Experimental report

29/09/2021

Proposal: 9-10-1674 **Council:** 4/2020

Title: Micelles in Chloride-Free Deep Eutectic Solvents.

Research area: Chemistry

This proposal is a new proposal

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Samples: 2 d8-glycerol:citric acid
C12EO4 (C12H25(OC2H2)OH)
C12TAN (C12H25N(CH3)3NO3)
C16TAN (C16H33N(CH3)3NO3)
2 glycerol:citric acid
3 d8-glycerol:d4-citric acid
C12EO23 (C12H25(OC2H4)23OH)
d34-C12TAN (C12D25N(CD3)3NO3)
d42-C16TAN (C16D33N(CD3)3NO3)

Instrument	Requested days	Allocated days	From	To
D11	2	2	11/03/2021	13/03/2021
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, composed of glycerol and citric acid. Nonionic and cationic surfactants have been found to be soluble in this DES and preliminary SAXS data demonstrates micellization but also micelle structures which differ from those found for these surfactants in water and in glycerol:choline chloride DES. 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.

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 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, composed of glycerol and citric acid. Nonionic and cationic surfactants have been found to be soluble in this DES and preliminary SAXS data demonstrates micellization but also micelle structures which differ from those found for these surfactants in water and in glycerol:choline chloride DES. 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 the 1:2 citric acid (CA):Glycerol DES: Cationic surfactants $C_{12}TANO_3$ and $C_{16}TANO_3$, and the non ionic surfactants $C_{12}EO_6$ and $C_{12}EO_{23}$, using 1mm thick rectangular quartz cells as sample holders in all cases. The neat DES and sample solutions were measured at 25°C, except for the $C_{16}TANO_3$ containing samples, which were measured at 50°C due to lower surfactant solubility. Four concentrations were measured for each type of surfactant and different contrasts for DES components and surfactants were used, where available. Components used were h & d8-Glycerol and h & d4-CA, h & d25- $C_{12}TANO_3$, h & d33-$C_{16}TANO_3$, h-$C_{12}EO_6$ and h-$C_{12}EO_{23}$ to form the sample mixtures:

- h-CA:h-Gly + d-$C_{12}TANO_3$, d-CA:h-Gly + h-$C_{12}TANO_3$, d-CA:d-Gly + h-$C_{12}TANO_3$, h-CA:d-Gly + h-$C_{12}TANO_3$
- h-CA:h-Gly + d-$C_{16}TANO_3$, d-CA:h-Gly + h-$C_{16}TANO_3$, d-CA:d-Gly + h-$C_{16}TANO_3$, h-CA:d-Gly + h-$C_{16}TANO_3$
- d-CA:d-Gly + h-$C_{12}EO_6$, d-CA:h-Gly + h-$C_{12}EO_6$, h-CA:d-Gly + h-$C_{12}EO_6$
- d-CA:d-Gly + h-$C_{12}EO_{23}$, d-CA:h-Gly + h-$C_{12}EO_{23}$, h-CA:d-Gly + h-$C_{12}EO_{23}$.

Overall samples 64 plus backgrounds were measured, using a wavelength of 6Å at detector distances of 1.7m, 5.5m, 16.5m and 30m, with collection times between 30s and 30 minutes depending on the degree of scattering at the specific distance for each sample. Longer measurements at very low q were only performed for samples that showed interesting behaviour in this range, such as for $C_{12}EO_6$ samples.

The data was reduced to 1D patterns using the Grasp software, and processing and fitting using IgorPro and SasView is currently in progress.

Results

All samples showed scattering characteristic of micelles. Example data is shown below in Figures 1 (different surfactants) and 2 (different concentrations).

Looking at the different surfactants at similar concentrations in Figure 1 the data shows the expected characteristic scattering for similar micelle shapes and sizes, as expected for micelles with similar tail lengths, while $C_{12}EO_6$ (Figure 1 c) shows the formation of more elongated structures, as is often seen for this type of non ionic surfactants in aqueous systems.

The concentration series in Figure 2 also shows the expected behaviour of similar micelle shapes and sizes, with a clearer structure factor and stronger intermicellar interactions at higher concentration. Using the different solvent contrasts we hope to be able to discriminate between headgroup solvation in the different systems, and to determine more about the interaction of specific DES components with the different headgroups in these systems. This will help explain, for example why nonionic surfactants are soluble in these DES while remaining insoluble in others.

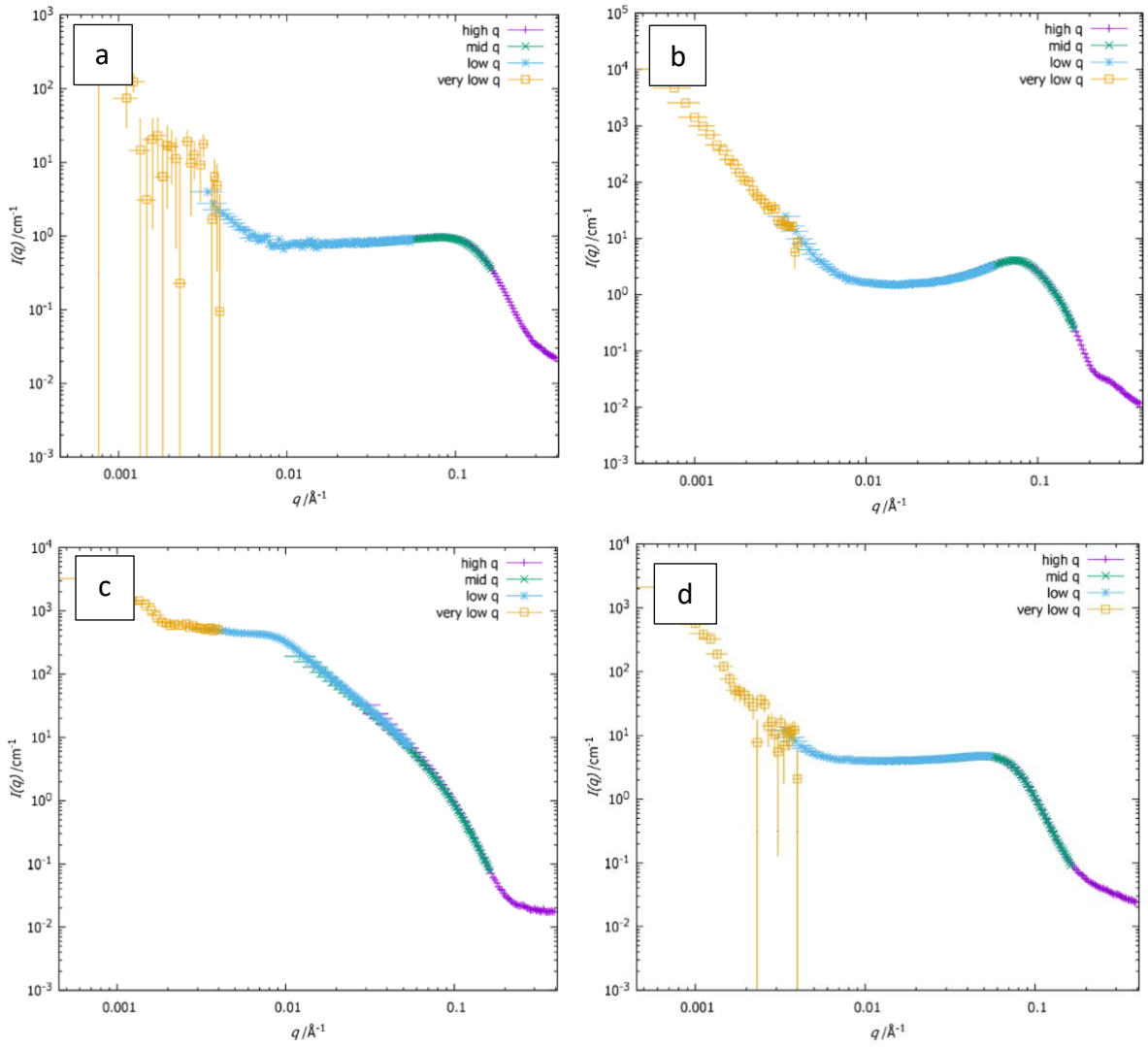

Figure 1: SANS data for 5wt% h-$C_{12}TANO_3$ (a), h-$C_{16}TANO_3$ (b), h-$C_{12}EO_6$ (c) and h-$C_{12}EO_{23}$ (d) in 1:2 d-CA:h-Gly

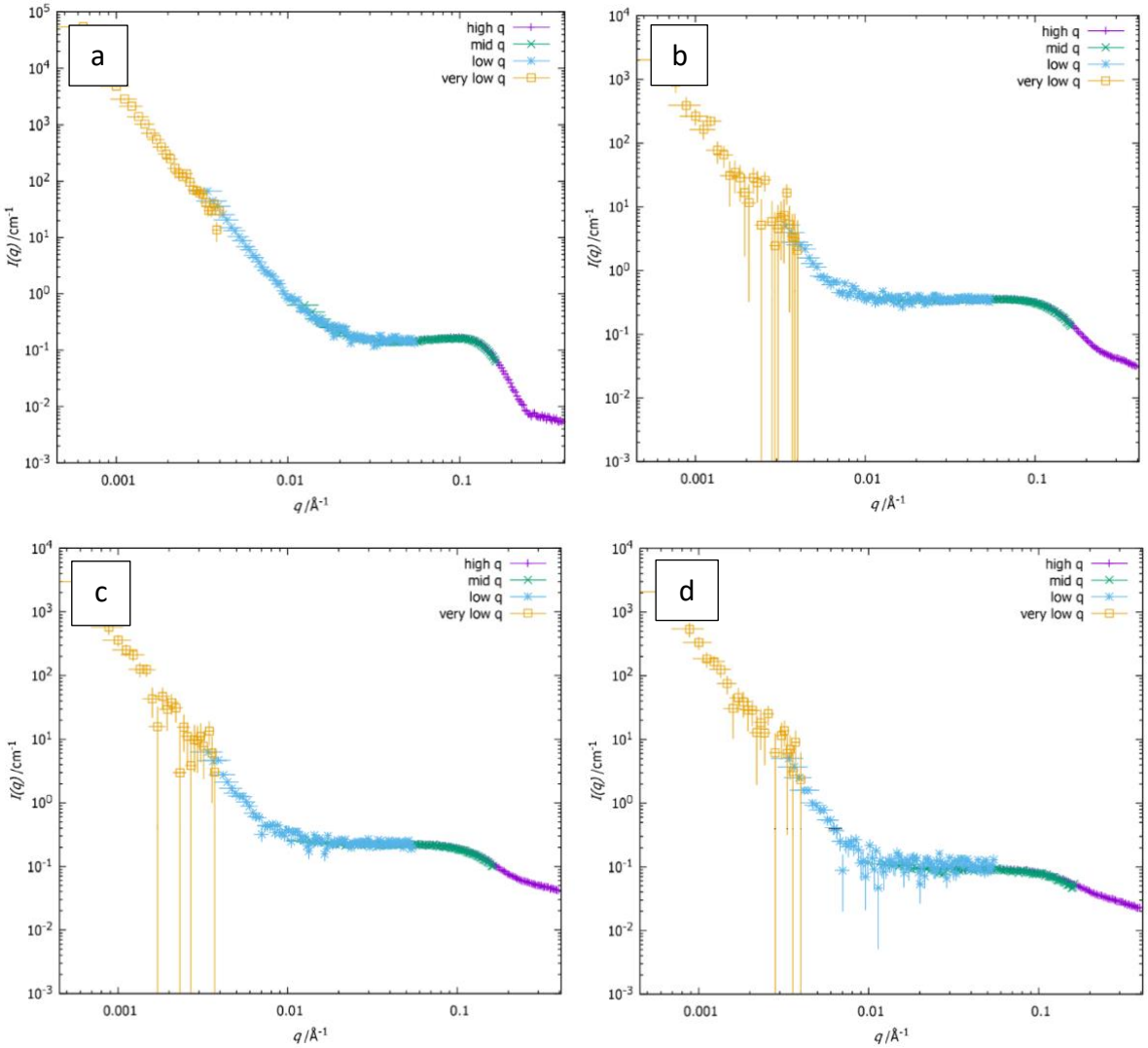

Figure 2: SANS data for 10wt% (a), 5wt% (b), 4wt% (c) and 3wt% (d) d-$C_{12}TANO_3$ in 1:2 d-CA:h-Gly.

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 halogen free systems, as well as the more rarely observed formation of nonionic surfactant micelles in DES. 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. Due to COVID-19 related travel restrictions we were unable to run these experiments ourselves, so had to send our samples to ILL and our biggest thanks goes to Sylvain Prevost, who ran the experiment and helped with data processing, as well as lending excellent support during and after the experiment.