Experimental report

05/10/2018

Proposal: 9-13-747 **Council:** 4/2017

Title: Adsorption of amino-acid based surfactants at the air-water interface

Research area: Chemistry

This proposal is a new proposal

Main proposer: Karen EDLER

Experimental team: Karen EDLER
Julien SCHMITT
Joseph THOMPSON
Naomi ELSTONE

Local contacts: Armando MAESTRO

Samples: C12, C14, C16-glutamine, tail d-C12, C14, C16-glutamine
C12, C14, C16-glycine, fully d-C12, C14, C16-glycine
C12, C14, C16-proline, fully d-C12, C14, C16-proline

Instrument	Requested days	Allocated days	From	To
FIGARO Adsorption troughs	4	3	06/04/2018	09/04/2018

Abstract:

There has been a recent revival of interest in preparation of surfactants from natural starting materials as they are more biodegradable and thus more environmentally friendly than traditional surfactants. We have begun a research project aimed at using a grain residue from brewing, containing the amino acids glycine, proline and glutamine as a source of polar components for surfactant synthesis. Little has been done to characterise these surfactants so far, so we are studying these materials both as pure surfactants and importantly as mixtures, with the goal of avoiding costly separation steps both before synthesis and before use. Here we wish to continue our studies on these surfactants by studying the surface adsorbed layers formed by soluble C12, C14 and C16 chain surfactants with these amino acid headgroups alone and in binary mixtures. These experiments will provide information on the interfacial properties of these materials which are important for emulsification and cleaning applications.

Introduction:

The potential of amino acids as surfactant headgroups has been recognized and investigated since their discovery in in the early 1900's.[1] There has been a resurgence in interest in surfactants prepared from amino acids and other naturally occurring compounds in recent years due to their green credentials, such as renewability and biodegradability.[1, 2] However, the majority of surfactants currently in use are produced from petrochemical sources at a rate of 13 million tons per year (2008).[3]

Amino acid based surfactants research has expanded into a range of areas including; solubilisation of hydrophobic drugs, determination of their interactions with proteins and use in enantiomeric separations due to their racemic purity.[4-6] The high availability and biodegradability of these compounds combined with the already extensive range of applications and the fact the compounds are not irritating to the skin means they are likely to find applications in a range of industries.

In this project we are preparing and investigating amino acid based surfactants and the effect of mixing them with one another and commercial surfactants as a preliminary study into their potential for use in formulations. Prior to this experiment we measured the micellar structure of mixtures of these amino acid surfactants using SANS at ISIS and the measurements we carried out at Figaro are complimentary to these and will allow us the determine the relative surface affinity of the different surfactants in these mixtures to the interface.

Experimental:

The reflectivity experiment carried out aimed to investigate the effect of mixing amino acid based surfactants on the composition of the adsorbed layer at the solution surface. The surfactants investigated were myristoyl glycine (C14Gly), myristoyl proline (C14Pro) and myristoyl glutamine (C14Gln). Both hydrogenated and deuterated surfactants were prepared and used for this experiment.

Samples were run in D_2O and ACMW, as appropriate, in order to achieve optimum contrast and to allow the ratio of the species at the surface to be determined. The surfactants were dissolved in phosphate buffer prepared at pH7.2 to facilitate the dissolution of the surfactants and measurements were taken below the CMC to avoid problems with solubility observed at higher concentrations. All measurements were carried out at 25°C. Samples were measured on the FIGARO beamline, in the standard Teflon adsorption troughs which hold ~30 ml of solution, using two incident angles which allowed a Q range of 0.006 to 0.27$Å^{-1}$ to be recorded.

Results:

Measurements were taken for 3:1, 1:1 and 1:3 molar ratios of binary pairs of the surfactants in line with the measurements carried out at SANS2d at ISIS Neutron and Muon Source, we also measured the pure surfactants to allow for direct comparison with the mixtures.

Figure 1 shows an example of the data collected, for mixtures of the C14 glycine and C14 glutamine surfactants. Initial fits to a one layer model were carried out and we found that for 1:3 mixtures of the C14Gln:C14Gly surfactant the ratio of the surfactants absorbed at the surface is close to 1:1, with the 3:1 mixture showing contributions closer to the solution mixture ratio. In order to more accurately determine the relative surface affinities further refinement of the models will be carried out and the data fitted to a two layer model if that proves to be more appropriate.

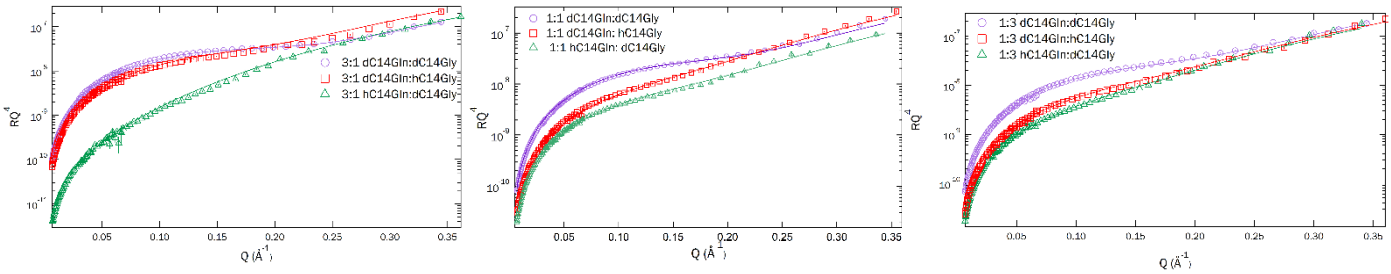

Figure 1: Measurements taken for 3:1 (left) 1:1(centre) and 1:3(right) mixtures of C14 Glycine and C14 Glutamine surfactants below the CMC at room temperature, fitted to a single layer model

During this experiment we measured the planned mixtures at concentrations below the CMC however due to time constraints only a single measurement above the CMC was carried out, this sample produced an identical reflectivity pattern to that of the sample measured at lower concentration suggesting that the surface was close to saturated at the concentrations used.

Conclusions

Initial fits indicate that these sample show some interesting non-ideal adsorption behaviour and that the data collected during this experiment will be a useful addition to studies already carried out in this project. We expect that once fully analysed this data will allow us to better understand these systems. The data will form a core part of the PhD thesis of Naomi Elstone, and we expect to publish the work shortly.

References:

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