

# Chain–Chain Interaction between Surfactant Monolayers and Alkanes or Alcohols at Solid/Liquid Interfaces

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**Abstract:** Sum-frequency surface vibrational spectroscopy was used to study chain conformation of self-assembled surfactant monolayers at various quartz/alkane and quartz/alcohol interfaces as a function of surfactant surface density and chain lengths of both surfactant and alkane or alcohol molecules. We found that, in comparison with fully packed monolayers such as octadecyltrichlorosilane (OTS) on glass or alkanethiols on gold, the chain conformation of loosely packed monolayers is considerably more sensitive to their environment. With sufficiently high surfactant surface density and sufficiently long chain lengths of both surfactant and alkane, the chain–chain interaction between surfactant and alkane molecules can effectively eliminate all the gauche defects initially present in the surfactant chains. With alkanes replaced by alcohols the hydrophobic effect appears to be dominant, as the alcohol molecules like to form a hydrogen-bonding network at an interface with the hydroxyl groups facing the surfactant monolayer. This causes the surfactant chains to curl up. However, if the long-chain alcohols are diluted in a nonpolar liquid, the hydrogen-bonding network is disrupted and the alcohol can now adsorb individually at the interface. Then again, the chain–chain interaction dominates and if it is sufficiently strong, the chains become all-trans. Our results are relevant for proper interpretation of wetting phenomena on self-assembled monolayers and provide a microscopic understanding of the interplay between interfacial structure and intermolecular interactions between monolayers and the surrounding liquid.

## Introduction

Surfactants play an important role in a variety of technological processes. Detergency, emulsification, coatings, lubrication, mineral flotation, and oil recovery are just a few examples.<sup>1,2</sup> They have therefore been studied extensively. In most commercial applications, surfactant solutions are composed of many ingredients to attain the desired properties. For instance, the addition of alkanes and alcohols to surfactant solutions has a profound influence on their bulk behavior<sup>3,4</sup> and adsorption properties.<sup>5</sup> The presence of ionic surfactants dramatically modifies the adsorption of nonionic surfactants.<sup>6,7</sup> Alcohol in cationic surfactant solutions changes the interaction between mica surfaces immersed in the solutions.<sup>8</sup> In microemulsions, the interaction of the oil phase with surfactant monolayers

determines their stability.<sup>9</sup> Clearly, understanding the interactions among different surfactants in a mixture or between oil and surfactants is a fundamental problem that has far-reaching consequences in applications.

Toward this goal, many authors have studied coadsorption of surfactants at solid/liquid interfaces using techniques such as adsorption isotherms,<sup>6,7,10</sup> fluorescence probes,<sup>11</sup> ellipsometry,<sup>12</sup> and sum-frequency generation.<sup>13–16</sup> They reveal strong synergistic effects in the adsorption of ionic/nonionic surfactant mixtures. The interaction of surfactants with alkanes has been studied in microemulsions and monolayers at the air/water interface with techniques such as surface tension<sup>17–19</sup> and neutron reflection measurements,<sup>20</sup> small-angle neutron scat-

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tering,<sup>21</sup> and X-ray reflectivity.<sup>22</sup> It was found that depending on the chain length, the interacting alkane could spread on the monolayer and form a macroscopic film on the air/water interface or stay as a bulk phase in equilibrium with a mixed monolayer of surfactant and alkane. The extent of alkane penetration in the monolayers depends on the surfactant density at the air/water interface. These results serve as models for the oil/water interfaces,<sup>22</sup> important for understanding microemulsion formation and biological systems.<sup>23</sup> Despite all these advances, a detailed microscopic picture of the various interfaces is still lacking, or at most incomplete.

The interaction of liquids with self-assembled monolayers is of fundamental importance in connection with wetting phenomena.<sup>24–26</sup> If a contacting liquid can alter the structure of the monolayers,<sup>25,27,28</sup> this will in turn affect the wetting properties of the interface by the liquid. It is known that compact monolayers are rather insensitive to the liquid environment,<sup>24,29–32</sup> due to limited penetration of solvent molecules and lack of available space for conformational defects. The conformation of loosely packed monolayers, on the other hand, is considerably more sensitive to the liquid environment around them,<sup>33,34</sup> and has a profound implication on the interpretation of contact angle measurements. In the case of long-chain alkanes, it has long been suggested that they can penetrate and affect the properties of loosely packed monolayers<sup>35–37</sup> or mixed monolayers of alkanethiols with different chain lengths.<sup>25,27,38</sup> A very recent molecular dynamics simulation<sup>39</sup> shows that penetration of hexadecane into loosely packed monolayers with different chain lengths can induce conformational changes in the monolayers.

In this paper we use infrared-visible sum-frequency vibrational spectroscopy (SFG), a surface specific technique with a unique sensitivity to alkyl chain conformation, to study the microscopic structure of surfactant monolayers interacting with various alkanes and alcohols. We have prepared self-assembled surfactant monolayers on fused silica with different chain densities and different chain lengths. These monolayers were put in contact with bulk alkanes or alcohols of various chain

lengths. We found that in the case of alkanes, the van der Waals chain–chain interaction between alkanes and surfactant could straighten the initially disordered surfactant chains if it is strong enough. In the case of long-chain alcohols, they form an ordered hydrogen-bonding layer above the surfactant monolayer. Then as in the cases of methanol and water, the hydrophobic effect causes the surfactant chain conformation to become highly disordered.<sup>34</sup> This situation can however be reversed by dilution of the long-chain alcohols in a nonpolar solvent. Then the alcohol molecules can no longer be hydrogen bonded to form a layer. They can now penetrate the surfactant layer and straighten the surfactant chains via the chain–chain interaction.

Infrared-visible sum-frequency generation (SFG) as a unique surface vibrational spectroscopic tool has been described in detail elsewhere and will not be repeated here.<sup>40–42</sup> The crucial aspect of the spectroscopy that will be used throughout this work is its capability of probing the conformation of long hydrocarbon chains. If the alkyl chains are in the all-trans conformation, the CH<sub>2</sub> groups are in a configuration that has a near inversion symmetry and SFG from the CH<sub>2</sub> groups becomes nearly forbidden.<sup>43</sup> The CH<sub>3</sub> groups can, however, contribute strongly to SFG if the all-trans chains have an orientational order at the interface. This is the case of a fully packed surfactant monolayer at the air/water interface. With gauche defects in the chains, the local inversion symmetry is broken and the CH<sub>2</sub> modes can become allowed. Yet increasing amounts of gauche defects also randomize the orientations of CH<sub>2</sub> and CH<sub>3</sub> groups of the monolayer, thus reducing their contributions to the SFG spectra. This was first demonstrated by Guyot-Sionnest *et al.*<sup>43</sup> and has been extensively used to probe surfactant chain conformation.<sup>13,44</sup> If the number of gauche defects per chain is large, the orientations of CH<sub>2</sub> and CH<sub>3</sub> could be so randomized that the SFG signal again becomes vanishingly small.<sup>34</sup> In this respect, a qualitative analysis of the SFG spectra of alkyl chains can readily reveal information about their conformation.

## Experimental Section

In our experimental setup, an active–passive mode-locked Nd:YAG laser system was used to produce 0.5 mJ visible pulses at 532 nm with a ~28 ps pulse width and 0.2 mJ tunable infrared pulses (from 2500 to 4200 cm<sup>-1</sup>) with a ~15 ps pulse width. The pulse repetition rate was 10 Hz. The line width of the infrared beam varied from about 8 cm<sup>-1</sup> around 2900 cm<sup>-1</sup> to about 45 cm<sup>-1</sup> at 3700 cm<sup>-1</sup>. The infrared and visible beams were incident on the sample interface from the solid side at angles of 51° and 42°, respectively. The beam spots overlapped spatially and temporally on the sample and the spot sizes were approximately 500 μm for the infrared and 300 μm for the visible. The sum-frequency output in the reflected direction was detected by a photomultiplier and a gated detection system. The acquisition time for each spectrum was about 30 min.

The surfactant monolayers were prepared by self-assembly on infrared-grade fused quartz windows (Esco Products Inc). The windows were thoroughly cleaned in hot chromic acid for several hours and then extensively rinsed with purified water (resistivity higher than 18.0 MΩ·cm, Barnstead NanoPure II). The pH value of the final rinse was allowed to equilibrate to 5.6–5.8. The substrates were then dried in a stream of N<sub>2</sub> gas and placed in an oven at 120 °C for 1 h to remove any remaining water layer. This cleaning procedure produces a fully hydroxylated quartz surface that becomes negatively charged in water with sufficiently high pH due to partial ionization of the surface silanol

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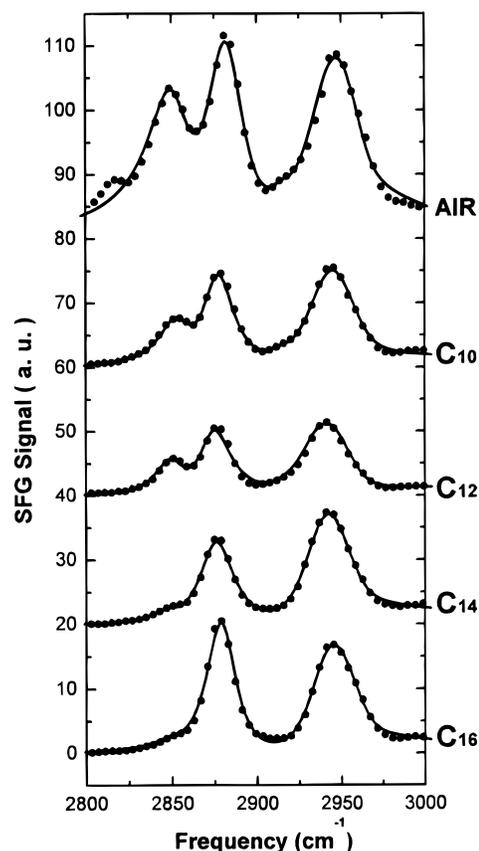
groups.<sup>45,46</sup> Cyclohexane, carbon tetrachloride, and butanol were purchased from J. T. Baker and octanol (anhydrous) and hexadecanol from Aldrich. All solvents used had purities above 99% and were used as received, except hexadecanol, which was recrystallized twice from acetone. The deuterated alkanes and alcohols were obtained from Cambridge Isotopes or Isotec and had isotope enrichments higher than 98%. Three different cationic surfactants were used: DOAC (dioctadecyldimethylammonium chloride,  $(\text{CH}_3(\text{CH}_2)_{17})_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$ ), DDAC (didecyldimethylammonium chloride,  $(\text{CH}_3(\text{CH}_2)_9)_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$ ), and DMOAP (*N*-octadecyldimethyl[(3-trimethoxysilyl)propyl]ammonium chloride,  $\text{CH}_3(\text{CH}_2)_{17}\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_3\text{Si}(\text{CH}_3\text{O})_3\text{Cl}^-$ ). Purified DOAC and DDAC were obtained from KAO Corporation and used as received. DMOAP was purchased from United Chemical Technologies as a 50% solution in methanol and filtered (0.45  $\mu\text{m}$  pore size) before use.

The self-assembly procedure of DOAC and DDAC monolayers is similar to the method described in ref 47. The cleaned substrates were first immersed in a heated ( $\sim 60^\circ\text{C}$ ) cyclohexane solution of the surfactants ( $c = 0.2\text{ mM}$ ) for 30 min. They were then rinsed in warm cyclohexane for another 30 min and blow-dried with  $\text{N}_2$  gas. The DMOAP monolayer was prepared by immersing the clean substrates in an aqueous solution<sup>48</sup> of the surfactant containing acetic acid (100:3:2 water:acetic acid:DMOAP, by volume) for 30 min. Afterward, they were rinsed with pure water for about 1 min, blow-dried with  $\text{N}_2$ , and then baked at  $120^\circ\text{C}$  for 1 h. All these samples could be stored in a vacuum desiccator under  $\text{P}_2\text{O}_5$  for more than 2 months with no degradation. The water advancing contact angle on a DOAC monolayer was about  $66^\circ$ .

DOAC and DDAC are double-chained cationic surfactants with two  $\text{C}_{18}$  and  $\text{C}_{10}$  chains, respectively. The chain density of a DOAC monolayer on quartz was found to be 2.8 chains/ $\text{nm}^2$ , by comparing its SFG spectrum to the spectra of a DOAC Langmuir film on water at various surface densities.<sup>49</sup> The surface density of a DDAC monolayer is assumed to be the same because the self-assembly mechanism is dominated by electrostatic interaction between the cationic surfactant and the negatively charged substrate. Hydrophobic effect on adsorption should be negligible since a nonpolar solvent was used in the self-assembly process. Therefore, the surface density of surfactant should be rather insensitive to the chain length. Indeed, in ref 47, surfactant monolayers of various chain lengths prepared in a similar way on mica substrates were found to have very similar surface densities. DMOAP is a single-chain silane surfactant (chain length  $\text{C}_{18}$ ) that forms chemisorbed monolayers on glass<sup>48</sup> with a chain density of about 2 chains/ $\text{nm}^2$  because of its large headgroup area.<sup>33</sup>

## Results

**A. Interaction between Surfactants and Alkanes.** We start by studying the interaction of various surfactant monolayers with long-chain alkanes. Figure 1 shows a series of SFG spectra for a DOAC monolayer at the quartz/deuterated alkane interface. The top curve is the SFG spectrum for the DOAC monolayer in air. The spectrum is dominated by three distinct peaks. Following the assignments of IR and Raman spectra,<sup>50</sup> the first at  $2850\text{ cm}^{-1}$  is identified as the  $\text{CH}_2$  symmetric stretch and the other two peaks at approximately  $2875$  and  $2940\text{ cm}^{-1}$  can be attributed to the  $\text{CH}_3$  symmetric stretch and its Fermi resonance with overtones of bending modes, respectively. The two  $\text{CH}_3$  asymmetric stretch modes at around  $2955$  and  $2965\text{ cm}^{-1}$  are rather weak and cannot be resolved from the Fermi resonance peak at  $2940\text{ cm}^{-1}$  due to the large bandwidth of



**Figure 1.** SFG spectra for a DOAC monolayer at the quartz/deuterated alkane interface. The alkane chain length is indicated on each curve. The spectrum for the DOAC monolayer at the quartz/air interface is shown for comparison (top curve). The polarizations of the sum-frequency output, visible input, and infrared input are *s*, *s*, and *p* (denoted by SSP, respectively). The spectra have been separated vertically by 20 units. The solid line is a fit to eq 1.

our laser. The presence of the  $\text{CH}_2$  symmetric stretch at  $2850\text{ cm}^{-1}$  indicates that the alkyl chains are *not* in the all-trans conformation and they must contain some gauche defects (see Introduction). This is to be expected from the lower surface density of the monolayer (2.8 chains/ $\text{nm}^2$ ) when compared to fully packed monolayers of alkyl chains with typical chain densities of  $\sim 5$  chains/ $\text{nm}^2$ .<sup>43</sup> The other curves in Figure 1 show SFG spectra for the DOAC monolayer in contact with various deuterated alkanes. The alkane chain length is indicated on each curve. The alkanes used were deuterated so that their vibrational modes are outside the frequency range of the surfactant chain modes. The spectra in Figure 1 reflect the conformational order of surfactant chains.

To help the discussion of our results, the spectra have been fitted with a surface nonlinear susceptibility of the form

$$\chi^{(2)}(\omega_{\text{IR}}) = \chi_{\text{NR}} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q} \quad (1)$$

where  $\chi_{\text{NR}}$  is a weak nonresonant contribution and  $A_q$ ,  $\omega_q$ , and  $\Gamma_q$  are the strength, frequency and line width of the  $q$ th vibrational mode, respectively. All the fitting parameters are assumed to be real, since the laser wavelengths are away from electronic transitions. The ratio of the peak strength of the  $\text{CH}_2$  symmetric stretch to that of the  $\text{CH}_3$  symmetric stretch ( $R = A_{\text{CH}_2}/A_{\text{CH}_3}$ ) is often used as a measure of the relative conformational order of alkyl chains, with this ratio decreasing as the

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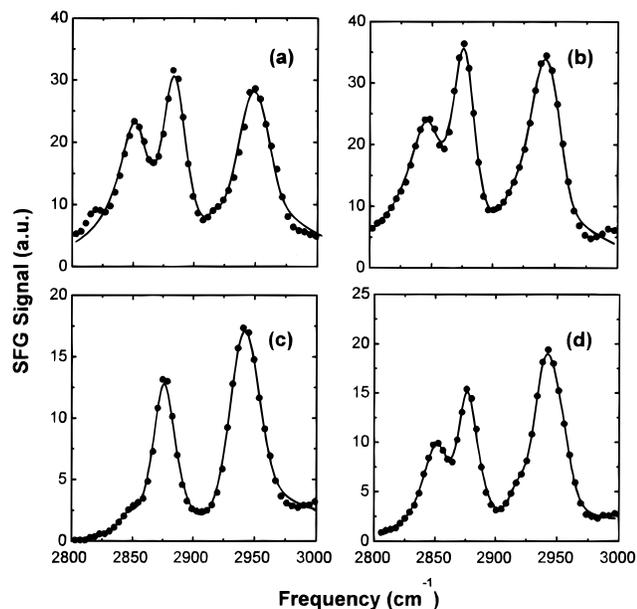
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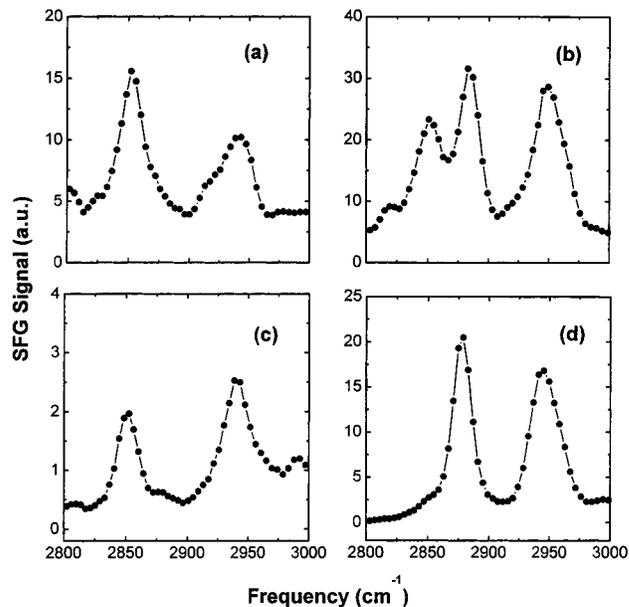
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**Figure 2.** SFG spectra (SSP) for (a) DOAC and (b) DDAC monolayers at the quartz/air interface and (c) DOAC and (d) DDAC monolayers at the quartz/deuterated tetradecane interface. The solid line is a fit to eq 1.

amount of gauche defects in the chains decreases.<sup>42,44,51</sup> In Figure 1, this ratio  $R$  is 0.70, 0.56, and 0.64 for a DOAC monolayer in contact with air, decane, and dodecane, respectively. The difference is not significant as it is within experimental uncertainty ( $\sim 10\%$ ) due to sample-to-sample variations and inaccuracy of the fitting procedure. All we could say is that the surfactant conformation is not significantly changed by interaction with these alkanes. For alkane chain lengths of  $C_{14}$  and  $C_{16}$ , the DOAC spectrum exhibits hardly any trace of the  $CH_2$  mode at  $2850\text{ cm}^{-1}$ :  $R$  is 0.16 in tetradecane and 0.07 in hexadecane, suggesting that the surfactant chains are nearly in the all-trans conformation. Apparently, the alkane molecules wedging into the surfactant monolayer now have a sufficiently long chain length to provide enough chain–chain interaction between alkane and surfactant molecules for the surfactant chains of length  $C_{18}$  to straighten up.

One may expect that for the surfactant chains to get straightened by sufficiently strong chain–chain interaction, both alkane and surfactant chains should be long enough. To verify this we repeated the same experiment as above but replaced DOAC by DDAC, which has a chain length of  $C_{10}$ . As mentioned earlier, DDAC is expected to have nearly the same surface chain density as DOAC. This is supported by their very similar SFG spectra at the quartz/air interface shown in Figure 2, spectra a and b, as it is known that the SFG spectra of surfactant monolayers depend strongly on surface density<sup>43,49</sup> but not much on alkyl chain length.<sup>52</sup> We found that none of the alkanes used in the experiment of Figure 1 were able to straighten the surfactant chains. As an example, the results for DOAC and DDAC monolayers in contact with deuterated tetradecane ( $C_{14}$ ) are shown in Figure 2, spectra c and d, respectively. Note that while the chain conformations of the molecules in air are very similar, they are very different when interacting with tetradecane: the DOAC chains are straightened



**Figure 3.** SFG spectra (SSP) for (a) DMOAP and (b) DOAC monolayers at the quartz/air interface and (c) DMOAP and (d) DOAC monolayers at the quartz/deuterated hexadecane interface.

but the DDAC chains are not. (The ratio of  $CH_2$  and  $CH_3$  peak strengths  $R$  is 0.60, 0.86, and 0.99 for DDAC in contact with air, tetradecane and decane, respectively.) This shows that indeed *both* surfactant and alkane must have long enough chains to effect straightening of surfactant chains. For lack of surfactants with intermediate chain length, we can only conclude at present that the minimum chain length for the surfactant chains to observe the straightening effect is between  $C_{10}$  and  $C_{18}$ .

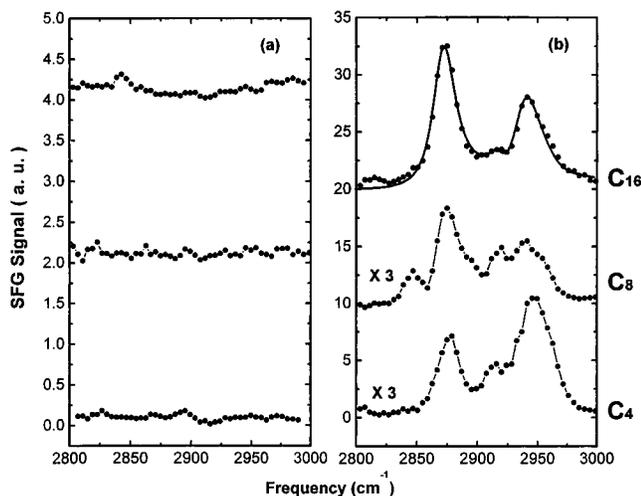
Another parameter of importance in this phenomenon must be the chain density of the surfactant monolayer.<sup>35,36,53</sup> We expect that for surfactant monolayers of too low a surface density, the chain–chain interaction between alkane and surfactant is also not strong enough to cause straightening of surfactant chains. To see whether this is true, we have obtained SFG spectra of DOAC and DMOAP monolayers in air and deuterated hexadecane, which are displayed in Figure 3. Both surfactants have the same chain length ( $C_{18}$ ), but the chain density for the DMOAP monolayer ( $2.0\text{ chains/nm}^2$ ) is about 70% of that for DOAC. Spectra a and b in Figure 3 are for the DMOAP and DOAC monolayers in air, respectively. Because of the lower chain density, the DMOAP monolayer is expected to have more gauche defects,<sup>25,30</sup> as evidenced in the spectrum of Figure 3a by a more prominent  $CH_2$  symmetric stretch ( $2850\text{ cm}^{-1}$ ), a shoulder at  $\sim 2920\text{ cm}^{-1}$  due to the  $CH_2$  asymmetric stretch, and a very weak  $CH_3$  symmetric stretch ( $2875\text{ cm}^{-1}$ ). When the monolayers are immersed in deuterated hexadecane their spectra show markedly different behaviors. The DMOAP spectrum (Figure 3c) is qualitatively similar to that in air. On the other hand, the DOAC spectrum (Figure 3d) undergoes a dramatic change with the disappearance of the  $CH_2$  modes that implies straightening of surfactant chains. We then conclude that the minimum chain density of the surfactant monolayer for the chain straightening to happen in alkanes is between 2.0 and  $2.8\text{ chains/nm}^2$ .

**B. Interaction between Surfactants and Alcohols.** In a previous publication,<sup>34</sup> we have studied the effect of hydrogen-bonding liquids on the chain conformation of loosely packed

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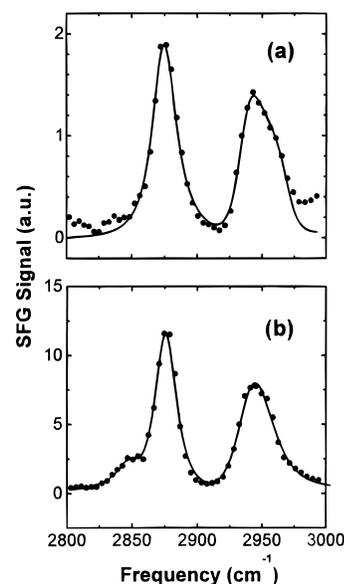


**Figure 4.** SFG spectra (SSP) for a DOAC monolayer at the quartz/alcohol interface: (a) with deuterated alcohols; (b) with regular alcohols. The chain length of the alcohols is indicated on each curve. The spectra have been separated vertically by 2 units in (a) and by 10 units in (b) for clarity. The solid line in the spectrum with regular hexadecanol (b) is a fit to eq 1.

surfactant monolayers. As in the case of water, methanol was also able to dramatically induce disorder in the surfactant chains because of the hydrophobic effect. The alkyl chains get “curled up” to reduce their exposed area to the solvent and minimize the number of broken hydrogen bonds at the interface. In light of our experiments with alkanes (section A, above), some interesting questions arise. What would happen to the chain conformation of a surfactant monolayer immersed in a long-chain alcohol? Would the chain–chain interaction between alcohol and surfactant be strong enough to overcome the hydrophobic effect and induce straightening of the surfactant chains? To answer these questions we have carried out SFG spectroscopic experiments with DOAC monolayers in contact with alcohols of different chain lengths.<sup>54</sup> The results are presented in Figure 4. The spectra in Figure 4a, obtained with three deuterated alcohols with very different chain lengths, show hardly any visible peaks from the surfactant chains. Apparently, the alcohols had induced curling up of the surfactant chains as water or methanol would do. Again, this is presumably due to the hydrophobic effect: the alcohols would form a hydrogen-bonding interfacial layer with OH facing the surfactant chains, which in turn become “curled up” to minimize the area of exposure to the alcohol layer. The spectra in Figure 4b were obtained with regular (perprotonated) alcohols of the same length as those listed in Figure 4a. They do show the characteristic CH<sub>2</sub> and CH<sub>3</sub> stretch peaks for alkyl chains. Since as in the case of deuterated alcohol no signal should be expected from the surfactant chains, the SFG spectra of Figure 4b must have come from oriented alcohol molecules at the interface.<sup>55</sup> We note that the spectrum of hexadecanol shows pronounced CH<sub>3</sub> modes and no CH<sub>2</sub> mode, suggesting that hexadecanol at the interface had formed an ordered hydrogen-bonded layer with a nearly all-trans chain conformation. With decreasing alcohol chain lengths, the SFG spectra (not shown, except for C<sub>8</sub> and C<sub>4</sub>) reveal that the alcohol layer of chain lengths C<sub>5</sub> to C<sub>12</sub> at the interface has a considerable amount of gauche defects in

(54) The alcohols which are solid at room temperature were kept several degrees above their melting point in a temperature-controlled Teflon cell during the experiments.

(55) This description demands that the DOAC monolayer is not being removed by solvents or replaced by alcohol molecules. See the discussion section below.



**Figure 5.** SFG spectra (SSP) for a DOAC monolayer at the quartz/hexadecanol solution interface: (a) with deuterated hexadecanol and (b) with regular hexadecanol. The solvent is CCl<sub>4</sub> and the alcohol concentration is 0.5 M. The solid line is a fit to eq 1.

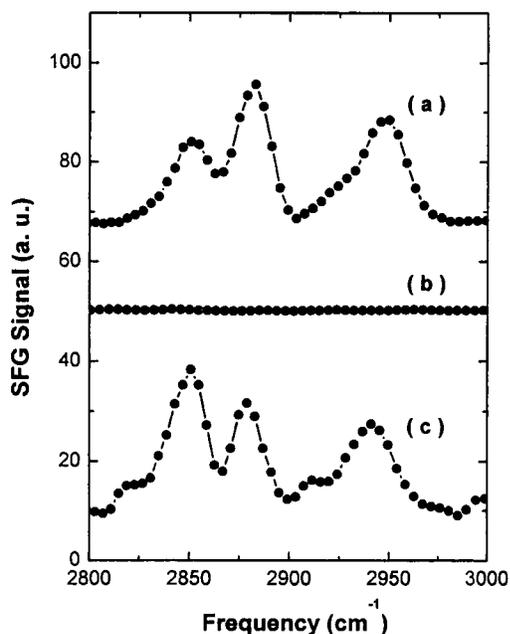
their chains. For butanol (C<sub>4</sub>) and propanol (C<sub>3</sub>), the amount of defects is less because of their short chain lengths.

One can reduce the hydrophobic effect of alcohol at the interface by diluting the hexadecanol in a nonpolar solvent, disrupting the interfacial hydrogen-bonded network. Figure 5 shows the SFG spectra for a DOAC monolayer in contact with a 0.5 M solution of hexadecanol in carbon tetrachloride. Deuterated hexadecanol was used in Figure 5a and therefore the spectrum comes only from the DOAC monolayer. Instead of a vanishingly weak SFG trace as seen in Figure 4a, the spectrum now exhibits distinct peaks characteristic of all-trans alkyl chains. Clearly, the alcohol chains must have wedged into the surfactant monolayer and the resultant chain–chain interaction has straightened the surfactant chains. This is only possible if the hydrogen-bonding network of alcohol is disrupted and the alcohol molecules individually penetrate the surfactant monolayer. To determine in this case the orientation of hexadecanol molecules adsorbed at the solution/DOAC interface we compare in Figure 5 the SFG spectra for this system using deuterated and regular alcohols in CCl<sub>4</sub>. Both are dominated by CH<sub>3</sub> resonances, although with regular alcohol, a shoulder due to the CH<sub>2</sub> mode at 2850 cm<sup>-1</sup> can be seen. This indicates that both surfactant and alcohol chains at the interface are nearly all-trans, the latter being slightly disordered. The peak strengths of the CH<sub>3</sub> modes are however significantly stronger in the case of regular alcohol, allowing us to conclude that the alcohol chains must be oriented in the same direction as the surfactant chains. If they were oriented oppositely, their contribution to SFG would interfere destructively with that from the surfactant chains and the spectrum would be much weaker.

## Discussion

**Dissolution of the Monolayers.** The above interpretations regarding disappearance of SFG signal from DOAC monolayers in hydrogen-bonding liquids assume that the DOAC monolayers are not dissolved by any of the solvents used. This is indeed what we found experimentally.<sup>56</sup> When the samples were soaked in various solvents, including water, for periods longer

(56) Details will appear in a forthcoming publication.



**Figure 6.** SFG spectra (SSP) for a DOAC monolayer on quartz: (a) in air, freshly prepared, (b) immersed in water ( $D_2O$ ), and (c) blow-dried by  $N_2$  gas after being immersed in water and then stored in a vacuum desiccator with  $P_2O_5$  for a few days.

than our data acquisition time ( $\sim 30$  min) and subsequently dried, the SFG spectrum from the monolayer in air was recovered almost to the level before the solvent exposure. The case with water is depicted in Figure 6. It shows the spectra for a DOAC monolayer on quartz (a) in air, freshly prepared, (b) immersed in water, and (c) blow-dried by  $N_2$  gas after being immersed in water and then stored in a vacuum desiccator with  $P_2O_5$  for a few days. While the spectrum of DOAC is completely suppressed in water, it recovers after the monolayer is dried, although the chain conformation is not as ordered as that of the freshly prepared sample. Similar results were obtained with other solvents. Therefore, any appreciable dissolution of the monolayers can be ruled out. In fact, removal of a DOAC monolayer from quartz can only be attained by cleaning with strongly oxidizing solutions ("piranha" solution, chromic acid) or by etching the substrate in a concentrated alkaline solution. We have also observed disappearance of the SFG spectrum of DMOAP monolayers in the same hydrogen-bonding solvents.<sup>57</sup> DMOAP is a silane that chemisorbs onto the quartz surface<sup>48</sup> and certainly cannot be dissolved in these solvents. The same effect has also been observed<sup>58</sup> for loosely packed surfactant monolayers on different substrates (quartz and mica). These results clearly indicate that conformational disordering of alkyl chains in water and other hydrogen-bonding solvents is responsible for the observations. This is expected to be a generic phenomenon although it becomes less important for densely packed monolayers due to limited solvent penetration into the monolayers.<sup>29–32</sup>

**Interaction with Alkanes.** Our results are directly relevant to the general use of contact angle wetting measurements to probe the structure of adsorbed monolayers.<sup>25,27,59,60</sup> Alkanes

(especially hexadecane) are widely used as probe liquids in such experiments. We now know that when loosely packed monolayers are being probed, one must be careful in interpreting the results due to the possibility of solvent penetration into the monolayer leading to its restructuring. This has long been suggested in connection with wetting experiments on incomplete monolayers,<sup>35,36</sup> where it appeared that hexadecane and tetradecane could penetrate the octadecylamine partial monolayers and make them highly oleophobic, resembling fully packed monolayers of alkyl chains. The solvent penetration had much less dramatic effects if the amine chain length was reduced to  $C_{12}$  or if solvents with bulky molecules were used. Also, if the amine monolayer had a surface density below  $\sim 40\%$  of a full monolayer, oleophobicity was quickly lost. All these observations are in remarkable agreement with our spectroscopic results on the interactions of surfactant monolayers with alkanes presented earlier.

The ability of alkanes to penetrate loosely packed monolayers and restructure the interfacial layer has also been suggested more recently to explain wetting measurements on partial surfactant monolayers<sup>37</sup> and mixed alkylthiol monolayers of different chain lengths.<sup>27,38</sup> Bain and Whitesides<sup>27</sup> have studied wetting on various mixed monolayers of  $C_{12}$  and  $C_{22}$  thiols on gold. They found that as the fraction of  $C_{12}$  chains on the surface was increased from 0 to about 0.5 the hexadecane contact angle varied from  $46^\circ$  to  $\sim 20^\circ$ . This reduction in oleophobicity was attributed to the disorder of the exposed ends of the  $C_{22}$  chains above the compact  $C_{12}$  layer. By using decane instead of hexadecane, the drop in oleophobicity occurred more abruptly and at a larger fraction of  $C_{12}$  chains in the monolayer. They attributed this result to the fact that the length of a decane molecule fits nearly exactly into the vacancies left in the mixed monolayer by the replacement of  $C_{22}$  by  $C_{12}$ . With decane molecules penetrating the partial monolayer it would produce a fully packed layer of alkyl chains with mainly methyl groups in contact with the liquid. This would increase the oleophobicity in comparison to a disordered layer of alkyl chains. When the surface density of  $C_{22}$  chains became less than 80% of a monolayer, decane penetration could no longer sustain a fully packed ordered layer of alkyl chains and the oleophobicity started to drop. This observation is qualitatively consistent with our results although in our case the minimum surfactant and alkane chain lengths to render the formation of a fully packed monolayer of alkyl chains are longer than  $C_{10}$ . However, our result is related to a chain density of about 2.8 chains/ $nm^2$  (56% of a full monolayer), and one expects that the minimum surfactant and alkane chain lengths for forming a fully packed monolayer via chain–chain interaction should depend on the surface density of vacancies in the surfactant monolayer.

One more recent experimental work reported in the literature can be directly related to our results. Allara *et al.*<sup>61</sup> have studied the wetting behavior of self-assembled alkoxy monolayers on  $SiO_2$  with chain densities of  $2.6 \pm 0.3$  chains/ $nm^2$  and several different chain lengths. They found a hexadecane contact angle ( $\theta_{HD}$ ) of  $\sim 10^\circ$  for chain lengths shorter than  $C_{15}$ , a rapid increase of  $\theta_{HD}$  from  $C_{15}$  to  $C_{18}$ , and  $\theta_{HD} \sim 36^\circ$  for  $C_{18}$  or longer, but a water contact angle  $\theta_W$  of  $\sim 100^\circ$  for all chain lengths. Their interpretation was that a structural transition in the monolayers (*in air*) from a more disordered to a more ordered chain conformation had happened when the alkoxy chain length increased from  $C_{15}$  to  $C_{18}$ . Knowing our results, we can now have a better understanding of their observations. All alkoxy

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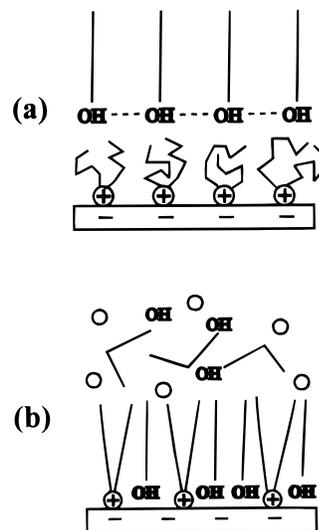
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monolayers, regardless of their chain lengths, will have their chains curled up when exposed to water because of the hydrophobic effect.<sup>34</sup> They therefore look the same to water, thus giving rise to the same water contact angles. The observed conformational transition of the alkoxy monolayer in hexadecane with increasing alkoxy chain length can be understood from the possible change of chain conformation induced by chain–chain interaction with hexadecane. For alkoxy monolayers with chain lengths varying from C<sub>15</sub> to C<sub>18</sub>, the chain–chain interaction between alkoxy chains and hexadecane penetrating the monolayer must have become increasingly stronger and at C<sub>18</sub> strong enough to induce straightening of the alkoxy chains. The mixed monolayer of alkane and alkoxy chains formed with C<sub>18</sub> or longer would appear similar to a compact layer of alkyl chains (as monolayers of alkylthiols on gold or OTS on glass). Therefore,  $\theta_{\text{HD}}$  should increase to a value close to what has been observed<sup>27,61</sup> for fully packed monolayers ( $\sim 46^\circ$ ). If their wetting experiments were done with decane instead of hexadecane probably no such transition would be observed, knowing that decane has little effect on the surfactant chain conformation for this surfactant density.

The above work of Allara *et al.*<sup>61</sup> has been complemented by molecular dynamics simulations.<sup>39</sup> The result shows that alkane penetration into the monolayer indeed can cause restructuring of the monolayer. However, although their simulation reproduces the observed change in the wetting behavior of hexadecane at the proper surfactant chain length, the physical picture deduced from the simulation is very different from what we have described: the hexadecane penetration into the surfactant monolayers is significant for surfactant chain lengths shorter than C<sub>15</sub> and *reduced* considerably for longer ones. Only a small increase in ordering of the chain conformation appears for the *shorter* surfactant monolayers ( $\leq C_{14}$ ) upon contact with hexadecane; conversion to a nearly all-trans conformation is *not observed* for any chain length. These predictions disagree with our experimental findings and are opposite to the picture we described earlier.

**Interaction with Alcohols.** As we mentioned earlier, the DOAC monolayers cannot be removed by alcohols or other common organic solvents. Therefore, the only interpretation for the vanishingly weak SFG spectrum of DOAC in contact with pure deuterated long-chain alcohols (Figure 4a) is that the surfactant chains must have contained a large amount of gauche defects or, in other words, “curled up”. This suggests that the situation is similar to what we have previously observed in the cases of water and methanol,<sup>34</sup> in which the liquid molecules like to form a hydrogen-bonding network at the solid/liquid interface to minimize the number of broken hydrogen bonds at the interface. The surfactant chains in turn become “curled up” to reduce their exposed area to the liquid and minimize disruption to the hydrogen-bonded network at the interface. For this to happen, the alcohol molecules must adsorb at the interface with their OH groups forming a hydrogen-bonding network and facing the disordered surfactant monolayer. To show that this is indeed the case, we use the SFG spectra of DOAC taken with regular alcohols (Figure 4b). In this case, the SFG spectra comes only from oriented alcohol molecules at the interface, since Figure 4a already shows that the signal from DOAC is negligible when in contact with deuterated alcohols. For sufficiently long alcohol molecules, e.g. hexadecanol, the spectrum in Figure 4b indicates that the chain–chain interaction is strong enough to straighten their chains. Comparing this spectrum to that of DOAC in contact with deuterated hexadecane (Figure 1) allows us to determine the absolute orientation of



**Figure 7.** Schematics of the structures of (a) quartz/DOAC/neat hexadecanol and (b) quartz/DOAC/0.5 M hexadecanol in CCl<sub>4</sub> interfaces. Chains are represented by solid lines, surfactant headgroups by plus signs within circles, and CCl<sub>4</sub> molecules by open circles.

the alcohol layer. This is done as follows.<sup>41,42,62</sup> The SFG spectra of hexadecanol/DOAC (Figure 4b) and hexadecane/DOAC (Figure 1) interfaces can be fit to eq 1. We found that in both cases the mode amplitude  $A_{\text{CH}_3}$  has the same sign as the nonresonant background  $\chi_{\text{NR}}$ . This indicates that the CH<sub>3</sub> groups of alcohol molecules and DOAC in the two cases point in the same direction. Since the nearly all-trans DOAC chains must point away from the quartz substrate, we can conclude that alcohol molecules at the interface must also have their chains pointing away from the substrate, and consequently OH groups facing the DOAC monolayer. Figure 7a shows a cartoon of the structure of the hexadecanol/DOAC interface inferred from our experiment.

One may argue that the alcohols at the interface should have their alkyl chains facing the hydrophobic surfactant monolayer. This is opposite to what we observed. In addition, this structure is also inconsistent with our spectra: if the alcohol chains faced and interacted with the DOAC monolayer, the situation would be similar to the case of DOAC in contact with alkanes discussed above. The chain–chain interaction should make the chains more ordered or straightened instead of curled up. The vanishing signals from DOAC in Figure 4a indicate that this is definitely not the case. While we have no detailed free-energy calculation to support the structure sketched in Figure 7a, we can make some plausible arguments. It is known, theoretically<sup>63,64</sup> and experimentally,<sup>13,65–69</sup> that chain molecules with an OH terminal tend to form an oriented hydrogen-bonding network at interfaces to minimize the number of broken hydrogen bonds. This is even possible with the OH terminals facing a hydrophobic medium. For example, both molecular

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dynamics simulations<sup>63</sup> and infrared spectroscopy<sup>68</sup> have shown that the OH-terminated alkylthiol molecules adsorbed on gold tend to have their OH terminals hydrogen bonded together and form a highly ordered monolayer with the bonded OH groups facing the air or vacuum. The question is which orientation of the alcohol layer is energetically more favorable, one with OH terminal groups facing the surfactant monolayer or one with the alkyl chains facing the surfactant monolayer. In terms of chain–chain interactions, we expect the two configurations to be comparable. With the OH groups pointing toward the surfactant monolayer, however, there is an entropy gain resulting from curling up of the surfactant chains. This configuration is then likely to have a lower free energy.

We now discuss the case of DOAC/hexadecanol-in-CCl<sub>4</sub>. When hexadecanol is diluted in CCl<sub>4</sub>, the fraction of associated alcohol molecules is reduced and the fraction of isolated alcohol molecules is increased.<sup>70–72</sup> The hydrophobic effect at the DOAC/liquid should be reduced due to disruption of the hydrogen-bonding network at the interface. Figure 5 clearly shows that both DOAC and hexadecanol at the interface now have their chains mostly in the all-trans conformation. Apparently individual alcohol molecules in solution can now adsorb at the interface, filling the empty sites in the surfactant monolayer. The hexadecanol chains are long enough to induce a straightening of the surfactant chains via the chain–chain interaction, as in the case of alkanes (Part A of the Results section). A similar effect due to the coadsorption of alcohol and soluble surfactants at a hydrophobic-solid/solution interface has been observed previously by SFG spectroscopy.<sup>13,16</sup>

As mentioned earlier, we can determine from the spectra in Figure 5 the relative orientation of the adsorbed alcohol molecules with respect to the DOAC monolayer. If the alkyl chains of both molecules are pointing away from the substrate, their CH<sub>3</sub> modes should contribute to the SFG signal constructively. On the other hand, if the adsorbed alcohols have their chains pointing toward the DOAC monolayer, the SFG signals from the CH<sub>3</sub> modes of alcohol and DOAC would interfere destructively. The spectra in Figure 5 show that the signal from the (alcohol + DOAC) layer (Figure 5b) is much stronger than that from the DOAC monolayer alone (Figure 5a), implying that the adsorbed alcohol molecules have the same orientation as the DOAC molecules. Fitting the spectra in Figure 5 to eq 1 yielded the mode amplitudes  $A_{\text{CH}_3}$ . We found that they have the same sign compared to the nonresonant background  $\chi_{\text{NR}}$  and compared to  $A_{\text{CH}_3}$  for the spectra of Figures 1 and 4b. This means that in all these cases, the alkyl chains of DOAC and alcohol are pointing away from the substrate. Figure 7b shows a cartoon of the DOAC/hexadecane-in-CCl<sub>4</sub> interface as deduced from our data. This configuration should indeed be energetically

favorable. In the bulk solution, alcohol molecules are surrounded by CCl<sub>4</sub> so that the solution is strongly hydrophobic. It is highly unfavorable to have alcohol molecules adsorbed with the OH groups facing the solution.

## Conclusion

In summary, we have studied the interaction of long-chain alkanes and alcohols with loosely packed self-assembled surfactant monolayers at the solid/liquid interface. We found that if both alkane and surfactant molecules have sufficiently long chains (longer than about C<sub>14</sub>) and the surfactant surface density is sufficiently high (higher than  $\sim 2.5$  chains/nm<sup>2</sup>), the penetration of alkane molecules into the surfactant monolayer can effectively eliminate the gauche defects initially present in the surfactant chains, due to a strong enough chain–chain interaction.

In the case of long-chain alcohols, they prefer to form a hydrogen-bonding network at the interface. Because of the hydrophobic effect, the surfactant chains become highly disordered (“curl up”) to reduce their surface area exposed to the liquid alcohol. The surface alcohol molecules are well oriented; their chains are nearly all-trans if they are long, thus forming a highly ordered layer above the highly disordered surfactant monolayer. However, diluting the alcohol in a nonpolar solvent can disrupt the surface hydrogen-bonding network and the alcohol molecules can now wedge into the surfactant monolayer. They adsorb at the interface with the same chain orientation as the surfactant molecules, providing enough chain–chain interaction to transform both surfactant and alcohol chains into all-trans.

Although the set of data presented here is far from being complete enough for us to be able to draw detailed conclusions, we have obtained some rough ideas on how long-chain molecules interact and affect their chain conformation at interfaces. While the work presented here is for self-assembled monolayers at solid/liquid interfaces, the general picture should be valid also for other interfaces such as air/liquid or liquid/liquid. However, the quantitative parameters (critical chain length, critical surface chain density) could be different at these interfaces owing to the lateral mobility of the monolayers.

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