

Anionic surfactant - biogenic amine interactions: the role of surfactant headgroup geometry

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ABSTRACT

Oligoamines and biogenic amines (naturally occurring oligoamines) are small flexible polycations. They interact strongly with anionic surfactants such as sodium dodecyl sulfate, SDS. This results in enhanced adsorption and the formation of layered structures and the formation of layered structures at the air-water interface which depends on surfactant concentration and solution pH. The effect of changing the surfactant headgroup geometry on that interaction and subsequent adsorption is reported here. Neutron reflectivity, NR, results for the surface adsorption of the anionic surfactant sodium diethylene glycol monododecyl ether sulfate, SLES, with the biogenic amine, spermine, are presented, and contrasted with previous data for SDS / spermine mixtures. The enhancement in the adsorption of the surfactant at the air-water interface where monolayer adsorption occurs is similar for both surfactants. However the regions of surfactant concentration and solution pH where surface multilayer adsorption occurs is less extensive for the SLES / spermine mixtures, and occurs only at low pH. The results show how changing the headgroup geometry by the introduction of the ethylene oxide linker group between the alkyl chain and sulfate headgroup modifies the polyamine – surfactant interaction. The increased steric constraint from the polyethylene oxide group disrupts the conditions for surface multilayer formation at the higher pH values. This has important consequences for applications where the modification or manipulation of the surface properties are required.

Keywords: Surfactant adsorption, biogenic amines, air-water interface, surface multilayers

INTRODUCTION

The aliphatic biogenic amines, such as spermine, and the oligoamines, such as tetraethylenepentamine, have similar structures and can be considered as small flexible polycations. The naturally occurring biogenic amines are involved in a range of biological functions (1-5). They are sources of nitrogen and precursors for the synthesis of hormones, alkaloids, nucleic acids and proteins, and are food aroma components and precursors to the formation of some carcinogenic compounds. They are involved in a variety of physiological roles associated with intercellular communication, cell growth and proliferation (6-9). Due to their cationic nature they interact strongly with phospholipids, proteins and nucleic acids. Their strong interaction with biomacromolecules such as DNA and RNA, resulting in enhanced stabilisation or precipitation, results in their potential gene therapy applications using polymeric complexes (10, 11). The oligoamines and amine based polymers, such as pol(ethyleneimine), PEI, have a high charge density at low pH and are important due to their potential for a wide range of diverse applications (12, 13); and hence have been extensively studied (14-18).

The particular focus of this paper is the surface adsorption behaviour of biogenic amine – surfactant mixtures at the air-water interface. It has been demonstrated that for the aliphatic biogenic amines (putrescine, spermidine and spermine) – SDS mixtures (19) and the oligoamine– SDS mixtures (20-22) the strong interaction of the biogenic amine with the SDS results in enhanced adsorption of the SDS at low SDS concentrations and regions of SDS concentration and solution pH where surface multilayer formation occurs. These studies illustrated how the oligoamine molecular weight (number of amine groups) and the structure (linear or branched) as well as the surfactant and oligoamine concentrations and solution pH

affect the surface behaviour. The importance of the oligoamine structure was further reinforced by a recent study where the effects of aromatic biogenic amines, such as melamine or histamine, on surfactant adsorption are reported (23). It has also been shown how modification of the polyamine, through ethoxylation or propoxylation, affects the polyamine – surfactant interaction and hence the pattern of adsorption (24). The addition of a cosurfactant (25, 26) and differently structured anionic surfactants (27) can have a significant impact upon the strength of the polyamine – surfactant interaction.

The ability of different polyions to induce enhanced adsorption, surface multilayer formation with their associated modification of surface wetting properties in anionic surfactants has stimulated our interest in the application of these polyion / anionic surfactant mixtures in a range of home and personal care products. Specifically in this paper we compare the surface interaction and adsorption properties of spermine / SDS and spermine / SLES mixtures. The effect of added electrolyte to anionic surfactants is well established (28) and leads to micellar growth and enhanced adsorption. The addition of multivalent counterions, such as Ca^{2+} or Al^{3+} , to anionic surfactants, such as SDS, leads rapidly to precipitation (29). This is the origin of the effect of water hardness on detergency and associated phenomena, and has been extensively studied (30-32). Modifying the alkyl sulfate structure of SDS by introducing a short ethylene oxide chain to form SLES improves solubility and tolerance to the addition of multivalent ions (33-36). Hence the degree to which softening of the charge interaction by the introduction of the ethylene oxide chain impacts upon the surface properties of the surfactant / spermine mixtures is the focus of this paper.

EXPERIMENTAL DETAILS

The neutron reflectivity, NR, measurements were made on the SURF reflectometer (37) at the ISIS neutron source. The reflectivity, $R(Q)$, is measured as a function of the wave vector

transfer perpendicular to the surface, Q ; where Q is defined as $Q=4\pi\sin \theta/\lambda$, θ is the grazing angle of incidence and λ is the neutron wavelength. On SURF a usable Q range ~ 0.045 to 0.5 \AA^{-1} is covered using a fixed θ of 1.5° and a λ range of 0.5 to 7 \AA .

In the kinematic approximation (38) $R(Q)$ is related to the square of the Fourier transform of the scattering length density distribution, $\rho(z)$, normal to the surface (where $\rho(z) = \sum_i n_i(z) b_i$, n_i and b_i are the number density and scattering length of the i th component and z is the direction perpendicular to the surface). Hence $R(Q)$ can be expressed as,

$$R(Q) = \frac{16\pi^2}{Q^2} \left| \int \rho(z) e^{-iQz} dz \right|^2 \quad (1)$$

As H and D have different scattering lengths ($b_H = -2.7 \times 10^{-6}$ and $b_D = 6.67 \times 10^{-6} \text{ \AA}$) in many organic / aqueous systems H/D isotopic substitution can be used to manipulate the scattering length density. This approach is commonly used in studying surfactant (39) and polymer / surfactant (40) adsorption at the air-water interface by deuterium labelling the surfactant and using null reflecting water, nrw (8 mole % D_2O / H_2O mixture with a scattering length density of 0.0, and so index matched to air) as the sub-phase; and this approach is used here in this study.

The measurements were all made in sealed Teflon troughs with sample volumes $\sim 25 \text{ mL}$ and at a temperature of 25°C . The reflectivity was calibrated on an absolute scale by reference to the direct beam intensity and the reflectivity from a pure D_2O surface. Each measurement took ~ 30 minutes and a series of measurements were made sequentially on a 5 position sample changer. Each measurement was repeated ~ 3 to 4 times, representing a total lapse time of up to ~ 6 to 8 hours, until each reflectivity profile reached a steady state.

The measurements were made for SLES / spermine mixtures at a fixed spermine concentration of 5 mM, SLES concentrations from 10^{-5} M to 10^{-2} M, and at pH values of 3, 7, and 10. Alkyl chain deuterated SLES was used, and was obtained from the Isotope Facility at ISIS. It was recrystallised twice in propanol / ethanol mixtures, and its purity was assessed by determining its adsorption above the cmc by NR and from the absence of a minimum in the surface tension, ST, behaviour. The spermine (1,12-dodecadiamine) was obtained from Sigma-Aldrich (>97% purity) and used as received. Deuterium oxide, D₂O, was obtained from Sigma-Aldrich and high purity water (Elga Ultrapure) was used throughout. The solution pH was adjusted by the addition of aqueous hydrochloric acid and sodium hydroxide solution. All the solutions prepared were clear and showed no signs of aggregation or precipitation. The structure of SLES, SDS and spermine are shown in figure 1.

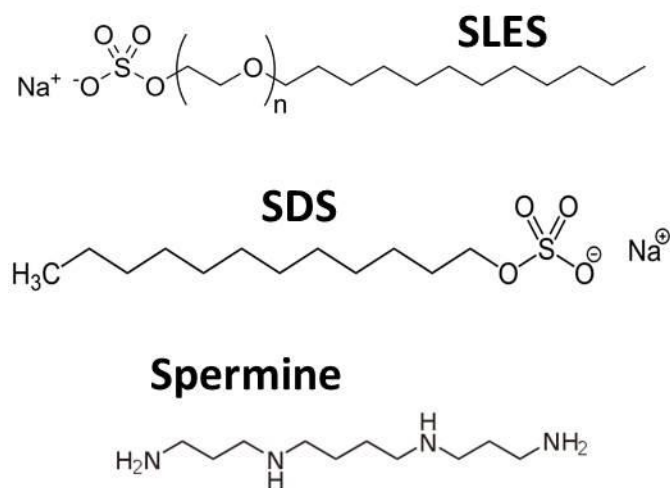


FIGURE 1. Molecular structure of SLES, SDS and spermine

RESULTS and DISCUSSION

(i) Results

The NR data for the SLES / 5 mM spermine mixtures at pH 7 and 10 over the SLES concentration range measured (10^{-5} to 0.1 M) and at pH 3 for SLES concentrations $< 10^{-3}$ M are consistent with a thin monolayer adsorbed at the interface. The mean thickness of the adsorbed layer is ~ 24 Å, and is dominated by the adsorption of the deuterium labelled SLES at the interface. The data are analysed quantitatively by modelling the adsorbed layer as a single thin layer of uniform density using the exact optical matrix method (38, 40) to obtain a thickness, d , and a scattering length density, ρ . From this the area/molecule or adsorbed amount can be estimated using $A = \Sigma b / d\rho$, where Σb is the scattering length of the alkyl chain deuterated SLES, 2.85×10^{-3} Å, and the adsorbed amount Γ is $\Gamma = 1/N_a A$, and N_a is Avogadro's number. From such NR data the statistical / systematic error in A at value of 50 Å² is $\sim \pm 2$ Å², and the errors quoted here are on that basis. The data are analysed assuming that the surface is dominated by the contribution from the deuterium labelled SLES. There is a finite but small contribution from the spermine, but assuming a stoichiometry of one SLES molecule per spermine that contribution will be $\ll 2\%$. In figure 2a the variation in the adsorbed amount for SLES / 5 mM spermine at pH 7 with SLES concentration, where only monolayer adsorption occurs, is shown. For comparison, the adsorption data for SLES in the absence of biogenic amine are also shown.

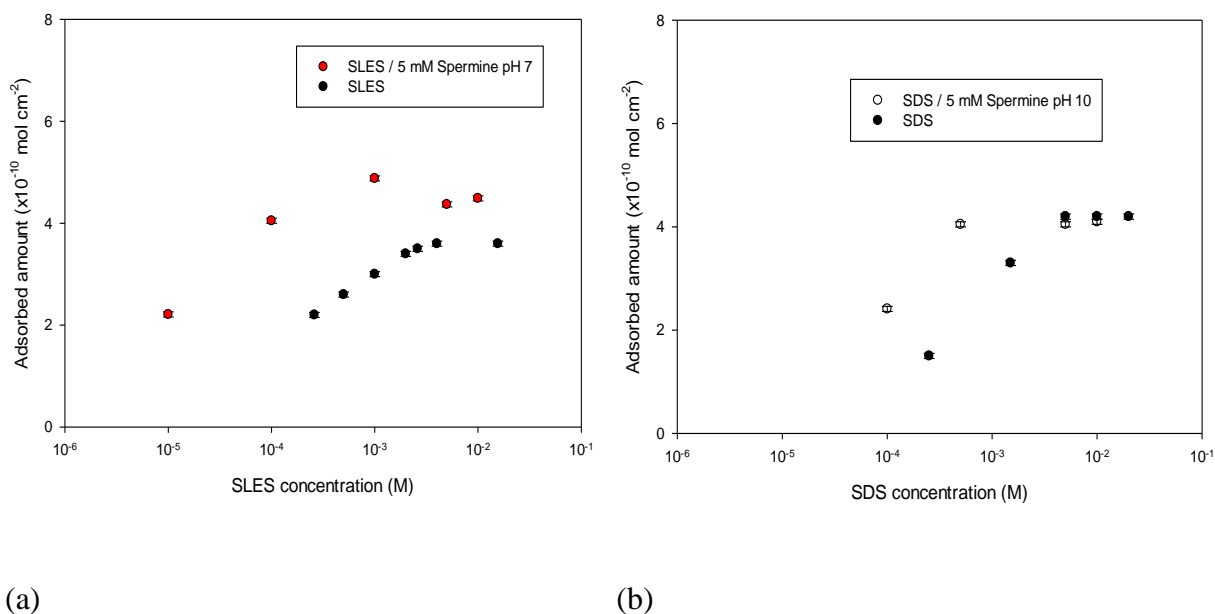


Figure 2. Adsorbed amount versus surfactant concentration for monolayer adsorption for (a) Spermine / SLES and (b) Spermine / SDS; for details of the individual plots see figure legend. The SLES only data are from reference 41 and for SDS only from reference 42.

At the higher SLES concentrations the area/molecule saturates at $\sim 37 \text{ \AA}^2$, corresponding to an adsorbed amount of $\sim 4.5 \times 10^{-10} \text{ mol cm}^{-2}$. In the absence of spermine the saturation adsorption of SLES at the cmc is $\sim 3.6 \times 10^{-10} \text{ mol cm}^{-2}$ (area/molecule $\sim 46 \text{ \AA}^2$) (41). Similar data are obtained for Spermine / SLES at pH 10 and 3, where monolayer adsorption occurred or was measured (see table S1 in the Supporting Information). Hence over the SLES concentration range measured the addition of spermine results in an enhanced adsorption of SLES at the interface. The contrasting behaviour of monolayer adsorption for SDS / spermine at pH 10 is shown in figure 2b. It was not possible to make the comparison at the same pH, as for SDS / spermine the only region of extensive monolayer adsorption was at pH 10 (19). There are two noticeable differences between the SLES / spermine and SDS / spermine behaviour. Firstly the enhanced adsorption at low surfactant concentrations, $< 10^{-3} \text{ M}$, is more pronounced for SLEs than for SDS. Secondly at high surfactant concentrations, \geq

$5 \times 10^{-3} \text{ M}$, where the adsorption is not changing with surfactant concentration, the addition of spermine has little impact upon the adsorption, whereas for SLES the adsorption has increased by $\sim 25\%$.

The NR data for 5mM spermine / SLES at pH 3 and SLES concentrations of 10^{-3} , 5×10^{-3} and 10^{-2} M have a fundamentally different form, and exhibit a strong time dependence as illustrated in figure 3 for 5 mM spermine and 1 and 5 mM SLES.

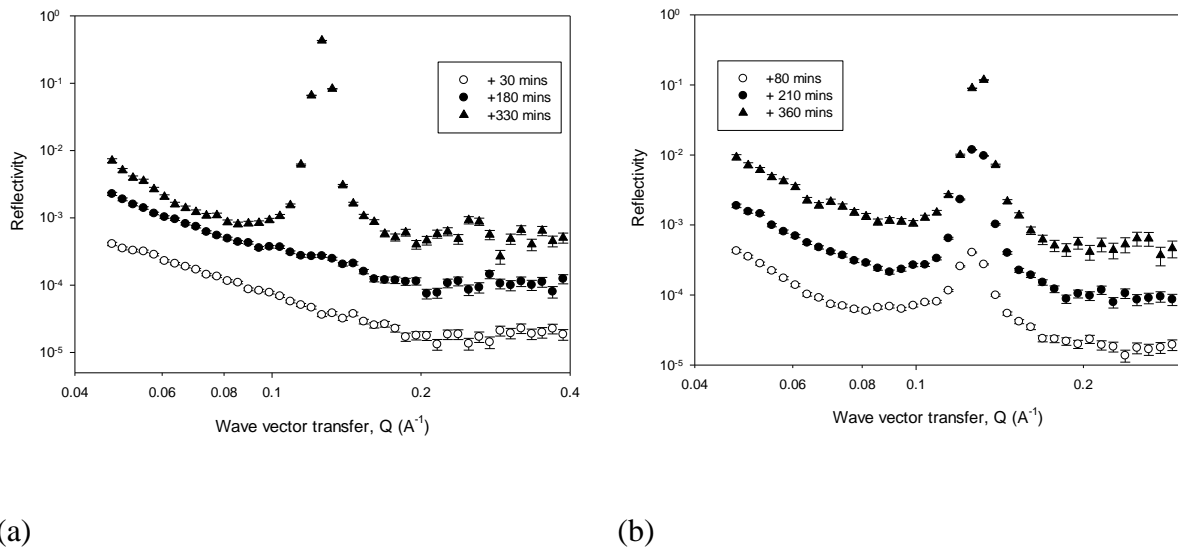


Figure 3. Time dependence of neutron reflectivity for (a) 5 mM spermine / 5 mM SLES, (b) 5 mM spermine / 1 mM SLES; see legend for details of the individual plot. Starting with the bottom curve each subsequent curve is shifted vertically by $\times 5$ with respect to the previous curve

The data in figure 3a for 5 mM spermine / 5 mM SLES evolves with time from a monolayer to a profile with a broad interference fringe evident, and ultimately to a structure with a pronounced Bragg peak at a $Q \sim 0.13 \text{ \AA}^{-1}$. The evolution in the reflectivity in figure 3b for 5 mM spermine / 1 mM SLES is different, with a Bragg peak at a $Q \sim 0.13 \text{ \AA}^{-1}$ present in all three measurements, but with increasing intensity. The ultimate profile in each case is very similar, and reflects the different time intervals of the measurements (see figure legends).

The ultimate reflectivity profiles are consistent with the formation of surface multilayer structures, as has been demonstrated in related systems (19-23).

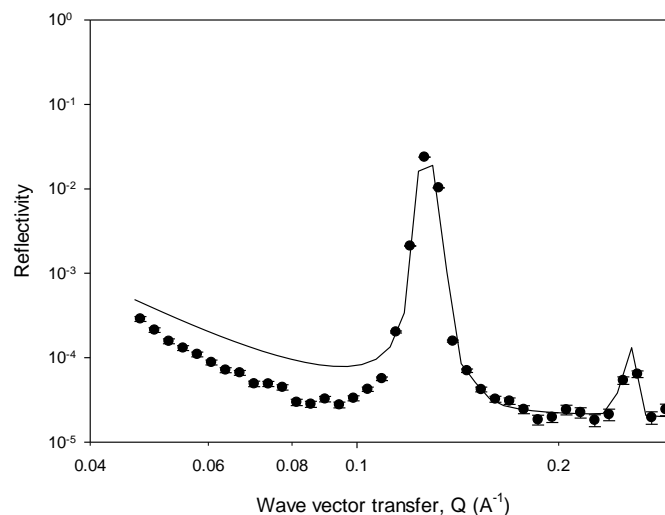


Figure 4. Neutron reflectivity for 5 mM spermine / 10 mM SLES. The solid line is a model fit as described in the main text and for the key model parameters listed in the main text.

The NR data corresponding to a surface multilayer structure, as shown in figure 3, are analysed quantitatively using a surface multilayer model based on the kinematic approximation (43, 44) and used extensively in related studies (19-23, 41). The key model parameters are the number of bilayers, N , the bilayer thickness d_t , where $d_t = d_1 + d_2$ and d_1 and d_2 are thicknesses of the alkyl chain and hydrated headgroup regions of the bilayer structure, and the scattering length densities of those two regions, ρ_1 , ρ_2 . The width of the Bragg peak is proportional to $1/N$ convolved with the instrumental resolution $\Delta Q/Q$ ($\sim 5\%$). The widths of the Bragg peaks in these data are dominated by the contribution from ΔQ . This and the absence of any subsidiary interference fringes from the total film thickness at the interface indicate that N is relatively large. Hence with only the 1st order Bragg peak, and sometimes the 2nd order (as shown in figure 4) the modelling is determined predominantly by N , d_t , $\Delta\rho$ ($\rho_1 - \rho_2$), and ΔQ . The data in figure 4 is for 5 mM spermine / 10 mM SLES, and the solid line

is a representative model fit. The data are modelled with $N=120$, $d_t=48$, $d_1=26$, $d_2=22$ Å, $\Delta\rho=3.5 \times 10^{-6}$ Å⁻², $\rho_1=4.5 \times 10^{-6}$, $\rho_2=1 \times 10^{-6}$, and $\Delta Q=0.06$. The associated model fits and summary of the key model parameters for the data in figure 3 are shown in figures S1 and S2 and tables S2 and S3 in the Supporting Information. The model parameters for the final multilayer structures shown in figures 3a and b are broadly similar to those for figure 4. The intermediate structure associated with the broad interference fringe in figure 3a is consistent with a three layer structure (see table S3 in the Supporting Information). Such structures can be considered as a precursor to the onset of multilayer formation and are frequently encountered in a range of polyelectrolyte / surfactant mixtures and related systems (16, 24-27, 39, 41).

Comparing the data for the surface multilayer structures for spermine / SLES mixtures in figure 4 and the associated model parameters with those previously reported for spermine / SDS mixtures (19) there are some notable difference. The Q value for the 1st order Bragg peak is ~ 0.13 Å⁻¹ for spermine / SLES whereas it is ~ 0.16 Å⁻¹ for spermine / SDS. This corresponds to a bilayer thickness of 48 Å for spermine / SLES compared to 38 Å for spermine / SDS. Xu et al (41) investigated the impact of ethylene oxide chain length on the surface multilayer structures in SLES / AlCl₃ mixtures, where for small N the bilayer thickness varied systematically with the degree of ethoxylation (in the range 1 to 3 ethylene oxide groups) of the SLES. For large N the bilayer thickness was independent of the degree of ethoxylation and was ~ 48 Å, similar to that obtained here for SLES / spermine. Going from SDS to SLES the bilayer thickness increases by ~ 10 Å. This can be readily accounted for by the contribution from the ethylene oxide spacer. Assuming ~ 3.5 Å per fully extended ethylene oxide the increased thickness per bilayer would be ~ 14 Å. A schematic representation of the surface structure for both Spermine / SLES and Spermine / SDS is shown in figure 5.

The 1st order Bragg peak is more intense for the SLES / spermine mixture than for SDS / spermine. This is reflected in a greater number of bilayers, ~120 compared to ~40; with the SLES / spermine multilayer structure extending further into the subphase than for SDS / spermine. In both mixtures the value for $\Delta\rho$ is similar and indicative of a relatively high surface coverage.

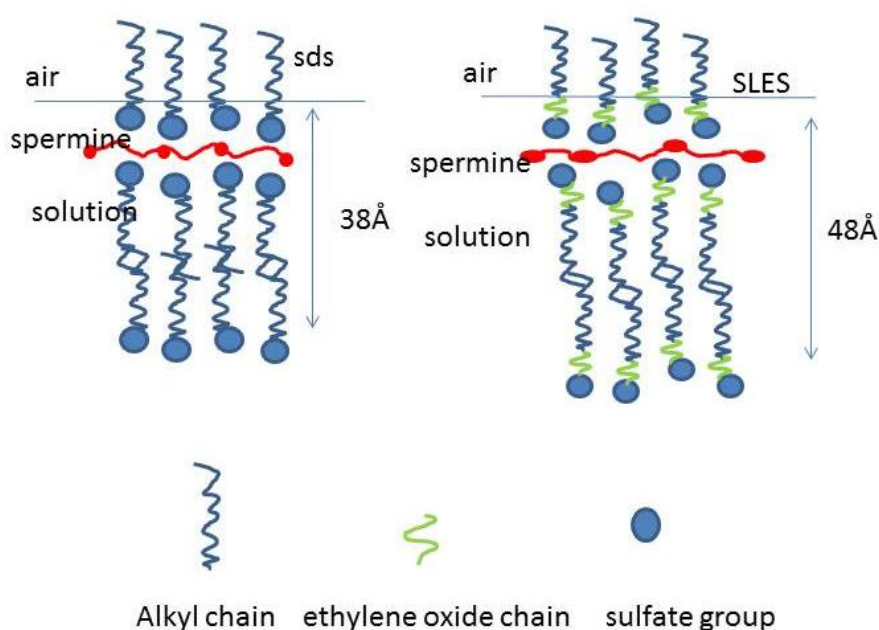


Figure 5. Schematic representation of the surface structure for Spermine / SLES and Spermine / SDS, showing the surface monolayer and initial bilayer structure only of a surface multilayer structure

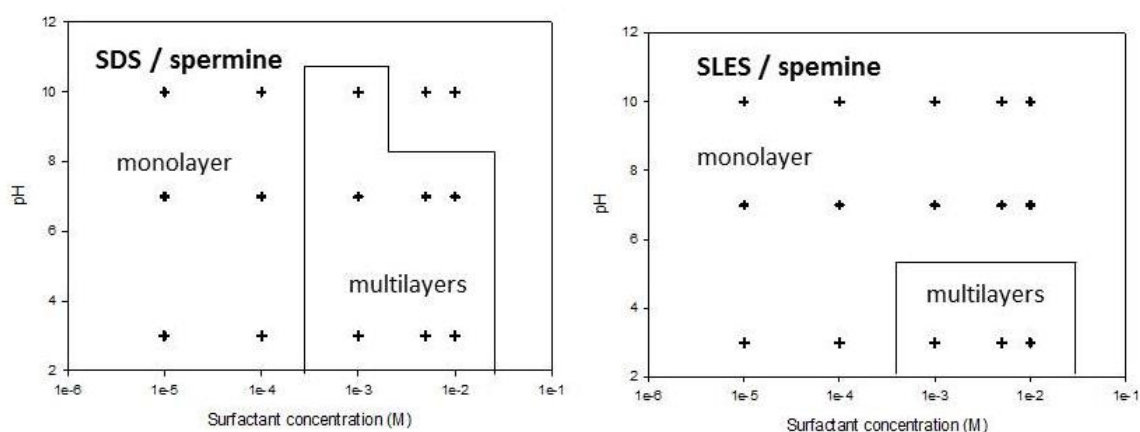


Figure 6. Approximate surface phase diagrams for surfactant / spermine mixture, SDS / spermine, and SLES / spermine; where the regions of monolayer adsorption and surface multilayer formation are indicated.

In figure 6 the approximate surface phase diagrams for SDS / spermine and SLES / spermine are compared. For SDS surface multilayer formation occurs at in the SDS concentration range 10^{-3} to 10^{-2} M at pH 3 and 7 and at pH 3 to 10 for the SDS concentration of 10^{-3} M. For SLES surface multilayer formation occurs over a more restricted pH range, and is only observed at pH for SLES concentrations between 10^{-3} and 10^{-2} M.

(ii) Discussion

The adsorption data presented in figure 2 show that the addition of spermine to SLES results in an enhanced surfactant adsorption down to relatively low SLES concentrations. The results are compared with those for SDS (19), and show a greater shift in the pattern of adsorption to lower concentrations with the addition of SLES than for SDS. The enhanced adsorption is attributed to the strong surface interaction between the anionic surfactant and biogenic amine, as previously observed and discussed for biogenic amines (19, 23) and in other oligoamine / surfactant mixtures (16, 20-22). At low pH when the oligoamines are highly charged the

interaction arises from the electrostatic attraction between the amine groups and the sulfate groups of the anionic surfactant. As the pH increases the charge on the oligoamine decreases such that at pH 10 it is essentially neutral. The surface interaction between the oligoamine and surfactant is observed to be also strong at high pH, and the enhanced adsorption observed is often largely independent of pH. The strong interaction at high pH has been attributed to the combination of an ion-dipole interaction between the surfactant sulfate headgroup and the amine nitrogen group and the inter-alkyl chain interaction between neighbouring attached surfactant molecules (45). This description of the nature of the interaction is reinforced by a wider range of studies (16, 19-25) and corroborated by the evidence from other studies (14, 15, 46-48). The results presented here are consistent with that overall description. The general pattern of ST behaviour for anionic surfactant / biogenic amine mixtures is illustrated in reference 19 for SDS / putrescine and SDS / spermidine mixtures, and that for SDS / spermine is expected to follow a similar pattern. It is analogous to that observed for anionic surfactants in the presence of multivalent counterions, as shown in reference 41 for SLES / AlCl_3 mixtures. In this respect the biogenic amine can be considered as acting like a flexible multivalent cation. For the SLES / AlCl_3 mixtures the addition of AlCl_3 shifts the ST pattern of SLES to lower SLES concentrations and results in a lower interfacial tension. In the absence of electrolyte SLES has a lower cmc (~ 2.5 mM) than SDS (~ 9 mM) (41), and the differences in the adsorption patterns in figure 2 for SLES / spermine and SDS / spermine are in part associated with the relative impact of the spermine on the surfactant cmc / cac.

The impact of an anionic surfactant with a different structure on its interaction and surface properties with PEI was investigated through a comparison between sodium dodecyl benzene sulfonate, LAS and SLES (27). It was found that the impact on the interaction, surface adsorption and surface complex formation was less pronounced for LAS than for SDS,

especially at high pH. This was attributed to the steric disruption associated with the LAS phenyl ring on the strength of the ion-dipole interaction which dominates the high pH interaction and behaviour. Related studies on surface multilayer formation in anionic / multivalent counterion mixtures (41, 50) showed that surface multilayer formation occurred in LAS / Ca^{2+} mixtures but not in SLES / Ca^{2+} mixtures. However surface multilayer formation was induced for SLES with the addition of trivalent counterions such as Al^{3+} (41). Adsorption and self-assembly data for SLES show that the sodium counterions are more tightly bound for SLES than in other anionic surfactants such as SDS and LAS (41), and this accounts for the difference response to the addition of Ca^{2+} and Al^{3+} ions. Indeed the experimental evidence implies that SLES is only weakly ionic. This is attributed to the presence of the ethylene oxide group modifying the dielectric constant in the headgroup region resulting in a stronger counterion binding due to the increased electrostatic attraction. Here the presence of the ethylene oxide group of the SLES modifies the interaction between the sulfate group and the amine nitrogen over the whole pH range where the interaction is dominated by the ion-ion attraction at low pH and the ion-dipole interaction at high pH. The subtle change in these interactions affects the balance of interactions which drive surface multilayer formation.

Surface multilayer formation at the air-water interface, induced in a range of polyelectrolyte . surfactant (39), poly(ethyleneimine) / surfactant (24-27), oligoamine / surfactant (20-22, 45), biogenic amine / surfactant (19, 23) and multivalent counterion / surfactant (41, 49) mixtures, has been extensively studied and reported. Thomas and Penfold (51) have recently reviewed the surface multilayer formation in a range of surfactant systems induced by multivalent counterions, oligoamines and polyelectrolytes. The surface multilayer formation is described primarily as associated with wetting or pre-wetting at the air-water interface by phases in the bulk solution, whose structures depend upon the attractive forces between the

associated constituents. The concentrated lamellar phase that forms at low surfactant concentrations, and is characteristic of that presented here, is driven by strong specific ion binding and bridging between surfactant layers.

In particular the recent studies on a range of small linear and branched oligoamines (20-22, 45) and biogenic amines (19, 23) have illustrated the importance of the oligoamine structures, MW, and charge density on the tendency to form surface multilayer structures. The more rigid branched oligoamines with a lower charge density have a greater tendency to promote multilayer structures at low pH (20). The more flexible linear oligoamines promote multilayer formation predominantly at higher pH. From the studies on a range of linear oligomers it is evident that surface multilayer formation is strongly dependent on MW. If the MW is too low there is a lack of cooperativity to drive multilayer formation. At higher MWs the entropic penalty due to the flexibility of the polymer chain is too great for multilayer formation (22). For the lower MW oligoamines the number of amine groups affects the pH dependence of multilayer formation (21). For the oligoamine triethylenetetramine and smaller multilayer formation occurs predominantly at low pH, whereas for tetraethylenepentamine and larger multilayer formation occurs at higher pH. For the biogenic amines (19) the increased spacing between the amine groups appears to make the conditions more optimal for surface multilayer formation compared to the equivalent oligoamines. All these observations point to the importance in the balance between the electrostatic attraction between the anionic surfactant headgroup and amine nitrogen group, the attraction between neighbouring surfactant alkyl chains and the repulsion between neighbouring surfactant headgroups in promoting surface multilayer formation. The results presented here show how adjusting the strength of the surfactant headgroup interaction with SLES rather than SDS can affect the surface multilayer formation. For SDS / spermine multilayer formation occurred over a wide range of surfactant concentrations and solution pH. In contrast for SLES it occurred only at

pH 3 and in a similar surfactant concentration range. As illustrated in other related studies (41, 49) the stronger counterion binding associated with SLES results in a weaker interaction with the oligoamine and a shift in the balance of competing interactions controlling surface multilayer formation.

CONCLUSIONS

Surfactant surface multilayer structures, induced by polyelectrolytes (24-27, 39), oligoamines (19-23, 45) or multivalent counterions (41, 49) have been extensively demonstrated (51). They offer a range of interesting potential applications in lung surfactancy (50, 52), tissue lubrication (53 54), fibre and hair conditioning (55) and in increasingly efficient detergency, soft lubrication and efficient delivery of perfumes and other active agents to surfaces (56) and in encapsulation. In the surfactant – oligoamine mixtures the criteria for surface multilayer formation arise from a balance between the surfactant-oligoamine inter molecular interactions and the surfactant inter-molecular interactions. It has been shown here how a relatively subtle change in the anionic surfactant headgroup from SDS to SLES results in a change in that balance of interactions and conditions for surface multilayer formation.

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SUPPORTING INFORMATION

Tables of some key model parameters and associated figures associated with the data analysis of monolayer and surface multilayer structures are available in the Supporting Information.

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GRAPHICAL ABSTRACT

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