Experimental report

08/08/2022

Proposal: 9-10-1718 **Council:** 4/2021

Title: Anionic surfactant self-assembly in halide free deep eutectic solvents

Research area: Chemistry

This proposal is a resubmission of 9-10-1700

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Samples: betaine:glycerol with sodium d-25-dodecylsulfate
betaine:glycerol with sodium dodecylsulfate
betaine:glycerol with sodium lauryl sarcosinate

Instrument	Requested days	Allocated days	From	To
D11	2	2	17/09/2021	19/09/2021
D22	2	0		
D33	2	0		

Abstract:

Deep Eutectic Solvents (DES) are mixtures of organic salts and hydrogen bond donors, that form strongly hydrogen-bonded room temperature liquids. DES share many features with ionic liquids (ie. tunable physicochemical properties) which make them viable green solvents that are less toxic than typical ILs. We have studied amphiphile self-assembly in DES with the aim of developing templated deep eutectic-solvothermal syntheses for catalytic porous metal oxide structures, and have studied self-assembly in a range of choline chloride based DES. The halide anion however is known to poison many catalytic particles, so here we wish to probe surfactant self-assembly in a halide free DES, betaine:glycerol. We have previously studied a glycerol:citric acid solvent which supports micellization for cationic and nonionic surfactants, but not anionics. Betaine:glycerol in contrast solubilised anionic surfactants but not the others. We hypothesis that headgroup interactions with solvent components alter the solubility and self-assembly in these solvents and propose to use contrast variation SANS to better understand the structures formed in these solutions.

Objectives

Deep Eutectic Solvents (DES) are mixtures of organic salts and hydrogen bond donors, that form strongly hydrogen-bonded room temperature liquids. DES share many features with ionic liquids (ie. tunable physicochemical properties) which make them viable green solvents that are less toxic than typical ILs. We have studied amphiphile self-assembly in DES with the aim of developing templated deep eutectic-solvothermal syntheses for catalytic porous metal oxide structures and have previously studied self-assembly in a range of choline chloride based DES. The halide anion however is known to poison many catalytic particles, so here we studied surfactant self-assembly in a halide free DES, composed of betaine (Bet) and glycerol (Gly) or ethylene glycol (EG). Different anionic surfactants have been found to be soluble in this DES and preliminary SAXS data demonstrates the formation of micelles. We hypothesis that headgroup interactions with solvent components alter the micelle shape and propose to use contrast variation SANS to better understand the structures formed in these solutions.

Experimental

Scattering data was collected on beamline D11 for four different surfactants in Betaine (Bet):Glycerol (Gly) DES at molar ratios of 1:2 and 1:3, and Betaine:Ethylene Glycol (EG) at 1:3: Anionic surfactants sodium dodecyl sulfate (SDS) and sodium lauryl succinate (SLS), using quartz cells as sample holders in all cases. The neat DES and sample solutions were measured at 25 °C. Four concentrations were measured for each type of surfactant and different contrasts for DES component and surfactants were used, where available. Components used were h & d8-Glycerol and h & d11-Betaine, h & d- SDS and h-SLS to form the following sample mixtures:

- 1 h-Bet : 2 h-Gly + d-SDS, 1 h-Bet : 2 d-Gly + d-SDS, 1 d-Bet : 2 d-Gly + h-SDS
- 1 h-Bet : 2 d-Gly + h-SDS, 1 d-Bet : 2 d-Gly + h-SDS
- 1 h-Bet : 3 h-Gly + d-SDS, 1 h-Bet : 3 d-Gly + d-SDS, 1 d-Bet : 3 d-Gly + h-SDS, 1 h-Bet : 3 d-Gly + h-SDS
- 1 h-Bet : 3 d-Gly + h-SLS, 1 d-Bet : 3 d-Gly + h-SLS
- 1 h-Bet : 3 h-EG + d-SDS, 1 d-Bet : 3 d-EG + h-SDS
- 1 h-Bet : 3 d-EG + h-SLS, 1 d-Bet : 3 d-EG + h-SLS

Overall samples 56 plus backgrounds were measured, using a wavelength of 6Å at detector distances of 1.7m, 8m and 28m, with collection times between 30s and 30minutes depending on the degree of scattering at the specific distance for each sample. Longer measurements at very low q were only performed for selective samples to check for interesting behaviour in this range.

The data was processed using the Grasp software, processing and fitting using IgorPro and SasView is currently in progress.

Results

All of the above samples showed scattering characteristic of micelles. Example data is shown below in Figures 1 and 2.

For different surfactants at similar concentrations in the different DES (Figure 1) characteristic scattering for similar micelle shapes and sizes can be seen, as expected for micelles assembled from surfactants with similar tail lengths. Similar to the preliminary SAXS data, intermicellar interactions can be seen as

a peak in the data, indicating a structure factor from micellar interactions. Some differences in peak shape are directly visible.

An example of a concentration series is shown in Figure 2. It also shows the expected behaviour of similar micelle shapes and sizes, with a clearer structure factor and stronger intermicellar interactions at higher concentrations.

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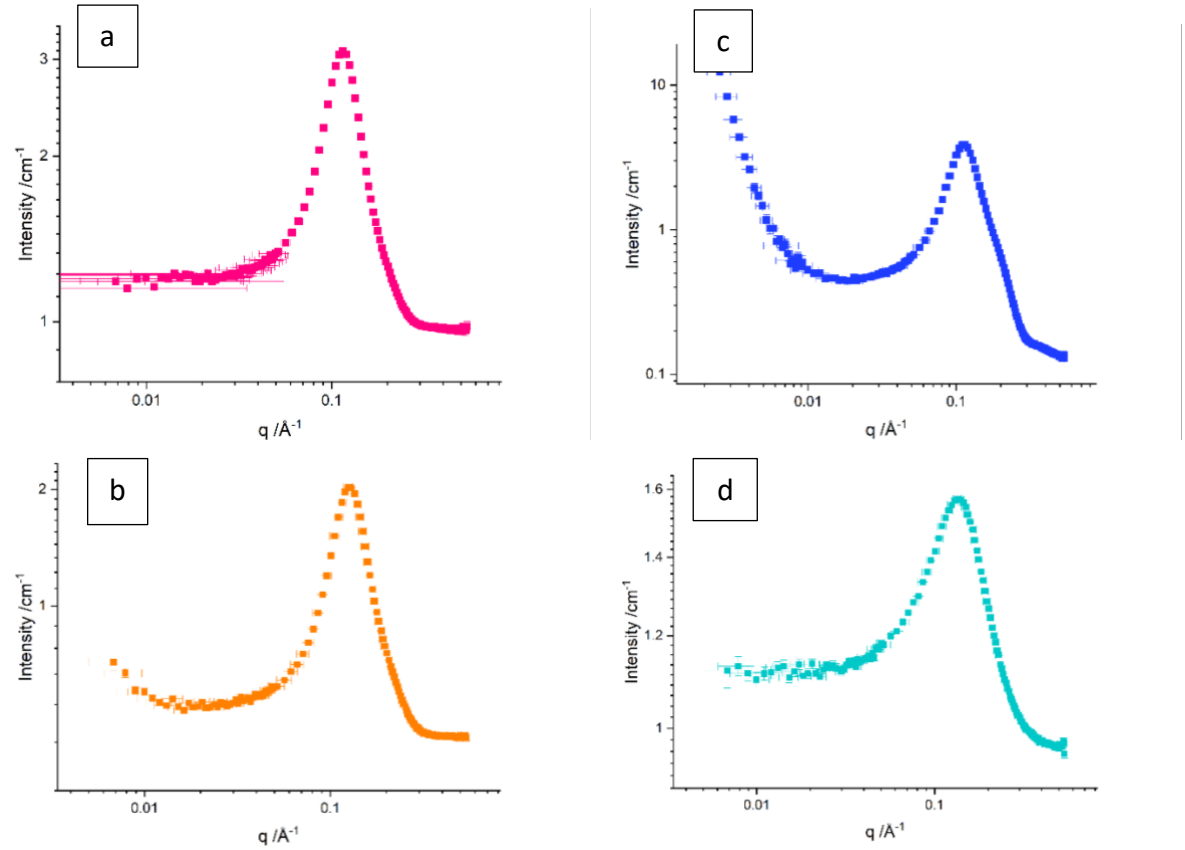
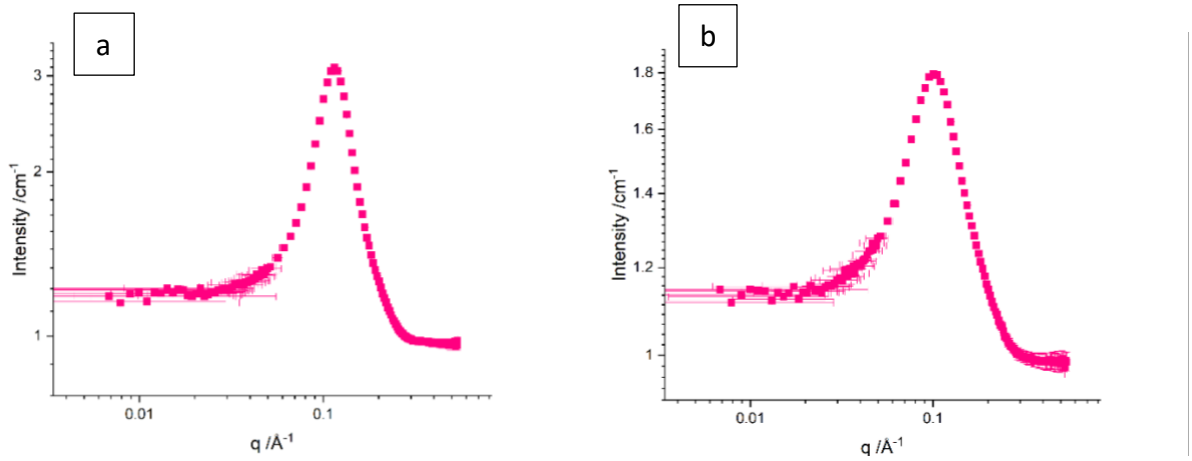


Figure 1: Example data for 10wt% d-SDS in 1:3 h-Bet:h-Gly (a), h-SLS in 1:3 h-Bet:d-Gly (b), h-SDS in 1:2 d-Bet:d-Gly (c), d-SDS in 1:3 h-Bet:h-EG (d).



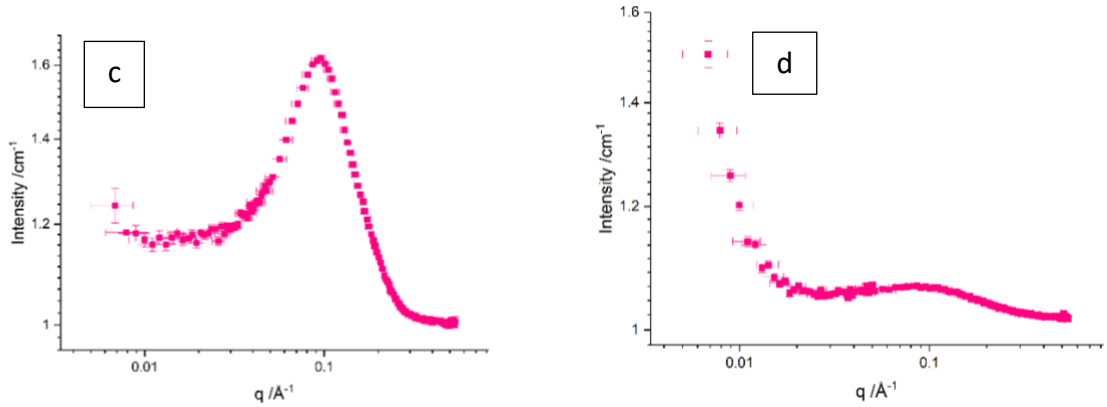


Figure 2: Example data for 10wt% (a), 5wt% (b), 4wt% (c) and 2wt% (d) d-SDS in 1:3 h-Bet:h-Gly.

Concluding remarks

The results agree well with the preliminary SAXS data and expectations formed before the experiment and will help to elucidate the behaviour of anionic surfactants in betaine-based halogen free DES systems. We are currently working on fitting the data using the appropriate models using SASView. These experiments will contribute to the PhD thesis of Elly Bathke, and are expected to be published within the next couple of months. Our biggest thanks goes to Olga Matsarskaia, who helped with running the experiment and data processing, as well as lending excellent support during and after the experiment.