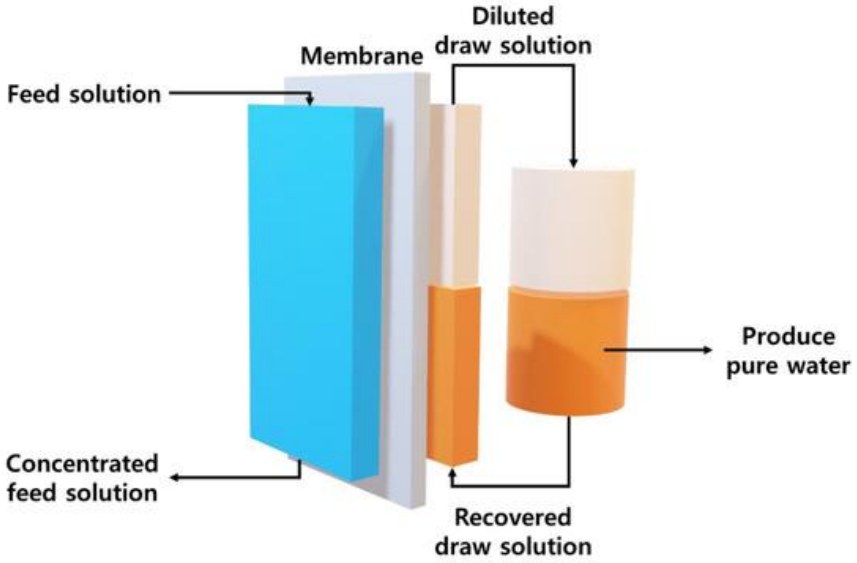


Figure adapted from Kim et al, Polymers 2019, 11(3), 571

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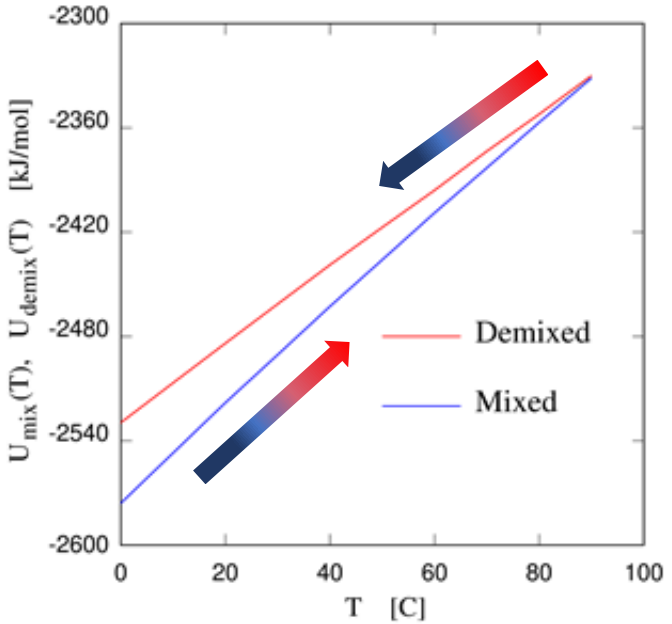
# Energy and environmental applications: From our simulations

## Permanent heat storage

- Heat storage in thermal fluids relies on phase-change materials.
- UCST and LCST are a special case of phase change.
- The mixing enthalpy at low T can be stored permanently by physically separating two phases.

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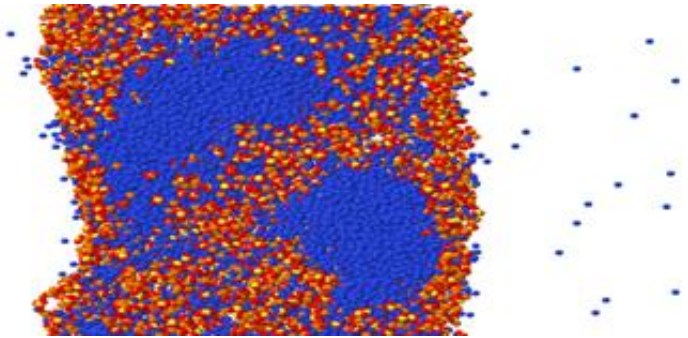
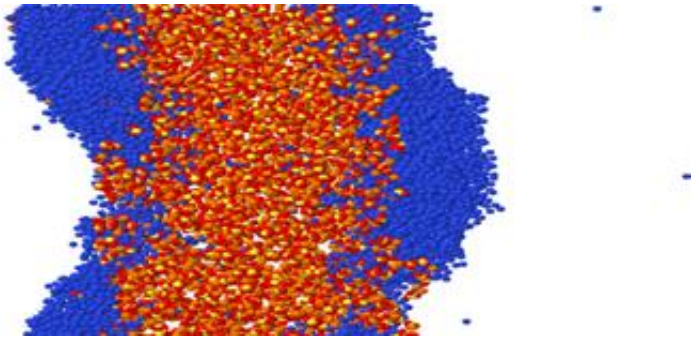
# Energy and environmental applications: From our simulations
## Water harvesting from the atmosphere

Absorbing water at low T



Releasing water at high T



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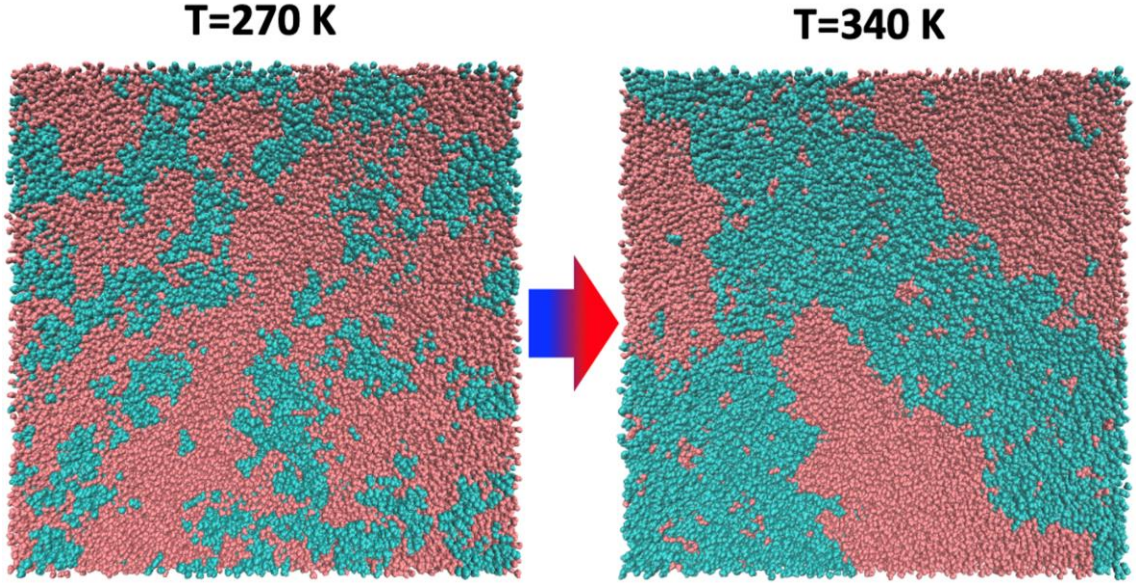
# Take-home message




- Goal: Understand the microscopic mechanism of the mixing/demixing transition.
- Goal: Characterisation of the transition aiming at energy applications.

$\mu$s molecular dynamics simulation of IL / water solutions at 50-50 wt% composition. Samples of 1 – 1.2 x $10^6$ atoms (Linear size of the simulation box ~22 nm).

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# THANK YOU

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