

Exploring asymmetry induced entropy in tetraalkylammonium–urea DES systems: what can be learned from inelastic neutron scattering?

Catarina F. Araújo¹, Paulo Ribeiro-Claro¹, Pedro D. Vaz², Svemir Rudić³, Rafael Serrano¹, Liliana P. Silva¹, J.A. P. Coutinho¹, Mariela M. Nolasco¹

¹ Department of Chemistry, Universidade de Aveiro CICECO, Aveiro, Portugal

² Champalimaud Centre for the Unknown, Lung Unit, Champalimaud Foundation, Av. Brasília, Lisboa, Portugal

³ ISIS Neutron & Muon Source, STFC Rutherford Appleton Laboratory, Didcot, UK

The behaviour of deep eutectic solvents (DES) is a hot topic in contemporary chemistry. The term “deep eutectic” stems from the peculiar phenomenon that the melting point of a DES is significantly lower than that of an ideal mixture of its components. The most often cited rationalization for this phenomenon is that newly formed intermolecular interactions amongst the DES components lead to negative deviations from ideality, a result of entropic and enthalpic effects which are often difficult to tell apart. In general, most studies on DES focus on enthalpic factors while the influence of entropic changes remains unclear, with only a handful of recent studies exploring the role of entropy in deep eutectic formation.

In this work¹, a combination of inelastic neutron scattering (INS) spectroscopy and periodic density functional theory calculations is used to investigate the impact of entropic factors on the behaviour of deep eutectic solvents. Deviations from ideality in the mixtures of tetraalkylammonium salts with urea are readily determined through a simplified thermodynamic approach. This study reports and discusses the relationship between the cation's asymmetry, the INS spectra of the eutectic mixture and its deviation from ideality. Contrary to the majority of systems studied so far, the deep eutectic system comprised of $[N_{2,2,2,1}]Cl$ and urea appears to owe its deviation from ideality to entropic rather than enthalpic factors.

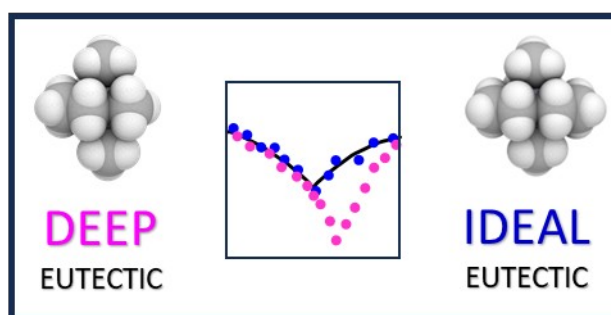


Figure 1. In the center, schematic representation of the solid-liquid equilibrium diagrams of eutectic mixtures comprised of urea and tetraalkylammonium salts with a symmetric (blue dots, $[N_{2,2,2,2}]Cl$) or asymmetric (pink dots, $[N_{2,2,2,1}]Cl$) cation. Simplified molecular structures of the symmetric and asymmetric cations are depicted on the right and left sides, respectively, along with the description of the behaviour of their eutectic mixtures with urea.

References

[1] C.F. Araujo, P. Ribeiro-Claro, P.D. Vaz, S. Rudić, R. Serrano, L.P. Silva, J.A.P. Coutinho, M.M. Nolasco, *Physical Chemistry Chemical Physics* **26** (2024) 5969-5977.