

A molecular dynamics study of ionic thermoresponsive fluids for desalination by forward osmosis

Nancy C. Forero-Martinez

*Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany and
Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudingerweg 9, 55128 Mainz, Germany*

Robinson Cortes-Huerta*

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Pietro Ballone

*School of Physics, University College, Dublin, Ireland and
Conway Institute for Biomolecular and Biomedical Research, University College, Dublin, Ireland*

Securing the water supply to a growing population with increasing water demands for agriculture and industry is a considerable challenge confronting society for the next few decades. Desalination of sea water or other brackish water resources is increasingly viewed as the primary approach to achieving this goal.

In the last few years, forward osmosis (FO) has emerged as an appealing approach to desalination, in which osmosis is used to extract water from a salty feed solution, absorbing it into an even more concentrated draw solution. This approach can only be advantageous if the draw solution may be easily and inexpensively separated into nearly pure water and nearly dry draw solute, suitable to restart the process.

In FO, this crucial step may be carried out using thermoresponsive systems, in which a solubility gap develops through a change of temperature. Demixing can take place either with decreasing T (UCST systems) or with increasing T (LCST systems), and the latter case is preferred for engineering reasons. Selected organic salts belonging to the room temperature ionic liquid (IL) family represent promising candidates for the role of draw solute, since, upon absorbing water, they give LCST thermoresponsive solutions. The temperature increase required for demixing is limited to $\sim 50^\circ$, allowing to achieve desalination using moderately concentrated solar power, or inexpensive low-grade heat recovered from industrial processes.

Thermodynamic evidence and limited theoretical exploration have identified criteria for rationalising and predicting the ability of any given organic salt to act as a draw solute, consisting in the moderate hydrophobicity of the compound, resulting from the near compensation of hydrophobic and hydrophilic groups in the structure of the salt molecule. A likely mechanism for demixing with increasing T is represented by the entropy gain in breaking the tight association between ions and solvent molecules, often attributed to hydrogen bonding between water and IL anions. However, a detailed understanding of the thermoresponsiveness of IL/water solutions based on microscopic evidence is still lacking.

To fill this gap and ease the development of draw solutions with improved energy efficiency and lower carbon footprint, we undertook a large scale MD investigation of IL/water thermoresponsive systems, considering ~ 10 different ILs and covering a wide T -range. Demixing is at most a weakly first-order transition, culminating in a critical point both at the UCST and LCST states. Fluctuations, therefore, are crucial, require large sizes and long times to be adequately described, and make it imperative to use large supercomputers.

Preliminary results show that simulation based on atomistic models can reproduce the demixing transition at conditions close to the experimental ones. Demixing, moreover, is anticipated by the marked nanostructuring of the solution already in the nominally homogeneous phase. The two phases forming through demixing consist of nearly pure water, and IL with non-negligible water content. The last stage of the project, now underway, consists of the quantitative characterisation of thermodynamic functions, and of the scaling analysis of nanostructuring in approaching the demixing point from the macroscopically homogeneous phase. Results available up to now highlight the important role of cations for the transition, beyond the role of anions and hydrogen bonds emphasised in previous studies.

A better understanding of all these features and properties might greatly ease the optimisation of the RTIL choice, opening the way to economically viable applications on the field, primarily targeting the conditions of less favoured, solar energy-rich countries.

* Electronic address: corteshu@mpip-mainz.mpg.de