Coadsorption of Sodium Dodecyl Sulfate and Dodecanol at a Hydrophobic Surface

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Sum-frequency spectroscopy has been used to study coadsorption of dodecanol and sodium dodecyl sulfate (SDS) at the interface between aqueous solutions and a monolayer of octadecanethiol on gold. Selective deuteration was employed to distinguish between the two adsorbed surfactants. Mixed monolayers were studied over a range of SDS concentrations with dodecanol present at a level of 1 mol %. The results are compared with other data published previously and with literature studies of the air/water interface. A quantitative analysis of the monolayer adsorbed from 6 mM SDS + 10 μM dodecanol showed that the monolayer comprised 63% dodecanol and 37% SDS and had a packing density comparable to that of a monolayer of pure dodecanol. The composition of the monolayer was found to be isotope dependent. This dependence might arise from a highly surface active impurity in the SDS but can also be explained quantitatively by a lattice model of the monolayer within regular solution theory.

Introduction

Commercial samples of the important anionic surfactant sodium dodecyl sulfate (SDS) are invariably impure. The principal organic contaminants are homologous alkyl sulfates, *n*-alcohols (from which alkyl sulfates are formed and to which they are readily hydrolyzed[1]), and carboxylic acids (formed by oxidation of alcohols[2]). It is extremely difficult to prepare SDS that is sufficiently pure for surface chemistry, and much of the early work on SDS solutions may be unreliable due to the influence of contaminants.[2,3] Dodecanol is the most important contaminant and one of the hardest to remove. Even at impurity levels below 0.1%, dodecanol reduces the surface tension, γ, of SDS solutions and leads to the well-known minimum in γ below the critical micelle concentration (cmc).[4] The presence of dodecanol in SDS solutions has a dramatic effect on the surface properties, such as surface tension,[4] dilational modulus,[5] and shear viscosity,[6,7] and consequently on physical behavior, such as foam stability.[7,8] Numerous studies have attempted to establish the adsorption isotherms of SDS/dodecanol mixtures at the air−water interface by a variety of techniques, including radiotracer measurements,[9] surface tensiometry,[10] foam fractionation,[11] and neutron reflection.[12] SDS/dodecanol mixture have also been investigated at the oil−water interface. In contrast to the air−water interface, traces of dodecanol have little effect on the oil−water interface because dodecanol is highly soluble in the oil phase.[13]

An extensive literature exists on the adsorption of SDS alone at the interface between water and both polar and nonpolar solids.[14] There have, however, been surprisingly few studies on the effect of dodecanol on the adsorption of SDS at the solid−water interface. Rosen used a hydrophobic silica HPLC column to purify SDS[15] but did not report any quantitative measurements on the preferential adsorption of dodecanol at the solid−water interface. In an attempt to understand the adsorption process at a molecular level, we have used sum-frequency spectroscopy (SFS) to study mixtures of SDS and dodecanol adsorbed at a model hydrophobic surface: a self-assembled monolayer of octadecanethiol (ODT) on gold.[16] In a preliminary communication, we showed that SFS could discriminate between the coadsorbed SDS and dodecanol and demonstrated the sensitivity of SFS to the packing density and conformational order in the adsorbed monolayer.[17] This paper begins with a qualitative description of the adsorption isotherms of mixtures of dodecanol and SDS at a hydrophobic surface. The main part of the paper contains a quantitative analysis of SF spectra obtained for one set of concentrations and a detailed discussion of the assumptions underlying the analysis. The concentrations (6 mM SDS + 10 μM dodecanol) were chosen to reflect the behavior of a "pure" commercial sample below the cmc. Finally, adsorptions of SDS/dodecanol mixtures at the solid−water and air−water interfaces are compared.

SFS of the solid−liquid interface has been reviewed recently.[18] The basic principles are summarized in Figure 1 for readers unfamiliar with the technique.[19] SFS has several useful features for studying the adsorption of mixtures of surfactants at the solid−water interface.[18] First, SFS is interface specific: only molecules adsorbed at the interface are detected; no signal arises from molecules in solution. Second, since SFS is a form of vibrational spectroscopy, we can distinguish between the adsorbed dodecanol and SDS, and between the surfactants and the ODT monolayer, by deuterating one or two of the species. The C−H stretching modes fall between 2800 and 3000 cm^{-1}, and the C−D stretching modes fall between 2000 and 2250 cm^{-1}. Water is sufficiently transparent in both these regions for the detection of protonated and deuterated surfactants. Third, the methylene and methyl stretching modes in SF spectra are very sensitive to conformational order in the hydrocarbon chain. Since all-trans hydrocarbon chains are locally centrosymmetric,

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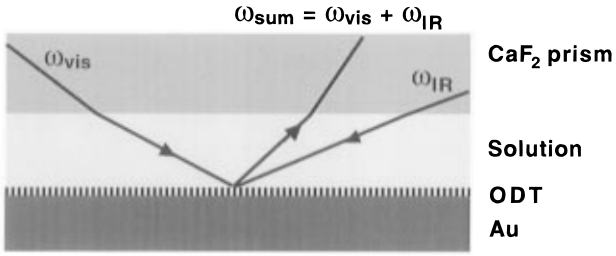

Figure 1. Schematic diagram of sum-frequency spectroscopy of the solid−liquid interface. A thin film (∼micrometers) of surfactant solution is sandwiched between a CaF_2 prism and a hydrophobic substrate (a monolayer of octadecanethiol on gold). A pulsed visible laser and a tunable pulsed infrared laser are overlapped at the interface, and the light emitted at the sum-frequency is detected. The SF emission is coherent and in a well-defined direction. The intensity of the emitted light changes when the IR laser is in resonance with a vibrational mode of an adsorbed molecule. The line strength depends on the product of the IR and Raman transition moments and on the polar orientation of the molecules. Scanning the frequency of the IR laser yields a sum-frequency spectrum.

the rule of mutual exclusion applies to the normal modes of the methylene groups. The line strength in SFS depends on the product of the IR and Raman transition dipole moments, and hence the methylene modes in an all-trans chain are SF inactive. Gauche defects may break this local centrosymmetry and give rise to methylene modes in a SF spectrum. The intensity of the CH_3 stretching modes depends on the average orientation of the terminal methyl groups. In a densely packed monolayer, the methyl groups are highly oriented and the CH_3 modes in a SF spectrum are strong. In a conformationally disordered monolayer, the methyl groups have a wide distribution of orientations and the CH_3 modes are consequently weak. The relative strength of the methylene and methyl stretching modes is thus a good indicator of conformational disorder.[20,21] Finally, the intensity of the SF signal depends on the surface coverage:[22] the composition of a mixed monolayer can be calculated provided that the orientational distribution of the methyl groups in the two components is the same.

Experimental Section

The design of the sum-frequency spectrometer at Cambridge and the experimental procedures for obtaining SF spectra from monolayers at the solid−liquid interface have been described elsewhere.[17,20,22,23] The visible laser beam (532 nm, 0.6 mJ/pulse, 8 ns, 2.5 mm diameter, angle of incidence = 60°) and the IR laser beam (2000−3000 cm^{-1}, 1−2.5 mJ/pulse, ca. 4 ns, 1 mm diameter, angle of incidence = 65°) were incident on the substrate through a CaF_2 prism and a thin film of solution. The detected SF signal at 459−481 nm was 30−80 photons/pulse.

The solid substrates were prepared by evaporation of 5 nm of Cr and 200 nm of Au onto polished Si wafers followed by immersion of the wafers in a saturated solution of octadecanethiol (ODT) or octadecanethiol-d_{37} (dODT) in methanol. SF spectra in the C−H stretching region were acquired with a substrate of dODT/Au, and spectra in the C−D stretching region were acquired with ODT/Au in order that no resonances from the substrate distorted the SF spectra of the adsorbed surfactants.

Before a spectrum was acquired, the sample was positioned 5 mm away from the prism and allowed to equilibrate with the surfactant solution for 30 min. To minimize the effect of depletion of the bulk dodecanol concentration caused by adsorption in the cell, the solution was flowed through the cell at a rate of 0.5 cm^3/min for 15 min. The sample was then brought toward the prism in order to trap a micrometer-thick film of solution to prevent significant attenuation of the IR laser beam. In order to test whether adsorption was complete, two sequential spectra were taken, separated by equilibration with the bulk solution for 15−30 min. All spectra were taken at a temperature of 292 ± 1 K.

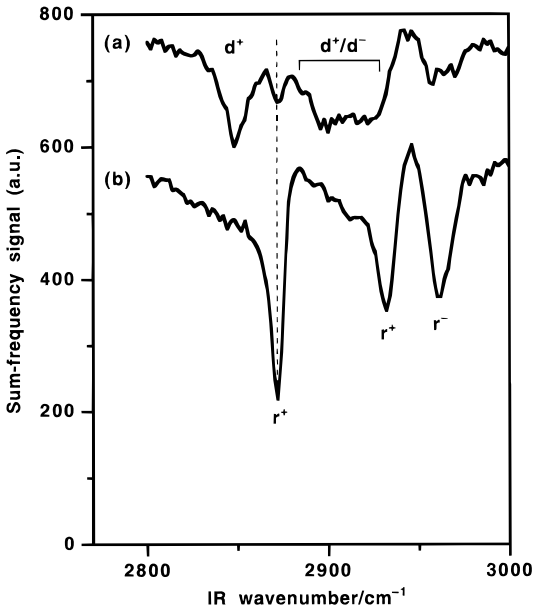

Figure 2. SF spectra in the CH stretching region of monolayers of pure surfactants adsorbed at the interface between an aqueous solution and a monolayer of dODT on gold: (a) 16 mM SDS, (b) saturated DD solution. Vibrational modes are labeled as follows: symmetric methyl stretch (r^+), antisymmetric methyl stretch (r^-), symmetric methylene stretch (d^+), antisymmetric methylene stretch (d^-). The spectrum in (a) has been offset vertically by 200 au.

To prepare mixtures of SDS and dodecanol, solutions of dodecanol in CH_2Cl_2 (BDH, Analar) were placed in dry vials, the CH_2Cl_2 was allowed to evaporate, and 9 cm^3 of 12 mM SDS in UHP water (Elga) was added. The mixtures were sonicated and swirled at 55 °C for 3 min to ensure complete mixing and then diluted with UHP water to a final concentration of SDS = 6 mM and dodecanol = 10 μM. For each hydrophobic substrate, a set of eight SF spectra were then acquired, two of each of the four isotopic combinations. The spectrum with the strongest peaks was fitted by computer, and the same resonant frequencies and line widths were used to fit the other spectra. The model used to fit the spectra has been described elsewhere.[22] This procedure was repeated three times with fresh substrates and solutions. Five or six spectra were analyzed for each isotopic combination. Average line strengths were calculated and are quoted with errors at the 1σ level.

Unlabeled SDS (BDH, 99.5%) and SDS-d_{25} (MSD, 99% isotopic purity) were crystallized three times and once, respectively, from ethyl acetate/methanol (9:1 by volume). The SF spectrum taken at a concentration of 16 mM of hSDS purified by recrystallization agreed with the spectrum of a foam fractionated sample kindly provided by J. Hines.[2] Unlabeled dodecanol (Fluka, 99%) and dodecanol-d_{25} (gift from Dr. R. K. Thomas, nominal isotopic purity 99%) were used as received.

Results and Discussion

Qualitative Features of SF Spectra. Figure 2 shows SF spectra of monolayers of pure $CH_3(CH_2)_{11}SO_4^-Na^+$ (hSDS) and pure $CH_3(CH_2)_{11}OH$ (hDD) adsorbed at the interface between an aqueous solution and a monolayer of $CD_3(CD_2)_{17}SH$ (dODT) on gold. This monolayer provides a reproducible hydrophobic surface with no molecular vibrations in the C−H stretching

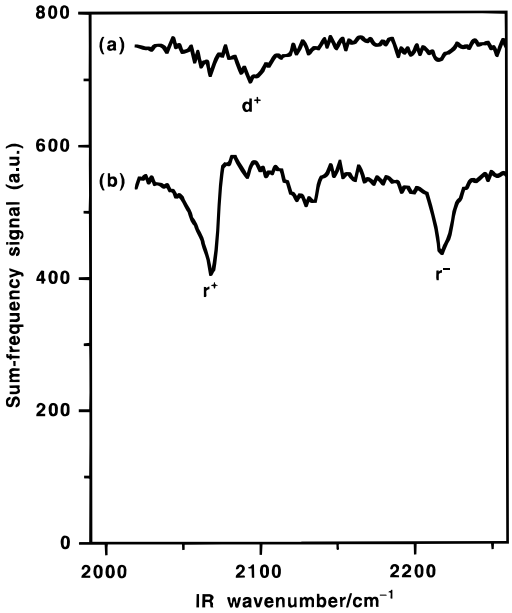

Figure 3. SF spectra in the CD stretching region of monolayers of pure surfactants adsorbed at the interface between an aqueous solution and a monolayer of hODT on gold: (a) 16 mM dSDS, (b) saturated dDD solution. Mode labels as in Figure 2. The spectrum in (a) has been offset vertically by 200 au.

region. Figure 3 shows comparable SF spectra of the deuterated surfactants $CD_3(CD_2)_{11}SO_4^-Na^+$ (dSDS) and $CD_3(CD_2)_{11}OH$ (dDD) adsorbed at the interface between an aqueous solution and a monolayer of $CH_3(CH_2)_{17}SH$ (hODT) on gold. In each case the monolayer was at saturation coverage. The background signal in all these spectra arises from the nonlinear optical response of the gold surface. The molecular vibrations appear as dips due to destructive interference between the SF fields of the molecules and the gold surface. The phase of the peaks demonstrates that the molecules are adsorbed with their hydrocarbon chains oriented toward the solid surface.[24]

The assignment of peaks in sum-frequency spectra of hydrocarbon chains has been discussed in detail elsewhere.[20] The spectrum of hDD (Figure 2b) shows strong features associated with the C−H stretching modes of the terminal methyl groups (labeled r^+ and r^-)[25] but only weak shoulders from the methylene modes (labeled d^+ and d^-). The line strength of the methyl modes is comparable to that in a monolayer of hODT,[26] suggesting that the area per molecule of dodecanol is comparable to that of hODT (22 Å^2).[27] For comparison, the area per molecule in adsorbed monolayers of dodecanol at the air−water interface is 21 Å^2.[28] The strong signal also rules out bilayer formation. In a bilayer, the sum-frequency signals from the two layers have opposite phases and therefore cancel.[29] The weakness of the methylene modes shows that polymethylene chains are predominantly in an all-trans conformation. This conformation is expected since dodecanol forms a close-packed, crystalline monolayer at the air/water interface.[30] In contrast, the spectrum of hSDS (Figure 2a) is dominated by the methylene modes with only weak methyl modes, indicating a highly disordered monolayer.[20] This structure is consistent with a low surface coverage caused by electrostatic repulsions between the charged sulfate groups. SFS does not distinguish between a monolayer of uniform thickness and an array of hemimicelles. Similar behavior is observed in monolayers of SDS at the air/water[21] and CCl_4/water interfaces.[31]

In the C−D stretching region, methyl modes predominate in the SF spectrum of dDD (Figure 3b). The size of the peaks, relative to the constant nonresonant background, is smaller than in the C−H region due to the lower amplitude of the C−D vibrations. The SF signals from dSDS (Figure 3a) are very weak indeed, but the strongest modes are once again assignable to methylene vibrations.

In Figure 4 we show SF spectra of solutions containing both hSDS and dDD in a molar ratio of 100:1 (0.7% DD by weight), as a function of the concentration of SDS. The cmc of pure SDS (8.2 mM) is used as a convenient reference marker: any dodecanol present is likely to depress the cmc.[32] The methyl modes are sharp, and the methylene modes are virtually absent in all the spectra of hSDS below the cmc (Figure 4b), in marked contrast to the spectrum of pure SDS (Figure 2a). In the spectrum taken at 1.5 × cmc, the methyl modes are weaker and the methylene modes reappear. The sharp CD_3 modes of deuterated dodecanol (Figure 4a) are observed from the mixed monolayer at all concentrations below the cmc but fall below the noise level at 1.5 × cmc. Below the cmc, the spectra of both hSDS and dDD are qualitatively similar to the spectra of monolayers of pure dodecanol, but the features are weaker due to the lower surface coverage of the individual components in the mixed monolayer. We infer that the monolayer is densely packed, has few conformational defects, and contains both SDS and dodecanol. Above the cmc, most of the dodecanol is solubilized in the micelles in bulk solution, though a small amount must remain in the monolayer since the hSDS spectrum indicates significantly greater conformational order than is present in a monolayer of pure hSDS.

The intensity of the r^+ modes is an indicator of the composition of the monolayer below the cmc. The SDS coverage increases as the bulk concentration increases, reaching a maximum at the cmc. Above the cmc, the structure of the monolayer changes and we cannot compare the intensity of the r^+ mode directly with the spectra below the cmc. The coverage of dodecanol molecules reaches a maximum at 0.1 × cmc and decreases gradually as the cmc is approached (Figure 4a).[33]

In our preliminary communication, we reported data for a lower fraction of added dodecanol (0.5 mol %, 0.3% by weight of the SDS concentration). Similar behavior was observed to that reported here, except that a higher total concentration was required to produce a well-ordered monolayer.[17] We have also investigated the effect of varying the amount of dodecanol at a fixed concentration of SDS = 0.8 mM, well below the cmc to minimize effects arising from aggregation in solution.[18] The monolayer became progressively more ordered as the concentration of dodecanol increased until a limiting structure was reached for [dDD] > 0.5% [hSDS]. Even at very low concentrations of dodecanol (1 μM), the structure of the monolayer was significantly different from a monolayer of pure SDS.

Quantitative Analysis of Composition. The intensity of the sum-frequency signal depends on the second-order nonlinear electric susceptibility of the interface, $\chi^{(2)}$. The susceptibility can be separated into two terms, the resonant susceptibility, $\chi_R^{(2)}$, arising from the molecules at the interface, and the nonresonant susceptibility, $\chi_{NR}^{(2)}$, of the gold substrate.

$$I_{SF} \propto |\chi_R^{(2)} + \chi_{NR}^{(2)}|^2 \quad (1)$$

If local field effects are ignored, $\chi_R^{(2)}$ can be written in terms of the number of molecules, N, per unit area and the molecular hyperpolarizability, β, averaged over all the orientations of the molecule at the surface. β depends on the molecular structure and the frequency and is negligible except when the IR laser is in resonance with a molecular vibration that is both IR and Raman active. If there are two species in the monolayer, with

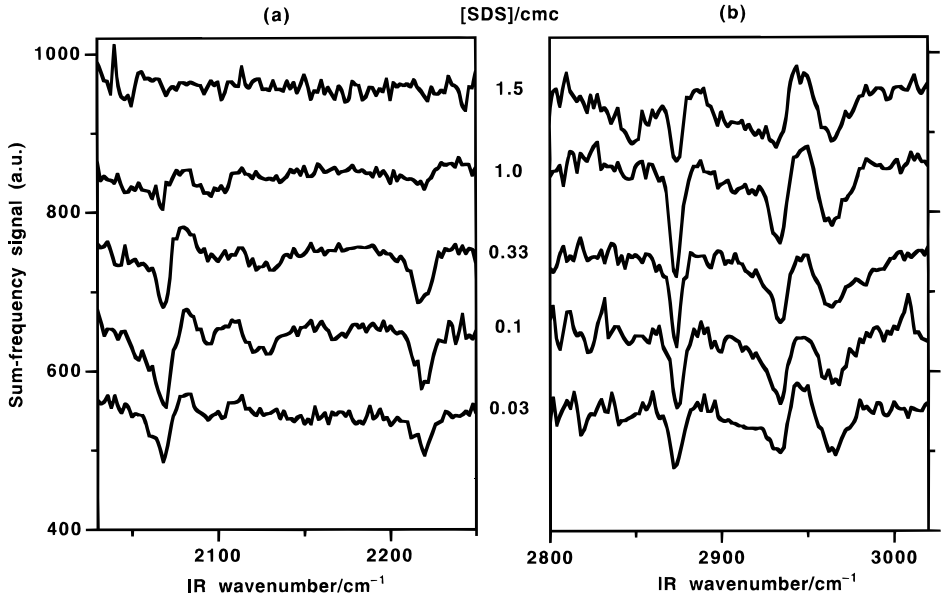

Figure 4. SF spectra of mixed monolayers of SDS and dDD adsorbed at the interface between an aqueous solution and a monolayer of (a) hODT/Au and (b) dODT/Au. The molar ratio of dodecanol to SDS was fixed at 0.01. The bulk concentration of SDS normalized to the cmc of pure SDS (8.2 mM) was, from top to bottom, 1.46, 1.00, 0.33, 0.10, and 0.03. The spectra in (a) show the C−D modes of adsorbed dDD, and the spectra in (b) show the C−H modes of coadsorbed SDS. Successive spectra have been offset vertically by 100 au. The scale on the ordinate refers to a concentration of 0.03 cmc.

mole fractions f_1 and f_2, and the molecules are well mixed, then

$$\chi_R^{(2)} = \frac{N}{\epsilon_0}(f_1\langle\beta_1\rangle + f_2\langle\beta_2\rangle) \qquad (2)$$

where the angle brackets $\langle\rangle$ indicate that β is averaged over the orientations of all the molecules in the monolayer. Assuming that the hydrocarbon chains in the two components in the monolayer have the same orientation, $\langle\beta_1\rangle = \langle\beta_2\rangle$. This assumption is reasonable in the C−H stretching region if both species have the same chain length. When both species are protonated, the line strength derived from a computer fit[22] of eq 1 will then be proportional to N and independent of f_1 and f_2. Note that the intensity of a peak in a SF spectrum is not simply related to the line strength due to the convolution of the resonant and nonresonant terms in eq 1. If species 2 is deuterated, β_2 vanishes and the line strength depends only on N and f_1. If species *1* is deuterated, β_1 vanishes and the line strength depends only on N and f_2. Provided that f_1 and N are unaffected by isotopic substitution *(vide infra)*, the ratio of line strengths gives f_1/f_2.

In principle, the composition of the monolayer can be determined from just two isotopic combinations involving only one deuterated molecule, hSDS + hDD and hSDS + dDD. To reduce errors and identify experimental artifacts, it is prudent to build some redundancy into the experiment. A comparison of the two combinations hSDS + dDD and dSDS + hDD permits the evaluation of f_{DD}/f_{SDS} independently from the SF spectra of the CH_3 and CD_3 modes. The two analyses should give the same result. The remaining combinations, hSDS + hDD and dSDS + dDD, are used as controls. The sum of the line strengths in the two isotopic mixtures (hSDS + dDD and dSDS + hDD) should equal the line strength measured with both species protonated or both species deuterated.

Figure 5 shows SF spectra in the C−H stretching region for the four isotopic combinations at a bulk concentration of 6 mM SDS and 10 μM dodecanol in contact with a substrate of dODT/Au. Figure 5a demonstrates that the deuterated surfactants and dODT give no detectable SF signals in the C−H stretching region. Figure 5b,c thus shows the contributions of hSDS and

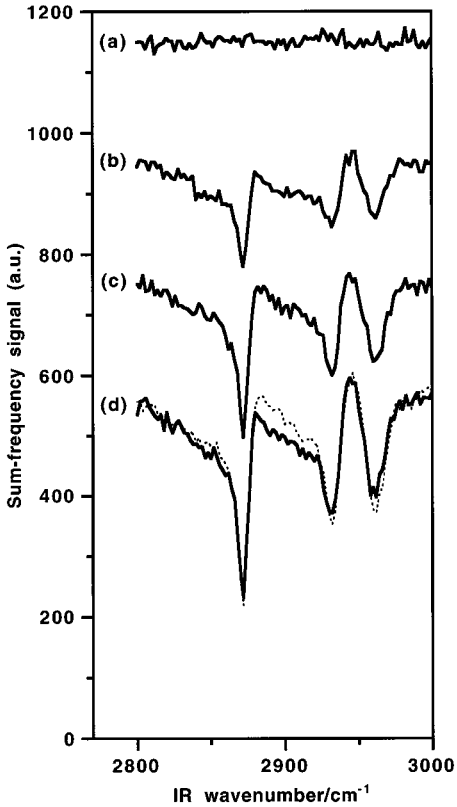

Figure 5. SF spectra in the CH stretching region of (a) dSDS + dDD, (b) hSDS + dDD, (c) dSDS + hDD, and (d) hSDS + hDD. The substrate was dODT/Au, and the bulk concentrations were [SDS] = 6 mM, [DD] = 10 μM. The broken line in (d) is the spectrum obtained from a saturated solution of hDD. Spectra a, b, and c have been offset by 600, 400, and 200 au, respectively.

hDD alone. Even a casual inspection of Figure 5 reveals that the monolayer contains more dodecanol than SDS. To quantify the composition, we calculated the line strengths of the methyl modes at 2874, 2935, and 2961 cm^{-1} from computer fits to six sets of spectra. The line strengths, S, of the methyl modes derived from the computer fit are sensitive to the choice of

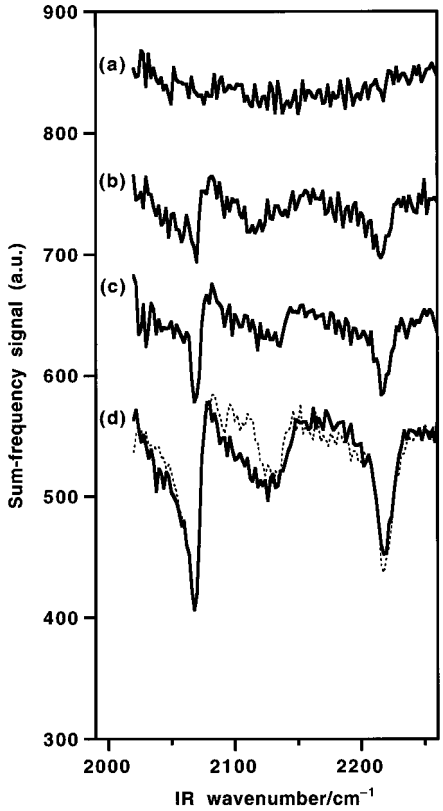

Figure 6. SF spectra in the CD stretching region of (a) hSDS + hDD, (b) dSDS + hDD, (c) hSDS + dDD, and (d) dSDS + dDD. The substrate was hODT/Au, and the bulk concentrations were [SDS] = 6 mM, [DD] = 10 μM. The broken line in (d) is the spectrum obtained from a saturated solution of dDD. Spectra a, b, and c have been offset by 300, 200, and 100 au, respectively.

parameters used to model the broad methylene modes. A consistent set of parameters was employed for each spectrum so that any systematic fitting errors acted in the same direction. The analysis of all three methyl modes further reduced the likelihood of fitting errors influencing the result. The fitting procedure was then repeated with significantly different parametgers for the CH_2 modes: the effect on the calculated composition of the monolayer was negligible. The average value *S*(hDD)/*S*(hSDS) obtained from the six pairs of spectra was the same for all three modes, to within experimental error. Combining the data from the three modes, the ratio of the mole fractions of dodecanol and SDS in the monolayer, f_{DD}/f_{SDS}, = 1.65 ± 0.1.

SF spectra in the C−D stretching region from solutions of the same composition in contact with hODT/Au are shown in Figure 6. The control experiment with hSDS + hDD is featureless (Figure 6a). Figure 6b,c shows spectra of dSDS + hDD and hSDS + dDD and therefore provides information on the SDS and dodecanol, respectively, in the mixed monolayer. We have analyzed the intensities of the r^+ mode at 2070 cm^{-1} and the r^- mode at 2219 cm^{-1} as before. The molecular features are weaker than in the C−H stretching region and the asymmetry in the r^+ mode makes peak fitting more difficult, so the error associated with the analysis of the C−D modes is higher. The mean ratio of *S*(dDD)/*S*(dSDS) is 1.9 ± 0.2, within experimental error of the value obtained from the C−H modes. Combining the data from the two spectral regions and giving greater weight to the C−H modes, we finally obtain a value of f_{DD}/f_{SDS} = 1.7 ± 0.1, i.e. 63 ± 1% of the monolayer is dodecanol.

It is revealing to compare the spectrum of hSDS + hDD with the spectrum of pure hDD (Figure 5d). The strengths of the methyl modes in the two monolayers are the same to within experimental variation. Monolayers of dodecanol adsorbed at the Au/ODT/water interface show a first-order phase transition at 40.5 °C from a conformationally ordered "liquid-condensed" phase[34] to a conformationally disordered "liquid-expanded" phase.[35] This phase transition is accompanied by a 30% decrease in the intensity of the r^+ and r^- modes. The similarity of the spectra in Figure 5d suggests that the mixed SDS + DD monolayer is also in a dense ordered phase and raises the possibility of a phase transition to a disordered phase at higher temperatures. Such a phase transition has been observed in SDS/dodecanol mixtures at the air/water interface.[36] The existence of crystalline order in the hydrocarbon chains would explain the similarity in the SF spectra of the two components in the mixed monolayer, despite the different interactions between the head groups and water. The spectra of the pure hDD and the mixed hSDS + hDD monolayers are not, however, identical. The methylene modes are slightly more intense in the mixed monolayer, particularly around 2900 cm^{-1}, consistent with a higher population of gauche defects.

Figure 6d shows a spectrum of dSDS + dDD with the spectrum of pure dDD overlaid. Once again, there is excellent agreement between the two spectra except in the vicinity of the CD_2 stretch at 2100 cm^{-1}, which is stronger in the mixed monolayer. These spectra confirm the conclusion that the packing densities of the mixed monolayer and the pure dodecanol monolayer are comparable but that there are more gauche defects in the mixture.

The quantitative analysis of the composition of the mixed monolayer rests on two key assumptions: (i) the orientational distribution of the terminal methyl groups in the SDS and the dodecanol molecules is the same; (ii) isotopic substitution of deuterium for hydrogen affects neither the composition nor the structure of the monolayer. Several features of the spectra support the former assumption. First, the relative intensities of the r^+ and r^- modes depend on the orientation of the methyl group;[37], yet, they are the same for dodecanol and SDS in the mixed monolayers. Second, the ratio of intensities of the symmetric methyl stretch at 2874 cm^{-1} and the symmetric methylene stretch at 2850 cm^{-1}, $I(r^+)/I(d^+)$, is a sensitive measure of conformational order in hydrocarbon chains. This ratio is not significantly different for the two components in the mixed monolayer. Third, the similarity between the pairs of spectra in Figures 5d and 6d would be remarkable coincidence if the SDS chains adopted a conformation very different from that of dodecanol. We can evaluate the effect on our calculations of any breakdown in this assumption. If $\langle\beta_1\rangle$ and $\langle\beta_2\rangle$ were to differ by 10%, the calculated mole fraction of dodecanol in the monolayer would be in error by only 2%.

The second assumption can be tested directly. If isotopic substitution has no effect on the composition and structure of the monolayer, the line strength of the CH_3 modes in the hSDS + hDD monolayer (Figure 5d) would be equal the sum of the line strengths in the hSDS + dDD monolayer (Figure 5b) and the dSDS + hDD monolayer (Figure 5c). In fact, the sum of the parts exceeded the whole by an average of 13 ± 4%. While small, this difference is statistically significant. The same analysis was carried out for the CD_3 modes (Figure 6). Here, the sum of the line strengths in the spectra of hSDS + dDD and dSDS + hDD monolayers fell short of the line strength in the spectrum of the dSDS + dDD monolayer by 12 ± 4%. These results are summarized in Table 1, which presents the average line strength of the methyl modes in the C−H and C−D regions, normalized to a value of 100 for hSDS + hDD and dSDS + dDD, respectively.

TABLE 1: Normalized Line Strengths, *S*, of the Methyl Stretching Modes in the CH and CD Stretching Regions

monolayer	CH_3 modes	CD_3 modes
hSDS + hDD	100	0
hSDS + dDD	43	57
dSDS + hDD	70	30
dSDS + dDD	0	100

There are three possible explanations for these observations. First, it could be an artifact of the model used to fit the SF spectra. It is, however, unlikely that such an artifact would overestimate line strengths in the C−H region and underestimate them in the C−D region.

Second, a hydrogenous contaminant in the solutions could be adsorbed, increasing the apparent concentration of the protonated component in some, or all, of the monolayers. Highly surface active molecules can be incorporated into a monolayer at submicromolar concentrations, and it is exceedingly difficult to rule out impurities at this level. The second and third rows in Table 1 each sum to 100, so any impurity would have to substitute for SDS or dodecanol without changing the packing of the monolayer. The spectrum in Figure 5a, obtained from a solution of dSDS + dDD in H_2O, is completely featureless. Since even a 10% impurity of hydrogenous material would be detected readily, the putative contaminant must therefore arise from one of the protonated surfactants. The hSDS is the only plausible candidate as dodecanol is present at such low concentrations. The effect we observed could be reproduced if the true composition of the monolayer were 70% dodecanol and 30% SDS and one-fifth of the dodecanol in the mixed monolayer of hSDS + dDD were replaced by an isomorphous hydrogenous contaminant. Such a contaminant could plausibly be dodecanoic acid or dodecanol itself. Given that the impurity would have to compete effectively with the added dodecanol, it is surprising that there is no evidence for an impurity in the behavior of the pure hSDS. SF spectra of hSDS above (16 mM) and below (6 mM) the cmc were indistinguishable, whereas one would normally expect the impurity to dissolve in the monolayer below the cmc but partition principally into the micelles above it.

Third, there could be a small thermodynamic preference for incorporation of the protonated surfactants in the monolayer. Deuterated hydrocarbons are smaller ($\Delta V_m = 0.5\%$) and less polarizable ($\Delta\alpha = 1.0\%$) than their protonated analogues due to the smaller amplitude of the zero-point vibration of the C−D bonds.[38] The effect on monolayer properties is certainly measurable. For example, deuteration lowers the phase transition temperature of a monolayer of dodecanol at the air−water interface by 3 K,[39] a value similar to that observed in bulk hydrocarbons.[40] The greater well-depth associated with the protonated surfactants would favor their incorporation in a densely packed monolayer.

We can use a lattice calculation to estimate the isotope effect in mixed monolayers. Consider, for simplicity, a monolayer comprising the fully deuterated and fully protonated isotopomers of the same molecule, e.g. hDD and dDD. Let ϵ_{hh}, ϵ_{dd}, and ϵ_{hd} be the well depths associated with the chain−chain interactions in the monolayer. If each molecule in the monolayer has n nearest neighbors and the molecules are randomly mixed (ideal entropy of mixing),[41] the chemical potentials of the two species in the monolayer are given by

$$\mu_h(\text{surf}) = \mu^{\ominus}(\text{surf}) + nf_h\epsilon_{hh} + nf_d\epsilon_{hd} + RT(\ln f_h - \ln f_e) \tag{3a}$$

$$\mu_d(\text{surf}) = \mu^{\ominus}(\text{surf}) + nf_h\epsilon_{hd} + nf_d\epsilon_{dd} + RT(\ln f_d - \ln f_e) \tag{3b}$$

where $\mu^{\ominus}(\text{surf})$ is the molar free energy associated with noninteracting molecules on isolated sites, f_h and f_d are the fraction of sites occupied by protonated molecules and deuterated molecules, respectively, and f_e is the fraction of empty sites. In equating $\mu_h^{\ominus}(\text{surf})$ and $\mu_d^{\ominus}(\text{surf})$, we have neglected the small isotope dependence of the interaction between the adsorbate and the hydrophobic solid. We assume further that differences in the intramolecular contributions to the free energy between the two isotopomers do not influence the free energy of adsorption. Equating chemical potentials in the solution and in the monolayer and eliminating $\mu^{\ominus}(\text{surf})$, we obtain

$$n\,[(f_d - f_h)\epsilon_{hd} + f_h\epsilon_{hh} - f_d\epsilon_{dd}] + RT\ln(f_h/f_d) = \Delta\mu(l) \tag{4}$$

where $\Delta\mu(l)$ is the difference in chemical potentials in the bulk solution. In the limit of saturation coverage, $f_d = 1 - f_h$. Writing $\Delta\epsilon = \epsilon_{dd} - \epsilon_{hh}$ and noting that $\epsilon_{hd} \approx \sqrt{(\epsilon_{dd}\epsilon_{hh})} \approx (\epsilon_{dd} + \epsilon_{hh})/2$, we can rewrite eq 4 as

$$RT\ln\left(\frac{f_h}{1 - f_h}\right) = \frac{n\Delta\epsilon}{2} + \Delta\mu(l) \tag{5}$$

Dorset et al.[40] use a corresponding states argument to show that $(\epsilon_{hh} - \epsilon_{dd})/\epsilon_{dd} \approx 0.012$ for bulk alkanes. ϵ_{hh} can be estimated from molecular dynamics simulations. Ryckaert et al.[42] calculated the internal energy in the rotator phase[43] of solid tricosane ($C_{23}H_{48}$) to be −120 kJ mol^{-1}, which we take to be approximately twice the intermolecular internal energy in a 12-carbon monolayer.[44] From the relation of Dorset et al., we then find that $n\Delta\epsilon/2 = 720$ J mol^{-1}.

The influence of isotopic substitution on the monolayer composition is greatest when there is no isotope effect in the bulk solution, i.e. when $\mu_h^{\ominus}(l) = \mu_d^{\ominus}(l)$. Assuming ideal dilute behavior, $\Delta\mu(l) = RT\ln(m_h/m_d)$, where m_h and m_d are the molalities in solution. To simulate the average composition in the mixed monolayer of SDS and dodecanol, consider the two cases where $m_h/m_d = 1.7$ and $m_d/m_h = 1.7$. In the former case, eq 5 yields $f_h = 0.70$ and $f_d = 0.30$, and in the latter case $f_h = 0.44$ and $f_d = 0.56$. The mole fractions in the monolayer differ from the ideal values (0.63 and 0.37) by ±0.07. The calculated compositions mimic those observed in our experiments almost exactly (Table 1). While this simple calculation does not establish the existence of an isotope effect in the mixed SDS/dodecanol monolayers—it is only an upper limit based on the assumption of no isotope effect in the solution phase—it does demonstrate that isotopic substitution could have an effect on the composition of mixed monolayers comparable to that observed experimentally.[45]

This analysis suggests that the possibility of an isotope effect should be taken into account in the design of an experiment. If the composition of the monolayer were calculated from spectra of hSDS + dDD and dSDS + hDD in the C−H region alone, an isotope effect would lead to an underestimation of the proportion of dodecanol in the monolayer. A similar measurement in the C−D region would overestimate the amount of dodecanol. The errors are, however, small (∼2% of a monolayer) and are eliminated if the composition is taken to be an average of the ratios obtained in the two regions. Much larger errors would arise if only one deuterated species were used to determine the composition, e.g. from a comparison of hSDS + hDD and hSDS + dDD (Table 1).

Comparison with Mixed Monolayers at the Air−Water Interface. The most complete characterization of mixed monolayers of SDS and dodecanol at the air−water interface has been carried out by Lu et al. using neutron reflection.[12] The qualitative features of the adsorption isotherms at the air−water and solid−water interfaces are similar. For bulk concentrations below the cmc, dodecanol is incorporated into the mixed monolayers at either interface, even when it is present at very low levels in absolute terms (1 μM) or as a proportion of the SDS concentration (0.1%). The amount of SDS in the monolayer increases monotonically with increasing bulk concentration below the cmc. If the concentration of the solution is varied while keeping [DD]/[SDS] fixed, the amount of dodecanol in the monolayer reaches a maximum below the cmc and then decreases as the bulk concentration passes through the cmc. When [DD] $\sim$ mol 1% of [SDS], the maximum amount of adsorbed dodecanol is reached at an SDS concentration of about $0.1 \times$ cmc at both interfaces, while at lower levels of dodecanol the maximum adsorption is reached at higher concentrations.

At the quantitative level differences between the two interfaces emerge. The neutron study included a measurement of the surface excess of dodecanol, Γ_{DD}, at a composition very similar to that studied here. For a solution containing 6.7 mM SDS and 10 μM dodecanol, Lu et al.[12] found $\Gamma_{DD} = 1.8 \times 10^{-6}$ mol m^{-2} at the air−water interface. The surface excess of SDS, Γ_{SDS}, was not measured for this composition (0.1% by weight), but we can interpolate between measurements on a solution of pure SDS ($\Gamma_{SDS} \approx 3.8 \times 10^{-6}$ mol m^{-2}) and SDS containing 0.5% dodecanol by weight ($\Gamma_{SDS} \approx 3.4 \times 10^{-6}$ mol m^{-2}). Since these values are so similar, a value of $\Gamma_{SDS} \approx 3.6 \times 10^{-6}$ mol m^{-2} at the concentration used in our experiment can be adopted with reasonable confidence. The monolayer at the air−water interface therefore comprises 33% DD and 67% SDS and has a total coverage only 70% of that of a pure dodecanol monolayer ($\Gamma_{DD} = 7.7 \times 10^{-6}$ mol m^{-2}). When the concentration of dodecanol was increased to 26 μM, the density of the monolayer at the air−water interface approached that of pure dodecanol, but even then the amount of dodecanol in the monolayer only equaled that of SDS. Thus, the monolayer at the solid−water interface is denser and much richer in dodecanol than comparable monolayers on the surface of water.[46]

The similarities between the interfaces are easy to comprehend. From an energetic perspective air acts like a hydrophobic wall; for example, the relative values of the surface tension of water and the interfacial tension between water and a hydrocarbon suggest that the polar contribution to the interfacial energy is similar in each case.[47] The differences are more subtle. At an impenetrable solid surface, such as that provided by ODT/Au, the density profile of the monolayer falls sharply from the density of bulk hydrocarbons to zero at the solid surface. In contrast, the chains of the surfactant can penetrate into the air, and the density profile at the air−water interface drops off much more gradually. At the solid surface, the interfacial roughness is defined by the roughness of the solid, independent of the nature of the adsorbed film. At the surface of water, the roughness is determined by capillary waves and by the intrinsic roughness of the surfactant monolayer on a molecular scale. There is a virtual absence of comparative data on the same surfactant system adsorbed at the solid−water and air−water (and water−oil) interfaces. As a consequence we have little understanding of how these factors affect adsorption.

Conclusion

The principal object of this paper has been to establish that SFS can be used quantitatively to determine the composition of mixed monolayers in which the hydrocarbon chains of the two species have similar conformations and orientations. A detailed analysis of the SF spectra of one particular mixture, 6 mM SDS + 10 μM dodecanol, in contact with a hydrophobic solid showed that the adsorbed monolayer contained 63% dodecanol and 37% SDS. The total surface coverage was comparable to that of a monolayer of pure dodecanol. A comparison of different isotopic mixtures showed a small preference for incorporation of protonated surfactants over deuterated surfactants. While these results may have arisen from a contaminant in the SDS, a genuine isotope effect arising from different pair potentials in the two isotopes could account for the differences observed. A simple lattic model based on regular solution theory predicts changes of up to ± 0.07 in the mole fractions of the two components in the monolayer due to H/D isotopic substitution. The largest effects would be expected in densely packed monolayers. The possibility of isotope effects should be reflected in the design of any experiment that uses isotopic substitution to study mixed surfactant aggregates, whether by vibrational spectroscopy, neutron reflection, or magnetic resonance.

The adsorption isotherms of SDS/dodecanol mixtures at the solid−water and air−water interfaces have been compared. While the isotherms share a number of common features, there are quantitative differences. When [SDS] = 6 mM and [DD] = 10 μM, the monolayer at the solid−water interface is denser and much richer in dodecanol than the corresponding monolayer at the surface of water.

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