

To gel or not to gel? A curious case of molecular self-assembly in deep eutectic solvents

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Deep Eutectic Solvents (DES) are binary mixtures of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), with a eutectic point (melting point) significantly lower (by around 100°C) than that of either components [1]. One of the main features of these hydrogen-bond rich non-aqueous media is the possibility to support amphiphile self-assembly [2-4]. However, different aspects of molecular self-assembly in DES are yet to be fully understood [2-4].

We have investigated the (surprising) role of the counter-ions in the self-assembly of a series of alkyltrimethylammonium surfactants – with either bromide (Br^-) or chloride (Cl^-) as counterions – in the DES choline chloride:glycerol (1:2) and compared the self-assembled nanostructures of the same surfactants in glycerol. We observed the formation of a gel of the chloride-counterion surfactants in DES, but *not* in glycerol. Vice versa, the bromide-counterion surfactants showed the tendency to form gels in glycerol, but *not* in DES. This peculiar observation was corroborated by the analysis of the birefringent textures observed by polarised light microscopy (PLM) and the viscoelastic response measured by rheology. Most importantly, small-angle neutron scattering (SANS) experiments unveiled the nanoscale organisation and its correlation with the bulk behaviour of the aggregated structures, showing clear differences in the size and shape of the surfactant aggregates in glycerol and in the choline chloride:glycerol DES. Collectively, these results demonstrate an interconnection between the solvent structure, the counter-ion identity, and surfactant self-assembly, opening new perspectives in tuning the properties of self-assembled materials within DES.

Keywords:

deep eutectic solvents, surfactant self-assembly, counterion effects, gelation, small-angle neutron scattering

References:

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