Experimental report

03/09/2015

Proposal: 9-10-1357 **Council:** 4/2014

Title: Understanding surface excess and structure of cationic surfactants atalumina interfaces

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: C12TAB, C14TAB, H2O, D2O, Al2O3

Instrument	Requested days	Allocated days	From	To
D17	3	3	02/10/2014	05/10/2014

Abstract:

This proposal seeks to determine the explanation of a pronounced maximum in the surface excess observed at a solid/liquid interface by studying systematically the effects of pH on aqueous solutions of alkyl trimethyl ammonium bromide (CnTAB) surfactants against sapphire substrates. This is thought to arise from the balance of different influences on adsorption such as electrostatic attraction to the surface, repulsion between charged adsorbates and the solvent interactions that can cause a rich variety of behaviour. T he new data will allow sensitive tests of models of adsorption that depend on ionic association and surface potential close to the critical micelle concentration.

Aims

The main aim of this experiment was to investigate some aspects of the adsorption of simple cationic surfactants to sapphire/solution interfaces. In particular previous preliminary measurements had suggested that (a) the layers are thin and (b) the surface excess might not just increase monotonically to a maximum plateau value. The experiment used hexadecyltrimethyammonium bromide (C16TAB) and tetradecylammonium bromide (C14TAB) to study these issues.

Results

The opportunity was taken to exploit the latest development of reflection sample cells with a stirred sample volume to ensure good mixing and homogeneous concentration as well as the possibility to locate a mask to limit background scattering and thus extend the effective measurable range of momentum transfer. Typical data is shown in Figure 1. This new sample cell design worked well and data showing the reduction in background has been published in a new publication that describes these developments.[1] The improved shielding reduced the background by approximately a factor of five.

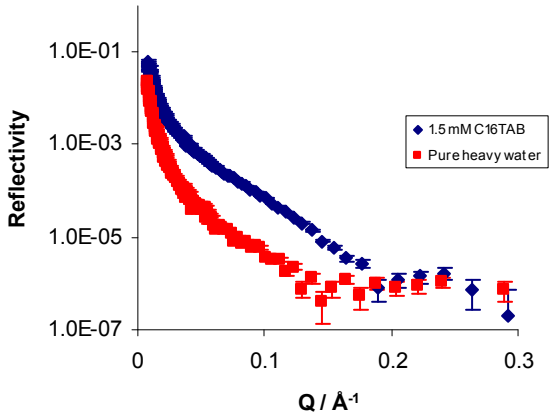

Figure 1 Comparison of reflectivity for a sapphire (Al_2O_3) interface with 1.5 mM C16TAB and pure D_2O.

Analysis of the data in terms of bilayers has used specific software that uses molecular parameters such as the volumes and scattering lengths of hydrophilic and hydrophobic moieties and solvent molecules.[2] Preliminary fitted parameters for the surface excess and thickness of C16TAB in pure D_2O against sapphire (Al_2O_3) are shown in Figure 2.

The results for C16TAB did not give any indication of a maximum in the surface excess. However the overall layer thickness displays an interesting trend as the adsorbed layer becomes thinner but significantly denser as the concentration increases. The length of the region of hydrophobic tails is markedly less than that of two extended C_{16} hydrocarbon chains[3] as reported previously for layers on silica.[4] This can be rationalised in terms of the crystal structure

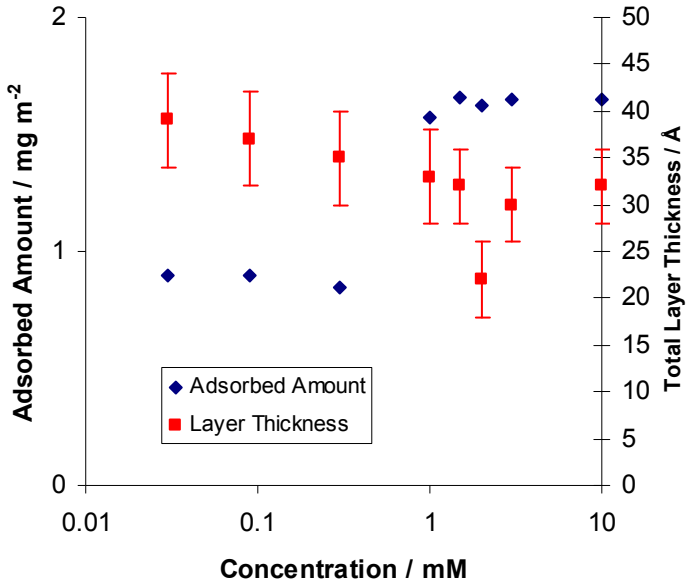

Figure 2. Surface excess (adsorbed amount) and thickness of bound layer of C16TAB on Al_2O_3.

Other data is now being prepared for publication in the context of new studies of chain packing and mobility of several alkyl trimethyl ammonium surfactants at variable temperatures.

The reduced background allows reliable data fitting to larger momentum transfer and gives better information about the layer thickness and analysis of details of the internal structure of the adsorbed layers is in progress.

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[1] A. R. Rennie, M. S. Hellsing, E. Lindholm, A. Olsson 'Note: Sample cells to investigate solid/liquid interfaces with neutrons' Rev. Sci. Instrum. 86, (2015), 016115.

[2] wwww.reflectometry.net/fitprogs/bike.htm

[3] C. Tanford 'Micelle Shape and Size' *Journal of Physical Chemistry* **76**, (1972), 3020-3024.

[4] G. Fragneto, R. K. Thomas, A. R. Rennie, J. Penfold, 'Neutron Reflection from Hexadecyltrimethylammonium Bromide Adsorbed on Smooth and Rough Silicon Surfaces' *Langmuir* **12**, (1996), 6036-6043.