

An Unusual Maximum in the Adsorption of Aqueous Surfactant Mixtures: Neutron Reflectometry of Mixtures of Zwitterionic and Ionic Surfactants at the Silica–Aqueous Interface

Kun Ma,[†] Pei Xun Li,[†] Robert K. Thomas,^{*,†} and Jeffrey Penfold^{‡,¶}

[†]*Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ, UK.*

[‡]*Rutherford-Appleton Laboratory, Chilton, Didcot, Oxon*

[¶]*Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ, UK.*

E-mail: robert.thomas@chem.ox.ac.uk

Abstract

The adsorption of two zwitterionic surfactants, dodecyldimethylammonium propane-sulfonate (C₁₂PS) and dodecyldimethyl ammonium carboxybetaine (C₁₂CB) and of their mixtures with the cationic dodecyltrimethylammonium bromide (C₁₂TAB) and the anionic sodium dodecylsulfate (SDS) at the silica-water interface has been studied by neutron reflection (NR). The total adsorption, the composition of the adsorbed layer, and some structural information have been obtained over a range of concentrations from below the critical micelle concentration (CMC) to about 30× the mixed CMC. The adsorption behaviour has been considered in relation to the previously measured micellar equilibrium of these mixtures in their bulk solutions and their adsorption at the air-water interface.

$C_{12}CB$ adsorbs cooperatively close to its CMC to form an almost complete bilayer on its own, whereas $C_{12}PS$ adsorbs more weakly in a fragmented bilayer structure. Although SDS does not normally adsorb at the silica-water interface, SDS adsorbs strongly and cooperatively with $C_{12}PS$ at fractional SDS compositions up to about 0.5. This cooperativity is lost when the adsorbed fraction of SDS rises above about 0.5. At this point adsorption drops sharply, creating an unusual maximum in the variation of adsorption with total concentration above the mixed CMC. Neither the increase in cooperativity nor the subsequent decline in adsorption result directly from variations of the independently determined monomer concentrations in the bulk solution. The adsorption maximum is predominantly the effect of strong cooperative interaction, possibly accompanied by partial segregation of SDS within the layer, followed by charge repulsion from the surface. Although the solution aggregation and adsorption at the A-W interface are similar for SDS with $C_{12}CB$, the addition of SDS to $C_{12}CB$ at the silica-water interface promotes the opposite behaviour to that of SDS with $C_{12}PS$, and SDS simply disrupts the cooperative binding of $C_{12}CB$.

Unlike SDS the cationic surfactant $C_{12}TAB$ adsorbs on silica. It therefore coadsorbs at the SiO_2 -W interface with either $C_{12}CB$ or $C_{12}PS$. However, in neither case is there any pronounced cooperativity and, even though the presence of $C_{12}TAB$ might be expected to favour adsorption, the adsorption is generally unexpectedly low.

Keywords: Adsorption maximum, surface mixing, nonideal mixing, excess free energy of mixing, surface layer structure, surfactant fragment distribution

Introduction

The adsorption of surfactants at a hydrophilic solid-water interface is primarily driven by the combination of the interaction of the head group of the individual surfactant with the surface and the strongly cooperative hydrophobic interaction between the hydrophobic units.^{1,2} The result is a cooperative adsorption that has sometimes been regarded as a surface critical aggregate concentration (SCAC),³ analogous to the critical micelle concentration (CMC) in

bulk solution. Non-invasive structural techniques such as neutron reflection (NR),⁴⁻⁶ null ellipsometry,⁷ x-ray reflection (XRR),⁸ and spectroscopy⁹ have shown that surface structures at the widely studied silica-water ($\text{SiO}_2\text{-W}$) and mica-water interfaces are often fragmented bilayer structures, whereas atomic force microscopy (AFM), which is a more invasive probe of the layer, mostly gives the result that spherical micelles and hemimicelles of cationic surfactants occur on silica and mica respectively.^{10,11} However, more recent AFM measurements using the less invasive peak force tapping mode confirm that the structure of hexadecyltrimethylammonium bromide on mica evolves from a fragmented structure at low concentrations to a complete bilayer as the CMC is approached.¹²

In addition to the essential role of the hydrophobic effect in adsorption of surfactants at hydrophilic-aqueous surfaces, the charges on surfactant and surface also strongly affect adsorption. The levels of adsorption observed for surfactants of opposite charge to that of the surface are often higher than the known charge on the bare surface and charge regulation of the surface must therefore involve a mix of ion exchange, induced ionization on the surface and the adsorption of surfactant ion-counterion pairs, all of which involve electrostatic and entropic contributions.¹³ Such adsorption is illustrated by the adsorption of sodium dodecyl sulfate (SDS) as a complete bilayer on sapphire,¹⁴ and by the adsorption of a phosphate derivative of AOT on sapphire.¹⁵ In the former, an adjustment of charge at the surface is thought to be associated with a maximum in the adsorption at the CMC, which was attributed to adsorption only of the surfactant ion, with the counterion being preferentially incorporated into the micelles of the solution with increasing concentration.¹⁶⁻¹⁸ A maximum with pH has also been found for the weak anionic hexanoic acid on alumina,¹⁹ which was attributed to replacement of OH^- groups on the surface with RCO_2^- .¹⁹

The surface and surfactant ion do not need to be of opposite charge for adsorption to occur. Different counterions, especially divalent ions, can induce adsorption between like charged surfactants and surface, as shown by the strong adsorption of the negative surfactant ion of Aerosol OT on the negative surfaces of both silica²⁰ and mica^{21,22} when divalent ions

are present. Zwitterionic surfactants, which usually contain a more or less closely spaced pair of opposite charges can also adsorb on a charged surface. Thus, it has been shown that cooperative adsorption of zwitterionic surfactants on powdered silica substrates, which are generally negatively charged, occurs around the CMC.^{23,24} Zajac et al²⁵ have observed weak adsorption at low concentration of zwitterionic surfactants on silica as well as adsorption with the positive enthalpy characteristic of cooperative hydrophobic interaction at around the CMC. Harvigsson et al. have described the cooperativity of the adsorption of a series of dodecylalkylammonium alkanecarboxylates on a single silica surface in terms of an SCAC.³ Nonionic surfactants may also adsorb as aggregates on a charged surface, e.g. hexaethylene glycol monododecyl ether ($C_{12}E_6$), which forms a bilayer on silica.⁴

The use of mixed surfactant systems gives a flexible means of probing the effects of charge at a surface because the interaction can be used to tune the composition of the adsorbed layer. This is especially the case when the interaction between the two surfactants is strong as in pairs of ionic and zwitterionic surfactants. Lokar and Ducker have shown that adsorption of mixtures of cationic dodecylpyridine chloride and dodecyldimethylammonium propanesulfonate is enhanced relative to the separate components at the hydrophilic silica and mica surfaces.²⁶ However, even when one of the components is nonionic, a strong interaction with a charged species can enable adsorption on a surface of the same charge.²⁷ Thus, a mixed SDS- $C_{12}E_6$ bilayer containing up to about a third of SDS will adsorb on the negatively charged silica surface.²⁸ The cooperative adsorption of mixtures is also an important means of enhancing the efficiency of formulations. However, the use of mixtures introduces more degrees of freedom, especially above the CMC, where most formulations are used in practice. For example, one of the components may be preferentially fractionated into the solution micelles, possibly leading to maxima in the adsorption at either air-water (A-W) or solid-water interfaces.^{13,18,29,30}

Here, we examine the composition and structure of adsorbed layers of mixtures of each of the zwitterionics dodecyldimethylammonium propanesulfonate, $C_{12}H_{25}N^+(CH_3)_2-C_3H_6SO_3^-$,

abbreviated to C₁₂PS, and dodecyldimethylammonium carboxybetaine, C₁₂H₂₅N⁺(CH₃)₂-CH₂CO₂⁻, abbreviated to C₁₂CB (both structures are shown by Ma et al.³¹), with the anionic surfactant SDS and cationic dodecyltrimethylammonium bromide (C₁₂TAB) at the negatively charged hydrophilic silica-water interface (SiO₂-W), particularly above the mixed CMC. The difference from previous studies is that we have already measured the mixed micellization of these mixtures in the bulk solution as well as their adsorption at the A-W interface both above and below the CMC,³¹ which provides key information for interpreting the adsorption at the SiO₂-W interface.

Experimental Details

The materials were the same as those used by Ma et al.³¹ NR measurements were performed on the reflectometers CRISP and SURF at the Rutherford-Appleton Laboratory (Didcot, U.K) and D17 at the Institut Laue-Langevin (Grenoble). The instruments, the procedures for making the measurements, and the scattering lengths used for the analysis of the data are also described fully by Ma et al. Measurements were made over a range of momentum transfer, κ ($= (4\pi \sin \theta)/\lambda$), where θ is the glancing angle of incidence), from below the critical angle for total reflection from the SiO₂-D₂O interface out to about 0.35 Å⁻¹, and a flat incoherent scattering background was subtracted.

The experimental solution was held in a Teflon container with a volume of approximately 25 ml, which was clamped against the polished (111) face of a silicon single crystal of dimensions 125 x 50 x 25 mm³ between temperature controlled aluminum and magnetic stirrer plates. Sample changes were made through inlet and outlet ports located on opposite sides of the container, which could be connected to plastic tubes for injection by syringe. The silicon blocks were cleaned by immersion in Piranha solution (a 5:4:1 mixture of H₂O: H₂SO₄: H₂O₂) at 70 °C followed by UV/ozone treatment. They were rinsed and soaked in clean water (Elgastat Ultrapure). Following this treatment the silicon (111) surface typically has a layer of oxide of about 15 Å in depth. The oxide layer on the Si(111) substrate was char-

acterized using the NR profiles from Si/SiO₂/D₂O, Si/SiO₂/water_{2.07} and Si/SiO₂/water_{4.00} interfaces, where the subscripts indicate the scattering length densities of the water. The NR profiles could all be well fitted by single uniform layers of silica of thicknesses in the region of 17 ± 3 Å, scattering length density of 3.4×10^{-6} Å⁻², and roughnesses of 3 ± 0.5 Å.

The adsorption experiments on binary solutions of A and B surfactant mixtures were done in D₂O using two isotopic compositions, hA–hB and hA–dB, where h and d denote fully protonated or fully deuterated hydrocarbon (C₁₂) chains, over a range of concentration. The structure that gave the best fits to the reflectivity data consisted of three sublayers. The central layer (layer 2) consists mainly of the hydrophobic chains and the outer two layers (layers 1 and 3) consist of heads and water. The bilayer is assumed to occur in patches so that the average scattering length density of a sublayer is weighted by the volume fractions of bilayer and water. The calculation of the reflectivity was based on the optical matrix method using the Motofit program³² and the main adjustable parameters are the thicknesses of the three layers and the surface excess. The number of headgroups in inner and outer layers was constrained to be approximately identical. In addition, the interfacial roughness, σ , was taken to be the same for all sublayers and could be adjusted. As always with NR, the fits are extremely sensitive to the coverage. In this case, because of the thicker layers, they are also sensitive to the overall thickness. However, they are less sensitive to the division into the three sublayers unless the water fraction in the outer layers is very different from that in the inner layer. In particular, while it was possible to determine the composition of the layer in terms of the two surfactants, the experiment was not sensitive enough for it be possible to distinguish any segregation of the two surfactants along the normal direction to the surface, such as was done for SDS-C₁₂E₆ mixtures on silica.²⁸ Finally, the parameters of the silica layer were fixed as determined for the bare silica surface.

Results and Discussion

Adsorption of Pure Zwitterionics on Silica

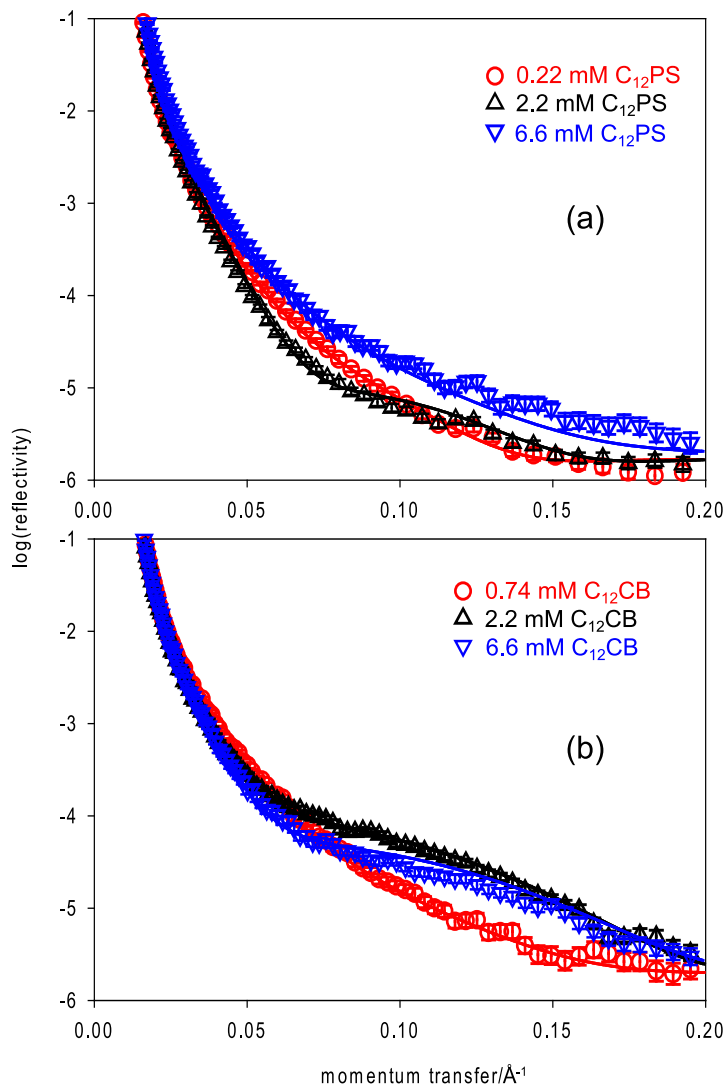


Figure 1: Neutron reflectivity profiles of (a) C₁₂PS at 308 K and (b) C₁₂CB at 313 K at different concentrations at the silica-D₂O interface, points (experiment) and lines (best fit to a three layer model).

Examples of the NR data for the two pure zwitterionic surfactants are shown in Figure 1 together with the best fits using the parameters given in Table 1. The temperatures were raised from room temperature because crystallization in some of the SDS–C₁₂CB mixtures

298 K had earlier been observed at 298 K by Hines et al.³³ A sharp onset of adsorption for C₁₂CB above the CMC is evident from the last column in Table 1, although there is some weak adsorption below the CMC (1.9 mM). At its highest the level of adsorption is comparable with cationic surfactants, e.g. C₁₆TAB,³⁴ and close to a complete bilayer. This and the fact that the thickness of the hydrocarbon region is about that of an extended chain indicates that the structure is an interdigitated bilayer. The high coverage on a negatively charged surface and its resemblance to a cationic surfactant suggests that the quaternary ammonium group is in close contact with the surface but that the molecules are still able to maintain a packing that allows strong cooperativity from the hydrophobic interaction. This is possible if the individual molecular configuration in the inner layer next to the surface is something like that shown for C₁₂CB in Figure 2(a), in which the head group adopts a bent rather than an extended conformation. This would allow the quaternary ammonium group to be close to the surface and to interact laterally with the carboxy groups within the immediate surface layer. The key factor is that the various contributions to the interactions within the head group and surface region should enable the strong hydrophobic interaction between the chains of the inner and outer layers to be maximized. C₁₂PS follows a quite different pattern. The adsorption at the low concentrations of 0.22 and 0.74 mM is larger than for C₁₂PS indicating a stronger individual interaction with the surface, although it is still low. There is also little evidence of cooperative hydrophobic interaction, even above the CMC, and the adsorption at about 3×CMC is much lower than for C₁₂CB. The stronger individual interaction is consistent with the positive part of the head group being attached to the surface while the negative part is held further away from the surface by the flexible 3 carbon spacer in a way that hinders the close approach of other molecules, as shown in Figure 2(d). The larger spacer with the opposite arrangement of the charge thus seems to block self-assembly of the layer. At the A-W interface these two surfactants form well packed monolayers with similar limiting areas per molecule, which indicates that the head groups adopt the fully extended conformation in these different circumstances.³¹ This will

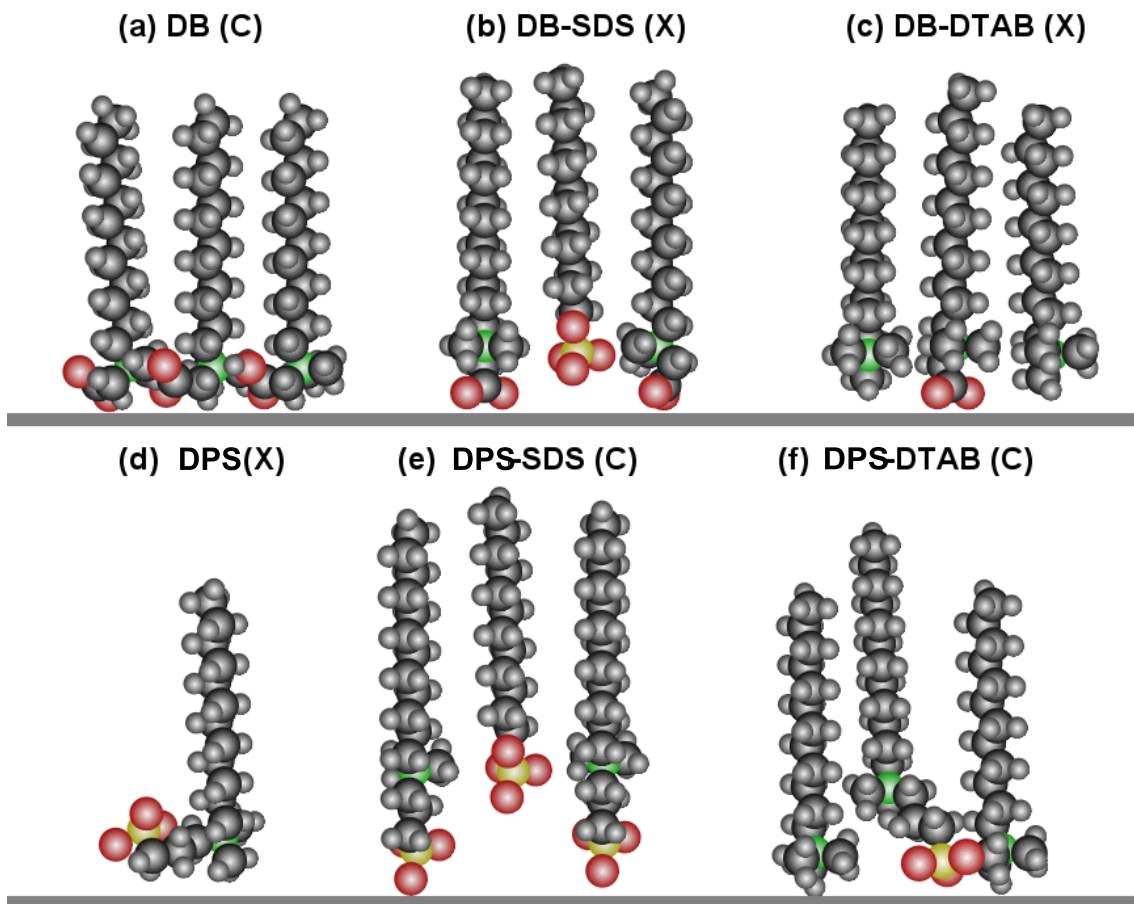


Figure 2: Possible configurations of $C_{12}CB$ and $C_{12}PS$ (abbreviated to DB and DPS) molecules in the inner layer next to the surface at the SiO_2 -W interface, (a) pure $C_{12}CB$, (b) a mixture of $C_{12}CB$ and SDS, (c) a mixture of $C_{12}CB$ and $C_{12}TAB$, (d) pure $C_{12}PS$, (e) a mixture of $C_{12}PS$ and SDS, and (f) a mixture of $C_{12}PS$ and $C_{12}TAB$. Cooperative adsorption is marked with a C and no or little adsorption with an X. The separation and stoichiometry in the two mixtures approximately match those observed and the colours are black/grey for C/H, red for O, green for N and yellow for S.

also occur in the outer set of molecules in the bilayer adsorbed on the solid but the much larger spacing of the inner layer is evidently still sufficient to prevent self-assembly of $C_{12}PS$ into a bilayer structure.

Harvigsson et al. have previously used ellipsometry to determine the level of adsorption of a set of $C_{12}C_nB$ with varying length of carbon spacer in the betaine head group on silica as substrate.³ For $C_{12}CB$ they observed the same sharp onset with concentration, although their value of the limiting coverage was slightly less than ours at 5 compared with 7 $\mu\text{mol m}^{-2}$.

Table 1: Layer thicknesses (τ_1 and τ_3 are the head group thicknesses, and τ_2 is the thickness of the alkyl chain region) and surface excess (Γ) of C₁₂CB at 313 K and C₁₂PS at 308 K derived from neutron reflectivity data. Italics indicate measurements below the CMCs of 1.9 and 2.2 mM for C₁₂CB and C₁₂PS respectively.

Surfactant	concentration mM	τ_1 ± 2 Å	τ_2 ± 2 Å	τ_3 ± 2 Å	Γ $\mu\text{mol m}^{-2}$
C ₁₂ CB	<i>0.22</i>	7	18	5	<i>0.2</i> \pm 0.2
	<i>0.74</i>	8	18	4	<i>0.3</i> \pm 0.2
	2.2	5	18	8	7.3 \pm 0.5
	7.4	5	18	7	6.8 \pm 0.5
C ₁₂ PS	<i>0.22</i>	6	14	6	<i>1.3</i> \pm 0.3
	2.2	4	19	8	3.0 \pm 0.4
	6.6	4	20	9	2.1 \pm 0.4

Lokar and Ducker, using attenuated infrared spectroscopy, found some signs of cooperative adsorption of C₁₂PS on oxidized silicon up to a higher limiting value (about 4 $\mu\text{mol m}^{-2}$) than here.²⁶ However, the limiting adsorption on silica is quite sensitive to factors such as roughness and is also expected to be sensitive to differences in the underlying crystal face and thickness of the oxide layer. On the silica (111) plane used here the oxide layer is about 15 Å thick but on the Si(100) face used for the ellipsometry it is often about 300 Å thick (the crystal face and level of oxidation were not specified by Lokar and Ducker).

Adsorption of Mixtures of SDS or C₁₂TAB with Zwitterionics on Silica

The mixtures of the two zwitterionics, protonated and deuterated, with hSDS and hC₁₂TAB in D₂O were measured as described above. The sensitivity of the NR signal to the different isotopic combinations is illustrated by the examples shown with fitted profiles in Figure 3. The combined results for the complete set of profiles, which can be found in Ma,³⁵ are given for SDS in Table 2 and for C₁₂TAB in Table 3, where concentrations below or at about the mixed CMC are given in italics (the experimental mixed CMCs for each composition are from Ma et al.³¹). These tables also include equivalent experimental measurements of the adsorbed fraction of the ionic surfactant at the A-W interface, also from Ma et al. The thicknesses of the hydrocarbon region of the bilayer were found to be about those of a single,

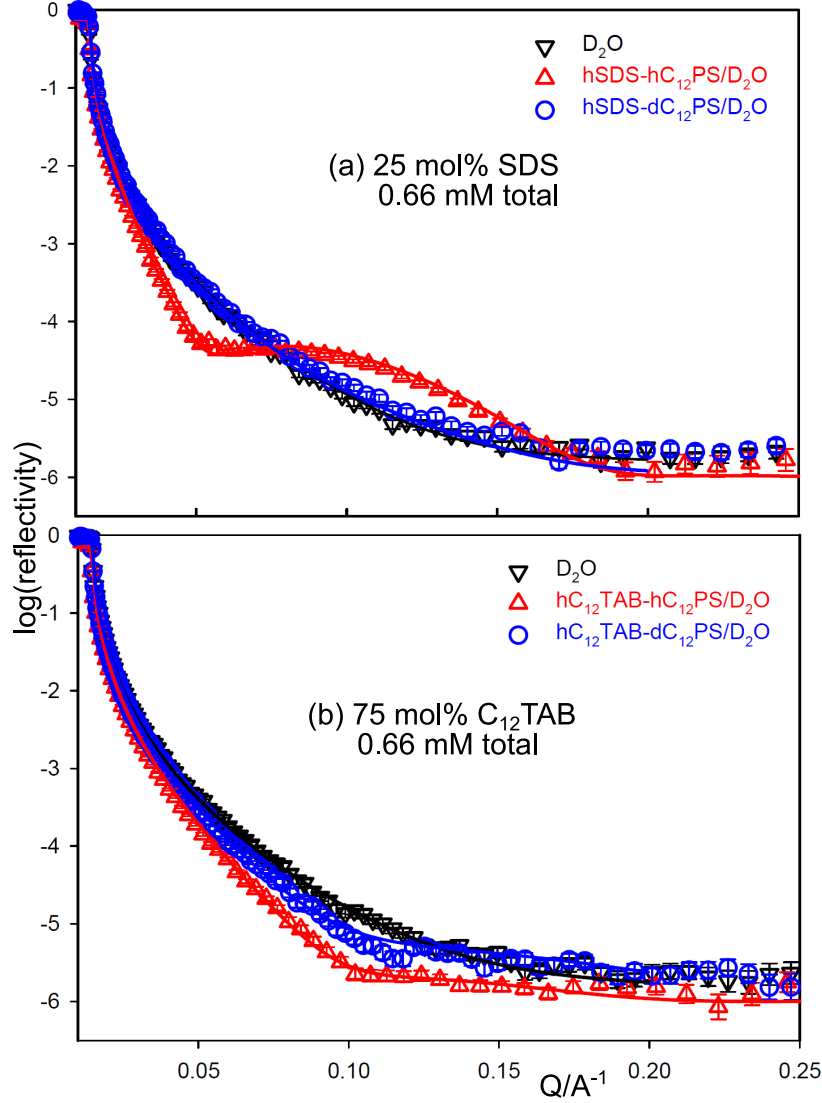


Figure 3: Neutron reflectivity profiles of (a) $h\text{SDS}-hC_{12}\text{PS}$ and $h\text{SDS}-dC_{12}\text{PS}$ in D_2O at a total concentration of 0.66 mM with 25 mol% SDS at 313 K and (b) $hC_{12}\text{TAB}-hC_{12}\text{PS}$ and $hC_{12}\text{TAB}-dC_{12}\text{PS}$ in D_2O at a total concentration of 0.66 mM and 75 mol% $C_{12}\text{TAB}$ at 308 K adsorbed at the $\text{SiO}_2\text{-W}$ interface, points (experiment) and lines (best fit to a three layer model).

approximately normally oriented chain which, together with the high coverage, suggests that this part of the layer is interdigitated, although in the present experiments the sensitivity is too low to distinguish this from a structure in which the chains are not interdigitated but are obliquely oriented at about 30° to the horizontal.

Figure 4 shows the experimental results for the total adsorption as a function of total

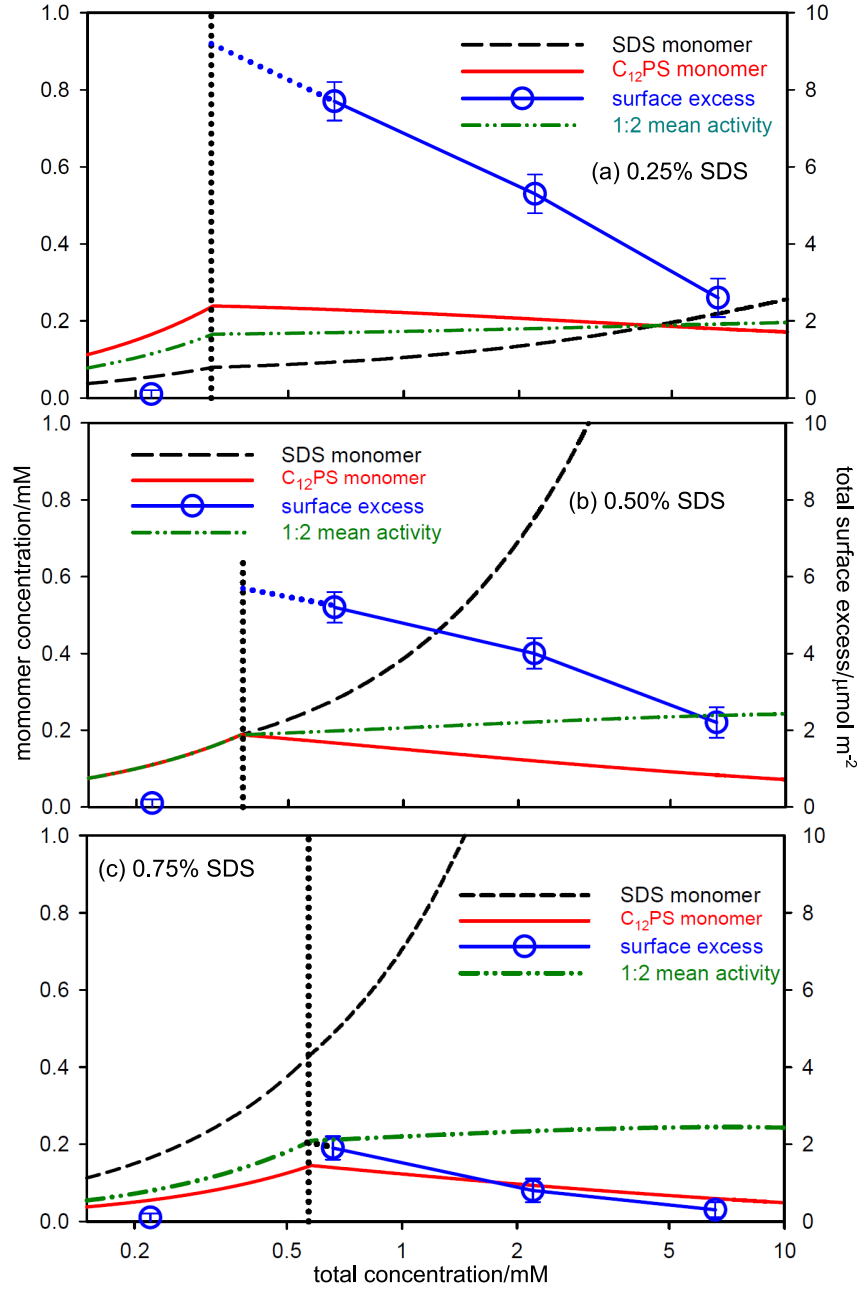


Figure 4: Total surface excesses adsorbed at the SiO₂-W interface as a function of total concentration of SDS-C₁₂PS at each of three different molar fractions of SDS, ϕ_{SDS} , of (a) 0.25, (b) 0.50 and (c) 0.75. The calculated mixed CMCs are shown as dotted lines and the experimental measurements are also extended to the CMC by dotted lines. Also shown are the calculated concentrations of the individual monomers of C₁₂PS (continuous red lines) and SDS (dashed black lines) from Ma et al.³¹ and the calculated mean concentration/activity (dashed-dotted lines) for a 1:2 SDS:C₁₂PS complex.

Table 2: Adsorbed amounts and compositions determined from fits to NR data from SDS-C₁₂PS (308 K) and SDS-C₁₂CB (313 K) mixtures adsorbed at the SiO₂-W interface. The observed mole fractions of SDS adsorbed at the A-W interface (from Ma et al. and Hines et al.) are also included for comparison. Italics indicate concentrations below the mixed CMC.

	x_{SDS} bulk	c mM	τ_1 $\pm 2 \text{ \AA}$	τ_2 $\pm 2 \text{ \AA}$	τ_3 $\pm 2 \text{ \AA}$	Γ $\mu\text{mol m}^{-2}$	x_{SDS} SiO ₂ -W ± 0.05	x_{SDS} A-W ± 0.03
C ₁₂ PS	<i>0.25</i>	<i>0.22</i>	-	-	-	<i><0.1</i>	-	<i>0.32</i>
	0.25	0.66	8	19	10	7.7 \pm 0.5	0.47	0.34
	0.25	2.2	7	17	9	5.3 \pm 0.5	0.41	0.35
	0.25	6.6	9	17	7	2.6 \pm 0.5	0.35	0.39
C ₁₂ PS	<i>0.50</i>	<i>0.22</i>	-	-	-	<i><0.1</i>	-	<i>0.32</i>
	0.50	0.66	10	19	6	5.2 \pm 0.4	0.42	0.40
	0.50	2.2	9	19	11	4.0 \pm 0.4	0.28	0.38
	0.50	6.6	6	17	8	2.2 \pm 0.4	0.20 \pm 0.08	0.41
C ₁₂ PS	<i>0.75</i>	<i>0.22</i>	-	-	-	<i><0.1</i>	-	<i>0.39</i>
	<i>0.75</i>	<i>0.66</i>	<i>7</i>	<i>21</i>	<i>7</i>	<i>1.9\pm0.3</i>	<i>0.33</i>	<i>0.40</i>
	0.75	2.2	7	15	4	0.8 \pm 0.3	0.21 \pm 0.08	0.42
	0.75	6.6	7	14	5	0.3 \pm 0.2	0.13 \pm 0.1	0.45
C ₁₂ CB	<i>0.25</i>	<i>0.074</i>	-	-	-	<i><0.1</i>	-	-
	<i>0.25</i>	<i>0.22</i>	<i>6</i>	<i>22</i>	<i>8</i>	<i>0.2\pm0.2</i>	<i>0.13\pm0.1</i>	<i>0.26^a</i>
	0.25	0.74	5	21	5	0.3 \pm 0.2	0.19 \pm 0.08	-
	0.25	2.22	7	19	7	0.8 \pm 0.3	0.24	-
C ₁₂ CB	<i>0.50</i>	<i>0.074</i>	-	-	-	<i><0.1</i>	-	-
	<i>0.50</i>	<i>0.22</i>	<i>5</i>	<i>20</i>	<i>7</i>	<i>0.2\pm0.2</i>	<i>0.17\pm0.08</i>	<i>0.32</i>
	0.50	0.74	9	19	7	0.5 \pm 0.2	0.24	-
	0.50	2.22	8	20	9	0.9 \pm 0.3	0.33	-
C ₁₂ CB	<i>0.75</i>	<i>0.074</i>	-	-	-	<i><0.1</i>	-	-
	<i>0.75</i>	<i>0.22</i>	<i>4</i>	<i>15</i>	<i>4</i>	<i>0.1\pm0.1</i>	<i>0.27</i>	<i>0.39^a</i>
	<i>0.75</i>	<i>0.74</i>	<i>5</i>	<i>17</i>	<i>8</i>	<i>0.6\pm0.2</i>	<i>0.39</i>	-
	0.75	2.22	4	17	4	2.9 \pm 0.4	0.40	-

concentration (c_{total}) for three SDS fractional concentrations (ϕ_{SDS}) as points joined by straight lines. There is a clear and strong maximum for each of the three values of ϕ_{SDS} . The coarse grid of the measurements does not locate the exact position of the maximum but there are reasons discussed below for supposing it occurs at the appropriate mixed CMC, as indicated in the figure. Comparison of the measurements in the figure with the adsorbed fractions of SDS in Table 2 shows that all the values of the measured fractional adsorption of SDS above the three maxima in Figure 4 *decrease* with an *increase* in either c_{total} or ϕ_{SDS} ,

Table 3: Adsorbed amounts and compositions determined from fits to NR data from C₁₂TAB/C₁₂PS (308 K) and C₁₂TAB/C₁₂CB (313 K) mixtures adsorbed at the SiO₂-W interface. The observed fractions of C₁₂TAB adsorbed at the A-W interface for C₁₂TAB-C₁₂PS mixtures are included for comparison.³¹ Italics indicate concentrations below the mixed CMC.

	$x_{C_{12}TAB}$ bulk	c mM	τ_1 $\pm 3\text{\AA}$	τ_2 $\pm 3\text{\AA}$	τ_3 $\pm 3\text{\AA}$	Γ μmol^{-2}	$x_{C_{12}TAB}$ (SiO ₂ -W) ± 0.1	$x_{C_{12}TAB}$ (A-W) (A-W) $\pm 0.03^a$
C ₁₂ PS	<i>0.25</i>	<i>0.22</i>	<i>7</i>	<i>14</i>	<i>6</i>	3.1 ± 0.4	0.61 ± 0.05	<i>0.27</i>
	<i>0.25</i>	<i>0.66</i>	<i>7</i>	<i>14</i>	<i>7</i>	4.5 ± 0.4	<i>0.65</i>	<i>0.23</i>
	0.25	2.2	7	13	6	5.0 ± 0.4	0.78	0.26
	0.25	6.6	8	12	8	4.9 ± 0.4	0.80	0.33
C ₁₂ PS	<i>0.50</i>	<i>0.22</i>	<i>6</i>	<i>12</i>	<i>6</i>	1.1 ± 0.3	<i>0.64</i>	<i>0.26</i>
	<i>0.50</i>	<i>0.66</i>	<i>6</i>	<i>11</i>	<i>8</i>	1.7 ± 0.3	<i>0.70</i>	<i>0.30</i>
	0.50	2.2	7	13	8	3.3 ± 0.4	0.86	0.36
	0.50	6.6	6	12	8	3.5 ± 0.4	0.87	0.39
C ₁₂ PS	<i>0.75</i>	<i>0.22</i>	<i>6</i>	<i>10</i>	<i>7</i>	1.0 ± 0.3	<i>0.62</i>	<i>0.33</i>
	<i>0.75</i>	<i>0.66</i>	<i>6</i>	<i>12</i>	<i>6</i>	2.9 ± 0.4	<i>0.69</i>	<i>0.33</i>
	<i>0.75</i>	<i>2.2</i>	<i>5</i>	<i>11</i>	<i>8</i>	3.2 ± 0.4	<i>0.69</i>	<i>0.33</i>
	0.75	6.6	6	13	6	3.8 ± 0.4	0.71	0.34
C ₁₂ CB	<i>0.25</i>	<i>0.22</i>	<i>7</i>	<i>19</i>	<i>8</i>	< 0.1	<i>0.05</i>	-
	<i>0.25</i>	<i>0.74</i>	<i>6</i>	<i>19</i>	<i>6</i>	0.2 ± 0.2	<i>0.16</i>	-
	0.25	2.22	6	19	6	0.3 ± 0.2	0.31	-
	0.25	7.4	8	17	7	1.8 ± 0.4	0.38	-
C ₁₂ CB	<i>0.50</i>	<i>0.22</i>	<i>9</i>	<i>18</i>	<i>6</i>	0.5 ± 0.3	<i>0.11</i>	-
	<i>0.50</i>	<i>0.74</i>	<i>8</i>	<i>19</i>	<i>9</i>	0.6 ± 0.3	<i>0.21</i>	-
	<i>0.50</i>	<i>2.22</i>	<i>8</i>	<i>15</i>	<i>7</i>	3.7 ± 0.4	<i>0.28</i>	-
	0.50	7.4	6	13	8	3.6 ± 0.4	0.39	-
C ₁₂ CB	<i>0.75</i>	<i>0.22</i>	<i>5</i>	<i>17</i>	<i>7</i>	< 0.1	<i>0.06</i>	-
	<i>0.75</i>	<i>0.74</i>	<i>6</i>	<i>19</i>	<i>8</i>	0.3 ± 0.2	<i>0.16</i>	-
	<i>0.75</i>	<i>2.22</i>	<i>5</i>	<i>18</i>	<i>8</i>	0.3 ± 0.2	<i>0.18</i>	-
	0.75	7.4	5	15	5	1.1 ± 0.3	0.33	-

whereas the corresponding measurements at the A-W interface do the opposite, i.e. they *increase* with either c_{total} or ϕ_{SDS} . In that adsorption of a species should increase with its activity, the A-W behaviour is in line with thermodynamic expectations but the SiO₂-W behaviour is apparently not.

Ma et al. used the extension of the pseudophase approximation (PPA) above the CMC, outlined by Rubingh,³⁶ to calculate both the state of micellar dissociation and the fractional adsorption of each component at the A-W interface. They used an expanded excess free

energy of interaction including terms up to cubic, i.e.

$$\Delta G_E = RTx_1x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots] \quad (1)$$

where x_i are the mole fractions and B, C and D are the coefficients that determine G_E , which are different for micelle and surface. The use of terms up to cubic avoids the usual assumption that G_E is symmetrical with respect to composition (the regular solution approximation). For SDS-C₁₂PS the minimum G_E for micellization was found to occur at a value of $\phi_{SDS} = 0.23 \pm 0.05$ and the equivalent minimum for adsorption at the A-W interface was found to occur at $\phi_{SDS} = 0.38 \pm 0.05$. Figure 4 shows the variation of the monomer concentrations resulting from this calculation (continuous red line for C₁₂PS and black dashed line for SDS). At all three ϕ_{SDS} the concentration of C₁₂PS shows the expected break in slope at the mixed CMC and then decreases with c_{total} with a decline that is greater as ϕ_{SDS} increases. The SDS concentration, however, increases with c_{total} , even at the lowest $\phi_{SDS} = 0.25$, and the increase becomes greater with increasing ϕ_{SDS} . There is thus extensive fractionation of the C₁₂PS into micelles, potentially reducing the surface activity of C₁₂PS, but the greatly increasing SDS concentration leads to a compensating increase in the surface activity of SDS. Paria and Khilar have presented PPA calculations that suggest that this fractionation of the more surface active component often leads to a maximum in the adsorption.¹³ However, in their calculations they assume that the sum of the two monomer concentrations above the mixed CMC equals the CMC. This is not the case in either the analysis including activity coefficients given by Rubingh³⁶ or even in the case of ideal mixing (see an example Figure 4 of Clint³⁷). In Figure 4 the sum of the SDS and C₁₂PS monomer concentrations clearly increases well above the mixed CMC as c_{total} increases. The effect of the more rapidly increasing concentration of the less surface active component is to offset significantly its lower surface activity. This can be seen in the SDS-C₁₂PS system at the A-W interface where the adsorbed fraction of SDS at the A-W interface increases with c_{total} exactly as

expected from the monomer concentrations calculated from the PPA at all three ϕ_{SDS} (last column in Table 2³¹). Paria and Khilar’s assumption is correct only at the mixed CMC. If the correct calculation is applied a maximum of the type suggested by Paria and Khilar remains a possibility but it is much less probable than suggested by their calculations.

The PPA strictly applies only to undissociated species and it is therefore surprising that it accounts so well for the pattern of adsorption at the A-W interface above the CMC. This may be because the neutrality requirement at the A-W interface ensures that matching amounts of the DS^- ion and its Na^+ counterion are adsorbed and hence adsorption of the SDS component is controlled by the mean activity (concentration) of SDS. A further important factor behind the successful application of the PPA to the calculation of composition at the A-W interface and in micelles is that the surface activities and micellization of surfactants are broadly comparable because they are all mainly driven by similar hydrophobic chains reducing their exposure to water. The effects of changes of composition on the interaction of the components can then have a significant effect against a background of comparable overall adsorption or aggregation determined only by the hydrophobicity. This allows the composition of a mixed layer to be successfully handled with the PPA, although the model does not extend to the calculation of the total adsorption. In the SDS- $C_{12}PS$ system the minimum free energy of mixing occurs at $x_{SDS} = 0.38 \pm 0.05$ and has a depth of $-2.8 \pm 0.3RT$. It would be surprising if such a large value of the excess free energy of mixing did not bring about some increase in the total adsorption near the free energy minimum. Ma et al. did indeed observe just such a strong synergy leading to an enhanced total adsorption nearly 50% higher than expected from the two limiting adsorptions at the CMC. Comparison of the excess adsorption with the measured surface composition showed that the synergy is a maximum at an SDS fraction of 0.4 with a narrow distribution from 0.3 to 0.45, i.e. it coincides with the minimum free energy in the PPA calculation. Although this synergistic adsorption occurs with a narrow range of surface stoichiometry, the enhanced adsorption will occur over a wider range of solution stoichiometry because it depends on the mean activity

of the solution components that are adsorbed.

It should be possible to describe the adsorption of a particular stoichiometry at the SiO₂-W interface in terms of the mean activity of the adsorbed “complex” incorporated into an adsorption isotherm, i.e. adsorption should be a function of the mean activity of the two components that are adsorbed. The range of observed compositions adsorbed at the SiO₂-W interface is from a mole fraction of SDS, x_{SDS} , of about 0.15 to 0.45 (Table 2, penultimate column). Figure 4 includes the calculated mean activity for an adsorbed complex of stoichiometry 1:2 SDS:C₁₂PS, i.e. $x_{SDS} \approx 0.33$. This was chosen as an illustration because it is at about the midpoint of the range of observed surface compositions. The calculation is based on the PPA parameters used to calculate the solution monomer concentrations and described above. The calculated mean activity for this 1:2 composition, $([SDS][C_{12}PS]^2)^{1/3}$, very slightly increases with c_{total} over the whole concentration range above the mixed CMC because the large increase of the SDS monomer concentration above the mixed CMC dominates the mean activity while x_{SDS} is above about 1/3. However, the total adsorption shows a sharp decrease for all three compositions studied, which requires the mean activity to decrease sharply, and this, in turn, requires a substantial decrease in x_{SDS} , preferably to less than about 1/6. This has the effect of giving much more weight to the free C₁₂PS concentration, which then declines with increasing c_{total} .

SDS is known not to adsorb at all at the negative SiO₂-W interface and, as shown in Table 1, the adsorption of C₁₂PS on its own is weak. That the adsorption of the mixture is much higher than for C₁₂PS on its own therefore suggests that it is the synergy between the two surfactants that mainly drives the adsorption. The highest observed value of x_{SDS} is 0.45 and this is accompanied by the highest observed total adsorption, which suggests that the cut-off may be at an even higher value of x_{SDS} . Thus, over the range of x_{SDS} from 0 to, say 0.6, the strength of the adsorption can be expected to reach a peak somewhere between the two values, while being approximately zero at each end of the range. Adsorption could then, in principle, be modelled by using the solution mean activity of the components that

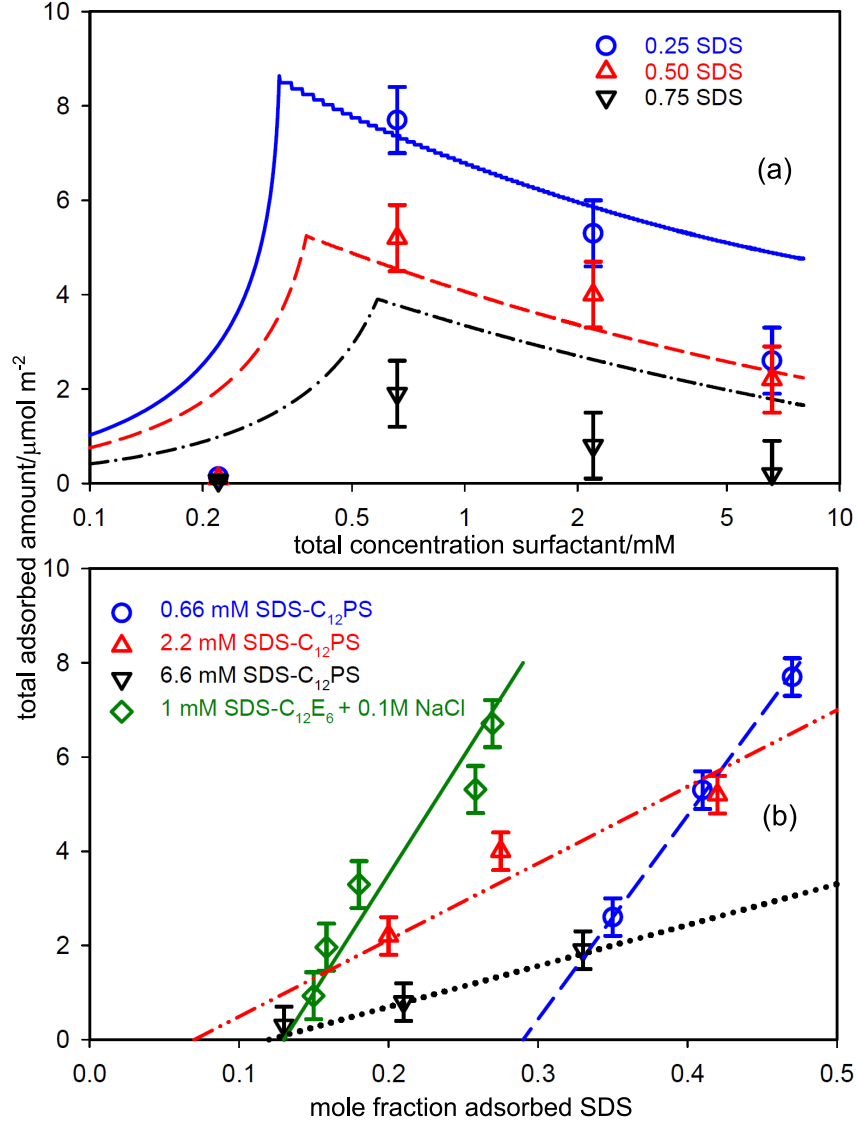


Figure 5: (a) Calculated total adsorption of SDS-C₁₂PS at the SiO₂-W interface as a function of total concentration of solutions at three SDS mole fractions, 0.25, 0.50 and 0.75. The fitted parameters are a stoichiometry of 0.15 mole fraction of SDS in the *adsorbed* complex, and Langmuir and Frumkin parameters (see Eqn (2)) of 0.7 and 1.95 respectively. (b) Total adsorption of SDS-C₁₂PS and of SDS-C₁₂E₆ in 0.1M NaCl as a function of the adsorbed mole fraction of SDS. Each linear plot is at a fixed total concentration in the solution and the individual points correspond to different SDS mole fractions of SDS relative to total surfactant. The data for SDS-C₁₂E₆ are from Penfold et al.²⁸ Note that the data in (b) are plotted in the direction of *decreasing* total surfactant concentration.

make up the adsorbed complex in combination with a model isotherm, which would have different parameters at each value of x_{SDS} . From the discussion above the isotherm obviously must be one that includes some cooperativity, such as the Frumkin isotherm, which can be written as^{14,38}

$$\lambda a_{mean} = \frac{\theta}{1 - \theta} \exp(-2\chi\theta) \quad (2)$$

where λ is the Langmuir parameter, χ is the Frumkin parameter, and θ the coverage. When $\chi = 0$ the equation reduces to the Langmuir isotherm and positive values of χ give a strongly cooperative shape to the isotherm. The mean activity, a_{mean} , is defined by $[SDS]^{x_{SDS}}[C_{12}PS]^{1-x_{SDS}}$ where the concentrations are those of the monomers in solution and are given by the PPA calculation described above. The difficulty in applying such an equation to the data here is that λ and χ are likely to vary with x_{SDS} , as discussed above. Nevertheless, this relatively simple approach with a single values for λ and χ leads to an overall adsorption pattern semiquantitatively similar to that observed, as shown in Figure 5(a). It is also clear from this simple model that relatively small variations of the values of λ and χ with ϕ_{SDS} could easily be used to obtain better individual fits. We have not done this because the surprising feature of the fit is that it can only be achieved by using a very low value of x_{SDS} less than 0.15, much lower than the observed values, which are mostly significantly higher. It is then not at all clear what would be physically reasonable to alter.

There are several possible reasons why this simple model might fail. The first has already been identified, which is that the adsorption isotherm may change significantly with the stoichiometry, x_{SDS} . A second is that if any adsorption of the DS^- counterion occurs this will both change the way the PPA is applied, because of partial micellar ionization,¹⁴ and change the mean activity that should be used in the analysis. We consider this unlikely because the similar charge of the surface makes adsorption of the DS^- ion unfavourable and hence improbable. The third is that the SDS may not be distributed evenly between the two halves of the bilayer. The present experiments did not have the sensitivity to identify this, but fractionation between inner and outer layers was found to be significant in the

closely related SDS-C₁₂E₆ system on silica.²⁸ To emphasize the connection between the two systems Figure 5(b) shows the change in total adsorption of SDS-C₁₂PS with x_{SDS} for the three total concentrations above the CMC used in Figure 4(a), i.e. each plot consists of three measurements at the same total concentration but at the three overall SDS fractions of 0.25, 0.5 and 0.75. The observations are the same as in Figure 4 but when plotted against x_{SDS} at constant total concentration they become three linear variations. The total adsorption is largest for the largest value of x_{SDS} and the increase is also steeper for sets with larger values of x_{SDS} . For all but one of these measurements the experimental value of x_{SDS} is significantly higher than the value of 0.15 used in modelling the data in Figure 5(a). A similar pattern of behaviour is observed for SDS-C₁₂E₆ in 0.1M NaCl²⁸ and the comparable plot for various overall SDS fractions at a constant concentration of 1 mM is included in Figure 5(b). Again, the total adsorption depends linearly on x_{SDS} and changes in the same direction as for SDS-C₁₂PS. Like SDS-C₁₂PS the total adsorption also decreases with increasing ϕ_{SDS} . The significance of the close similarity of the SDS-C₁₂E₆ and SDS-C₁₂PS behaviour is that the resolution of the SDS-C₁₂E₆ measurements with respect to the location of the SDS in the adsorbed layer was higher. This was partly because the adsorbed layer was thicker and partly because a better range of isotopic species could be used for the SDS-C₁₂E₆ measurements because the head group signal is larger. The results show that the fractional SDS composition of the layer adjacent to the surface is only 0.3 - 0.4 times that of the outer layer. This suggests the possibility that adsorption can be modelled in terms of a low inner layer fractional adsorption, which follows the model used for the calculated adsorption in Figure 5(a), and a larger outer layer fractional adsorption, in which more SDS can be adsorbed because of the reduced repulsion and in which the cooperativity of the adsorption of the two species is better utilized, i.e. closer to the optimum value of $x_{SDS} \approx 0.4$ observed at the A-W interface. Clearly, no outer layer adsorption can occur unless there is an inner layer and the occurrence of adsorption may then be controlled to a significant extent by the inner layer isotherm. There are therefore good reasons why adsorption at the inner and outer

layers of these two systems should follow different isotherms, although there must also be some interaction between the two, which would make modelling very difficult. However, the inner layer would be expected to dominate the onset of adsorption and hence to depend more strongly on the mean activity of the dominant surface active species, here either C₁₂PS or C₁₂E₆. A quantitative explanation of the adsorption in terms of the different characteristics of inner and outer layer could in principle also incorporate the possibility that the isotherm itself changes as a function of coverage.

An alternative approach to the adsorption is to consider the adsorbed layer essentially as adsorbed micelles, and this is close to models such as hemimicelle formation or critical surface aggregation. The micelle composition in the SDS-C₁₂PS system can be obtained using the PPA calculation and, over the range of total concentration of the measurements in Figure 4, the micellar molar fraction of SDS calculated by the PPA using the parameters of Ma et al. is respectively 0.21-0.22, 0.22-0.29 and 0.25-0.33 for values of ϕ_{SDS} of 0.25, 0.50 and 0.75. The reason that the molar fraction of SDS remains at these low values, even when the total fraction of SDS is much higher, is that the minimum free energy of mixing in the micelle is at $x_{SDS} = 0.23$. At $\phi_{SDS} = 0.25$ the measured x_{SDS} values in the surface layer are 0.33, 0.41 and 0.47 while the micellar x_{SDS} only changes from 0.21 to 0.20, i.e. there is little resemblance between the layer and micellar compositions either in their magnitude or in the way they change with overall composition.

Another potential cause of an adsorption maximum, especially for SDS, is the presence of an impurity. There are two commonly occurring potential sources of impurity in SDS, dodecanol originating from hydrolysis of the SDS, and traces of ions of higher valency, particularly Ca²⁺. The effect of dodecanol has been examined by many authors, e.g.³⁹⁻⁴¹ Dodecanol is highly surface active, has a low solubility, and does not micellize on its own. It adsorbs strongly as it approaches its solubility limit and, even at low levels of fractional impurity, it may approach this limit before the SDS reaches its CMC, in which case it preferentially adsorbs at the surface. Dodecanol is strongly solubilized into the SDS micelles

above the CMC. The overall effect is then a minimum in the surface tension, which is just below the CMC for low levels of impurity, and a maximum in the adsorption of dodecanol. Although the effect has been mainly studied at the A-W interface, the parallel effect has been observed at the solid-aqueous interface.⁴² For a given level of dodecanol as impurity, the surface tension anomaly can be greatly reduced by the addition of electrolyte because this lowers the CMC of the SDS relative to the solubility limit of dodecanol. The effect of mixing SDS with C₁₂PS also decreases the CMC but is a much larger effect because it brings about a greater reduction in the CMC while having no effect on the solubility of dodecanol. Thus, the presence of dodecanol is unlikely to affect adsorption in the SDS-C₁₂PS-SiO₂-W system. A further feature that is inconsistent with a dodecanol type of impurity is the decrease in the adsorption peak with *increasing* SDS fraction, the opposite of what would be expected from the explanation above. Other possible impurities are Ca²⁺ or other divalent cations. At the A-W interface small amounts of Ca²⁺ effectively create the low solubility Ca(DS)₂ salt and it affects the surface tension in a similar way to dodecanol SDS.⁴³ This is unlikely to be significant for the same reasons as dodecanol. However, small amounts of cations can have significant effects on the adsorption of anionic surfactants on silica and mica by reducing the charge repulsion, some examples of which have already been given in the introduction. Such examples have so far needed a higher level of added divalent ion than just a trace, and the strongly enhanced surface activity of the mixtures studied here should suppress any such effect.

The unusual features of the adsorption of SDS-C₁₂PS on SiO₂ result primarily from the combination of the unusually strong cooperative interaction between the two surfactants with the repulsive interaction of SDS with the SiO₂ surface. Although C₁₂TAB also interacts attractively with C₁₂PS with minima in the free energies of mixing at the same compositions as for SDS-C₁₂PS, the depths of the two minima are only 20-25% of the value for SDS-C₁₂PS, so there is little cooperativity. In addition, C₁₂TAB interacts strongly and attractively with SiO₂ and forms a complete bilayer at about 4 mM (1/3 of its CMC).⁴⁴ The effect

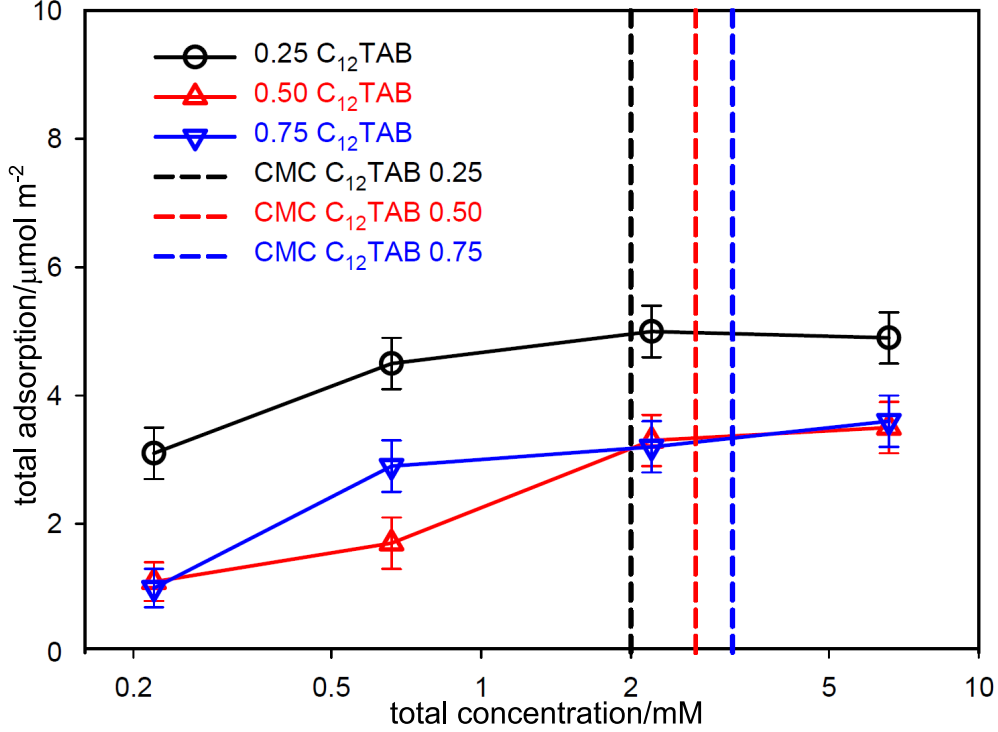


Figure 6: Adsorption isotherms of C₁₂TAB-C₁₂PS mixtures at the SiO₂-W interface as a function of total concentration at different total compositions.

of these differences in the pattern of adsorption is dramatic, as can be seen by comparing the total adsorption isotherms for C₁₂TAB-C₁₂PS in Figure 6 with those for SDS-C₁₂PS in Figures 4(a), (b) and (c), measured at identical concentrations and compositions. The strong cooperativity in SDS-C₁₂PS greatly increases the adsorption of either component from its value at the bare surface (SDS does not adsorb at all) and leads to a high total adsorption with a composition similar to that at the A-W interface. For the C₁₂TAB-C₁₂PS mixture, adsorption is dominated by the strong electrostatic interaction of C₁₂TAB with the surface, which makes it more competitive with the C₁₂PS at the SiO₂-W interface than at the A-W interface. Thus, the fraction of adsorbed C₁₂TAB is much higher than at the A-W interface, 0.61-0.80 at the SiO₂-W interface compared with 0.27-0.33 at the A-W interface. The only evidence of any attractive interaction between the two surfactants is that total adsorption is highest at the lowest value of $\phi_{CTAB} = 0.25$, which corresponds to the composition where the free energy of mixing is at its highest.

In both micelles and at the A-W interface the interaction of SDS with the carboxy-betaine $C_{12}CB$ closely parallels its interaction with $C_{12}PS$ apart from a slight shift in the position of the minimum free energy of adsorption.³¹ However, as shown in Table 1, $C_{12}CB$ on its own adsorbs much more strongly at the SiO_2 -W interface than $C_{12}PS$, but the strong cooperative adsorption for $C_{12}CB$ on its own is completely destroyed by the presence of SDS. We examine below the possible differences in surface structure that could cause such an effect. However, from the point of view of understanding the unusual maximum in the adsorption of SDS- $C_{12}PS$ at the SiO_2 -W interface it is significant that the pattern of solution activities of the monomers in the two systems are almost identical. This shows very clearly that preferential fractionation of the zwitterionic into micelles is the same for the two systems and hence can *not* be the main cause of the maximum. The $C_{12}TAB$ - $C_{12}CB$ interaction is again much weaker than for SDS- $C_{12}CB$ so that there is no cooperative adsorption. Compared with $C_{12}TAB$ - $C_{12}PS$ the stronger adsorption of $C_{12}CB$ now competes more strongly with that of $C_{12}TAB$ with the result that the total adsorption of the $C_{12}TAB$ - $C_{12}CB$ mixture is lower even than that shown for $C_{12}TAB$ - $C_{12}PS$ in Figure 6 and also much lower than that for $C_{12}CB$ on its own. We now examine the structural features that might explain some of these features.

The schematic diagrams shown earlier in Figure 2 suggest a possible reason for cooperativity in one case but not the other. Thus, Figure 2(a) and (d) have already been used to argue that the configuration of an isolated $C_{12}PS$ makes it more difficult for adjacent $C_{12}PS$ molecules to pack together than for $C_{12}CB$. However, the addition of SDS, whose head group will interact preferentially with the quaternary ammonium on the zwitterionic, may be strong enough to force the spacer group to become more fully extended as shown in Figure 2(e). This structure would greatly improve the packing of the alkyl chains and hence promote cooperativity and self-assembly, although this might be offset by the layer presenting a negative charge to the surface. However, as discussed above the effect of the negative charge may not interfere with the cooperativity, as is strongly indicated by the

whole pattern of adsorption in the SDS- C_{12} PS system. A possible configuration for the C_{12} TAB- C_{12} PS mixture, where the stoichiometry drawn reflects the stronger interaction of C_{12} TAB with the surface, is shown in Figure 2(f). This has a partially bent spacer group, intermediate between those of (d) and (e), which allows some interaction between the sulfonate and the C_{12} TAB head groups, while maintaining a reasonably close spacing of the alkyl chains. In this way the cationic groups could ensure adsorption, although overall the adsorption would be less strong and less cooperative than for SDS- C_{12} PS. The failure of C_{12} CB to adsorb cooperatively with either SDS or C_{12} TAB is less easy to understand. The short spacer of the zwitterionic is such that the alkyl chains should always be able to pack well, as indicated in Figure 2(a), and the interaction of SDS with the cationic group is of similar strength for the C_{12} PS and C_{12} CB.³¹ This suggests that it is a weakening of the attachment to the surface that causes desorption and this is what would be expected from Figure 2(b), where the sulfate group of the SDS is much closer to the surface than for the mixture with C_{12} PS (Figure 2(e)). Figures 2(c) and 2(f) have the relative positions of the two cationic groups reversed. The reason for this is that the close proximity of the anionic surface to the carboxyl group will tend to make it revert to being a weaker acid (the natural pK of a carboxyl group is about 4.5 but with the single CH_2 spacer separating it from the quaternary ammonium the pK drops to 2.4⁴⁵). Harvigsson et al. found that lowering the pH reduces the adsorption of carboxybetaine surfactants and it is therefore possible that it is a combination of the close approach of the carboxy group to the surface and a reduction in the pK_a by the anionic surface that destabilizes the adsorption.

Conclusions

The adsorption of each of the two zwitterionic surfactants, C_{12} PS and C_{12} CB, at the SiO_2 -W interface is surprisingly different. The C_{12} CB has only a single CH_2 spacer between the charged carboxy and quaternary ammonium charged groups whereas the C_{12} PS has a $(CH_2)_3$ spacer. The C_{12} CB is therefore able to pack more efficiently and more cooperatively into

a bilayer at this surface, whereas the propane sulfonate forms only a fragmented bilayer of significantly lower coverage.

SDS interacts almost identically strongly with $C_{12}PS$ and $C_{12}CB$ in micelles and at the A-W interface and it does not on its own adsorb at the SiO_2 -W interface. However, the pattern of adsorption of SDS mixtures with each of the two zwitterionics at the SiO_2 -W interface is totally different. In the one case, SDS- $C_{12}CB$, the addition of SDS disrupts the cooperative adsorption of $C_{12}CB$ at the SiO_2 -W interface with the result that the total adsorption drops to a low value under most conditions. However, for SDS- $C_{12}PS$, where $C_{12}PS$ on its own only adsorbs weakly, strong cooperative adsorption is observed over a limited range of concentration and composition. Since the underlying monomer concentrations in the SDS- $C_{12}CB$ and SDS- $C_{12}PS$ systems follow a more or less identical pattern, the adsorption maximum in SDS- $C_{12}PS$ cannot be attributed to fractionation of $C_{12}PS$, although fractionation does occur for both systems. Instead, we propose that the strong cooperative interaction leads to an strongly adsorbed inner layer, i.e. next to the silica, containing a relatively low fraction of SDS and an outer layer richer in SDS that completes the bilayer. Since the latter cannot adsorb without the former, overall adsorption will be controlled by the pattern of adsorption of the inner layer. A semi-quantitative model of the adsorption into the inner layer reproduces the adsorption maximum and the pattern of decay of the adsorption as the total concentration of surfactant is increased. The NR experiments used here were not sufficiently sensitive to observe SDS fractionation between inner and outer layers in the SDS- $C_{12}PS$ system, but such segregation has been observed in the closely related SDS- $C_{12}E_6$ system in 0.1 NaCl, which also exhibits a similar adsorption anomaly.

In the comparable $C_{12}TAB$ - $C_{12}PS$ system the cooperativity is about 1/5 of the strength of that for SDS- $C_{12}PS$ and, unlike SDS, $C_{12}TAB$ adsorbs well on silica. The adsorption at the SiO_2 -W interface now follows a completely different pattern from that of SDS- $C_{12}PS$ and is dominated by the stronger adsorption of $C_{12}TAB$ and by the slightly greater intrinsic surface activity of $C_{12}PS$ with little evidence of cooperativity. Finally, in the $C_{12}TAB$ - $C_{12}CB$

system the strong adsorption of each component on its own on silica is almost completely lost. It seems that either steric constraints concerning the head group packing and/or the enhancement of the interaction of the anionic sulfonate with the surface lead to an increased nett repulsion of the mixed layer from the surface.

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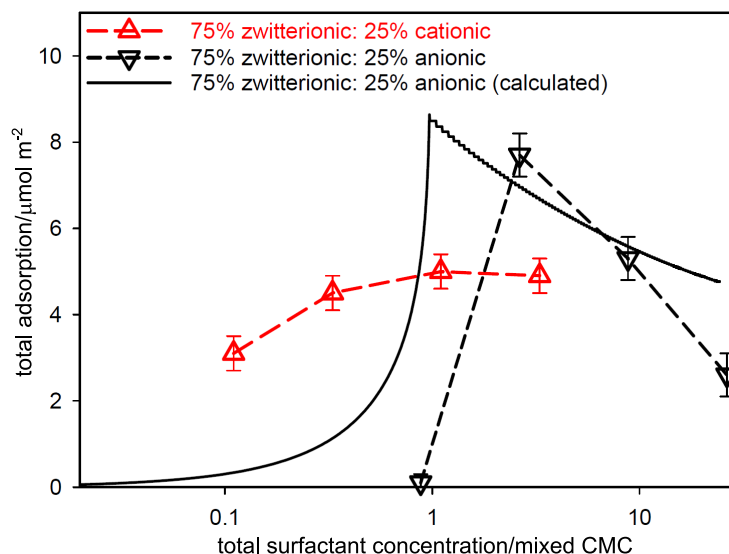


Figure 7: TOC.