Minicolloque n° 1 ☒ **Oral** ☐ **Poster**

Thermodynamics of Nanoconfined Aqueous Solutions

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Understanding the thermodynamic properties of Deep Eutectic Solvents (DESs) and their aqueous solutions is a matter of much current interest. The non-ideal character of DESs suggests the existence of molecular organizations at the nanometer scale [1], and raises questions about their influence on phase behavior [2] and molecular dynamics [3].

In the present talk, we demonstrate that an upper level of complexity emerges, when aqueous DES solutions are manipulated in nanoporous channels. Despite the very common use of solvents in confined media in various technologies, the specific implications of confinement for DESs remain to be studied fundamentally.

We elaborate on interfacial and finite size effects on the thermal phase behavior of prototypical aqueous polyol [4] and DES solutions. For sufficiently large pores (Rp = 4 nm), a consistent view of the phase behavior is achieved by a thermodynamic model accounting simultaneously for the cryoscopic (solutes) and the Gibbs−Thomson (confinement) effects. However, for smaller pores (Rp < 2 nm), it reveals a deviation of the apparent water activity from that of the bulk solution with the same composition, indicating the possible role of concentration heterogeneities in determining the onset of freezing in strongly nanoconfined solutions [5].

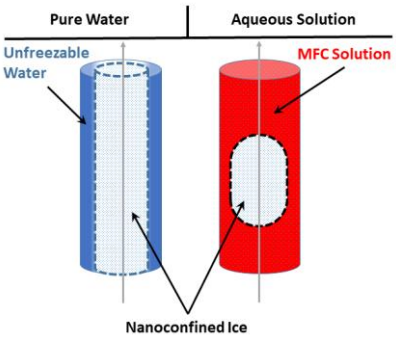

Figure : Sketch of the different physical states observed for the simple case of water (left) and for an aqueous solution (right) confined in a nanopore.

[1] 'Do Deep Eutectic Solvents Form Uniform Mixtures Beyond Molecular Microheterogeneities?' L. Percevault, A. Jani, T. Sohier, L. Noirez, L. Paquin, F. Gauffre, D. Morineau, . Phys. Chem. B, 124 (41), pp.9126-9135 (2020).

[2] 'Phase behavior of aqueous solutions of ethaline deep eutectic solvent' A. Jani, T. Sohier, D. Morineau, J. Mol. Liq., 304, pp.112701 (2020).

[3] 'On the Coupling between Ionic Conduction and Dipolar Relaxation in Deep Eutectic Solvents: Influence of Hydration and Glassy Dynamics' A. Jani, B. Malfait, D. Morineau, J. Chem. Phys., 154 (16), pp.164508 (2021).

[4] 'Extension and Limits of Cryoscopy for Nanoconfined Solutions' B. Malfait, A. Pouessel, A. Jani, D. Morineau, J. Phys. Chem. Lett., 11 (14), pp.5763-5769 (2020).

[5] 'La loi de la cryoscopie revisitée par les nanosciences', D. Morineau, Communiqué de l'INP du CNRS, Oct. 2020. https://inp.cnrs.fr/fr/cnrsinfo/la-loi-de-la-cryoscopie-revisitee-par-les-nanosciences