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Sodium Dodecyl Sulfate Adsorption onto Positively Charged Surfaces: Monolayer Formation With Opposing Headgroup Orientations

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Abstract

The adsorption and structure of sodium dodecyl sulfate (SDS) layers onto positively charged films have been monitored *in situ* with vibrational sum-frequency-generation (SFG) spectroscopy and surface plasmon resonance (SPR) sensing. Substrates with different charge densities and polarities used in these studies include CaF₂ at different pH values as well as allylamine and heptylamine films deposited onto CaF₂ and Au substrates by radio frequency glow discharge deposition. The SDS films were adsorbed from aqueous solutions ranging in concentration from 0.067 to 20 mM. In general the SFG spectra exhibited well resolved CH and OH peaks. However, at SDS concentrations between 1–8 mM the SFG CH and OH intensities decreased close to background levels. Combined data sets from molecular conformation, orientation, and order sensitive SFG with mass sensitive SPR suggest that the observed changes in SFG intensities above 0.2 mM are related to structural arrangements in the SDS layer. A model is proposed where the SFG intensity minimum between 1–8 mM is associated with a monolayer containing two head group orientations, one pointing towards the substrate and one pointing towards the solution phase. The SFG peaks observed at concentrations below 0.2 mM are dominated by the presence of adsorbed contaminants such as fatty alcohols (e.g., dodecanol), which are more surface active than SDS. As SDS solution concentration is increased above 1 mM SDS molecules are incorporated in the surface layer, with dodecanol continuing to be present in the surface layer for solution concentrations up to at least critical micelle concentration.

Keywords

Sodium Dodecyl Sulfate (SDS); Sum-Frequency-Generation (SFG) Spectroscopy; Adsorption; Surfactants

INTRODUCTION

Molecular level information about the interaction of surfactants with surfaces is of great interest for a range of industrial and scientific areas.^{1–5} Particularly sodium dodecyl sulfate (SDS) is used in such varied fields as cleaning applications, lubrication, stabilization of emulsions, preparation of nano- and microparticles, and even as model systems for

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biological membranes in protein research.^{6, 7} The formation of SDS layers also raises important questions about the dynamics of molecular self-assembly on surfaces. Surfactant adsorption is complex and involves a delicate, concentration dependent balance of forces between charge interactions of the headgroups with the surface,⁸ intermolecular van der Waals interactions,³ electrostatic repulsion between the headgroups,⁹ and interactions with the surrounding liquid phase.⁵ On charged surfaces, SDS head groups with negative charge bind at the interface and anchor the molecules to the surface. Upon completion of monolayer coverage, the surface charges are increasingly screened by surfactant headgroups.¹⁰ At higher concentrations typically around the critical micelle concentration (cmc) it has been suggested that a second – inverted – surfactant layer is formed by hydrophobic interactions of the tail groups in the first and second layer.¹¹

Studies of surfactants at interfaces have been done with a number of techniques including neutron reflectivity,^{12, 13} spectroscopic ellipsometry,^{14, 15} optical reflectometry,¹⁶ quartz crystal microbalance,¹⁷ filter viscometry,² atomic force microscopy^{18, 19} and vibrational sum-frequency-generation (SFG) spectroscopy.^{5, 8, 9, 20–34} While most of these techniques can accurately determine the amount of surfactant adsorbed at the interface, SFG spectroscopy is the only technique capable of providing insight into the molecular conformation, orientation, and order of surfactant layers *in situ*. The adsorption kinetics and energetics of a variety of surfactants including SDS have been studied in great detail, but the number of spectroscopic studies is still very limited. For a detailed understanding of SDS at surfaces it is essential to combine molecular-level structural information directly with adsorbed mass information to obtain a full understanding of the surfactant film structure.²⁶

The investigation of SDS at interfaces is further complicated by contaminants with high surface activity making it exceedingly difficult to prepare sufficiently pure SDS for surface studies.^{35, 36} In fact, concentrations of dodecanol at 0.1% can significantly reduce the surface tension at the air/water interface at solution concentrations up to the cmc.³⁷ Commercially available ‘as-received’ SDS typically contains 0.1–1% dodecanol, so unless extensive purification is done, impurities will be present in the SDS films and have a significant effect on their surface structure and composition.^{37–40} This is especially true at low SDS solution concentrations, but dodecanol will continue to present and have an effect for solution concentrations up to at least the cmc. To address effects of dodecanol on the structure of SDS, Bain and coworkers performed SFG studies of mixed dodecanol/SDS monolayers at hydrophobic solid surfaces.^{29–31} These studies showed that dodecanol has an effect on SDS conformation and packing density at concentrations below the SDS cmc.

Importantly, the above-cited studies clearly show that any SDS layer prepared under technologically and commercially relevant conditions, where it is not feasible or practical to invest the time and money required to produce ultra-high purity SDS, will be affected by contaminants in the SDS to varying but significant degrees. In this work, we therefore chose to use ‘as-received’ SDS without further purification as a realistic system that can be directly related to the use of SDS in practical applications. We recognize that impurities will change the recorded spectra and the structure of the materials at the interface, thus we will discuss the obtained data in this context.

We here combine SFG measurements with mass sensitive SPR data for SDS solutions ranging from micro- to millimolar concentrations to study the binding of SDS to positively charged surfaces. Using radio frequency glow discharge deposited allylamine (AAM) and heptylamine (HApp) surfaces as positively charged model surfaces allowed us to prepare identical substrate chemistries for both SFG and SPR.⁴¹ The latest SFG-based model of SDS adsorption onto positively charged surfaces, put forward by Richmond and co-workers, describes neutralization of net surface charge near 0.2 mM SDS solution concentration

related to monolayer coverage and onset of bilayer formation at higher concentrations.^{8, 22} The data reported here indicate that the monolayer-bilayer transition observed by Richmond et al. is most likely caused by contaminants and that the related adsorption model needs to be extended to account for additional film structure transitions.

MATERIAL AND METHODS

SDS solution preparation

Surfactant Dodecyl Sulfate (SDS) was purchased from Bio-Rad (99% purity). Experiments with both as-received and recrystallized SDS were done. SDS consists of a 12-carbon tail and anionic sulfate headgroup (see Figure 1). The as received powder was dispersed in degassed, deionized, and distilled water at room temperature. A 20 mM SDS solution was prepared by heating at 40°C overnight with moderate stirring. After dissolution, the solution was cooled to room temperature and then aliquots from the 20 mM SDS solution were diluted to obtain lower SDS solution concentrations. The SDS solutions were adjusted to pH 3.5 and pH 5.4 with acetic acid or 1M NH₄OH. For recrystallization the as-received SDS was dissolved into ethanol (Decon Labs, Inc., King of Prussia, PA) and then filtered with a 20 μ m syringe-filter. The ethanol was removed from the SDS solution via evaporation in a vacuum dessicator.

Radio Frequency (RF) Glow Discharge Coating

The radio frequency glow discharge (RFGD) deposition was performed using published procedures.^{42, 43} AAm (98% purity) and HApp (99% purity) were purchased from Sigma-Aldrich (see Figure 1). AAm and HApp films were deposited in an RFGD system. The vacuum system consisted of a rotary pumped glass vacuum chamber with an external RF electrode. The coupled external electrode was connected to the 13.56-MHz RF power source.

After loading the samples into the reactor and evacuating it to the base pressure of 10 mTorr with a rotary vacuum pump, oxygen was introduced inside the chamber and the pressure was maintained at 350 mTorr. The samples, holder and interior walls of the chamber were then cleaned by an 80 W oxygen discharge for 30 min. After oxygen etching, the chamber was evacuated to base pressure. The substrates were further cleaned and activated using a 30 W Ar discharge for 30 sec at 350 mTorr. AAm and HApp films were then coated onto Au pieces and CaF₂ prisms. First an adhesion-promoting layer of AAm was deposited at 80 W and 350 mTorr for 30 sec. Then the final AAm coating process was done at 10 W and 350 mTorr for 5 min. The deposition process for HApp was 80 W for 1 min (adhesion layer) followed by 10 W for 5 min (final layer), both at a pressure of 250 mTorr. The effective thickness of the deposited coatings was determined by spectroscopic ellipsometry (J.A. Woolam Co M-2000) to be 130 nm (AAm) and 220 nm (HApp). The refractive index of the AAm was determined to be 1.581. The rms roughness of the HApp film was determined by atomic force microscopy (Bruker Dimension Icon) to be 0.5 nm.

X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) experiments were carried out using an S-Probe XPS instrument (SSI, Mountain View, CA). The base pressure was below 10⁻⁹ Torr. XPS studies were performed using a monochromatized AlK $\alpha_{1,2}$ X-ray source and an analyzer pass energy of 150 eV. The Au substrates and the CaF₂ prism were mounted on standard sample stubs by means of double-sided adhesive tape and core-level spectra were recorded at a 55° photoelectron take-off angle. The photoelectron take-off angle is defined as the angle between the surface normal and the axis of the analyzer lens. The x-ray beam spot size was about 800 μ m and the x-ray power was 200 W. All binding energies (BEs) were

referenced to the hydrocarbon C 1s peak at 284.6 eV. Atomic % compositions were calculated using the Hawk Data Analysis v7 software, which incorporates the appropriate sensitivity factors for the S-Probe XPS instrument.

Vibrational Sum-Frequency-Generation (SFG) Spectroscopy

SFG spectra were acquired using a picosecond Nd:YAG laser (PL2241, EKSPLA) with a pulse duration of 35 ps at a repetition rate of 50 Hz. Visible (532 nm) light and tunable IR pulses are overlapped at the sample interface. The substrate films were deposited onto one side of an equilateral CaF₂ prism, which was brought into contact with the sample solution in a Teflon liquid cell as shown in Figure 2. The laser beams were brought in through the backside of the prism to probe the substrate/solution interface *in situ* in near-total internal reflection geometry. The visible and IR beams were overlapped at the sample spatially and temporally with incidence angles of 67° and 55° relative to the surface normal, respectively. The energy for both beams was 190–240 μJ per pulse in the CH and OH spectral regions and approximately 50 μJ per pulse for the IR beam in the SO spectral region. A spectral resolution of 2 cm⁻¹ was used for the *ppp* polarization combination (in the order of increasing wavelength; SFG, visible, and IR) between 2800 and 3000 cm⁻¹ with 200 shots accumulated at each wavenumber. For the *ssp* polarization combination between 2800 and 3850 cm⁻¹ and 1000 and 1100 cm⁻¹, the spectral resolution was 4 cm⁻¹ with 100 shots accumulated at each wavenumber. All spectra were divided by the visible and IR intensities and plotted without further smoothing.

The recorded SFG intensities I_{SFG} in the SO region were fitted in accordance to the following equation:

$$I_{SFG} \propto \left| \chi_{Res.}^{(2)} \right| I_{Vis} I_{IR} \quad \text{with} \quad \chi_{Res.}^{(2)} = \sum_k \left| \frac{A_k}{(\omega_{IR} - \omega_k) + i\Gamma_k} \right| e^{i\phi_k} \quad (1)$$

where $\chi_{Res.}^{(2)}$ is the second-order susceptibility, A_k the amplitude of the k -th resonance, ω_k its frequency and ϕ_k the phase difference between substrate and resonant response. Γ represents the linewidth of the k -th vibration and I_{Vis} , I_{IR} the intensities of the two incident beams.

Surface Plasmon Resonance (SPR)

The SPR sensorgrams were measured using a commercial T100 spectrometer (Biacore, GE Healthcare, NJ) with a 760 nm LED light source and a sample interface assembly (SIA Au kit). The SPR detection was based on the p-polarized reflected light from the AAm or HApp coated gold substrate, which was mounted in a micro-fluidic flow system. The reflection spectra are represented as a function of time. The flow rate was maintained at a slow speed (10 μl/min) to prevent the delamination of the plasma coated films. The data were obtained by first introducing pure water into the flow cell containing a fresh RFGD film, then switching from pure water to an SDS solution of known concentration while recording the SPR signal in real time.

The SDS solutions were flowed over the samples for 30 s (SDS concentrations <2 mM) or 10 s (SDS concentrations >2 mM). The spectra were collected with a computer using the standard Biacore software. The SPR measurements were repeated three times for each SDS solution concentration. After each injection of an SDS solution, the flow system was completely rinsed with flowing pure water for 1 hour. Each SPR spectrum was collected using a fresh AAm or HApp film.

Since the SPR signal did not fully saturate after 30 s of SDS adsorption for solution concentrations below 3 mM, the final signal was estimated by extrapolating the kinetic data using the following equation (see inset of Figure 9(A)): $y = y_0 + Ae^{-x/t}$.

The SPR signal values were then converted into adsorbed layer thickness, d (in nm) by using the following equation:

$$d = \frac{l_d}{2} \cdot \frac{\Delta R}{S(\eta_a - \eta_s)}, \quad (2)$$

where l_d is a characteristic decay length, S is the SPR sensitivity value, R is the SPR response, η_a and η_s are the refractive indices of the adsorbed film and SDS solution.⁴⁴ The sensitivity value (1.041×10^6 SPR units/RIU) was determined from calibration using ethylene glycol/water solutions with known refractive indexes (data not shown). The decay length is typically defined as 37% of the laser wavelength (760 nm). The SDS refractive index of 1.461 was used for η_a . Measured refractive indices of the SDS solutions showed them to be the same, within experimental error, of pure water. So the refractive index of pure water was used for η_s . Using the refractive index of solid SDS in equation (2) results in the calculation of an effective thickness, where the closer the structure of the adsorbed SDS film is to the structure of solid SDS the closer this effective thickness is to the actual film thickness. Further discussion regarding thickness calculations with equation (2) and the errors associated with those calculations are provided in reference 44.

RESULTS AND DISCUSSIONS

Stability of the AAm and HApp films

The compositions of the RFGD coatings were examined by XPS before and after exposure to water and an 11 mM SDS solution (Table 1) to characterize their stability and adhesion to the Au and CaF₂ substrates during the SFG and SPR experiments. The 11 mM SDS concentration were chosen to be above the cmc where the SFG signals are also maximized (see following SFG discussion). The XPS experiments were done at 3 different spots on the same sample. The XPS data in Table 1 shows the composition of the pristine HApp films were very similar to those of films soaked in the SDS solution. However, the AAm/Au film composition changed slightly after the longest exposure time (30 min) to the SDS solution. Sulfur was detected (3.2 atomic %) with a S2p BE of 168.6 eV. Also, this SDS-soaked AAm films had an approximately 5 atomic % higher oxygen concentration, 5 atomic % higher carbon concentration and 10 atomic % lower nitrogen concentration than the unsoaked AAm film. The detection of a S2p peak at 168.6 eV and an increase in the oxygen signal are consistent with SDS being retained on the AAm surface. The significant decrease in nitrogen concentration along with a small increase in the carbon concentration also suggest partial removal of the outer AAm film could be occurring at long SDS exposure times. To minimize the effects of residual SDS and film erosion from previous exposures to SDS solutions, fresh RFGD films were used for each SDS solution concentration in the SPR experiments. Thus, the total exposure time of the RFGD films to the SDS solutions was < 1 min, well below the time where XPS detected changes in the AAm films.

The C, N, and O atomic % values in Table 1 were renormalized to 100 atomic % to show the composition of the RFGD coating on the Au and CaF₂ substrates. The only sample where substrate peaks were detected was the AAm/Au film after 30 min water exposure (0.4 atomic % Au). The only sample where sulfur was detected was also the AAm/Au film after 30 min SDS solution exposure (3.2 ± 0.6 atomic % S).

ppp polarization SFG spectra in the CH stretching region

After verifying with XPS that the RFGD films were stable on the CaF_2 surfaces, SFG spectra were collected using the CaF_2 prism with RFGD deposited films and the bare CaF_2 prism. SFG spectra of AAm and HApp films, as well as bare CaF_2 in increasing SDS concentrations are shown in Figure 3 (with as received SDS used to prepare the SDS solutions). The spectra were collected using ppp polarization combination (sum-frequency, visible and IR beams all p-polarized). Since AAm films are hydrophilic and the AAm film becomes charged at lower pH values,⁴⁵ the SDS solution was maintained at a pH of 3.5. The spectra of the AAm coated substrate (Figure 3(A)) below 37 μM SDS concentration are featureless, while at 47 μM and higher SDS concentrations the spectra exhibit resonances near 2870 cm^{-1} , 2934 cm^{-1} , and 2958 cm^{-1} (data below 67 μM not shown). These modes can be assigned to the symmetric CH_3 stretching vibration, a CH_3 Fermi resonance and the asymmetric CH_3 stretching vibration.⁴⁶ Given that 'as-received' SDS was used to form these films, the observed CH peaks for SDS solutions below 0.2 mM are likely due to the presence of the highly surface active ordered fatty alcohol contaminants (e.g., dodecanol) and not ordered SDS. The spectra at both 0.2 mM and 1 mM solution concentrations show extremely weak signals. The presence of methyl bands and the almost absence of methylene resonances is indicative of well-aligned, all-trans hydrocarbon chains with few gauche defects (both dodecanol and SDS contain C12 alkyl chains). This is due to symmetry considerations of an alkane chain in an all-trans configuration. In this case a center of inversion is present between the methylene groups, making the methylene CH stretches SFG inactive. This is a consequence of the SFG selection rules, which precludes signals from molecules possessing inversion symmetry or isotropic arrangements.⁴⁷

To verify that the transitional features observed on AAm are general phenomena and valid for other positively charged interfaces, we have also collected SFG spectra for SDS adsorption onto positively charged HApp surfaces. CH stretching SFG data for SDS adsorbed onto HApp surfaces are shown in Figure 3(B). The HApp films are more hydrophobic compared to the AAm films, but also remain uncharged at neutral pHs.⁴⁸ Therefore, the SDS adsorption was done from aqueous acidic solution (pH of 3.5) as well, so the HApp films will have a positive charge. The spectra contain the expected CH_3 resonances near 2871 cm^{-1} , 2938 cm^{-1} and 2957 cm^{-1} similar to those recorded on AAm films. However, the signal to noise ratio is somewhat lower on the HApp films compared to the AAm films, which might be explained by a rougher surface.⁴⁹ The main difference is that for HApp films the lack of SFG signal was observed at solution concentrations of 0.2 mM and between 1 and 5 mM, compared to solution concentrations of 0.2 and 1 mM for AAm films.

To further confirm that the adsorption mechanism depends on SDS concentration, SFG spectra from SDS adsorption onto a CaF_2 substrate were acquired at pH 3.5 (Figure 3(C)) and pH 5.4 (Figure 3(D)). Streaming potential measurements indicate that the point of zero charge of CaF_2 is at pH 6.2,⁵⁰ so CaF_2 should be positively charged at both pH 3.5 and 5.4. The SFG spectra at pH 5.4 and pH 3.5 are very similar. Only the 0.067 mM spectral intensity was observed to vary significantly, which is not unexpected since at this solution concentration the surface film should be predominately comprised of the fatty alcohol contaminants. SDS adsorption onto the CaF_2 substrate exhibits no SFG signal for solution concentrations of 0.2 and 3.5–8 mM. In the other concentration ranges the peaks around 2870 and 2934 cm^{-1} , and 2957 cm^{-1} appear with comparable intensities to those observed on the HApp and AAm films.

For all samples studied the CH region exhibits two minima in spectral intensity. The first minimum is at 0.2 mM SDS solution concentration and is independent of the substrate used. The second minimum ranges from 1 to 5 mM SDS solution concentration, depending on the

surface. The lack of an SFG signal can, in principle, be explained by a disordered layer, low surface coverage, or centrosymmetric molecular arrangements such as bilayers or monolayers with opposing head groups. It is also interesting to note that the shape of the three resonances (i.e., the relative signal phases) changes dramatically across the transitional concentrations above 0.2 mM and additionally, in the case of AAm, at concentrations above 11 mM. The phase changes of the SFG signals are indicative of structural changes in the film and will be further discussed in the section analyzing the SO_3 stretching vibrations of SDS.

ssp polarization SFG spectra in the CH and OH stretching regions

The ordering of SDS and water at the AAm, HApp, and CaF_2 surfaces was studied in the CH and OH regions using the ssp polarization combination (Figure 4). The SFG response in the OH stretch is generally stronger in ssp polarization compared to ppp polarization.^{51, 52} For SDS solution concentrations above 1 mM the OH stretching regions exhibit broad resonances between 3000 and 3650 cm^{-1} . The peaks observed at 2862 and 2932 cm^{-1} can be assigned to the CH_3 symmetric stretching mode and the CH_3 symmetric stretching Fermi resonance.²² Similar to the ppp polarization spectra, the presence of primarily methyl stretches in the C-H stretching regions indicates a considerable degree of alignment of all-trans fatty alcohol and SDS alkyl chains.

The OH stretching signals only become significantly stronger at concentrations above 0.2 mM. This increase in intensity is most probably related to electrostatic interactions between the charged SDS molecules starting to assemble at the interface (see next section) and polar water molecules in the vicinity of the interface. Increasing the SDS solution concentration leads to a minimum in intensity that is observed at 3 mM for films of AAm (Figure 4(A)), 5 mM for HApp (Figure 4(B)), 8 mM for CaF_2 at pH 3.5 (Figure 4(C)), and 8 mM CaF_2 at pH 5.4 (Figure 4(D)). This decrease in OH signal intensity is accompanied by a decrease in CH signal intensity, with the exception of CaF_2 at pH 5.4. In this case the OH stretch minimum occurs at an SDS solution concentration of 8 mM, whereas the CH stretch has its minimum at an SDS solution concentration of 5 mM. Assuming that electrostatic interactions have the largest influence on the OH signal strengths, this suggests that the surface becomes neutralized near the SDS solution concentration range where the second minimum in the CH stretch is observed.

Contributions of contaminants to the SFG spectra

In both polarization contributions, a strong SFG CH signal was obtained from 67 μM SDS solutions and no SFG signal was observed from 0.2 mM SDS solutions. The appearance of signals below 0.2 mM are likely from impurities such as unsulfated alcohols, which have been observed in various commercial SDS products.^{39, 53} These fatty alcohols can successfully compete with SDS for surface adsorption sites at SDS solution concentrations below 0.3 mM and remain in the surface film at least until the solution concentrations reaches the SDS cmc.^{38, 54, 55}

The as-received SDS purity was 99%. To remove some of the fatty alcohol impurities from the 'as-received' SDS, solutions of recrystallized SDS were examined. The corresponding SFG CH spectra shown in Figure 5 are featureless for recrystallized SDS solutions below 0.2 mM, but exhibit CH vibrational peaks above 0.4 mM. No SFG signal was observed from 5 mM recrystallized SDS solutions, similar to 'as-received' SDS solutions (see Figure 3(C)). It is interesting to note that the CD region of the SFG spectrum recorded from a 67 μM fully deuterated SDS solution is featureless (see insert in Figure 5), as is the spectra from a 0.2 mM fully deuterated SDS solution (data not shown), suggesting the amount of deuterated fatty alcohol contamination in the deuterated SDS solutions is lower than the undeuterated

fatty alcohol contamination in the as-received undeuterated SDS solutions. Since the fatty alcohol is a contaminant, it is not surprising its concentration varies among different types and sources of SDS. Thus, results from the recrystallized SDS and deuterated SDS solutions are consistent with SDS present on the surface only above SDS solution concentrations of 0.2 mM. Contaminants such as dodecanol from the as received SDS are likely the dominant adsorbed species contributing to the SFG spectra observed at solution concentrations below 0.2 mM. Dodecanol will continue to be present in the SDS films as the solution concentration is increased to the SDS cmc.

ssp polarization SFG spectra in the O–SO₃ stretching region

While the previous paragraph discusses spectral contributions at higher frequencies, this section discusses the SFG O–SO₃ SDS headgroup stretching vibrations between 1000 and 1150 cm⁻¹.⁵⁶ Figure 7 shows the ssp polarization SFG spectra recorded at the SDS/CaF₂ interface at a fixed pH 3.5 value and different SDS concentrations. The first observation is the absence of SFG intensity at SDS solution concentrations $\leq$ 2 mM. This further confirms that SDS is not adsorbing onto the CaF₂ surface in an ordered fashion at sufficient surface density from the low concentration SDS solutions. However, the presence of strong CH bands for the as received SDS solutions at concentrations below 0.2 mM indicates the existence of an ordered layer at these concentrations, but the absence of SO₃ vibrations makes it unlikely that SDS is the source for these CH spectral features. Bain et al. previously showed that low concentrations of dodecanol form well-ordered films, suggesting dodecanol or similar fatty alcohol is responsible for the CH signals observed at solution concentrations below 0.2 mM made with as-received SDS.³⁰ At solution concentrations above 0.2 mM the alkyl chains in both dodecanol and SDS will contribute to the CH signals.

Furthermore, starting at 3.5 mM a double peak with frequencies of 1074 and 1087 cm⁻¹ appears and continues to grow in intensity at concentrations where the CH signals are vanishing (between 5 and 8 mM, see Figs. 3 and 4). The presence of SO₃ vibrations and the absence of the CH signals in this concentration range can, therefore, be related to a molecular SDS arrangement where the methyl groups are in a symmetric environment while the sulfate headgroups are in an ordered, non-symmetric environment. A symmetric methyl group arrangement can be accomplished by an equal number of opposing SDS chains. This can be realized in a bilayer or a monolayer with opposing orientations of SDS molecules. The most likely bilayer configuration would have the SDS headgroups in the inner layer facing the substrate and the SDS headgroups in the outer layer facing the water phase. The most likely monolayer configuration would require interdigitating SDS chains. If an SDS bilayer does form at solution concentrations between 3 and 8 mM, the reappearance of methyl vibrations at higher solution concentrations would suggest the formation of an additional layer on top of the bilayer as shown in Figure 6(A). This seems energetically unfavorable due to the adjacent location of the charged headgroups from the second and third layers as well as the hydrophobic chains extending into the water phase. A more plausible explanation is a single layer with opposing headgroups and interdigitating alkyl chains as shown in Figure 6(B). Other SDS adsorption models such as hemi-micelles have been considered (e.g., see references 11 and 26). However, the arrangement of the SDS molecules in these models is not consistent with the results of these study. So only the planar, layered models are discussed in detail here.

As the effective surface charge becomes neutralized with increasing SDS adsorption, it becomes more favorable for SDS molecules to expose their headgroups towards the water phase. At the highest SDS solution concentrations (i.e., above 8 mM) this would lead to an unequal population of sulfate headgroups pointing towards the water phase and methyl groups pointing towards the substrate, thus, breaking the methyl group symmetry and resulting in the reappearance of the CH bands. At the SDS solutions above the cmc the

presence of fatty alcohol molecules in the film should be minimized since Bain et al have shown that above the cmc dodecanol mostly resides in the SDS micelles.³⁰ Following this, SDS continues to adsorb with both headgroups pointing towards the substrate as well as headgroups pointing towards the water phase. As the sulfate headgroup is experiencing a different environment in both orientations, e.g. one is exposed to a charged surface while the other is adjacent to water, their vibrational stretching frequencies are different. It has been shown that for SDS at the air/water interface with the headgroups pointing towards the water phase, only a single peak close to 1070 cm^{-1} is observed.^{9, 34} Therefore, we assign the 1074 cm^{-1} peak to sulfate groups pointing towards the water phase and the 1087 cm^{-1} peak to sulfate groups pointing towards the substrate.

The double peak also explains the absence of an intensity minimum in the SO_3 vibrations (see Figure 7), in contrast to the intensity minima observed in the CH vibrations. Fig. 8 shows also a curve fit of these spectra using Equation (1). The two peaks can be separated and their phase can be determined. Before discussing the phase, it is important to realize that nonpolar methyl groups are not affected by the surface charge or the presence of the water phase. Therefore, an opposing orientation would result in opposing orientation of IR transition dipole moments (TDMs) and, therefore, a phase shift around π that leads to a cancellation of the signals (destructive interference). The same holds true for the headgroups, except that the energy is split. This is further illustrated in Figure 8 showing the phases from the 2 peaks as well as their intensities as a function of solution SDS concentration. Fitting 2 peaks with similar phases was not possible with physically meaningful peak widths. The difference in phases is close to 120° indicating a change in sign of $\chi_{\text{res.}}^{(2)}$ as a result of an opposing orientation of TDMs, e.g. upward and downward. Most importantly, the energetic splitting does not lead to a vanishing signal, even if the phases are closer to 180° than to 0° . The 2 peaks located at 1074 and 1087 cm^{-1} become easily visible at 3.5 mM SDS solution concentration. Both contributions are increasing with SDS solution concentration until the cmc is reached. (Note that, in consideration of the error bars, a thorough quantitative analysis of relative headgroup orientations, i.e. if more SDS molecules are pointing up than down, cannot be performed unambiguously.) Finally, the signal becomes generally lower at 20 mM SDS solution concentrations, possibly due to the presence of micelles in the vicinity of the interface disrupting the organization of the SDS monolayer or due to the release of the remaining dodecanol from the SDS monolayer.

As a summary of the SFG spectroscopy data, SDS only starts to adsorb at the CaF_2 interface for solution concentrations of 0.2 mM and above. Below these solution concentrations fatty alcohol impurities (i.e., dodecanol) are absorbing at the interface that are responsible for the CH signals. Above 0.2 mM contributions of SDS with the headgroup orientated towards the substrate lead to neutralization of the surface charge. In addition SDS with headgroups orientated towards the water interface are present. The doublet SO_3 peaks are increasing with SDS solution concentration while the CH peak intensities reach a minimum, the latter due to destructive interference of opposing methyl group TDMs at the same vibrational frequency. Above this concentration micelles are formed in the solution phase. This will be discussed further in a following section. While the SFG data, which provides information about the molecular structure of the SDS layer suggests different headgroup orientations, it is not sensitive to the thickness of the corresponding layer (e.g., whether the arrangement corresponds to a bilayer or a monolayer with opposing headgroup orientations). The amount of material in the SDS layer needs to be determined with a technique sensitive to the surface coverage and thickness of the SDS layer.

SPR data of SDS adsorbed to AAm and HAp films

The SPR results in Figure 9 show that a small amount of material is adsorbed on the films at SDS solution concentrations below 0.2 mM. As-received SDS was used for these experiments, so the SPR signal detected from these solutions is likely due to adsorption of the fatty alcohol contaminant in the as-received SDS. The SPR signal shows a slight decrease near a solution concentration of 0.2 mM where the SFG CH intensity disappears, likely due to SDS molecules beginning to co-adsorb with the fatty alcohol, causing the adsorbed fatty alcohol to disorder and suggesting that this change in the structure and morphology of the adsorbed film could be responsible for the slight decrease in the SPR signal. Most importantly, the surface concentration of the adsorbed species is sub-monolayer at SDS solution concentrations below 1 mM (see next paragraph), ruling out the possibility that the minimum in the SFG CH intensity observed for solution concentrations of 0.2 mM is due to formation of an SDS monolayer, as proposed in previous studies. Above solution concentrations of 0.2 mM the SPR signal continues to increase as the solution concentration increases. From SDS solution concentrations of 0.2 mM up to the cmc, this increase is primarily due to an increase in adsorbed SDS, consistent with the observed increase in the SFG sulfate peaks. Above the cmc the further increase in the SPR signal is likely due to the presence of micelles in the region sampled by the evanescent wave, since its sampling depth extends beyond the adsorbed SDS film and into the liquid phase.

The thickness of the adsorbed film was determined by converting the SPR response to a thickness using equation (2). Based on the length of the SDS molecule an SDS monolayer should have a thickness between 1.5 and 2 nm, depending on the exact tilt of the SDS molecules from the surface normal. The calculated thicknesses for the adsorbed film only reach the lower limit of this range (1.5 nm) at an SDS solution concentration of 11 mM. Thus an SDS monolayer is not formed until at or slightly above the SDS cmc. At the lower SDS solution concentrations the thicknesses are below those expected for a monolayer (e.g., ~0.6 nm for 1 mM SDS and ~1 nm for 3 mM SDS). Thus, at SDS solution concentrations where the second minimum in the CH intensity occurs (1–5 mM) the SDS surface coverage is still in the submonolayer to monolayer regime and well below the thickness expected for an SDS bilayer (~3.5 nm).

SDS adsorption model: Monolayer with opposing headgroups

In Figure 10 a model is proposed for how the SDS monolayer with opposing head group orientations is formed as the SDS solution concentration increases. With increasing number of adsorbed SDS molecules, the charged substrate becomes neutralized. Since the tail groups of SDS are hydrophobic, further adsorption leads to an SDS monolayer with opposing headgroup orientation. This is supported by (i) a minimum intensity for the methyl vibrations because of an equal number of methyl groups in downward and upward orientations in the monolayer (between solution concentrations of 3 and 8 mM), (ii) SFG spectral analysis for the SO_3 band that exhibited two contributions with positive and negative phases (see Figure 8). Since SDS is in an upright orientation in the 3 to 8 mM concentration range, this indicates one sulfate group points toward liquid phase and the other sulfate group binds to the substrate. Finally, the surface coverage determined by SPR corresponds to a monolayer rather than a bilayer, all of which is consistent with a model where an SDS monolayer is formed at the interface with opposing headgroup orientation.

The observed decrease in both SO_3 and CH band above 14 mM can be interpreted as a disordering of the sulfate and methyl groups. These solutions are well above the cmc, so it is likely the micelles present in solution may pass close enough to the SDS monolayer to influence its order and orientation. For example, the sulfate headgroups from the SDS layer that point towards the water phase could experience an electrostatic repulsive interaction

with the charged sulfate groups on the outer surface of the micelles, resulting in a disordering of those SDS molecules. Another possible explanation for the decrease in SO_3 and CH band intensities above 14 mM is that removal of dodecanol from the adsorbed monolayer at these SDS solution concentrations causes some disordering of the adsorbed SDS molecules.

Conclusion

In summary, based on the SFG and SPR results, the formation of films from solutions made with as-received SDS (i.e., SDS containing fatty alcohol contaminants) on positively charged surfaces exhibits five structural phases. (i) $c < 57 \mu\text{M}$: At micro-molar solution concentrations the film coverage and order is very low, if any. The ordered species observed at these low concentrations are likely due to contaminants such as fatty alcohols adsorbing onto the substrate. (ii) $57 \mu\text{M} < c < 0.2 \text{ mM}$: In this lower part solution concentration range the film consists predominately of adsorbed fatty alcohols. In the higher part of this solution concentration range, SDS molecules start to co-adsorb onto the surface. (iii) $0.2 \text{ mM} < c < 3\text{--}8 \text{ mM}$: A formation of a monolayer is characterized by initial adsorption of the SDS with the headgroups pointing towards the surface to compensate and screen surface charges. With decreasing surface potential, some SDS molecules begin adsorbing in the opposite orientation (headgroups pointing towards the water phase). This leads to the formation of a monolayer with opposing headgroup orientations at solution concentrations in between 3 and 8 mM, depending on the initial surface charge of the substrate. The opposing headgroup orientation results in an inversion symmetry for the methyl groups and loss of SFG CH peak intensities. (iv) $3\text{--}8 \text{ mM} < c < 11 \text{ mM}$: As the solution concentration continues to increase, more SDS molecules are adsorbed with an unequal distribution between up and down orientations, resulting in the reappearance of the SFG CH signal. (v) $c > 11 \text{ mM}$: Micelles in the water phase interact with SDS headgroups in the SDS monolayer that point towards the water phase, resulting in some disordering within the SDS monolayer. Removal of dodecanol from the adsorbed monolayer at these solution concentrations could also be responsible for some disordering in the SDS film.

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Figure 1.
Chemical structures of (A) Allylamine, (B) Heptylamine and (C) Sodium Dodecyl Sulfate.

Figure 2.
Schematic of the SFG experimental geometry.

Figure 3.

CH region SFG spectra of SDS/AAM at pH 3.5 (A), SDS/HApp at pH 3.5 (B), CaF_2 at pH 3.5 (C), and CaF_2 at pH 5.4 (D). The SFG spectra were collected in the ppp polarization combination. As received SDS was used to prepare the SDS solutions for the experiments shown in this figure.

Figure 4.

CH and OH region SFG spectra of SDS/AAm at pH 3.5 (A), SDS/HApp at pH 3.5 (B), CaF₂ at pH 3.5 (C), and CaF₂ at pH 5.4 (D). The SFG spectra were collected in the ssp polarization combination. As received SDS was used to prepare the SDS solutions for the experiments shown in this figure.

Figure 5. CH SFG data acquired from a CaF_2 substrate and SDS solutions made with recrystallized SDS. The spectra were collected in the ppp polarization combination. The inset shows the CH SFG spectrum of 0.067 mM deuterated SDS. The SDS solution pH was 3.5.

Figure 6. Two possible SDS adsorption models. (A) Formation of an SDS bilayer on the surface. (B) Formation of an SDS monolayer with half the SDS headgroups pointing towards the surface and half the SDS headgroups pointing towards the water phase.

Figure 7.

The ssp polarization SFG spectra near 1100 cm^{-1} obtained from the SDS/CaF₂ interface at pH 3.5. The spectra have 2 contributions that are related to SO₃ vibrations pointing towards the water phase (1074 cm^{-1}) and the CaF₂ substrate (1087 cm^{-1}). The thicker lines represent fits of the spectra using eq. (1).

Figure 8.

Fitting results for the phases and amplitudes of the SO_3 band as a function of SDS solution concentration. The black and red data points correspond to the bands at 1074 cm^{-1} and 1087 cm^{-1} , respectively. The phases for the two contributions differ by $\sim 120^\circ$ and their intensities increase where the signal in the CH spectra reaches a minimum.

Figure 9.

SPR signal vs time during exposure of SDS solutions to AAm films (A) and HApp Films (B). Before time 0, only water was flowing across the clean surfaces. SDS was introduced starting at time 0 and then after the SPR response approaches saturation, the surface was rinsed with water. Most SDS is removed upon rinsing, thus SDS adsorption is predominantly reversible on both AAm and HApp surfaces.

Figure 10. Proposed schematics for different phases of SDS adsorption onto positively charged substrates.

Table 1

Elemental composition (atomic %) of the AAm and HApp films before and after soaking in water and 11 mM SDS solution as determined from the XPS data. The numbers in parentheses represents the standard deviation for each atomic percentage.

Coating	Substrate	Solution	Soaked time	C	N	O
AAm	Au	–	0	72.1 (0.2)	19.8 (0.3)	8.0 (0.3)
			1 min	72.8 (0.4)	17.9 (0.3)	8.8 (0.2)
			3 min	72.6 (0.3)	18.0 (0.3)	9.0 (0.2)
			30 min	73.0 (0.2)	17.9 (0.3)	8.3 (0.2)
	11 mM SDS	11 mM SDS	1 min	72.0 (0.6)	19.3 (0.2)	8.5 (0.4)
			3 min	74.1 (0.3)	16.4 (0.3)	9.3 (0.2)
			30 min	75.1 (0.3)	8.4 (0.4)	13.2 (0.6)
HApp	Au	–	0	71.1 (0.3)	22.6 (0.3)	6.2 (0.7)
			1 min	74.4 (0.4)	21.7 (0.1)	8.9 (0.4)
			3 min	74.4 (0.3)	21.6 (0.2)	3.9 (0.4)
			30 min	71.5 (0.4)	22.2 (0.2)	6.4 (0.3)
	11 mM SDS	11 mM SDS	1 min	90.7 (0.9)	8.2 (0.6)	0.9 (0.2)
			1 h	90.7 (0.3)	8.2 (0.5)	1.0 (0.1)
			1 h	91.1 (0.9)	7.1 (1.0)	1.7 (0.1)
HApp	Au	–	0	91.0 (0.6)	8.3 (0.7)	0.6 (0.1)
			1 h	92.2 (0.4)	6.9 (0.4)	0.7 (0.1)
			1 h	91.4 (0.8)	7.8 (1.0)	0.7 (0.2)
	11 mM SDS	11 mM SDS	1 min	91.0 (0.6)	8.3 (0.7)	0.6 (0.1)
			1 h	92.2 (0.4)	6.9 (0.4)	0.7 (0.1)
			1 h	91.4 (0.8)	7.8 (1.0)	0.7 (0.2)