Experimental report

10/02/2017

Proposal: 9-10-1463 **Council:** 4/2016

Title: Amino-acid based surfactant monolayers and their mixtures

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: icosyl-L-glutamine on water
icosylglycine (3-(icosanoylamino) ethanoic acid) on water
icosyl-L-proline on water

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	3	3	09/10/2016	12/10/2016

Abstract:

Bioderived surfactants are becoming increasingly of interest to provide biodegradable amphiphiles from non-petrochemical sources. Ideally they should be derived from waste, so as not to impact upon food chains or the wider environment. However waste products generally contain mixtures of species, and separations are energy intensive, and costly. Here we begin a study on bioderived amino-acid based surfactants, ultimately to be made from grain residue wastes. Initially to understand the behaviour of these amphiphiles, we have prepared pure selectively deuterated C20-tail amino acid headgroup (glycine, proline, glutamine) surfactants. Since little is reported on their physicochemical properties we will first study these as Langmuir films using neutron reflectivity to determine layer thickness, headgroup orientation and spacings. Once individual components are characterised we will study the binary & ternary mixtures of these species to determine mixing behaviour, and structures formed in the mixed monolayers. This will provide information towards our ultimate goal to use amino acid mixtures to directly prepare surfactant mixtures with no purification, for use in formulation.

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, the structure of amino acid surfactant monolayers had not been determined using reflectometry.

Experimental:

The reflectivity experiment carried out aimed to investigate the effect of mixing amino acid based surfactants on the monolayer structure. The surfactants investigated were icosanoyl glycine (C20Gly), icosanoyl proline (C20Pro) and icosanoyl glutamine (C20Gln). Both fully hydrogenated and samples with deuterated tails were prepared and used for this experiment. Measurements were made for the pure surfactants and each of the possible 1:1 mixtures.

Samples were run on D_2O and ACMW, as appropriate, in order to achieve optimum contrast and to allow different molecules to be observed separately in the mixed monolayers. Langmuir monolayers were prepared by spreading solutions of the lipids in chloroform and methanol. The solvents were allowed to evaporate and an isotherm measured, to ensure the monolayer was in the equilibrated state, prior to reflectivity measurements being taken. Measurements were taken at constant surface pressure which for the two lowest pressures corresponded to fixed areas per molecule of 40Å^2/molecule and 30Å^2/molecule, measurements were also taken at 25mNm^{-1} and 35mNm^{-1} as these pressures were found to be at the beginning and near the end of the compressed region respectively in the pressure-area isotherms for all the surfactants and their mixtures. All measurements were carried out at 25°C.

Samples were measured on the FIGARO beamline, using two incident angles which allowed a Q range of 0.006 to 0.27Å^{-1} to be measured.

Results:

Measurements were taken at a range of surface pressures in order to determine the variation in the monolayer structure during compression as a range of phases were observed in previously recorded pressure-area isotherms.

The data shown in Figure 1 indicates a variation in the monolayer structures of the C20Pro and C20Gly surfactants and the reflectivity suggests that the structure of the 1:1 mixture is more similar to that of the C20Pro monolayer. The initial fit shown in Figure 2 for the C20Gln monolayer at 25mNm^{-1} gives a tail thickness of 25.9Å with a SLD of 7.9x10^{-6} Å^{-2}, (which is much higher than we expected from calculation of the SLD) and a headgroup thickness of 3 Å, which is much smaller than would be predicted from the molecular structure.

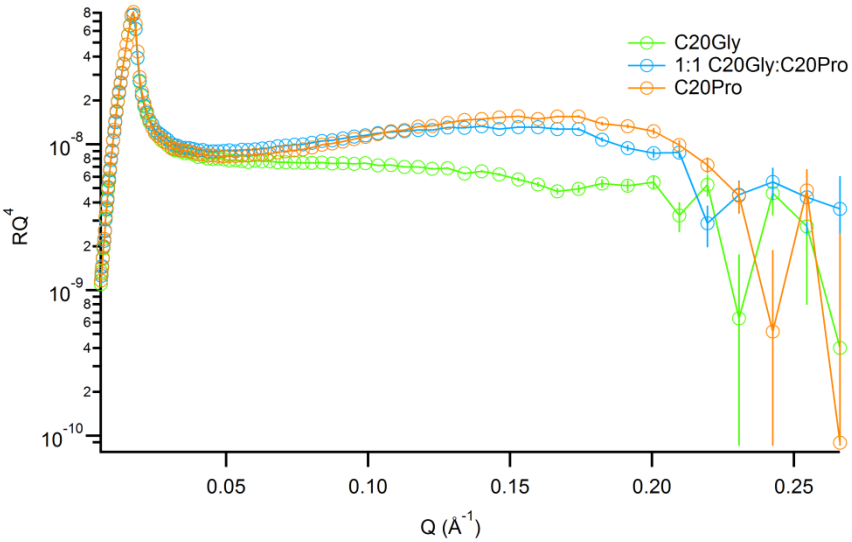

Figure 1: Reflectivity profiles of the tail deuterated compounds of C20Pro, C20Gly and the 1:1 molar mixture of both surfactants on D_2O at 25mNm^{-1}

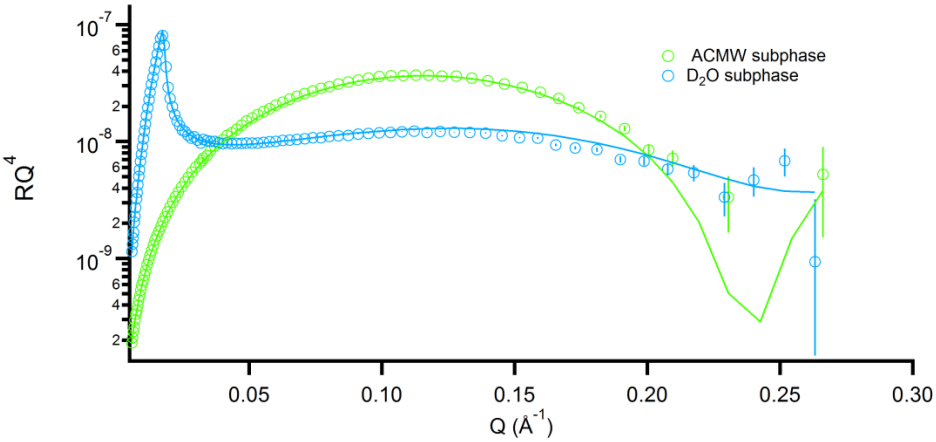

Figure 2: Initial fitting for the tail deuterated C20Gln system on ACMW and D_2O at 25mNm^{-1}

Due to these surprising results we ran extra analysis of the samples during the beamtime, to ensure that they had not degraded during transport, the IR spectroscopy and Langmuir isotherms recorded during the experiments were in line with expected results and so indicated that it was unlikely that the samples had degraded. As the additional experiments did not lead to an explanation for the high SLD we have decided to fit the data in tangent with data collected from the ISIS neutron facility on similar systems in December 2016 and X-Ray data collected at the Diamond light source on beamline I07 in order to determine whether this high SLD value is repeatable and to further improve the validity of the fit by co-refinement with the X-ray data. Data analysis is therefore on-going.

Conclusions

Initial fits and investigations indicate that the variation in the amino acid headgroup has a large effect on the structure of the monolayers. In addition, mixing these surfactants leads to interesting changes in the monolayer structure which does not appear to be simply an average of the two compounds reflectivity profiles, which suggests that the compounds are mixing rather than being in isolated regions. Initial inspection suggests that the mixed monolayer behaviour is dominated by that of the species with the most bulky headgroup. In order to further understand these systems additional measurements will need to be taken at different molar ratios, to determine whether the structure is always more similar to that of the more bulky single component system.

References:

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