Experimental report

03/02/2016

Proposal: **9-13-612**

Council: 4/2015

Title: Langmuir Film Formation on Deep Eutectic Solvents

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
choline chloride:glycerol mixtures with DPPC, stearic acid monolayers
choline chloride:glycerol mixtures with DMPC, DODAB monolayers

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	2	3	23/10/2015	26/10/2015

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. There is also some evidence that DES may form within the crowded environment in cells and could assist in solubilizing biological species in an intermediate environment between that of the hydrophobic phospholipids and highly polar water rich regions. Here we wish therefore to study the interaction of phospholipids, common components of cell membranes, and synthetic lipids relevant to emulsification in Langmuir films at the air-DES interface to determine how they interact with DES and whether comparable interfacial structures are found to those formed on water.

Introduction

In recent years many studies into green and designer solvents have been undertaken and Deep Eutectic Solvents (DES) have emerged as environmentally friendly alternatives in many processes. DES have common properties with ionic liquids such as (i) a melting point near or below room temperature with a negligible vapour pressure, (ii) highly thermal and chemical stability nonetheless (iii) wider liquid temperature range than molecular solvents. Until the last few years, the number of solvents with allowing amphiphile self-aggregation properties had been quite limited. However, the emergence of designer solvents has promoted the number of possibilities. Prior studies have shown self-assembly of amphiphile systems in ionic liquids. Our latest publication has shown the ability of DES to promote self-aggregation of an anionic surfactant and the particularities and differences of such system with water.[1]

We have therefore begun a systematic study of surfactants and phospholipids in this media, with the aim of finding the characteristics which drive the self-assembly in these novel media.

Experimental

The present reflectometry experiment was focused in the determination of the behaviour of different phospholipids and surfactants at the air-DES interface. Two different isotopic mixtures were used as the subphase, h-choline chloride:h-glycerol and h/d-choline chloride:h/d-glycerol, and were combined with protonated and deuterated phospholipids and surfactants in order to obtain the best contrasts between the different layers of the surfactant. DPPC, DMPC, sodium dodecylsulfate and alkyltrimethylammonium bromides were measured in this experiment. The phospholipids were studied as Langmuir films, ie insoluble monolayers deposited dropwise onto the solvent surface from a 0.1mg/ml chloroform solution. The chloroform was allowed to evaporate and the monolayers equilibrated for 10 mins before the measurement started. Measurements were made at 4 different area per molecule of phospholipid, from 500 $Å^2$/molecule to 75 $Å^2$/molecule. The soluble surfactants were measured as adsorbed layers from solution at various bulk solution concentrations (0.01 and 0.02 wt% for SDS, 0.02 and 0.04 wt% for C_{12}TAB and C_{16}TAB). These solutions were poured into the troughs, and the reflectivity measured sequentially until an equilibrium measurement was obtained. All measurements were carried out at ambient temperature.

Samples were measured on the FIGARO beamline, using incident angles of 0.623°, and 3.79° to cover the full reflectivity pattern. Two different sample environments were used in order to optimise the amounts needed of deuterated compounds. For the fully protonated subphase, a Langmuir trough (40ml volume) was used, whilst the partially deuterated subphases were supported by low-volume Delrin troughs holding ~5ml of solution.

Results

DPPC and DMPC monolayers were measured at different surface concentrations by controlling the surface pressure of the insoluble monolayer. Surfactants were measured at different concentrations below the CMC point and at the CMC point.

Figure 1 shows the reflectivity from a DPPC monolayer on choline chloride:glycerol DES at two different solution contrasts, along with preliminary fitting results. The results suggest that the thickness of the monolayer increases with the concentration of insoluble phospholipid as the area per molecule in the Langmuir film decreases, increasing the thickness of the tail layer and decreasing the presence of solvent in the headgroup layer. The different tail lengths between DPPC and DMPC show also some differences in film thickness, as expected, during the fitting procedure.

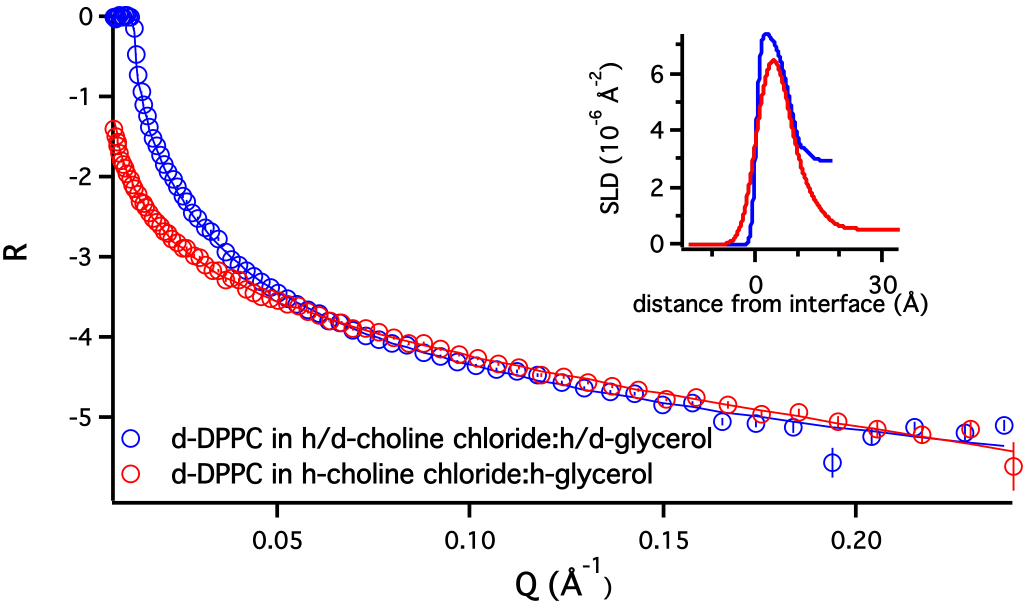

Figure 1: Reflectivity patterns from d-DPPC monolayers spread on choline chloride:glycerol subphase at 180 Å^2/molecule.

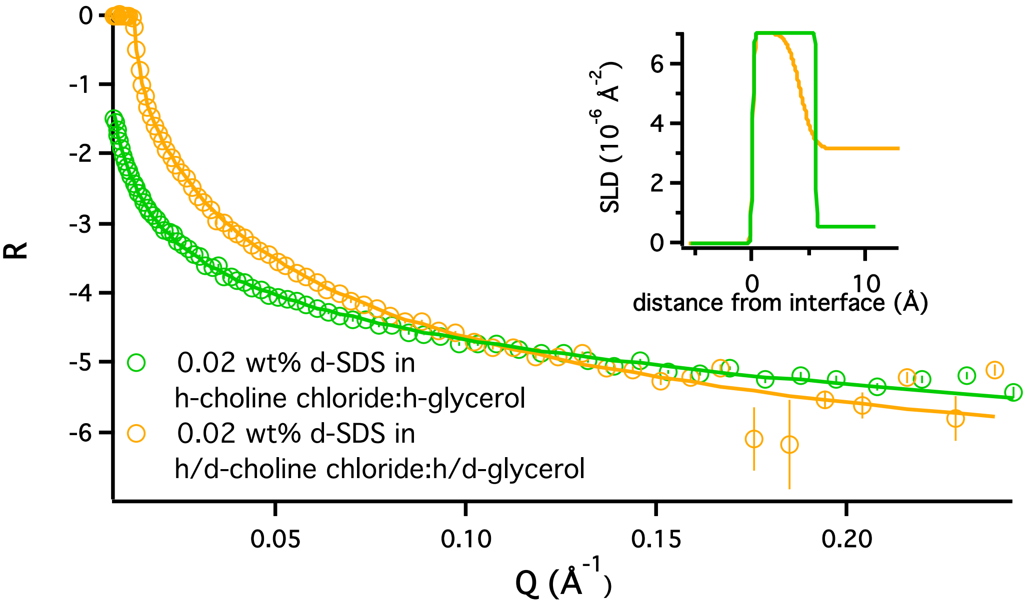

Figure 2: Reflectivity patterns from adsorbed monolayers at the surface of 0.02wt% SDS solutions in choline chloride:glycerol, with both contrasts fitted simultaneously to a single layer model.

Surfactants were found to remain surface-active at the air-liquid interface in this DES (Figure 2). The addition of surfactant below the CMC point increases the thickness of the layer (a 1-layer model was used during the surfactant data fitting), suggesting the segregation of these molecules to the air-solution interface. This is common behaviour for surfactants in water, and the behaviour of the studied surfactants in this DES appears to be similar. Fitting of the details of this adsorbed layer structure is ongoing, and will combine these neutron reflectivity measurements with x-ray reflectivity measurements on the same systems to provide a further contrast to assist with finding structural details in these monolayers

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Conclusion

DES have shown the ability to promote the formation of stable phospholipid monolayers at the air-liquid interface. Surfactants have also been shown to remain active at the interface. The information from this experiment will help to understand interesting effects, such as solvent-surfactant interactions and amphiphile behaviour within media with intermediate polarities.

Further analysis will be needed to draw conclusions about the headgroup-solvent interaction as well as the solvent penetration between layers. These data has also been found to be in good agreement with the previously collected X-Ray data. We therefore expect to carry on with the data analysis and include the present data in a journal publication.

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.