

Effect of Alkyl Chain Length on the Conformation and Order of Simple Ionic Surfactants Adsorbed at the D₂O/CCl₄ Interface as Studied by Sum-Frequency Vibrational Spectroscopy

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Received February 3, 1998. In Final Form: August 20, 1998

The conformational order of three alkanesulfonates, sodium hexanesulfonate (HS), sodium undecanesulfonate (UDS), and sodium dodecanesulfonate (DDS), adsorbed at the D₂O/CCl₄ interface are examined in detail by sum-frequency vibrational spectroscopy. An increase in surfactant concentration at the interface results in the reduction of gauche defects in the hydrocarbon chains as determined from the intensity ratio of the methyl to methylene symmetric stretch vibrational modes. The degree of disorder in the alkyl chains varies greatly with alkyl chain length. The alkyl chain of HS displays the fewest gauche defects while DDS and UDS display more disorder in their hydrocarbon chains at similar surface concentrations. This observation is interpreted as a reduction in the possible number of gauche conformations for the shorter alkyl chain.

I. Introduction

Amphiphilic molecules play an important role in many fields of chemistry due to their unique behavior at interfaces. The opposing interactions of the hydrophilic headgroup and hydrophobic tail with the surrounding medium is the basis for the interfacial properties of surfactants. In recent years, experimental methods have emerged which have allowed for a molecular level picture of how amphiphilic molecules adsorb at air/liquid interfaces.¹⁻¹⁰ In contrast, information on the molecular conformation and order of amphiphiles at the oil/water interface is sparse. This lack of information is primarily due to the absence of experimental methods for studying surfactants at a liquid/liquid interface on the molecular level. While studies have investigated the orientation and adsorption of surface-active dyes at the oil/water interface using fluorescence,^{11,12} resonance Raman scattering,¹³⁻¹⁵

and second harmonic generation (SHG),¹⁶⁻¹⁸ little is known about alkyl chain conformation of simple alkyl surfactants at the liquid/liquid interface and the role that alkyl chain length plays in conformational order. While neutron reflection and X-ray diffraction studies of surfactants have been conducted at the air/water interface^{6,8,9} only recently have such techniques been applied to the investigations at the liquid/liquid interface.^{19,20}

In this paper, we examine the effect of chain length on the relative conformational order and orientation of a series of alkanesulfonates at the water/carbon tetrachloride interface. The conformation of the alkyl chain within the amphiphilic molecule is known to contribute to the structure and quality of monolayers at interfaces.²¹ For example, a correlation between monolayer packing density and alkyl chain length has been observed at solid and liquid surfaces.²² Such studies have shown that longer alkyl chains generally form more ordered films than the corresponding shorter chains. An even-odd effect has also been observed in systems of alkanethiol monolayers on gold.²³⁻²⁵ In these systems, it is found that even and odd alkyl chains actually assemble with different packing arrangements, giving rise to a variation in order parameters for the two types of chain lengths. A similar trend is observed in the melting points of liquid crystals composed of even and odd alkyl chains. Even-numbered alkyl chain length liquid crystals display higher degrees

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of order, more crystalline structure and higher melting points than those liquid crystals composed of odd alkyl chain lengths.^{26–30} Similar behavior is observed in the heats of fusion of even- and odd-chained alkanes, with even-numbered alkanes having a greater heat of fusion.³¹

Molecular adsorption at a liquid/liquid interface is quite different than adsorption at the air/solid or air/liquid interfaces. Studies of monolayers on solid surfaces and at the air/water interface show that the van der Waals interactions between the alkyl chains of surfactants play a very important role in assembly at these interfaces.^{32,33} At a liquid/liquid interface, the van der Waals attractions between alkyl surfactants are diminished as solvent is introduced between the chains.³⁴ To what degree the solvent disrupts the molecular conformation of the alkyl chains has been impossible to measure directly. However, recent molecular dynamics calculations of sodium dodecyl sulfate at the water/carbon tetrachloride interface have begun to shed light on this subject.³⁵ Another consequence of the diminished chain–chain van der Waals interactions is that monolayers of adsorbed species at the liquid/liquid interface are typically more expanded than monolayers at the solid/liquid or liquid/air interfaces.^{36–38}

Recent studies from this laboratory have demonstrated the feasibility of obtaining molecular information about surfactant conformation at a liquid/liquid interface using total internal reflection sum-frequency vibrational spectroscopy (TIR-SFVS).^{10,39–41} With SFVS, the chemical sensitivity of vibrational spectroscopy is coupled with the interface specificity of this nonlinear technique to allow molecular characterization of buried interfaces. A total internal reflection geometry is used which significantly enhances the sensitivity of this technique.^{39,40,42} The focus of the work presented here is the use of this technique to provide information about the effect of chain length on the conformation and orientation of the alkyl chains of ionic surfactants at a liquid/liquid interface. Specifically, the conformational order of three alkanesulfonates, sodium hexanesulfonate (HS), sodium undecanesulfonate (UDS) and sodium dodecanesulfonate (DDS), adsorbed at the D₂O/CCl₄ interface are examined in detail by SFVS.

Information about molecular conformation of the hydrocarbon chains is obtained specifically from the C–H symmetric stretch region of the vibrational spectra. Conformational order is discussed in terms of the surface concentration of surfactant and the alkyl chain length of the hydrophobic tail.

II. Background

Sum-Frequency Vibrational Spectroscopy. Sum-frequency vibrational spectroscopy (SFVS) has a major advantage over conventional linear vibrational spectroscopic methods for the study of surfaces in that the method is inherently interface specific, and for this reason, it has been used extensively in the investigation of buried interfaces.^{5,42–54} In SFVS, two coherent laser beams, one visible and the other from a tunable IR laser source (ω_{vis} and ω_{IR}) impinge on a surface. The induced nonlinear polarization at the surface results in the coherent generation of light at the sum-frequency ($\omega_{\text{sum}} = \omega_{\text{vis}} + \omega_{\text{IR}}$).⁵⁵ The intensity of the sum-frequency light is given by

$$I(\omega_{\text{sum}}) \propto |\tilde{f}_{\text{sum}} \tilde{f}_{\text{vis}} \tilde{f}_{\text{IR}} \chi^{(2)}|^2 \quad (1)$$

where $I(\omega_{\text{sum}})$ is the nonlinear Fresnel factor for the generated sum-frequency light,^{56,57} $\chi^{(2)}$ is the second-order susceptibility tensor and \tilde{f}_{vis} and \tilde{f}_{IR} are the geometric linear Fresnel factors of the incident fields.⁴⁰ The symmetry constraints on $\chi^{(2)}$ prohibit nonlinear interactions in the bulk of centrosymmetric media. At an interface, this constraint is lifted due to the local break in symmetry and such processes are allowed. Consequently, the spectroscopic transitions of the molecules residing at the interfacial region can be probed selectively without any contributions from the molecules present in the more pervasive bulk liquids.

The second-order susceptibility $\chi^{(2)}$ can be separated into a nonresonant contribution $\chi_{\text{NR}}^{(2)}$ arising from the bare interface and a resonant contribution $\chi_{\text{R}}^{(2)}$ arising from the vibrational resonances of the molecules at the interface:

$$\chi^{(2)} = \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)}(\omega_{\text{IR}}) \quad (2)$$

For any given vibrational mode, the resonant component of the susceptibility can be expressed as

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$$(\chi_R^{(2)})_{lmn}(\omega_{IR}) = \sum_v \frac{NA_{n_v}M_{lm_v}}{(\omega_v - \omega_{IR} - i\Gamma_v)} \quad (3)$$

where N is the adsorbate surface density, A_{n_v} is the IR transition moment, M_{lm_v} is the Raman transition strength, ω_v is the transition frequency with a damping constant of Γ_v for a specific transition, v , and ω_{IR} is the frequency of the incident infrared beam. In order for a transition to be SFVS active, it must satisfy the constraint of Eq 3, which requires that the vibrational mode be both infrared and Raman allowed.

In the case of linear spectroscopic methods such as FTIR and FT Raman, attenuated total reflection (ATR) has been used to enhance the sensitivity of these methods.^{58–60} In a similar fashion, a total internal reflection geometry has been used here to enhance the otherwise weak sum-frequency response from the molecules residing at the liquid/liquid interface. In addition to the strong resonant coupling of the IR fields with the vibrational modes of the molecules residing at the interface, the optical geometry has a significant effect on the measured sum-frequency intensity. When the incident beams are directed on the interface in an internal reflection geometry at their respective critical angles, an enhancement of several orders of magnitude in the sum-frequency response is achievable over that for an external reflection geometry.^{39,40,42,56,57,61–65} This enhancement is a consequence of the evanescent field produced at the interface. The implementation of a TIR optical geometry in conjunction with SFVS has allowed for the vibrational spectroscopic investigation of liquid/liquid interfaces which has previously been inaccessible by conventional SFVS.^{39,40}

III. Experimental Section

Materials. The D₂O (99%) and HPLC grade CCl₄ (99%) used in the experiment were purchased from Aldrich. The CCl₄ was distilled in order to remove any residual hydrocarbon compounds, and its purity confirmed by transmission FTIR. The D₂O was shaken with purified CCl₄ prior to use and decanted. Sodium hexanesulfonate (HS) (TCI America, 99%), sodium undecanesulfonate (UDS) (TCI America, 99%), and sodium dodecane-sulfonate (DDS) (TCI America, 99%) were used as received. The molecular structures for the surfactants used, HS, DDS, and UDS, are shown in Figure 1.

Sum-Frequency Vibrational Spectroscopy Experiments. The SFVS experiments were performed with the frequency-doubled 532 nm output of a Q-switched Nd:YAG laser and IR light generated using a LiNbO₃ optical parametric oscillator (OPO), described elsewhere.⁶⁶ IR light pulses in the 2700–3100 cm⁻¹ region with a bandwidth of 6 cm⁻¹ and energies of 2–3 mJ were obtained over the entire spectral region. The OPO was calibrated with a polystyrene sample. The sum-frequency experiments were performed in a cylindrical quartz cell. To achieve the desired optical geometry for total internal reflection, both the visible and IR beams were directed onto the D₂O/CCl₄ interface through the CCl₄ high index phase, in a copropagating manner. D₂O was used due to the weak but significant absorption by H₂O in the spectral region of interest, which resulted in

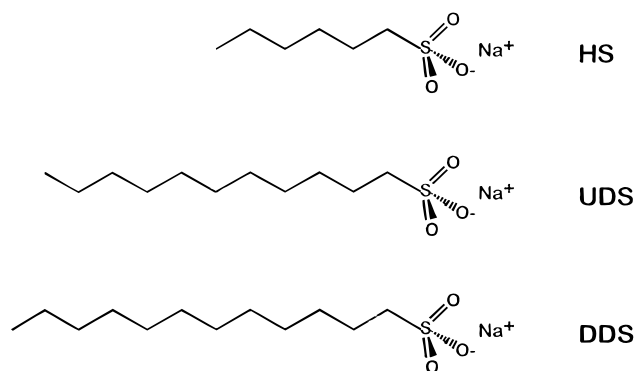


Figure 1. Molecular structure of sodium hexanesulfonate (HS), sodium undecanesulfonate (UDS), and sodium dodecane-sulfonate (DDS).

undesirable heating of the interface. The IR beam was focused on the interface at an angle of 70° from the surface normal. The visible 532 nm was collimated to a diameter of 1–2 mm and incident on the interface at an angle of 66°. Laser powers used were typically 1–2 mJ/pulse between 2800 and 3100 cm⁻¹ and 5 mJ/pulse at 532 nm.

Variation of the input IR polarization was accomplished with a Soleil-Babinet compensator and an IR polarizer. Polarization of the visible light was selected with a half-wave plate. The sum-frequency signal was collected in reflection at an angle of 66°. The resulting sum-frequency light was polarization selected with a broad band Glann–Taylor polarizer. The residual 532 nm light was removed by a combination of absorptive, interference and holographic notch filters. The resulting signal was detected using a PMT and gated electronics. Data points, collected every 2 cm⁻¹, were an average of 200 pulses. The sum-frequency spectra were corrected for Fresnel contributions for each polarization and for the intensity variation of the infrared beam throughout the spectral region.

The sample cell used in the sum-frequency experiments was cleaned with MicroCleaner and Nochromix solution and rinsed with NANOpure water which had a resistivity of 17.9 Mohm cm. The cell was dried in an oven at 100 °C to remove residual water. The solvents CCl₄ and D₂O were introduced into the sample cell and allowed to equilibrate. No detectable sum-frequency signal was measured from the bare D₂O/CCl₄ interface. This measurement also served as a means of determining the presence of any surface active contaminants. The surfactants were dissolved in an aliquot of D₂O, which was removed from the sample cell. The solution was then returned to the cell and mechanically stirred. SFVS spectra were collected after allowing the solutions to equilibrate for 20 min.

Interfacial Tension Measurements. Interfacial tension measurements of HS, UDS, and DDS at the H₂O/CCl₄ interface were obtained by means of the drop-volume method.⁶⁷ A Gilmont micrometer syringe was used for drop delivery of the CCl₄. Measurements were made at room temperature with aqueous surfactant concentrations ranging from 0.1 to 7.5 mM for UDS and DDS and 0.1 to 75.0 mM for HS. The interfacial tension was obtained from the drop volume by means of the method of Wilkinson.⁶⁸

IV. Results and Discussion

The adsorption isotherms for HS, DDS, and UDS at the H₂O/CCl₄ interface are shown in Figure 2. The Gibbs equation used for calculating the surface excess as a function of bulk concentration in the absence of any supporting electrolyte is given by eq 4, where π is the interfacial pressure in mN/m and a is the activity. For dilute solutions (less than 10⁻² M) the activity has been replaced with the bulk concentration C_i . A plot of the surface concentrations of HS, DDS, and UDS vs bulk

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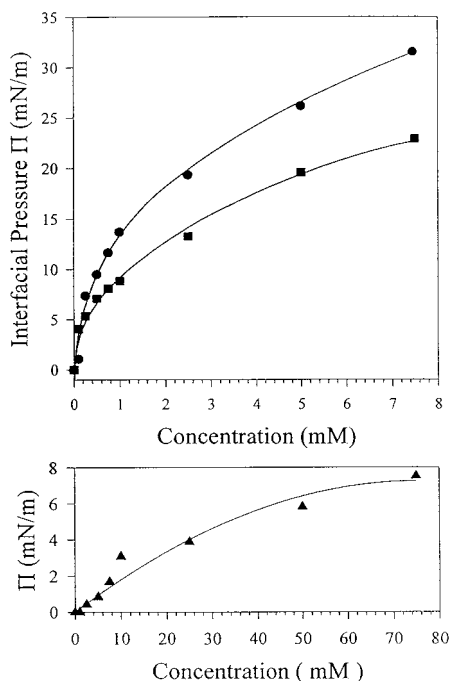


Figure 2. Plot of the interfacial pressure of (▲) HS, (■) UDS, and (●) DDS at the water/carbon tetrachloride interface vs the aqueous concentration. The solid line is shown as a guide to the eye.

$$\Gamma_i = \frac{1}{2RT} \left(\frac{\partial \pi}{\partial \ln(a_i)} \right)_T \quad (4)$$

concentration is shown in Figure 3. These values have been obtained from eq 4 and the interfacial tension data in Figure 2.

Sodium hexanesulfonate, which achieves a maximum surface pressure of ~ 8 mN/m, displays the lowest interfacial activity. The surface activities of UDS and DDS are nearly equivalent, with UDS achieving a slightly lower terminal surface pressure of approximately 23 mN/m compared to that of DDS at ~ 30 mN/m. This similarity is also reflected in the surface concentration data of Figure 3 and the area per molecule at monolayer saturation. The largest mean molecular area is found for HS at 200 ± 13 Å² whereas UDS and DDS have areas of 98 ± 5 and 61 ± 4 Å², respectively. The greater surface activity of UDS and DDS is a result of their longer alkyl chains. The addition of a single methylene unit to the alkyl chain results in a decrease in the free energy of transfer of the alkyl chain from the aqueous to the organic phase by approximately -3.45 kJ/mol.³⁴

Sum-Frequency Vibrational Spectra. Representative sum-frequency vibrational spectra of HS, UDS, and DDS adsorbed at the D₂O/CCl₄ interface are displayed in Figure 4. The spectra of UDS and DDS were collected at a bulk aqueous concentration of 5.0 mM. The spectra of HS was collected at a bulk aqueous concentration of 50 mM. The spectra in parts a, c, and e of Figure 4 were obtained with the polarization combination *ssp* (*s* polarized SF, *s* polarized visible, *p* polarized IR) and the adjacent spectra (Figure 4b,d,f) were obtained with the polarization combination *sps* (*s* polarized SF, *p* polarized visible, *s* polarized IR). All spectra have been corrected for Fresnel factors and the instrument response so that the intensities between the two polarizations can be compared quantitatively. The vibrational spectra of HS, UDS, and DDS are similar with differences apparent only in the relative peak intensities. The spectra were fit with a combination

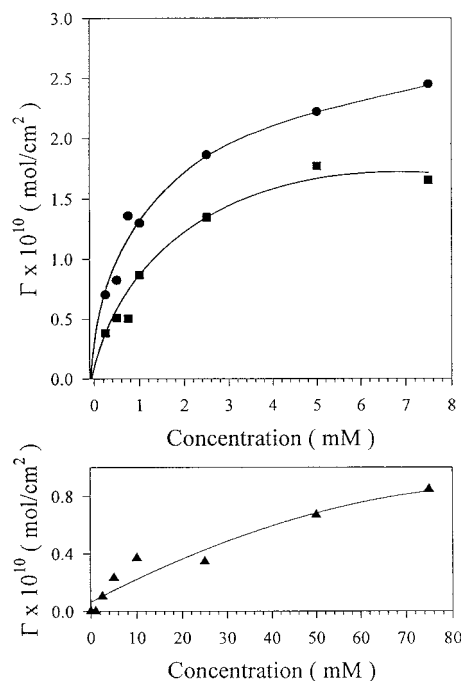


Figure 3. Surface excess concentration as a function of bulk aqueous concentration for (▲) HS, (■) UDS, and (●) DDS. The solid line is shown as a guide to the eye.

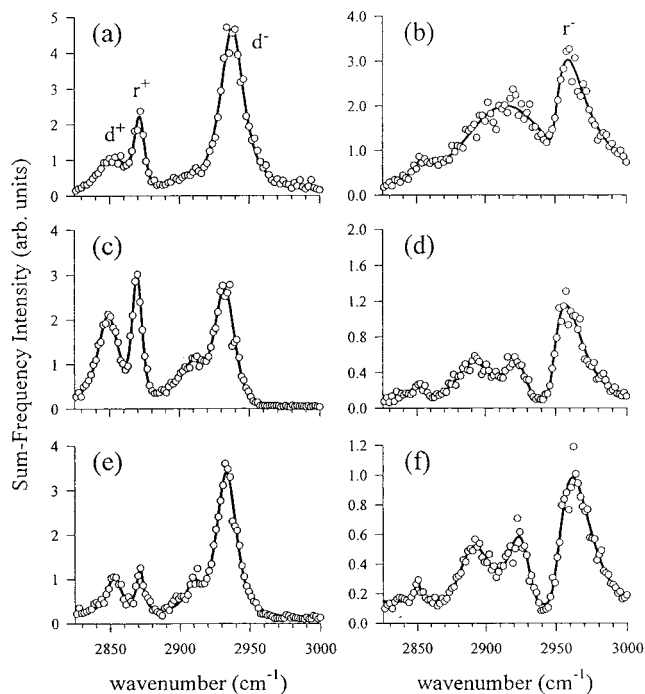


Figure 4. Sum-frequency vibrational spectra acquired with *p*-polarized infrared and *s*-polarized visible for (a) HS, (c) UDS, and (e) DDS. SF spectra acquired with *s*-polarized infrared and *p*-polarized visible for (b) HS, (d) UDS, and (f) DDS. Spectra are shown for 5.0 mM solutions of UDS and DDS in D₂O. The spectrum of HS is shown for 50 mM aqueous concentration. The generated output sum-frequency was *s*-polarized in both cases. The solid lines represent a fit to the spectra using a combination of Gaussian and Lorentzian functions for each peak.

of a Lorentzian and a Gaussian function for each peak. A Gaussian component was used in order to accommodate the limited bandwidth of the laser.

Spectral assignments for the SF spectra of HS, UDS, and DDS shown in Figure 4 have been made as follows.

The *p*-polarized IR (*ssp*) spectra for all the surfactants studied (Figure 4a,c,e) exhibit strong intensities for the methylene asymmetric stretch (d^-) at 2930 cm^{-1} , in agreement with the value observed in the IR spectrum, (2925 cm^{-1}).⁶⁹ Peaks of moderate intensity are observed for the methylene symmetric (d^+) and methyl symmetric (r^+) stretches at 2848 and 2872 cm^{-1} respectively. A weak methylene Fermi resonance (d^+_{FR}) at 2900 cm^{-1} , resulting from interaction of an overtone of the methylene bending mode with the methylene symmetric stretch, is observed as a shoulder of the methylene asymmetric stretch. This feature can be compared to the methylene Fermi resonance in polymethylene appearing in the IR ($d^+(\pi)_{FR}$) at $2898\text{--}2904\text{ cm}^{-1}$ and in the Raman ($d^+(0)_{FR}$) at 2890 cm^{-1} .^{70,71} For *s*-polarized IR (Figure 4(b, d, and f)), the asymmetric methylene (d^-) and methylene Fermi resonance (d^+_{FR}) are present in all cases at 2930 and 2900 cm^{-1} respectively. The most prominent feature in the *s* polarized spectra is the methyl asymmetric stretch (r^-) at 2960 cm^{-1} . A very weak methylene symmetric stretch is also apparent at 2850 cm^{-1} . The peak assignments above have been verified by deuteration studies.⁴⁰

Conformation of the Alkyl Chain. Information on the conformation of the alkyl chains can be obtained from the intensities of the spectral features seen in Figure 4. In linear absorption vibrational spectroscopy all vibrational modes can be accessed regardless of molecular symmetry. The nonlinear and coherent nature of SFVS means that the molecular symmetry and phase of a particular vibrational transition must be considered when interpreting sum-frequency spectra. To understand the relative intensities of the peaks in the sum-frequency spectra of Figure 4, it is necessary to consider the local symmetry of the CH_2 hydrocarbon backbone. An all-trans hydrocarbon chain is locally centrosymmetric with respect to the methylene groups. As a result, the methylene symmetric stretch is either IR or Raman allowed but never both.⁷² Referring back to eq 3, for a vibrational transition to be SFVS active, it must be simultaneously infrared and Raman allowed. Therefore, little contribution from methylene resonances should be observed for a system of well-ordered (all-trans), hydrocarbon chains. This criterion makes the methyl and methylene region of the SF spectrum an especially sensitive indicator of alkyl chain conformation. The presence of a strong methylene peak at 2850 cm^{-1} in the spectra of Figure 4 therefore suggests that the alkyl chains contain a number of gauche conformations which relax the local symmetry of the methylene vibrational mode.

To understand how the conformational order of the alkyl chains varies with surface concentration, the ratio of the intensities of the symmetric methyl and symmetric methylene stretch modes is used in conjunction with the interfacial tension data. We have previously demonstrated that the ratio of the intensities of the symmetric methyl and methylene modes, I_{r^+}/I_{d^+} , can be used as an indicator of the relative order within the hydrocarbon chains.³⁹⁻⁴¹ A variation in this ratio indicates a change in orientation of the average component of the methyl and methylene transition dipoles along the surface normal. In a previous study it has been determined that the C_{3v} axis of the methyl group lies principally along the *z* axis.^{39,40} As a result, the

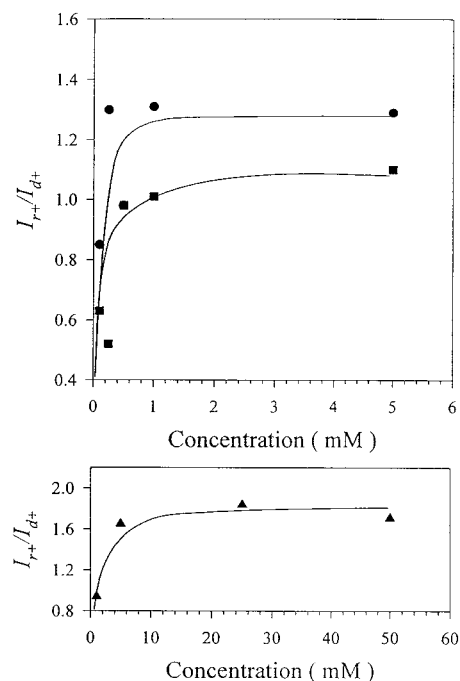


Figure 5. Plot of the methyl/methylene (I_{r^+}/I_{d^+}) ratio as a function bulk aqueous concentration for (▲) HS, (■) UDS, and (●) DDS. The solid line is shown as a guide to the eye.

change in the ratio of I_{r^+}/I_{d^+} is primarily due to a change in I_{d^+} caused by the introduction of gauche conformations in the alkyl chain.

Spectra were collected for a series of aqueous surfactant concentrations ranging from 1.0 to 75.0 mM for HS and from 0.1 to 5.0 mM for UDS and DDS. The peak intensities of the symmetric methyl and methylene vibrational modes were obtained from spectral fits. A plot of the I_{r^+}/I_{d^+} ratio vs bulk concentration is shown in Figure 5 for HS, DDS, and UDS. Examination of Figure 5 and the data presented in Figure 3 suggests that there is a correlation between alkyl chain order and surface concentration. This is consistent with the argument that as the surface density increases, the degree of conformational mobility within the alkyl chains decreases, due to confinement of the alkyl chains by their nearest neighbors. However, the I_{r^+}/I_{d^+} intensity ratios for HS, DDS, and UDS increases rapidly at the lowest surface coverages and then plateaus well before a full monolayer is formed. This suggests that the full extent of alkyl chain ordering occurs well before anything resembling a closest packed monolayer is formed.

The data in Figure 5 suggest that the length of the alkyl chain also plays a role in the conformational mobility of the alkyl chain. The C_6 alkyl chain of HS displays the largest I_{r^+}/I_{d^+} ratio even at the lowest surface concentrations. In contrast, UDS and DDS show much lower values of I_{r^+}/I_{d^+} overall and exhibit nearly identical behavior as a function of surface coverage. The data presented above suggest that there are fewer gauche defects in the alkyl chains of HS than for UDS and DDS. The technique of SFVS is not capable of distinguishing between the position and number of the gauche conformations in the alkyl chain. That is, a gauche defect in the portion of the chain near the headgroup is assumed to have the same effect as one further down the chain. Although the portion of the chain adjacent to the gauche site is reoriented, this part of the chain will still possess an all-trans conformation and will not contribute to the sum-frequency spectra. It is only the two methylene units forming the dihedral angle of the gauche conformation that will experience a disruption in

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the local symmetry and thus result in the appearance of a CH₂ resonance in the SF spectra. The intensity of the symmetric methylene resonance with *p*-polarized IR is therefore proportional to the number average of such defects oriented along the *z* axis within the ensemble of alkyl chains which are being sampled. The larger I_{r^+}/I_{d^+} ratios observed for HS can therefore be explained by the lower number of possible gauche conformations for the shorter alkyl chain of HS compared to the longer alkyl chains of UDS and DDS. This observation is not surprising, as the hexyl chain of HS intrinsically possess fewer geometrically allowed gauche conformations than the 11- and 12-membered alkyl chains of UDS and DDS.

There is also a slight difference in the alkyl chain order observed for UDS and DDS, with DDS appearing to possess more gauche defects. This observation is consistent with the arguments made above for HS, namely the longer alkyl chain possesses more possible gauche conformations. In addition, comparison of Figure 5 with Figure 3 suggests that this difference could be due to the surface concentration. There appears to be no evidence for preferential ordering of even-numbered alkyl chains (DDS) over odd-numbered ones (UDS). The diminished chain-chain interaction may account for the fact that no discernible difference is found in the conformation of alkyl chains composed of even or odd number of methylene units. Since the proximity of the alkyl chains to each other is reduced by the introduction of solvent, the tendency for a packing preference based on the structure of the alkyl chain should be greatly reduced.

Information about the orientation of the alkyl chain can be obtained from the relative intensity of the methyl peaks, which reflect the average orientation of the alkyl chain with respect to the surface normal. For example, polarization dependence of the symmetric methyl stretch has been used in the past as a means of determining the average tilt angle of the hydrocarbon chain in similar systems.^{43,48,50,73} However, this determination cannot be made for disordered systems such as those studied here because a molecular axis cannot be defined, due to the existence of gauche defects in the alkyl chains. However, the average orientation of specific C-H bonds can be determined relative to the surface normal. We have previously determined the orientation of the terminal methyl group for a series of anionic and cationic surfactants adsorbed at the D₂O/CCl₄ interface and found that the average orientation of the terminal methyl group is aligned normal to the surface.³⁹ The same result is found here for HS, UDS, and DDS and is consistent with an isotropic distribution of molecules in the interfacial plane.

V. Conclusions

The conformation and orientation of a series of alkane-sulfonates, HS, UDS, and DDS, adsorbed at the D₂O/CCl₄ interface have been examined by SFVS. The surfactants studied all display identical C-H vibrational resonances. The conformation of the surfactant hydrocarbon tail and the orientation of the terminal methyl group were determined by analysis of the sum-frequency spectra. The conformational order of the alkyl chains is seen to be determined by the spatial constraints imposed by neighboring alkyl chains as established by concentration dependence studies. In addition, the chain length was also found to affect the degree of conformational order of the alkyl chain.

The effect of surface concentration on the conformation of the hydrocarbon chain and the orientation of the terminal methyl group were examined in detail. A pronounced symmetric methylene resonance is observed in the vibrational spectra of all the surfactants examined and has been attributed to the relaxation of the local symmetry constraint for the CH₂ vibrations by the introduction of gauche defects. The ratio of the symmetric methyl/methylene intensity (I_{r^+}/I_{d^+}) which is used as a measure of chain conformation, increases with increasing surface coverage. This increase suggests that a reduction in the number of gauche defects occurs when the surface concentration is increased due to confinement of the alkyl chains. The I_{r^+}/I_{d^+} ratio is also seen to correlate very well with the surface concentration obtained from interfacial tension measurements. However, maximum ordering of the surfactants is seen to take place over a very narrow concentration range, well before full monolayer coverage is reached. From the spectral data, HS is found to display the least number of gauche defects relative to UDS and DDS at similar surface concentrations, as would be expected due to its shorter chain length. In addition, no preference for ordering is observed based on the even-odd character of the hydrocarbon chain.

Results from polarization studies indicate that the terminal methyl group is oriented primarily along the surface normal for all concentrations examined. This result is consistent with an isotropic distribution of molecules, as would be expected for species adsorbed at a liquid/liquid interface. Any conclusions regarding the absolute orientation or orientation distribution of the alkyl chains, however, are complicated by the fact that there appears to be a large number of gauche defects in the alkyl chains, evidenced by the strong symmetric methylene resonance in the sum-frequency vibrational spectra.

Acknowledgment. Funding is gratefully acknowledged from the U.S. Department of Energy, Basic Energy Sciences, DE-FG03-96ER45557.

LA980132U

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