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Anionic surfactant – Biogenic amine interactions: The role of surfactant headgroup geometry

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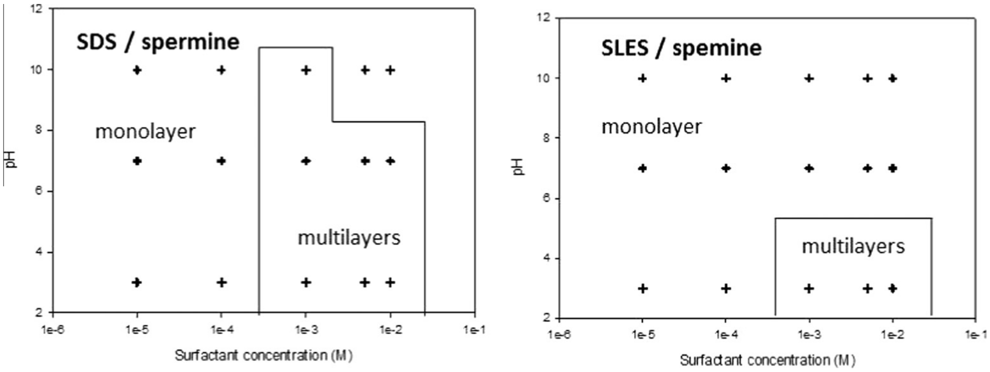
GRAPHICAL ABSTRACT



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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.

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1. 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 biomacromolcules 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 of 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 from 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.

2. 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 $\sim$ 0.045–0.5 Å^{-1} is covered using a fixed θ of 1.5° and a λ range of 0.5–7 Å.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 $\rho(z) = \sum_i n_i(z) \cdot b_i$, n_i and b_i are the number density and scattering length of the ith component and z is the direction perpendicular to the surface). Hence $R(Q)$ can be expressed as,

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

As H and D have different scattering lengths ($b_H = -2.7 \times 10^{-6}$ and $b_D = 6.67 \times 10^{-6}$ Å) 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 mol % 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 ~25 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 min and a series of measurements were made sequentially on a 5 position sample changer. Each measurement was repeated ~3–4 times, representing a total lapse time of up to ~6–8 h, 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, D_2O, was obtained from Sigma–Aldrich and high purity water (Elga Ultrpure) 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 spemine are shown in Fig. 1.

3. Results and discussion

3.1. 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 $\Gamma = 1/N_aA$, and N_a is Avogadro's number. From such NR data the statistical/systematic error in A at value of 50 Å^2 is