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Surfactant self-assembly structures and multilayer formation at the solid-solution interface induces by electrolyte, polymers and proteins.

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ABSTRACT

Recent developments in the study of the formation of self-assembled surfactant structures and multilayers at the solid-solution interface are presented. It covers a wide range of phenomena, but in this review the main focus is on the surface structures formed from dilute solution in the presence of electrolyte and in more concentrated solutions. Their formation under those conditions are set in the wider context of the more extensive observations of their occurrence in more complex polymer-surfactant mixtures. Although the sequential adsorption methods using layer-by-layer approaches are more well established for polyelectrolytes and their associated mixtures, the main emphasis is on the self-assembly. The opportunities to manipulate wetting properties and to generate enhanced wetting characteristics are discussed. The potential applications, modifying wetting behaviour, efficient near surface reservoir for enhanced and prolonged delivery of active components, and for the development of a range of smart functionalised surfaces are highlighted.

INTRODUCTION

The adsorption of surfactants at interfaces, air-solution, solid-solution and liquid-liquid, plays a central role in a wide range of technological, industrial and domestic applications; in detergency, cosmetics, pharmaceuticals, agrochemicals, enhanced oil recovery, mineral flotation, corrosion control, formation of solid and fluid dispersions and in foods and drinks. Surfactant adsorption at fluid interfaces, air-solution and liquid-liquid, is usually in the form of a monolayer, whereas the form of adsorption at the liquid-solid interface depends upon the nature of the solid surface. At hydrophobic surfaces it is also a monolayer, and at a hydrophilic surface it self-assembles to form predominantly bilayer structures. Recent reviews (1, 2) highlight the range of studies reported and the variety of techniques used to probe the adsorption. In this review there is a particular focus on the use of neutron reflectivity to probe surfactant adsorption at the solid-solution interface. It is now well-established that neutron reflectivity, NR, provides unique opportunities to probe the adsorption and structure of surfactants and mixed surfactants at the air-solution (3) and solid-solution (4, 5) interfaces.

This review considers more complex adsorption regimes, and the focus is specifically on the adsorption of self-assembled structures and multilayers at the solid-solution interface induced by increased concentration, or the addition of electrolyte, or polymer. Although indirectly inferred in some studies (6, 7) at the air-solution interface and observed in lung surfactants (8-10), it was the application of neutron reflectivity that provided the direct evidence for the existence of these more complex and extended surface structures. Recent reviews (11, 12) have given a comprehensive summary of their occurrence and the major factors promoting their formation at the air-solution interface. In particular at the air-solution interface (11) it was shown how for a range of anionic surfactants the addition of multivalent counterions in dilute solution resulted in the transition from monolayer adsorption, S_0 , to a series of layered surface structures, comprising a finite number of bilayers adsorbed beneath the initial monolayer, denoted as S_1 , S_2 , etc, to S_n which indicates a more extended multilayer structure. It was shown in some more recent studies how the evolution of these surface structures is affected by the surfactant structure, counterion type and surfactant / counterion concentrations; see, for example, the recent studies on the methyl ester sulfonate surfactants (13, 14). The addition of multivalent counterions results in a strong counterion binding

between neighbouring surfactant molecules, which significantly reduces the preferred curvature, and provides bridging across adjacent layers. These binding mechanisms are predominantly responsible for the attractive interaction required for the surface layering to occur. At higher surfactant concentrations the adsorption from bulk solution of a space filling lamellar phase, $L_{\alpha}(c)$ or $L_{\alpha}(sf)$, or a swollen lamellar phase, $L_{\alpha}(sw)$, is observed (11), and surface layering in a variety of polymer / surfactant mixtures has been reported (15, 16). Alternatively layer-by-layer, L-by-L, deposition and Langmuir-Blodgett, LB, or Langmuir-Schaeffer, LS, techniques (17) have been extensively used to sequentially construct more complex layered surface structures, using a combination of surfactants, polyelectrolytes and proteins. In this review the extent to which all these surface structures exist at the solid-solution interface is explored.

At the solid-solution interface the applications and potential applications of these extended surface structures have far reaching implications. They provide the opportunity for enhanced and prolonged delivery of active ingredients to surfaces, such as perfumes (18, 19). Their formation is often accompanied by extreme and persistent wetting properties, and this provides the opportunity to manipulate and tailor wetting behaviour (20, 21). Indeed there is an ability and flexibility to generate a variety of functionalised surfaces with applications in detergency, conditioning, corrosion inhibition, encapsulation, enhanced oil recovery, pharmaceuticals, agrochemicals, and food/drink formulations. In this respect the layer-by-layer methods have received more attention than the self-assembly routes to layered structures, but the latter offers a potentially more facile route.

SURFACE SELF-ASSEMBLY AND ORDERING FROM CONCENTRATED SOLUTION

In concentrated solution a range of different surface structures have been reported at different solid surfaces and for a range of surfactants, and some of those key observations are reviewed here.

Amongst the early studies was the work of Hamilton et al (22) and Gerstenberg et al (23, 24). Using grazing incidence small angle neutron scattering, GISANS, Hamilton et al (22) demonstrated the shear induced surface alignment of the extended rod-like micelles of cetyltrimethylammonium 3, 5 dichlorobenzoate, to form a highly ordered hexagonal array

adjacent to a hydrophilic quartz surface. Gerstenberg et al (23, 24) used neutron reflectivity to show how the triblock copolymer, Pluronic P85, micelles formed ordered layers adjacent to a hydrophilic quartz surface, with a structure which was different to the associated bulk BCC crystalline phase. The behaviour was modelled as the ordering of hard spheres against a structure less hard wall, resulting predominantly from the interaction of the polyethylene oxide chains on the outside of the micelles with the hydrophilic solid surface. Wolff et al (25, 26) used GISANS to probe in more detail the interfacial ordering of a range of pluronic micelles adjacent to both hydrophilic and hydrophobic solid surfaces. The ordered structures formed, which were cubic, hexagonal, or with no preferred orientation, depended upon the nature of the solid surface and the pluronic structure.

The integrity of the bulk phase adjacent to a solid surface is not always ensured, and the relationship between a bulk self-assembled phase and the surface adsorption was explored by Valdeperas et al (27). They investigated a complex system, which has applications in drug delivery and encapsulation, of sponge-like nanoparticles formed from a mixture of mono and di-glycerides and stabilised by a polymeric nonionic surfactant, polysorbate P80. The core-shell structure of the nanoparticles, with a P80 rich shell, was established using small angle neutron scattering, and their adsorption at a hydrophilic silica surface was probed using neutron reflectivity and QCM. The results showed that the nanoparticles disassemble at the interface to form a relatively thick lipid layer, due to the preferential interaction between the P80 head group and the silica surface.

Other non-lamellar surface structures were reported by Nylander et al (28). Grazing incidence neutron spin echo, specular and off-specular neutron reflectivity were used to study the structure and dynamics of the surface nanostructure formed from a mixture of soy phosphatidylcholine and glycerol dioleate. Both cubic and hexagonal phases were identified at the surface. The cubic phase was found to be more rigid and suppressed any surface fluctuations; whereas the hexagonal phase exhibited fluctuations with a spectrum which was modified by the proximity of the rigid interface. In a related study Nouhi et al (29) used grazing incidence SANS to probe the organisation of colloidal particles, charge stabilise polystyrene latex, in the region adjacent to sapphire and silica solid surfaces. In that case the ordered arrays observed showed powder-like patterns with no preferred orientation.

The adsorption of extended multilayer, or lamellar, surfactant structures at solid surfaces was reported by Li et al (30) and Helsing et al (31) for the di-alkyl chain anionic surfactant, Aerosol-OT, at both anionic silica and cationic sapphire surfaces. The occurrence of a series of sharp Bragg peaks is indicative of a highly ordered and extended lamellar structure at the interface. The Bragg spacing corresponds to a relatively large bilayer spacing, which varies from ~ 100 to ~ 200 Å, consistent with a surface $L_{\alpha}(sw)$ or $L_{\alpha}(sf)$ surface lamellar structure. An example is illustrated in figure 1 for 2 wt% AOT at the sapphire / D_2O interface.

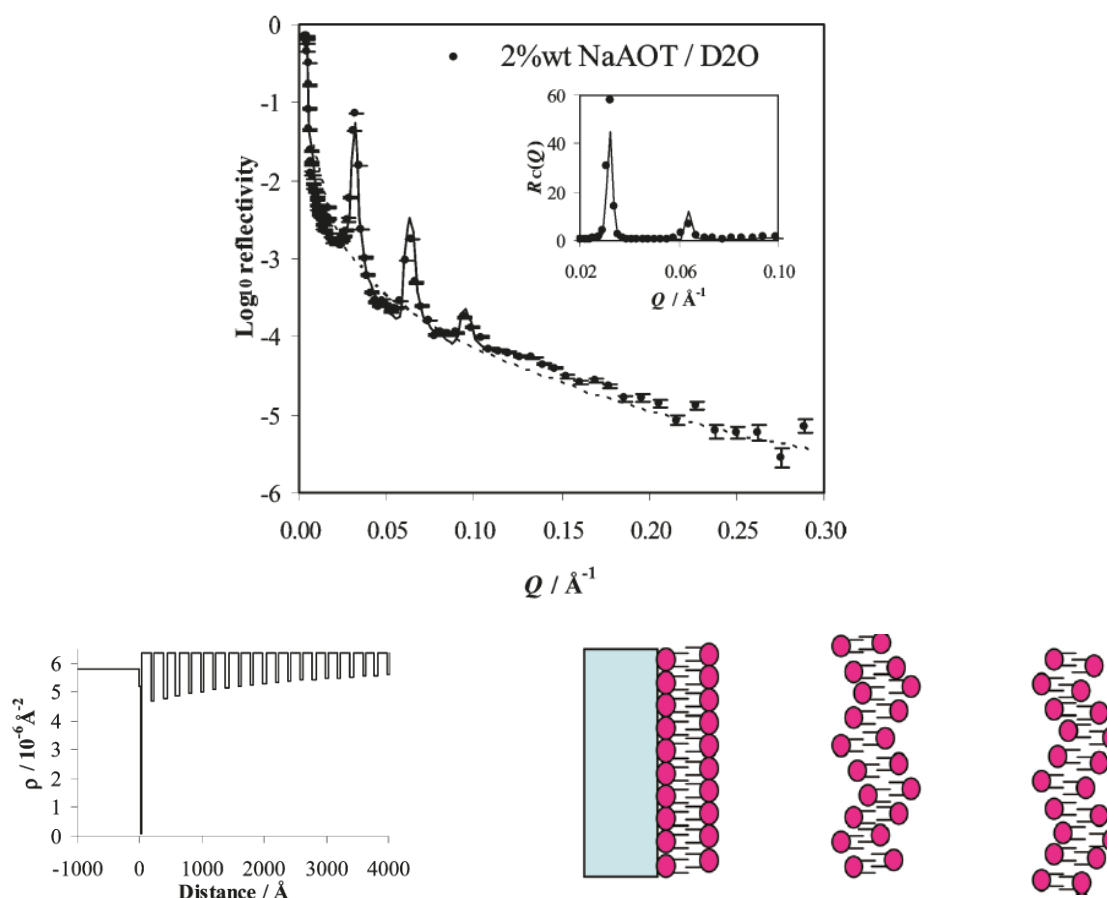


Figure 1. Neutron reflectivity and surface structure for 2 wt% AOT at the sapphire / D_2O interface; reproduced from reference 31.

At both interfaces the lamellar structure is highly sensitive to temperature, which results in changes in bilayer thickness and the spatial extent of layered structure at the interface. The similarity in the surface structure for both surfaces is consistent with an attractive force

associated with the self-assembly which is independent of the chemical nature of the surface. The sensitivity of the attractive force was demonstrated by Li et al (30) who showed that added electrolyte disrupted the surface lamellar phase formation but not the bulk phase behaviour. The highly ordered nature of this surface lamellar phase was illustrated by the observation of off-specular surface scattering associated with conformal roughness, as shown in figure 2.

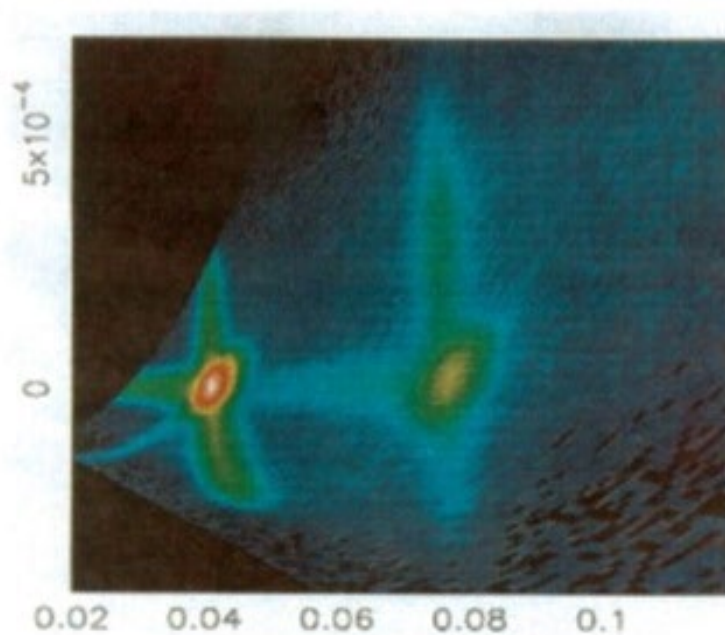


Figure 2. Off specular scattering for 2 wt% AOT at the silica / D₂O interface, produced from reference 30.

In a related study Nouhi et al (32) considered the impact of the roughness of the solid surface on the lamellar ordering at the solid-solution interface. For the nonionic surfactant, C₁₂E₄, they observed a highly ordered lamellar structure at the interface, which was less well ordered at the rougher surface. The surface roughness imposed perturbations on the structure which were larger than those associated with thermal fluctuations. It will be shown further in the next section how the surface morphology can have a significant impact upon the surface ordering (33).

In contrast to the extended multilayer structures formed by AOT and tetraethylene glycol monododecyl ether, $C_{12}E_4$, at the solid interface, the di-alkyl chain cationic surfactants, N,N-didodecyl-N,N-dimethyl ammonium bromide, DDAB, and the equivalent diundecyl compound, DUDAB, formed ordered structures but with a significantly lower number of layers (34). The visibility of the Bragg peaks and the intermediate interference fringes which characterised the reflectivity data are consistent with only 2-4 correlated layers with a relatively large spacing, $\geq 1000 \text{ \AA}$. Instead of a lamellar structure being formed at the surface, the data are consistent with either monodisperse unilamellar vesicles or a structured bicontinuous phase at the interface. This interpretation is consistent with complementary bulk scattering studies which indicate the coexistence of vesicles and lamellae in solution. The appearance of the surface structure showed a strong temperature dependence, and strong off-specular scattering consistent with conformal roughness is observed. Both observations are consistent with the interpretation of a vesicular or bicontinuous surface structure.

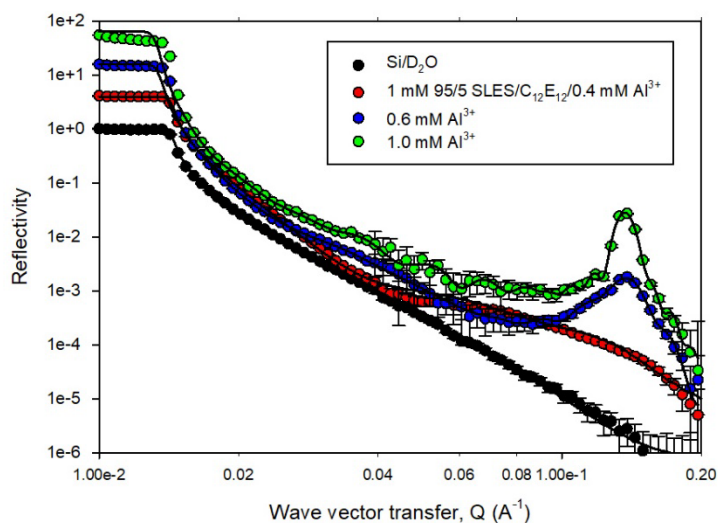
ELECTROLYTE INDUCED SURFACE MULTILAYER FORMATION

Surface multilayer formation in the presence of Al^{3+} counterions was extensively reported for the anionic surfactant alkyl ethoxy sulfate, SLES, from dilute solution at the air-water interface by Xu et al (35, 36). Xu et al showed how the evolution of the surface structures, from S_0 , S_1 , S_2 etc to S_n can be manipulated by changing the degree of ethoxylation and the alkyl chain length of SLES. The attractive interaction responsible arises from the strong binding of the multivalent ions between neighbouring surfactant head groups and a bridging mechanism across the adjacent layers, as described in the Introduction. Furthermore Petkov et al (37) showed how a nonionic cosurfactant, whilst minimising precipitation effects, disrupts the Al^{3+} binding to neighbouring SLES head groups, with an impact which is progressively greater with increasing ethylene oxide group size.

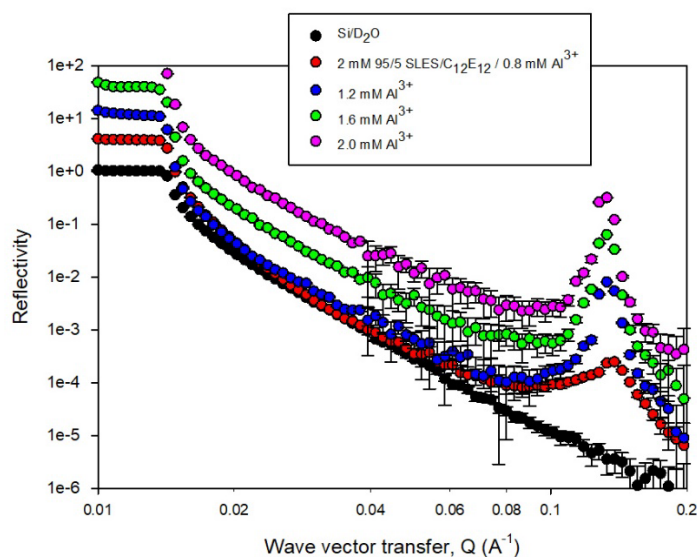
Penfold et al (33) extended those studies at the air-water interface to hydrophobic and hydrophilic solid-solution interfaces. Measurements were made at a hydrophilic silica surface and a hydrophobic silica surface, hydrophobized using hexamethyldisilazane. The results on silica were also contrasted with those at hydrophilic and hydrophobic cellulose surfaces. The measurements were made for the anionic / nonionic surfactant mixture of sodium dodecyl dioxyethylene sulfate, SLES, and monododecyl dodecaethylene glycol, $C_{12}E_{12}$, at a fixed mole

ratio of 95/5. The neutron reflectivity results at the hydrophilic and hydrophobic silica surfaces, as a function of Al^{3+} concentration, are shown in figure 3. Importantly the evolution in the surface structure with increasing Al^{3+} concentration at the solid-solution interface is broadly similar to that observed at the air-water interface, but some notable differences exist. At the hydrophilic silica surface (see figure 3a) there is no adsorption in the absence of Al^{3+} . The addition of Al^{3+} (0.4 mM) initially results in surface charge reversal and the appearance of a broad interference fringe, consistent with the adsorption of 2 bilayers. At higher Al^{3+} concentrations a Bragg peak occurs at a Q value $\sim 0.15 \text{ \AA}^{-1}$, corresponding to multilayer structure with a bilayer spacing $\sim 45 \text{ \AA}$. With increasing Al^{3+} concentration the structure of the Bragg peak sharpens as the number of bilayers adsorbed increases from ~ 8 (at 0.6 mM Al^{3+}) to ~ 12 (at 1.0 mM Al^{3+}). The variations in the scattering length density profiles associated with the ordered reflectivity patterns indicates a degree of both lateral and orthogonal disorder. This varies with the depth of the structure, which extends to $\sim 500 \text{ \AA}$ into the bulk solution, due to roughness, variations in bilayer thickness and variations in the orientation of the surface patches or surface multilayer domains. At the hydrophobic silica surface (see figure 3b) surface multilayer formation is also observed. The evolution in the surface structure is slightly different compared to that observed at the hydrophilic surface, and involves the more extended multilayer structures, S_n , over the entire Al^{3+} concentration range explored. Surface multilayer formation is also observed at hydrophilic and hydrophobic cellulose surfaces, but the adsorption was weaker and the multilayer formation was less well developed. This was attributed to a rougher cellulose surface and to surface inhomogeneity's which partially inhibit the lateral growth of multilayer domains on the surface.

Importantly Penfold et al (33) have showed that the multivalent counterion induced surface multilayer formation occurs at the solid-solution interface as well as at the air-water interface. Although this implies that the attractive interaction responsible is similar, the results also showed that the nature of the solid surface impacts upon the detailed nature of the layering.



(a)



(b)

Figure 3. Neutron reflectivity for 1 mM 95/5 mole ratio SLES / C₁₂E₁₂ / Al³⁺ at the (a) hydrophilic, (b) hydrophobic silica surfaces, as a function of Al³⁺ concentration, see legend for details (reproduced from reference 33).

The impact of the nature of the solid surface and the role of different surfactants on surface multilayer formation in the presence of electrolyte was further explored by Griffin et al (38), and Allen et al (39). Griffin et al (38) showed that Ca²⁺ promoted the formation of a condensed multilayer structure for AOT at the mica-solution interface, see figure 4. The number of

bilayers adsorbed was shown to vary from 3 to 4, and depended upon the solution pH. The pH dependence was attributed to changes in the head group screening from H^+ and OH^- ions.

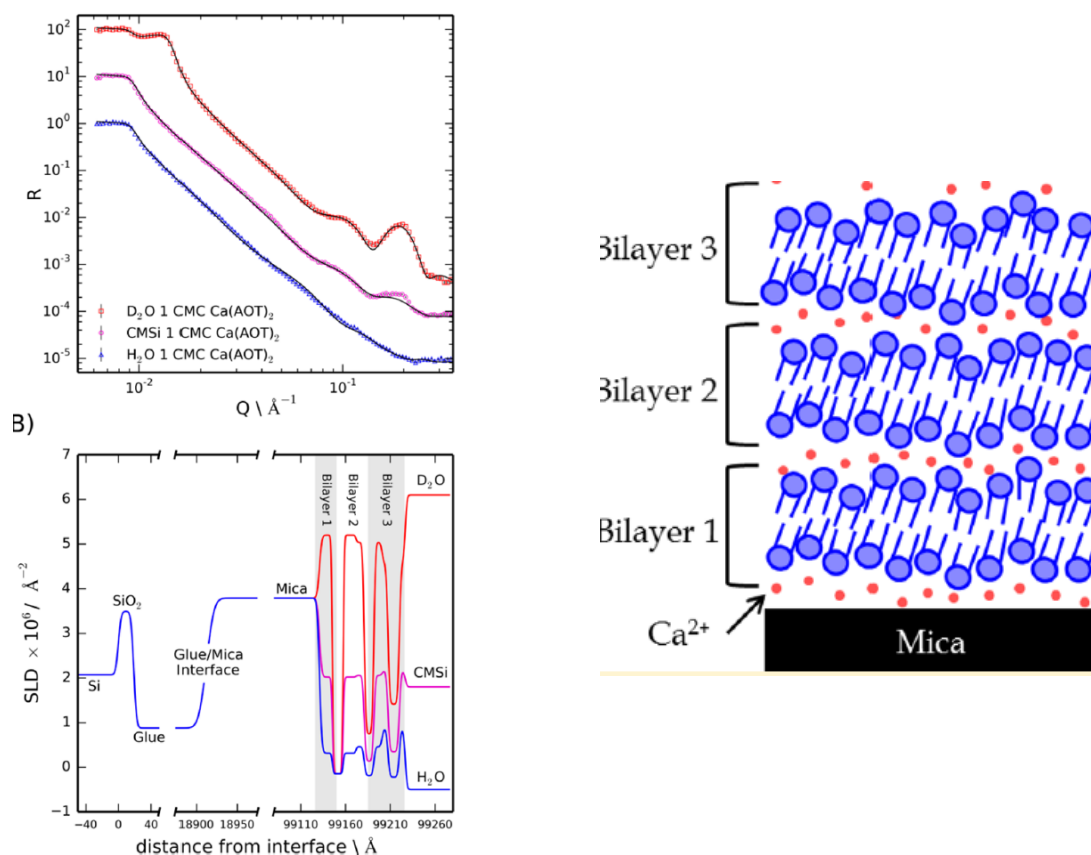


Figure 4. Variation in neutron reflectivity and surface structure for CaAOT at the solution/mica interface, reproduced from reference 38.

It was generally assumed that bridging does not occur with monovalent ions. However, it was reported by Allen et al (39) to occur for AOT with Cs^+ . In that case it was attributed to the relatively large ionic radius of Cs^+ and its associated lower charge density and weaker hydration. Allen et al (40) subsequently explored the counterion bridging mechanism in more detail, through the adsorption of the anionic surfactant AOT onto anionic mica. They investigated the impact of the divalent counterions Ca^{2+} and Mg^{2+} and a range of monovalent counterions. They reported surface adsorption for Ca^{2+} , Mg^{2+} and K^+ , but not for Na^+ . Furthermore Mg^{2+} and Ca^{2+} were shown to promote the onset of surface multilayer formation. Hence the valence of the ion is not the overriding criteria for bridging, and the ionic radius and hydration strength are important factors.

Liu et al (41) further investigated the role of calcium ion bridging in anionic surfactant adsorption to silica. In that case the increased adsorption with increasing pH was there attributed to an increase in the binding sites on the silica. It was shown that the introduction of excess of sodium ions exchanged with calcium ions near the surface to reduce adsorption, and that polystyrene sulfonate competed effectively to substantially reduce surfactant adsorption.

The type of surface for which multivalent ions induce layering has been observed was extended by the study of Xing and Rankin (42). Xing and Rankin used ATR-FTIR to probe the adsorption kinetics of an anionic fluorinated surfactant, tetraethylammonium perfluorooctyl sulfonate, TEA-FOS, onto a hydroxylated Germanium surface. In the presence of Ca^{2+} ions multilayer adsorption was observed. In their study Xing and Rankin highlighted the potential for aqueous cleaning, controlled surface modification and templating in such systems.

SURFACE COMPLEX FORMATION INVOLVING SURFACTANTS AND POLYMERS

The formation of structured surface layers involving polymers, and especially polyelectrolytes, using sequential adsorption techniques such as L-by-L, LB and LS methods, is well established (15-17), and have been applied to both planar solid surfaces and a range of nanoparticles. Such surface structures have attracted widespread interest and application in the development of functionalised surfaces and in the manipulation of wetting properties in a wide variety of industrial, technological, medical and domestic applications (16, 17, 20, 21, 43-45).

An alternative and in many ways more facile route is by the modification of adsorbed polyelectrolyte layer using surfactants or the self-assembly of polyelectrolyte – surfactant mixtures to form complex layered or self-assembled surface structures. This latter approach has been extensively demonstrated at the air-water interface (12, 46), where a range of polyelectrolyte-surfactant mixtures were shown to form extended self-assembled structures with a similarity to those induced using multivalent counterions (11). In those studies their significance and potential impact on the solid-liquid interface was recognised, and the reported extreme and persistent wetting of hydrophobic solid surfaces by polyethyleneimine / SDS mixtures is an example of this (47).

Recent studies have also shown how preadsorbed polyelectrolyte or polymer layers can modify surfactant adsorption and lead to more complex surface structures, and how adsorption from solution can be used to develop self-assembled surface structures.

Penfold et al (48) used NR to show how preadsorbed polyelectrolytes can be used to promote ionic surfactant by charge reversal of the surface, in a way similar to that encountered using multivalent counterions. It was further shown (49) that the presence of polyelectrolytes at the surface will modify the nature of mixed surfactant adsorption, and that the solution conditions can affect the nature of the surfactant and polyelectrolyte adsorption and the reversibility of the adsorption.

Moglianetti et al (50, 51) considered the effect of surfactant adsorption on more complex preadsorbed polymer surfaces involving comb polymers and polymer brushes. Moglianetti et al (50) demonstrated the impact of SDS on an adsorbed comb polymer consisting of a high charge density cationic backbone, with copolymer backbone units of methacryloxyethyl trimethyl ammonium chloride, METAC, and methyl ether methacrylate, MEMA, and polyethylene oxide, PEO, side chains. Although the adsorption of comb polymers onto solid surfaces has been previously investigated and the surface distribution of polymer chains established, the impact of surfactants on the adsorbed layer was largely unknown. A complex pattern of adsorption evolved, which depended upon the SDS concentration and the solution stoichiometry. Using contrast variation they were able to show the formation of micelle-like aggregates which swell the PEO side chains from a mushroom to brush-like configuration for one of the copolymer compositions. In a related study Moglianetti et al (51) used a similar approach to investigate surfactant adsorption in weak polyelectrolyte brushes at a sapphire-water interface. The weak polyelectrolyte brush of poly (2-(dimethylamino)ethyl methacrylate). PDMAEMA, was grown using surface initiated polymerisation at a sapphire-water interface. The nature of the SDS adsorption into the polymer brush depended strongly on pH. At low pH the addition of SDS initially swelled the brush, and at higher SDS concentrations multilayered structures are formed within the brush, as shown in figure 5. The repeat distance, $\sim 40 \text{ \AA}$, is comparable to the dimensions of a SDS bilayer or micelle, and the number of repeating layers depended upon the brush thickness.

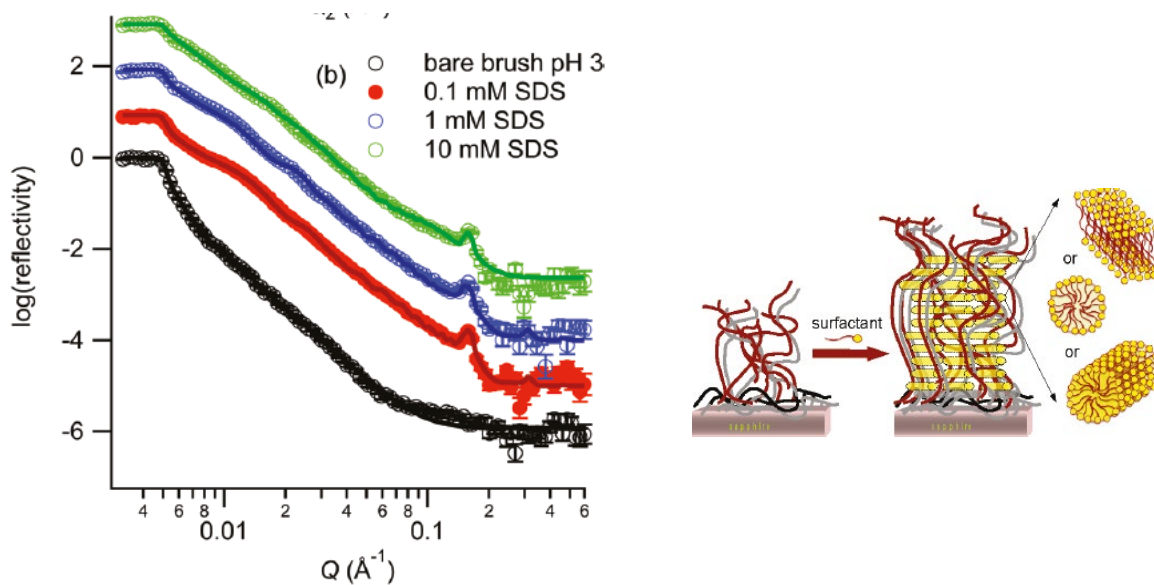


Figure 5. Neutron reflectivity and surface structure illustrating the development of a layered SDS structure within a PDMAEMA brush at a sapphire-solution interface, reproduced from reference 51.

At low pH the high local charge density in the brush provides screening of the interaction between the surfactant head groups which leads to the self-assembled structure. At high pH there is a significant adsorption of SDS into the brush, but there is no evidence of the formation of layered structures. The enhanced surfactant adsorption at high pH is due primarily to hydrophobic interactions.

Arteta et al (52) investigated the interaction of SDS and a cationic 4th generation dendrimer, polyamidoamine, PAMAM, at the silica solid-solution interface. The impact of SDS on a preadsorbed PAMAM layer is contrasted with the coadsorption of SDS / PAMAM from solution. PAMAM adsorbs irreversibly to form a compact layer. SDS adsorption to that layer results in an expansion of the dendrimer and at higher SDS concentrations surface aggregates with a bilayer-like structure is observed. For solution SDS / PAMAM mixtures close to neutrality a thick multilayered film is adsorbed.

Dedinaite et al (52) addressed specifically the differences associated with the adsorption of polyelectrolyte / surfactant complexes formed in solution with the adsorption of surfactant

onto a preformed polyelectrolyte layer on a solid surface. Consistent with related studies they observed self-assembled structures with a periodicity $\sim 40 \text{ \AA}$ from the adsorption of SDS onto a preadsorbed polypropionyloxyethyl trimethyl ammonium chloride, PCMA, polyelectrolyte layer. Fernandez-Peria (54) reviewed the impact of bulk aggregation of polyelectrolyte - surfactant mixtures on the adsorption onto solid surfaces, and considered further the contrast between adsorption of complexes from solution and the adsorption of surfactant onto preadsorbed polyelectrolyte surfaces. They highlighted in particular the potential complexity of the process, the competing factors at play and the potential importance of non-equilibrium effects. The review was very much focussed towards the impact on consumer products such as shampoos and conditioners. This was also very much the focus of the recent and specific study by Llamas et al (55), who studied the adsorption of poly(diallyldimethyl ammonium chloride) and sodium methyl-cocyl-tartrate complex on model surfaces and hair (keratin) fibres. Using a variety of techniques, which included AFM, QCM and ellipsometry, they reported the formation of inhomogeneous aggregate films which were randomly distributed across the surface. They observed that the adsorption correlated strongly with changes in the bulk aggregation, and that the kinetics of adsorption was controlled by bulk diffusion.

Using a slightly different approach Kundu et al (56) investigated the nature of polyelectrolyte-surfactant complex deposited onto hydrophilic silica surfaces using a modified L-S method. The deposition method involves the transfer of equilibrium structures established at the air-water interface to the solid surface. Using DNA and carboxymethyl cellulose, carboxyMC, as the polyelectrolyte and a cationic surfactant, dodecyltrimethyl ammonium bromide, DTAB, x-ray reflectivity revealed lamellar multilayer structures for DNA / DTAB complexes and coil-like structures for the carboxyMC / DTAB complexes. The results suggest a correspondence between the observed ordered structures and the MW and persistence length of the polyelectrolyte. These observation of Kundu et al are important in that they show conclusively that the equilibrium structures observed at the air-water interface (46, 47) can be successfully transferred to the solid surface.

SURFACE STRUCTURES INVOLVING PROTEINS

Given the ability of polyelectrolytes to promote complex surface structures by self-assembly, in combination with surfactants, and to form sequential layers with other polyelectrolytes and surfactants, it is evident that proteins should also perform similar functions, and a number of studies involving proteins also exist.

Caruso and Mohwald (57) described the stepwise assembly, by the L-by-L deposition, of protein multilayers onto colloidal particles. The deposition onto polystyrene latex particles involved bovine serum albumin, BSA, and immunoglobulin, IgG, with alternate polyelectrolyte layers. This approach provided a controlled mechanism to assemble such layers, with a wide range of potential applications for biologically functionalised surfaces in areas of biotechnology, biochemical engineering and in medical applications. In a recent extensive review Straeten et al (58) have charted the progress in the development and application of L-by-L techniques to produce multilayer films involving proteins. They highlight the wide range of systems that are used for the immobilisation and encapsulation of proteins at surfaces, with applications in chemical engineering, healthcare, diagnostics, pharmaceuticals, and tissue engineering.

In contrast Dickinson (59) reviewed the competitive and cooperative adsorption of proteins / biopolymers, and the formation of multilayer structures from mixed biopolymers at interfaces. The emphasis was on food related emulsions and foams, and so did not specifically consider the solid-solution interface. However the mechanisms of sequential and cooperative adsorption to form multilayer structures at the air-water and liquid-liquid interfaces also apply to the liquid-solid interface. This was demonstrated, for example, by Lundu et al (60) in the L-by-L deposition of Lysozyme / β -casein films onto hydrophilic surfaces. Holmberg et al (61) showed how competitive adsorption of albumin, IgG and other proteins can lead to surface protein aggregation and protein multilayer formation at the solid surface.

Hence it has been shown that both the L-by-L and surface self-assembly approaches offer great opportunities in the development of new bio-based surface functionalities.

The highly surface active, adhesive, compact and robust protein from filamentous fungi, hydrophobin, offers different and exciting possibilities. Wang et al (62) showed how proteins adsorb to a hydrophobin layer at solid surfaces to form a layered protein structure. This has interesting implications for a variety of protein related applications. In a related but slightly different study Tucker et al (63) demonstrated the formation of self-assembled protein-surfactant surface structures in hydrophobin and ethoxylated polysorbate surfactant mixtures, as shown in figure 6.

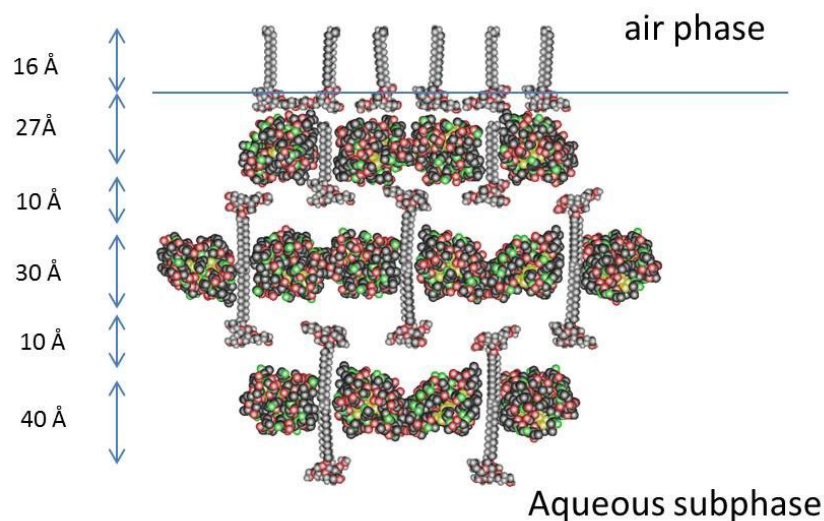


Figure 6. Surface structure of hydrophobin / ethoxylated polysorbate mixtures at the air-water interface: reproduced from reference 63.

The surface layered structure is due to the interaction between the hydrophobic patch of hydrophobin and the polysorbate alkyl chain, and the hydrophilic region of hydrophobin and the sorbitan head group; and occurs when the alkyl chain length and degree of ethoxylation are optimal. Although only demonstrated at the air-solution interface, the surface self-assembly has been shown to modify the properties of solid surfaces, and is discussed in a later section in the context of its associated wetting properties.

WETTING PHENOMENA ARISING FROM SURFACTANT SURFACE STRUCTURES

Surfactant induced wetting or enhanced wetting of solid surfaces is commonplace, and comprehensive reviews have considered their fundamental properties, characteristics and applications (64, 65) and more recent developments and applications in enhanced oil

recovery, medicine, and agriculture (66). A range of different surfactant structures, tailored for particular properties, have been exploited. The nonionic trisiloxanes (67, 68) and the polyoxyethylene alkyl ethers (68) have been widely studied and offer the possibility of tuning wetting / spreading with temperature. Recent examples in the literature have demonstrated the particular wetting properties of the di-alkyl chain surfactants by Lv et al (69) using branched cationic Gemini surfactants and by Biswal et al (70) using di-alkyl chain cationic and anionic surfactants.

Penfold et al (47) and Taylor et al (46) reported interesting and unusual wetting properties arising from polyelectrolyte / surfactant multilayer formation at interfaces, and these observations were reinforced by the similar observations Xu et al (35, 36) with the anionic surfactant / multivalent counterion induced surface multilayer formation. In a much earlier study Kilau et al (71) reported on the role of multivalent anions in enhancing the wettability of coals. More recently Arabloo et al (72) reported on the multilayer adsorption of a saponin-like surfactant onto solid surfaces, and the potential for enhanced oil recovery through the modification of the surface wetting properties.

Specifically Xu et al (35, 36) observed that the formation of surface multilayer structures for SLES / AlCl_3 mixtures resulted in hydrophobic surfaces such as Teflon becoming highly and persistently wetting. The adhesion of the wetting layer was such that vigorous cleaning and rinsing was required to restore the hydrophobic nature of the surface, to a degree not normally encountered in other systems. Similar observations were made by Penfold et al (47) and Taylor et al (46) for polyelectrolyte / surfactant mixtures which also formed multilayered structures at interfaces. Related solutions for which only monolayer adsorption occurs were, in contrast, readily rinsed. Penfold et al (33) characterised the unusual and extreme wetting properties of the SLES / nonionic surfactant mixtures in the presence of AlCl_3 using contact angle measurements. Figure 7 shows a comparison of the wetting of a hydrophobically treated silicon surface following surfactant adsorption (figure 7a) and following adsorption in the presence of multivalent counterions where surface multilayer structures are formed (figure 7b). The profiles were measured using a Kruss DSA100 drop shape analyser for a 1 mM 95/5 mole ratio SLES / $\text{C}_{12}\text{E}_{12}$ solution with added AlCl_3 (figure 7b) and without electrolyte (figure 7a), and following rinsing in water. In figure 7a the contact angle is $\sim 90^\circ$, similar to

that for a bare hydrophobic surface, whereas in figure 7b the contact angle is essentially zero. This contrast and the vigorous procedure required to remove the layer points to some exciting possibilities for such systems.

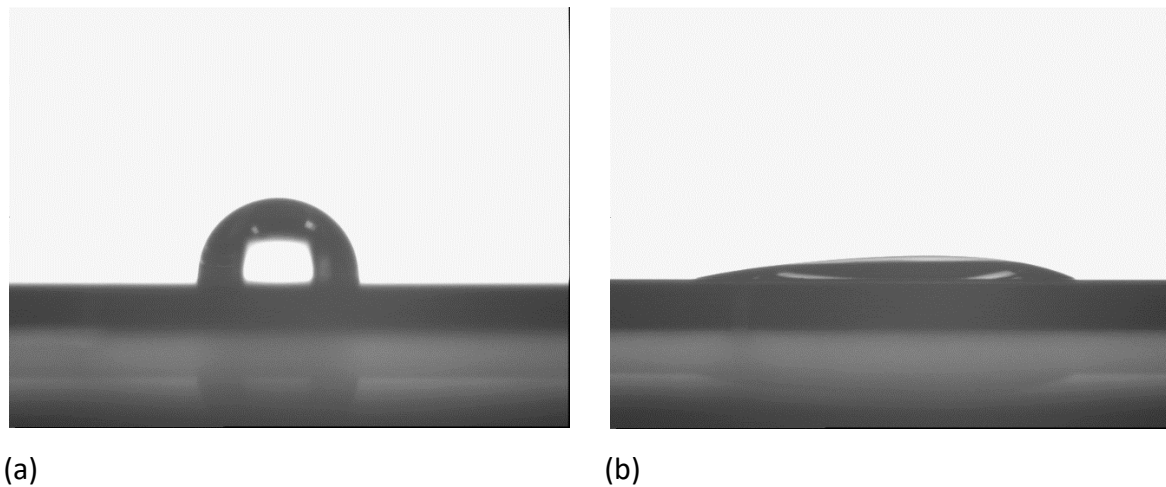


Figure 7. Profile of water droplet for (a) hydrophobic silica surface, (b) after exposure to multilayer adsorption and rinsing, reproduced from reference 33.

In the previous section on protein adsorption the spontaneous formation of surface multilayer structures in hydrophobin / ethoxylated polysorbate mixtures was reported (62), and their unusual wetting properties were alluded to. It is known that hydrophobin adheres strongly to hydrophobic surfaces (62, 63), rendering them hydrophilic. However when exposed to a hydrophobin / ethoxylated polysorbate mixture which forms multilayers a hydrophobic surface remains highly hydrophobic. This implies that the hydrophobin is preferentially incorporated into the multilayer structure and not adsorbed at the solid surface. Hence the wetting nature of hydrophobin can be manipulated by a suitable cosurfactant, and this leads to potentially interesting opportunities.

IMPACT OF FLOW AGAINST THE SOLID SURFACE

In the previous section it was shown that surface multilayer formation can have a profound impact upon the wetting properties of the surface. The extent to which the surfactant surface structure is affected by flow adjacent to the solid surface is important in terms of the wetting and the potential impact for lubrication.

In their pioneering study, presented earlier in this review, Hamilton et al (22) used Poiseuille flow to demonstrate the shear induced hexagonal ordering in a concentrated solution of rod-like micelles adjacent to a solid surface. Penfold et al (73) used a similar Poiseuille flow geometry to investigate the impact of shear flow on the adsorption of a nonionic surfactant, hexaethylene glycol monohexadecyl ether, C₁₆E₆, at a silica / solution interface. For a 50 mM solution lamellar ordering at the liquid-solid interface was observed, and the application of shear flow, up to an applied shear gradient of 10⁴ sec⁻¹, resulted in an enhancement of the lamellar ordering at the surface. Welbourn et al (74) used an adapted cone-plate rheological geometry to study the impact of shear on the adsorption of AOT at an alumina / solution interface. The adsorption of the bilayer structure observed at low surfactant concentrations was invariant with applied shear. At higher surfactant concentrations (~50 mM) multilayer adsorption occurs. There was a loss of surface structure with the application of both steady and oscillatory shear. The point at which the loss of surface structure occurred was similar to the impact of shear in disrupting the bulk lamellar structure. Wolff et al (75) extended their earlier studies (25, 26) on the ordering of pluronic micelles against solid surfaces by using a similar cone-plate geometry rheometer to probe the impact of shear on the surface ordering. They observed a transition from a more solid to a more liquid-like surface structure with increasing shear rate.

In a slightly different but related study, Singh et al (76) used a Poiseuille flow cell to investigate the impact of shear on the structure of a PEI / PSS polyelectrolyte L-by-L multilayer on quartz. The NR data showed a change in the structure associated with a decrease in the film hydration with applied shear. The structural changes were reversible and the initial structure was re-established under static conditions. Importantly this study extends the range of possibilities available and the potential for different effects due to flow against a solid surface.

Hence these examples imply that the impact of shear flow on the surfactant adsorption and the structure of the adsorbed layer will depend crucially upon the nature of the attractive interaction present and on the way the bulk properties are affected by shear. Depending upon the relative importance of the different mechanisms, disruption or enhancement of the surface ordering can occur.

SUMMARY AND FUTURE PROSPECTS

As illustrated in this review there are great opportunities for the modification of solid surface properties using surfactant self-assembly. This involves adsorption from concentrated solutions, sequential adsorption routes, and adsorption / self-assembly induced by different polyions.

The sequential adsorption, by different L-by-L techniques, of surfactants, polymers, proteins and colloidal particles have already been extensively used to manipulate and tailor surface properties, such as wetting, to provide a wide range of functionalised surfaces. Extensive applications in encapsulation, wetting, pharmaceuticals, food and drink formulations, and in agrochemicals have been identified and exploited.

Adsorption and self-assembly of surfactants, induced by polyelectrolytes, proteins and multivalent ions or polyions, at solid surfaces offer a potentially more facile route to the formation of a range of functionalised surfaces. This is a route that is yet to be fully explored and exploited, but a range of recent studies have demonstrated the potential and diversity of the surface structures available. Importantly the self-assembled structures have great potential for a range of applications involving the manipulation of wetting properties, encapsulation, and delivery of active components to surfaces. The key areas of application involve home and personal care products, lubrication, enhanced oil recovery, medication applications, pharmaceuticals, agrochemicals, and a range of smart functionalised surfaces.

An important aspect that remains underdeveloped is a theoretical treatment of multilayer formation at interfaces. Morgan et al (77) have developed a mathematical model which predicts some of the features observed, provides some initial insights into the adsorption kinetics, and is an excellent start. Such approaches also provide the potentially interesting link to kinetic studies, such as those involving depletion from the solution phase (78). Furthermore there remains scope for investigating further the role of flow / shear against the solid surface, and this has potential importance in terms of applications involving lubrication and wetting.

Neutron reflectivity and grazing incidence SANS, GISANS, provide complementary approaches for studying ordering at surfaces, and provide information orthogonal to the surface and in-

plane. Wolff et al (79) demonstrated that GISANS can be used to obtain directly depth resolved structural information. Probing the surface region with that extra depth sensitivity and distinction has so far been under used for such systems, but does provide great potential, especially in combination with external stimuli such as shear.

DECLARATION OF INTEREST

The authors declare that they have no financial or personal relationships which could have appeared to influence this review.

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