# Experimental report

17/09/2021

**Proposal:** **9-10-1699** **Council:** 10/2020

**Title:** Nanostructure in amphiphilic sulfobetaine based deep eutectic solvent

**Research area:** Chemistry

**This proposal is a new proposal**

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**Samples:** h-CSA:d-SB3-12 + D2O
h-CSA:d-SB3-12 + h-dodecane
h-CSA:h-SB3-12
h-CSA:h-SB3-12 + D2O
h-CSA:h-SB3-12 + d-dodecane
h-CSA:d-SB3-12
h-CSA:d-SB3-12 + H2O
h-CSA:d-SB3-12 + d-dodecane

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D11 | 2 | 0 | | |
| D33 | 2 | 0 | | |
| D22 | 2 | 1 | 22/06/2021 | 23/06/2021 |

## Abstract:

Deep eutectic solvents (DES) are mixtures of hydrogen bond donors and acceptors that form strongly hydrogen-bonded room temperature liquids. DES share many features with ionic liquids (i.e. tunable physicochemical properties), making them viable green solvents. Recently a series of DES based on amphiphilic sulfobetaines and camphor sulfonic acid have been reported, in which solvent structuring can be expected due to the nature of the DES components offering a unique potential for templating applications. We have initial indication that these solvents have internal nanoscale structure, and preferentially solubilise polar and non-polar additives. We wish to understand the interplay between the DES components by determining the nanostructure of DES, and how water (polar) and dodecane (non-polar) interact with hydrophilic and hydrophobic moieties found in the DES components by conducting SANS experiments on the DES along with additives and using contrast variation to highlight the relative position of solvent components vs additives. This will enable future experiments exploiting the solvent structuring for templated material synthesis to modify particle size, shape or porosity.

# Nanostructure in Amphiphilic Sulfobetaine Based Deep Eutectic Solvent – Experimental Report

## Introduction

Deep eutectic solvents (DES) are mixtures of hydrogen bond donors and acceptors that form strongly hydrogen-bonded room temperature liquids. DES have tunable physicochemical properties making them viable green solvents. Recently a series of DES based on amphiphilic sulfobetaines and camphor sulfonic acid have been reported, in which solvent structuring can be expected due to the nature of the DES components offering a unique potential for templating applications. Here we have explored the nanostructure of the DES, and how water (polar) and dodecane (non-polar) interact with hydrophilic and hydrophobic moieties found in the DES components by conducting SANS experiments on the DES without and with additives and using contrast variation to highlight the relative position of solvent components vs additives.

## Experimental Details

We prepared DES comprising (1S)-(+)-10-camphor-sulfonic acid (CSA) and N-alkyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (SB3-Cn) for varying alkyl chain lengths: SB3-12, SB3-14, SB3-16 and SB3-18; at molar ratio of 1.5:1 CSA/SB3-Cn. SANS was measured from the DES and their mixtures without and with water/dodecane at different contrasts of SB3-Cn (h- & d-SB3-Cn) and H2O/D2O or h/d-dodecane for a q range covering 0.0045 – 0.66 Å$^{-1}$. The sample contrasts and additive concentration measured are detailed below in **Table 1**.

***Table 1:*** *Sample contrast and additive concentration for the SANS measurements*

| | No Additive | +H2O | +D2O | +h-Dodecane | +d-Dodecane |
|---|---|---|---|---|---|
| **SB3-12** | h-CSA:d-SB3-12 (HD),<br>h-CSA:h-SB3-12 (HH) | HD DES: 10%<br>HH DES: 10%, 20% | HD DES: 10%<br>HH DES: 5%, 10%, 20% | HD DES: 10%<br>HH DES: 10%, 20% | HD DES: 10%<br>HH DES: 5%, 10%, 20% |
| **SB3-14** | h-CSA:d-SB3-14 (HD),<br>h-CSA:h-SB3-14 (HH) | | HH DES: 5%, 10%, 20% | | HH DES: 5%, 10%, 20% |
| **SB3-16** | h-CSA:h-SB3-16 (HH) | | HH DES: 5%, 10%, 20% | | HH DES: 5%, 10%, 20% |
| **SB3-18** | h-CSA:h-SB3-18 (HH) | | HH DES: 5%, 10%, 20% | | HH DES: 5%, 10%, 20% |

The concentrations are w/w percentage of the additives in the DES.

## Data and Preliminary Analysis

The SANS data from the CSA:SB3-Cn (molar ratio 1.5:1) for different alkyl chain lengths, SB3-12, SB3-14, SB3-16 and SB3-18, at two contrasts, h-CSA:h-SB3-Cn and h-CSA:d-SB3-Cn, are shown in **Figure 1**. The SANS patterns is characterized by a broad scattering peak and preliminary fitting was done using a Broad Peak model and is shown by the dashed lines in the figure. The model fits the data well and has peaks at 0.258 Å$^{-1}$ for h-CSA:h-SB3-12, 0.235 Å$^{-1}$ for h-CSA:h-SB3-14, 0.215 Å$^{-1}$ for h-CSA:h-SB3-16 and 0.201 Å$^{-1}$ for h-CSA:h-SB3-18 corresponding to d-spacing of 24.3 Å, 26.7 Å, 29.3 Å and 31.2 Å, respectively. The peak position for h-CSA:d-SB3-Cn contrast are consistent with the ones for h-CSA:h-SB3-Cn contrasts; 0.252 Å$^{-1}$ for h-CSA:d-SB3-12 (d-spacing = 24.9 Å) and 0.232 Å$^{-1}$ for h-CSA:d-SB3-14 (d-spacing = 27.1 Å). These structures can be attributed to the self-assembly of amphiphilic SB3-Cn to optimise interaction with the camphor sulfonic acid. The size of these scattering structures increases as the alkyl chain length of the SB3-Cn increases; evident from the shifting of the peak to lower *q* in **Figure 1** (increasing d-spacing) as chain length increases from SB3-12 to SB3-18.

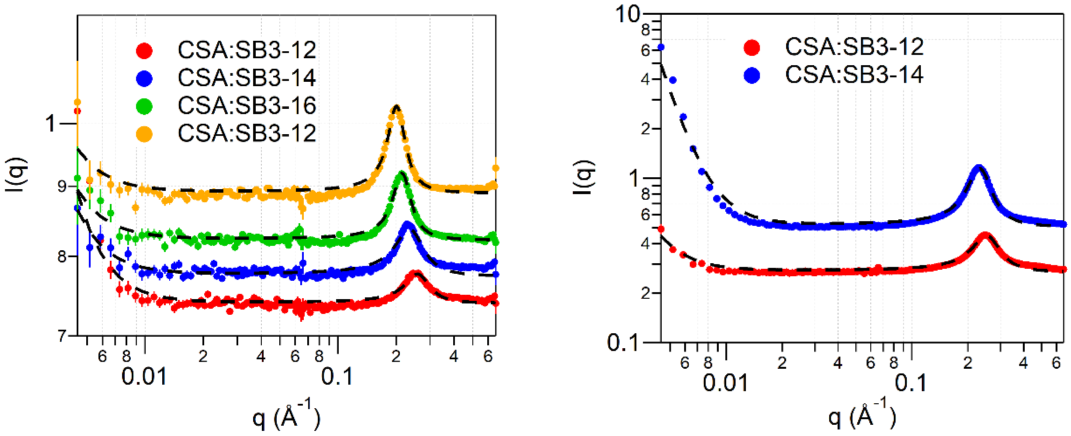

***Figure 1:*** *SANS data from CSA:SB3-Cn DES (molar ratio 1.5:1) for varying alkyl chain lengths, SB3-12, SB3-14, SB3-16 and SB3-18, at two contrasts, h-CSA:h-SB3-Cn (left panel) and h-CSA:d-SB3-Cn (right panel). The dashed lines show the fit to the data using a Broad Peak model. The various traces are offset along the y-axis for clarity.*

**Figure 2** shows SANS data for CSA:SB3-12 with the addition of water and dodecane at two contrasts of the DES (h-CSA:d-SB3-12; HD & h-CSA:h-SB3-12; HH) and additives (H2O/D2O or h-dodecane/d-dodecane). As with the neat DES, the SANS data for DES with water was fitted to the Broad Peak model and is shown by dashed lines in the figure. Upon the addition of water, the peak shifts to lower $q$, 0.240 Å$^{-1}$ corresponding to d-spacing of 26.2 Å. In the case of dodecane, along with the shift in the peak position some micellar scattering along with the shifts in peak position is observed. Detailed fitting of this is ongoing, but preliminary fitting of two contrast (HD DES + d-dodecane & HH DES + h-dodecane) to the Broad Peak model shows shifting of the scattering peaks to 0.204 Å$^{-1}$ (d-spacing = 30.7 Å). These results indicate that water and dodecane interact with the hydrophilic and hydrophobic moieties in the DES structure, primarily SB3-12, respectively, thereby solvating and swelling the entire structure causing the peak shifts to lower-$q$. The extent of the shift of the peak position, thereby the swelling, depends on concentration of the additive as observed from the concentration series of water/dodecane in the DES. Similar observations can be made for CSA:SB3-14, CSA:SB3-16 and CSA:SB3-18.

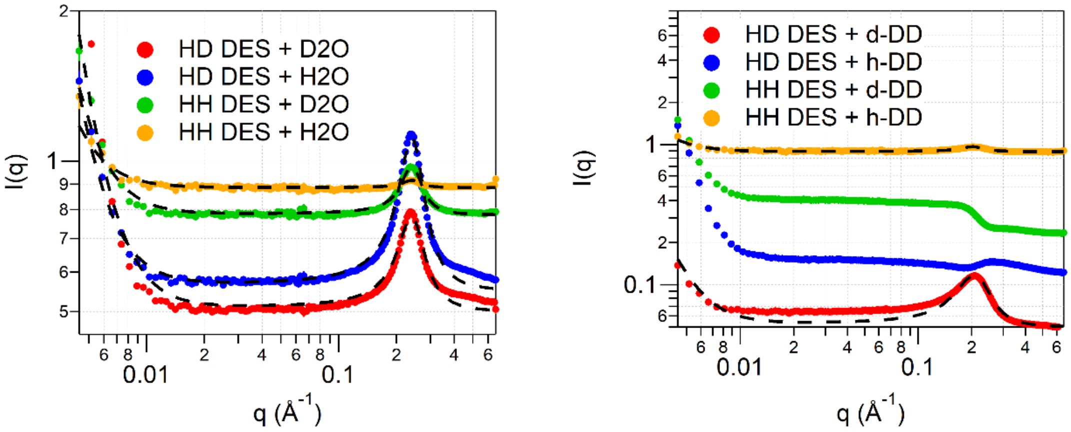

***Figure 2:*** *SANS data from CSA:SB3-12 DES (molar ratio 1.5:1) with addition of water (left panel) and dodecane (right panel) at two contrasts of DES and additives. The dashed lines show the fit to the data using a Broad Peak model. The various traces are offset along the y-axis for clarity.*

A more detailed analysis, especially for various contrasts of DES with addition of dodecane is ongoing to get further information about specific interaction of the additives with the hydrophilic and hydrophobic moieties in the DES using bicontinuous and/or micelle phase models.