

Experimental report

20/09/2021

Proposal: 9-10-1684

Council: 10/2020

Title: Surfactant Monolayers on Ternary Deep Eutectic Solvents

Research area: Chemistry

This proposal is a new proposal

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Samples: h-ChCl:d-Gly + dC12TAB
d-ChCl:h-Gly + dC12TAB
h-ChCl:h-Gly + d-SDS
h-ChCl:d-Gly + d-SDS
d-ChCl:h-Gly + d-SDS
h-ChCl:h-urea:h-Gly + d-C12TAB
h-ChCl:h-urea:h-Gly + d-SDS
h-ChCl:h-urea:d-Gly + d-C12TAB
h-ChCl:h-urea:d-Gly + d-SDS
h-ChCl:d-urea:h-Gly + d-C12TAB
d-ChCl:h-urea:h-Gly + d-C12TAB
h-ChCl:h-Gly + dC12TAB
h-ChCl:d-urea:h-Gly + d-SDS
d-ChCl:h-urea:h-Gly + d-SDS

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	04/06/2021	07/06/2021

Abstract:

Deep eutectic solvents (DES) are mixtures of organic salts and hydrogen bond donors (HBD) that form strongly hydrogen-bonded room temperature liquids. DES comprising urea have been used for solvothermal synthesis of metal oxide nanoparticles, which opens the field of templating nanostructured materials using surfactant self-assembly in DES. Cationic and anionic surfactants show varying solubility in different choline chloride (ChCl) based DES depending on the HBD: SDS micellises in both ChCl:glycerol and ChCl:urea DES whereas CnTABs micellise in ChCl:glycerol but not in ChCl:urea. In order to facilitate both micellisation and solvothermal synthesis a ternary DES based on ChCl:urea:glycerol was developed which shows ellipsoidal micelles for SDS and CnTABs. We wish to probe molecular interaction of SDS and CTAB with the ChCl:urea:glycerol DES components using neutron reflectivity to understand the micelle stabilisation mechanisms. This will have implications in the preparation of nanostructured materials in DES, by providing information about the selective capping of surfactant micelles by DES components, therefore affecting the self-assembly process.

Surfactants at DES/air interface – Experimental Report

Introduction

Deep eutectic solvents (DES) are mixtures of organic salts and hydrogen bond donors (HBD) that form strongly hydrogen-bonded room temperature liquids. DES comprising urea have been used for solvothermal synthesis of metal oxide nanoparticles, which opens the field of templating nanostructured materials using surfactant self-assembly in DES. Cationic and anionic surfactants show varying solubility in different choline chloride (ChCl) based DES depending on the HBD: SDS micellises in both ChCl:Glycerol and ChCl:Urea DES whereas CnTABs micellise in ChCl:Glycerol but not in ChCl:Urea. To facilitate both micellisation and solvothermal synthesis a ternary DES based on ChCl:Urea:Glycerol at varying ratio of the HBDs (1ChCl:1.5Urea:0.5Glycerol, 1ChCl:1Urea:1Glycerol & 1ChCl:0.5Urea:1.5Glycerol) was developed which shows ellipsoidal micelles for SDS and CnTABs. Here we have used specular neutron reflectivity and contrast variation to probe molecular interaction of SDS and C12TAB with the ternary ChCl:Urea:Glycerol DES components at two of the extreme molar ratios of the HBD (1ChCl:1.5Urea:0.5Glycerol & 1ChCl:0.5Urea:1.5Glycerol) and the binary ChCl:Glycerol DES.

Experimental Details

Specular neutron reflectivity was measured from SDS and C12TAB surfactants at the DES/air interface for the ternary ChCl:Urea:Glycerol DES at 2 molar ratios of the HBD in the DES; ChCl:1.5Urea:0.5Glycerol & 1ChCl:0.5Urea:1.5Glycerol. The measurements were done at the CMC of SDS (3-4 mM depending on the DES) & C12TAB (~22 mM) at 4 contrasts each of the DES; h-ChCl:h-Urea:h-Glycerol (HHH DES), h-ChCl:h-Urea:d-Glycerol (HHD DES), h-ChCl:d-Urea:h-Glycerol (HDH DES) & d-ChCl:h-Urea:h-Glycerol (DHH DES). The proposal also intended to measure SDS & C12TAB at the binary DES ChCl:Glycerol/air interface for three DES contrasts (h-ChCl:h-Glycerol, h-ChCl:d-Glycerol & d-ChCl:h-Glycerol), however, due to shipment delays these measurements could not be carried out. The measurements done using low volume (2 mL) Delrin troughs, dimension 60mm*40mm, to keep the sample volume to cost effective quantities. This experiment was done as a remote experiment due to COVID restrictions, therefore there are some gaps in the data.

Data and Preliminary Analysis

The neutron reflectivity patterns obtained from SDS and C12TAB at 1ChCl:1.5Urea:0.5Glycerol DES/air interface at different contrasts are shown in **Figure 1**. The figure shows the neat DES/air interface (blue data sets) and SDS (red data sets) & C12TAB (green data sets) at the DES/air interface at HHH DES, HHD DES, HDH DES and DHH DES contrasts. The reflectivity patterns from the neat DES/air interface can be fitted to a simple model with two layers, air and the DES with an interfacial roughness of 4 – 8 Å. Upon the addition of SDS or C12TAB, the reflectivity pattern changes showing an interfacially adsorbed layer of the surfactant. Preliminary fits suggest that the interfacially adsorbed layer comprising of a monolayer of the surfactant with the tails oriented towards the air and the heads towards the DES. For the DHH contrast the measurements were only done at one angle (low Q only), which means complete information is not available for this data set. Co-fitting for the available contrasts is ongoing.

Similar results were observed for SDS and C12TAB at the 1ChCl:0.5Urea:1.5Glycerol DES/air interface for HHH DES, HHD DES, HDH DES and DHH DES contrasts. In this case there are again some incomplete data sets, HHH contrast has only been collected at one angle (low Q), which makes fitting of the data challenging.

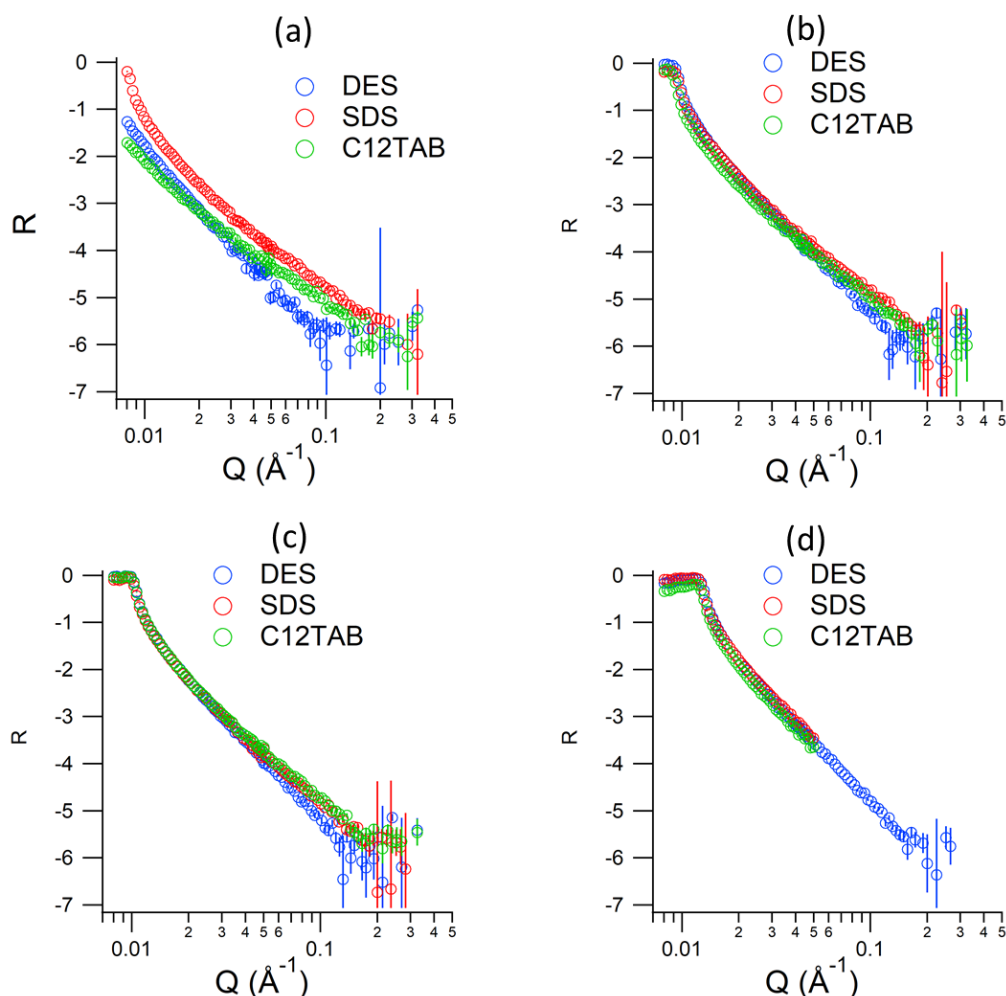


Figure 1: Reflectivity patterns from 1ChCl:1.5Urea:0.5Glycerol DES/air interface at different contrasts: (a) hhh DES contrast, (b) HHD DES contrast, (c) HDH DES contrast, and (d) DHH DES contrast. The blue data set shows the DES/air interface, the red data set shows the interface upon addition of SDS and the green data set upon addition of C12TAB.

In addition to the neutron reflectivity experiments, we have also recently (Aug 2021) collected X-ray reflectivity data at Diamond (I07 beamline; experiment number: SI27729-1) from SDS and C12TAB at the ternary ChCl:Urea:Glycerol DES/air interface. The incomplete neutron reflectivity data will be supplemented with the x-ray reflectivity data set and co-refined to obtain as accurate picture as possible of the surfactants at the DES/air interface.

Owing to problems with transportation resulting in reduced time on the beamline, complete data set for the originally planned experiment could not be collected. This limits the amount of information that can be obtained from the fitting of these data sets. Follow-up experiment at ILL or ISIS may be required to complete our understanding of the surfactants at the DES/air interface, especially preferential interaction with the DES components.