Experimental report

03/02/2016

Proposal: 9-12-399 **Council:** 10/2014

Title: Self Assembly in Deep Eutectic Solvents

Research area: Soft condensed matter

This proposal is a resubmission of 9-10-1389

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Samples: Malic Acid/Choline Chloride Mixture

Instrument	Requested days	Allocated days	From	To
D22	2	1	11/05/2015	12/05/2015
D33	2	0		

Abstract:

Deep Eutectic Solvents (DES) are molecular mixtures similar to ionic liquids, having melting points below room temperature. However instead of being composed of a salt, the mixture contains two molecules with strong interactions that hinder formation of an ordered crystalline network. DES share many of the 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. There is also some evidence that DES may form within the crowded cellular environment and could assist in solubilizing biological species in an intermediate environment between that of the hydrophobic phospholipids and highly polar water rich regions, particularly assisting survival under extreme conditions e.g. low temperature or drought where the water content of cells is restricted. Compared to ionic liquids, some DES are tolerant of high water content. Here we propose to examine the self assembly of a common surfactant, C12TAB, in a water containing DES as a function of water content.

Introduction

Deep Eutectic Solvents (DES) resemble ionic liquids but are formed from an ionic mixture instead of being a single ionic compound. In deep eutectic solvents, formation of a liquid at ambient temperatures relies on a large depression in freezing point coming from a favourable hydrogen bonding interaction between the constituents. DES share many properties with ionic liquids (negligible vapour pressure, adjustable physicochemical properties…) but they are easily prepared from cheap, biodegradable and non-toxic species; and tolerate addition of water, unlike some ionic liquids.

We have begun a systematic study of micellization occurring in DES and found interesting features regarding micelle structure.[1] In this experiment we had proposed to study the cationic surfactant C_{12}TAB, however although we found in our preliminary studies that this surfactant forms micelles in the choline chloride:urea DES, the range of solubility above the CMC turns out to be very limited. Thus although we have taken a little C_{12}TAB data at the range of possible (low) concentrations during this experiment, we have concentrated on another C_{12} tail surfactant system, choline chloride/urea and SDS. SDS micelles in choline chloride:urea have been shown an unusual rod-to-globular morphology transition with increasing concentration, unlike micelles formed by SDS in water and other polar solvents. We aimed to continue our studies in this system and expand the possibilities of tailoring these characteristics with studying the micellization in intermediate-polarity environments between the pure DES and water.

Experiment

This SANS experiment was focused on the structure determination of micelles in the DES choline chloride/urea and subsequent mixtures of this with water. Three different contrasts were measured for the pure DES with surfactant (h-choline chloride/h-urea + d-SDS, d-choline chloride/d-urea + h-SDS and h-choline chloride/d-urea + h-SDS) at high concentrations (2wt% to 12 wt%).

Furthermore the possibility of a morphology transition with water addition has been studied. Different water contents have been measured (1, 2 and 4 mole equivalents) to elucidate the effect of the water content.

Results

The figure 1 presents the SANS pattern for two of the contrasts.

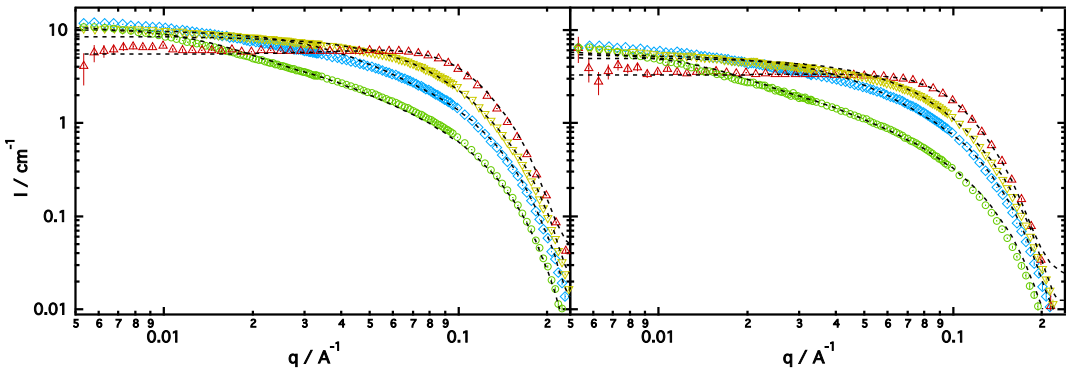

Figure 1. (a) dd solvent + 2, 5, 7.5 and 12 wt% h-SDS and (b) hd solvent + 2, 5, 7.5 and 12 wt% h-SDS and fits

The data was normalised to the concentration to check for the effect of a potential structure factor which would decrease the signal at low q and make the micelles look

smaller. However a significant structure factor was only found at the highest concentration (12 %) so we conclude that the decrease in the length of the micelles with concentration appears to be real, and cannot be ascribed to a structure factor effect. Also at the highest concentration a change in the slope in the Porod region suggests that the micelle shape changes to a more globular-like shape at high concentrations. The data fitting corroborates this idea, showing a rather constant radius (~16 Å) over the whole range of concentrations and a change in the length from ~400 Å at low concentration up to 25 Å at the highest.

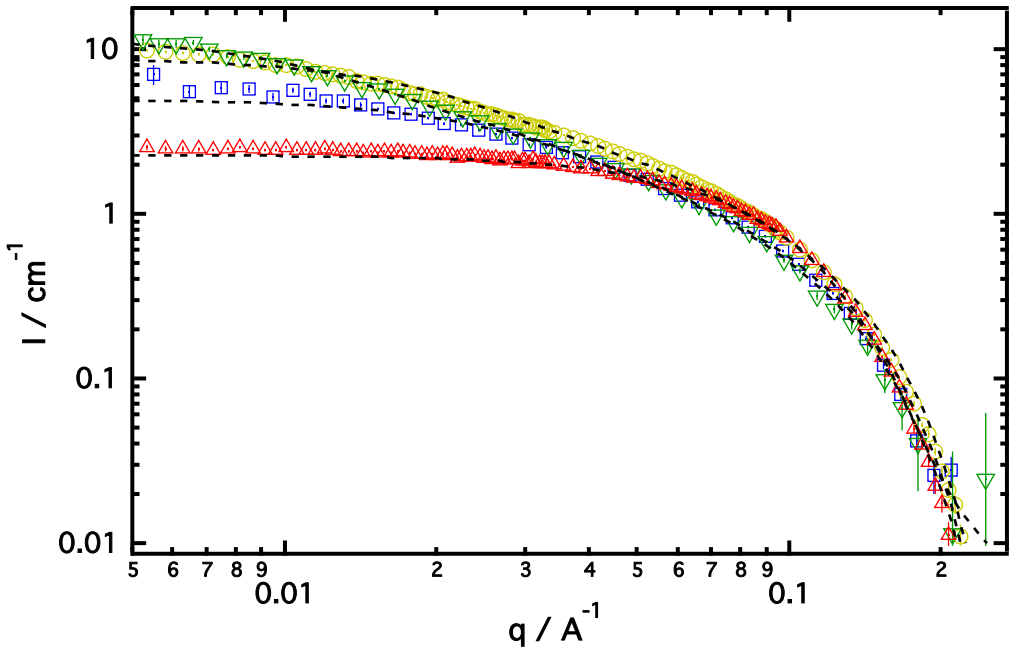

Figure 2. 1:2:n h-ChCl:h-Urea:H_2O + 2 wt% d-SDS with n= 0, 1, 2 and 4 mole equivalents

The addition of water to the DES was demonstrated to tailor the characteristics of the self-aggregates. It has been observed that increasing the water content in the system also promotes the change in the micelle shape from rod-like to globular. The initial length in the pure DES (~400 Å) is decreased to 26 Å as water is added up to 4 mole equivalents.

Conclusion

The outcome of this experiment has been highly positive. The system has shown an interesting and unexpected behaviour with increasing surfactant concentration and adding water. Furthermore, the data obtained is high quality with a good signal to noise ratio.

This data forms a central study to advance our work in this project. We expect to include it in a journal publication (currently in preparation). Furthermore it also provides essential contents for the thesis of ASF and will spark further studies. We will next evaluate the effect of temperature on the micellization process within this deep eutectic solvent. Additionally other alternatives to urea as the hydrogen bond donor in the solvent will be evaluated in the future.

References:

1. Arnold, T.; Jackson, A. J.; Sanchez-Fernandez, A.; Magnone, D.; Terry, A. E.; Edler, K. J., Surfactant Behavior of Sodium Dodecylsulfate in Deep Eutectic Solvent Choline Chloride/Urea. *Langmuir* **2015,** *31* (47), 12894-12902.