Experimental report

08/02/2017

Proposal: 9-10-1471 **Council:** 4/2016

Title: Micellization in alkyltriphenylphosphonium bromide:glycerol deep eutectic solvents.

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: ethyltriphenylphosphonium bromide:glycerol with C12TAB
2-hydroxyethyltriphenylphosphonium bromide:glycerol with C16TAB
methyltriphenylphosphonium bromide:glycerol with AOT
butyltriphenylphosphonium bromide:glycerol with SDS

Instrument	Requested days	Allocated days	From	To
D33	3	0		
D22	3	0		
D11	3	1	01/09/2016	02/09/2016

Abstract:

Deep Eutectic Solvents (DES) are molecular mixtures similar to ionic liquids, having melting points below room temperature. However instead of being a salt, the mixture contains two molecules with strong H-bonding that hinder formation of an ordered crystalline network. DES share many features of ionic liquids (low vapour pressure, adjustable polarity, etc) which make them interesting as green solvents while being far less toxic than typical ionic liquids. We have begun to study the formation of surfactant micelles in these novel, tailorable solvents, and discovered distinct differences in micelle shape and evolution with concentration compared to aqueous solutions. Here we wish to continue these studies by changing the cation component of the solvent and studying micelles formed with cationic and anionic surfactants. These results will be compared to our current results on the same surfactants for DES where the H-bond donor was altered. We aim to build up a systematic description of micellization in these non-aqueous solvents to promote their use in new amphiphile based applications such as templating and emulsification.

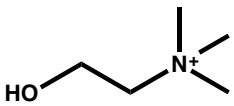
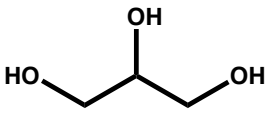
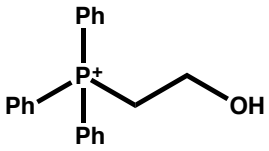
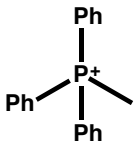
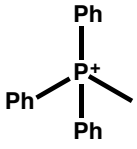
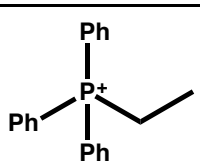
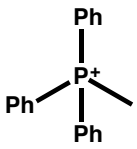
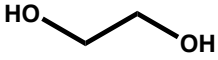
Introduction

Deep eutectic solvents (DES) are solvents obtained through the complexation of a halide salt with a hydrogen bond donor at a certain mole ratio, enabling solvent properties to be tuned for particular properties, including low toxicity and sustainability. We are undertaking a systematic study where we aim to correlate the unique hydrogen-bonded nanostructure of DES with their amphiphile aggregation behaviour. These investigations have shown that DES promote amphiphile self-assembly, with applications in templating of nanostructured materials. DES offer control over micelle morphology, as the solvent can be tuned to be interacting or non-interacting with the surfactant, altering the shape of the aggregates. We have demonstrated the formation of elongated anionic micelles in choline chloride:urea DES, unlike cationic surfactants which form globular micelles in that DES.

Experiment

The aim of this SANS experiment was to understand the role of the different components which form the DES and investigate the existence of possible selective interactions between the solvents and the surfactant headgroup. The DES were synthesised using different precursors. On one side the hydrogen bond donor was varied between glycerol and ethylene glycol. On the other side, choline chloride and different alkyltriphenylphosphonium halides were used as the halide salt. The full set of components measured are shown in Table 1.

Table 1: Components of the deep eutectic solvents used in this experiment.

Cation	Counterion	Hydrogen Bond Donor
	Cl^-	
		
		
	Br^-	
		
	Br^-	

Different concentrations of sodium dodecylsulfate (SDS, mole fraction 0.027 and 0.042), dodecyltrimethylammonium bromide (C_{12}TAB, mole fraction 0.056 and 0.12) and hexadecyltrimethylammonium bromide (C_{16}TAB, mole fraction 0.00085 and 0.022) were prepared in two different contrasts: deuterated surfactant (d_{25}-SDS, d_{25}-C_{12}TAB and d_{33}-C_{16}TAB) in protonated solvent and protonated surfactant in partially deuterated solvent (perdeuterated hydrogen bond donor, i.e. glycerol and ethylene glycol). Samples were loaded in 1 mm path length, 1 cm wide, quartz Hellma cells. Cells were equilibrated at 50 ˚C in the temperature-controlled sample changer. Two detector distances were measured, 1.5 and 8 m, providing a total q-range of 0.006-0.45.

Results

Figure 1 shows the SANS patterns for SDS micelles in different solvents.

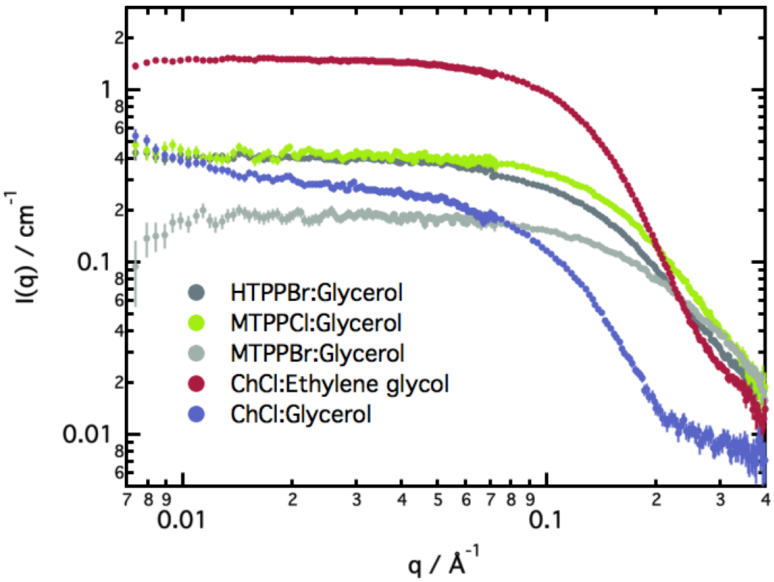


Figure 1 SANS data from solutions containing 0.027 mole fraction of d_{25}-SDS in fully protonated solvents: (HTPPBr:Glycerol) 1:3 2-hydroxyethyltriphenylphosphonium bromide:glycerol, (MTPPCl:Glycerol) 1:3 methyltriphenylphosphonium chloride:glycerol, (MTPPBr:Glycerol) 1:3 methyltriphenylphosphonium bromide:glycerol, (ChCl:Ethylene glycol) 1:2 choline chloride:ethylene glycol, (ChCl:Glycerol) 1:2 choline chloride:glycerol.

These data show distinct differences in the formation of micelles between the different solvents. We are currently working on the detailed analysis of this data, but our first results show a change in the aspect ratio of the micelles as the solvent constituents as altered, suggesting specific solvent-surfactant interactions occur in some cases. Furthermore, the volume fraction of micelles seems to differ between solvents, suggesting different solubility of surfactant molecules in the various solvents used.

Conclusions

The present data expands our knowledge of the micellization of amphiphiles in DES. The ability to selectively modify the characteristics of the micelles by varying the solvent constituents is demonstrated. This is also important with regards to tailoring the solvent for other applications where micelles are also required, since micelle size and shape cannot be assumed to be constant if the solvent is altered.

We can conclude that the outcome of this experiment has been positive. This study will be included in the thesis of ASF (due February 2018) and included in a scientific publication within a few months.