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sition but markedly change at the main transition within the very narrow temperature range of a few degrees.¹⁶

In the present DDPC-water system, on the other hand, the role of each group in the respective transitions is not so clear as in the case of the DMPC-water system. However, the comparison of the transition temperatures of DDPC with those of DMPC and the inspection of Figures 2 and 6 make the following points clear. If we consider the fact that the temperature of the transition I of DDPC with the amide group (16 °C) is higher than that of the pretransition of DMPC with the ester group (11 °C) and that the amide II band of DDPC exhibits a distinct peak at the transition I in Figure 6, this transition seems to be triggered by a loosening of the hydrogen-bonding network through the amide groups. It may induce the chain melting (see Figure 2) as well as the structural changes of the head groups as seen in Figure 6.

The temperature of the transition II agrees with that of the main transition of the DMPC-water system. As is also clear from Figure 6, all parts of DDPC are subjected

to the structural changes to the same extent at this transition.

Finally, at the transition III, the structural changes of the phosphate and choline groups mainly occur. Possibly, the hydrogen-bonding network among the amide groups still persists at this transition, because in DMPC, which is free from the amide group, the structural changes of head groups have already finished at lower temperatures.

In conclusion, the introduction of the amide group in DDPC gives rise to different structural aspects of the thermotropic phase transitions from those of DMPC with the ester group. First, for the 44 g % DDPC-56 g % water system, three phase transition take place between 16 and 28 °C. Second, the chain melting takes place in the wide range of temperature, including three transitions, and is completed at 35 °C. Third, the structural changes of the head groups occur at the highest temperature transition III.

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Orientation of Molecular Monolayers at the Liquid-Liquid Interface As Studied by Optical Second Harmonic Generation

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The molecular orientation of surfactants has been determined at air/water, decane/water, and water/carbon tetrachloride interfaces by optical second harmonic generation. The results show that the molecular orientation depends on the nature of the nonaqueous phase.

The study of molecular monolayers at the liquid-liquid interface has attracted attention from researchers in a variety of disciplines.¹ Interface-active monolayers are of interest in studying interfacial mass transfer and micellar structure, and as model membrane structures. Monolayers at the interface between two immiscible liquids have been extensively studied by classical techniques such as surface tension and surface potential measurements. However, there has been a noticeable lack of information at the molecular level at the liquid-liquid interface. A few studies have used total internal reflection excited fluorescence² and resonance Raman scattering³⁻⁵ of dye molecules at the liquid-liquid interface. In this paper we report the use of optical second harmonic generation (SHG) to determine the orientation of monolayers of sodium 1-dodecylphthalene-4-sulfonate (SDNS) (C₁₂H₂₅-C₁₀H₆SO₃Na) at the aqueous/decane and aqueous/carbon tetrachloride interfaces.

Optical techniques possess the obvious advantage of being able to probe interfaces between dense media, but generally they do not exhibit the surface specificity characteristic of the electron spectroscopies. Optical second harmonic generation (SHG), however, is intrinsically surface-specific as it is forbidden in centrosymmetric media but necessarily allowed at a surface or interface.⁶ In addition, it shares the usual advantages of optical probes such as high spatial and temporal resolution.

The surface nonlinear susceptibility $\chi_s^{(2)}$ arising from a monolayer of adsorbates can be written as⁷⁻⁹

$$\chi_{s,ijk}^{(2)} = N_s \langle T_{ijk}^{\lambda\mu\nu} \rangle \alpha_{\lambda\mu\nu}^{(2)} \quad (1)$$

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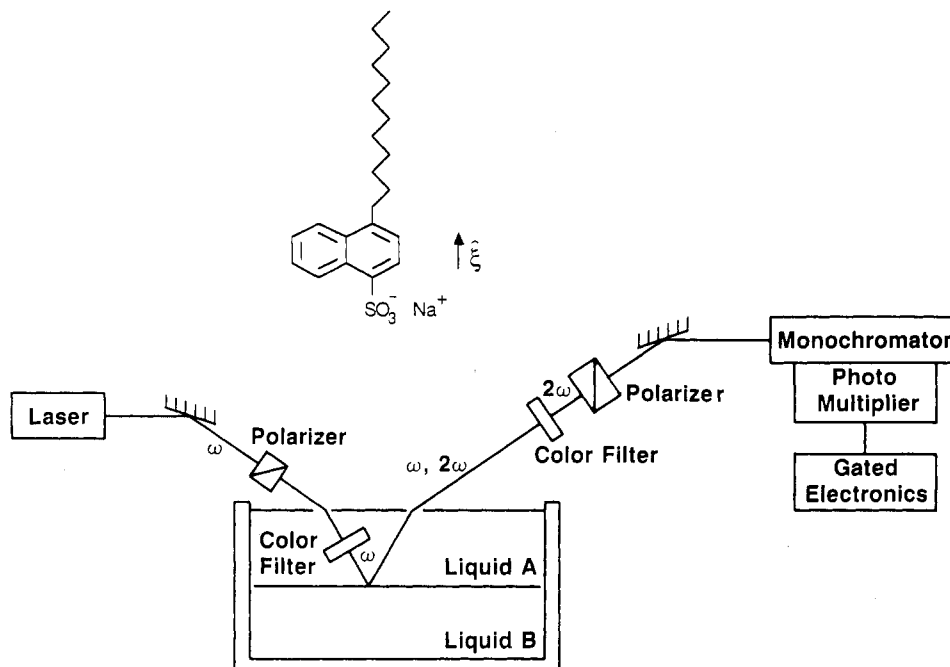


Figure 1. Schematic picture of the experimental apparatus used to observe SHG from monolayers at a liquid/liquid interface and the structure of the SDNS molecule studied.

where N_s is the surface density of molecules, $\tilde{\alpha}^{(2)}$ is the molecular nonlinear polarizability, $\langle T_{ijk}^{\lambda\mu\nu} \rangle$ is the coordinate transformation connecting the laboratory (x,y,z) and molecular (ξ,η,ζ) axes, and the angular brackets $\langle \rangle$ denote an average over the molecular orientations. From the SHG measurements, we can obtain $\chi_{s,ijk}^{(2)}$, but to find the molecular orientation, we need to know $\langle T_{ijk}^{\lambda\mu\nu} \rangle$, which is generally difficult to deduce. The analysis becomes tractable when $\tilde{\alpha}^{(2)}$ is dominated by a single component $\alpha_{\xi\xi\xi}^{(2)}$ along a specific molecular axis $\hat{\xi}$, which is randomly oriented with respect to the surface normal. In this case the nonvanishing elements of $\tilde{\chi}_s^{(2)}$ are⁷⁻⁹

$$\chi_{s,zzz}^{(2)} = N_s \langle \cos^3 \theta \rangle \alpha_{\xi\xi\xi}^{(2)}$$

$$\chi_{s,zii}^{(2)} = \chi_{s,izi}^{(2)} = \chi_{s,iiz}^{(2)} = \chi_{s,iii}^{(2)} = \frac{1}{2} N_s \langle \sin^2 \theta \cos \theta \rangle \alpha_{\xi\xi\xi}^{(2)} \quad (2)$$

$i = x, y$

where θ is the polar angle between the $\hat{\xi}$ axis and the surface normal \hat{z} . A measurement of the ratio between any two linear combinations of $\chi_{zzz}^{(2)}$ and $\chi_{zzx}^{(2)}$ can yield a weighted average of θ .

For the SHG experiments we used the frequency-doubled output of a Q-switched Nd:YAG laser at 532 nm as the pump beam with an energy of 15–20 mJ/pulse in a cross sectional area of 0.4 cm². The SH signal from the interface was sufficiently weak to necessitate the use of gated photon counting techniques. There was a nonnegligible signal from the bare interface proportional to $|\tilde{\chi}_{\perp}^{(2)}|^2$ while the interface with surfactant present gave a signal proportional to $|\tilde{\chi}_{\perp}^{(2)} + \tilde{\chi}_s^{(2)}|^2$. The phase difference between $\tilde{\chi}_{\perp}^{(2)}$ and $\tilde{\chi}_s^{(2)}$ was found to be negligible by a quartz interference technique.⁸

Figure 1 shows a schematic picture of the experimental apparatus and the structure of the molecule. The different $\tilde{\chi}_s^{(2)}$ components could be selectively measured by appropriate combinations of input and output polarizers. Possible polarization rotations at the air-liquid interfaces

must be taken into account. A color filter was placed in the input beam inside the liquid above the liquid-liquid interface in order to block the SH signal generated at the air-liquid interface. Another color filter was used in the output beam to separate the SH signal from the fundamental after its emergence from the liquid.

The SDNA surfactant was introduced by replacing by pipette approximately 10 mL of the aqueous phase (2% NaCl) with a saturated 2% NaCl solution of SDNS. The total aqueous concentration of SDNS was made to be approximately 10⁻⁵ M, which by our independently measured Langmuir adsorption isotherms was shown to lead to a condensed monolayer at the interface. Measurement of the surface pressure π versus surface area per molecule A at the air-water interface shows that the SDNS monolayer only shows an appreciable surface pressure close to a full monolayer and that there the area per molecule hardly changes ($A \approx 45 \text{ \AA}^2$, see ref 8). Therefore, although we have not measured the π - A diagrams at the liquid-liquid interface, we assume that in all cases $A \approx 45 \text{ \AA}^2$ for a fully condensed monolayer and use the surface pressure as an indication that this latter state has been reached.

Solvent purity was determined to be critical in these measurements. Both decane and carbon tetrachloride were from Burdick & Jackson Lab., Inc., spectroscopic grade with UV cutoffs at 193 and 261 nm, respectively. A lower grade solvent gave rise to a broad two-photon excited luminescence background, which even with extensive spatial filtering could interfere with the measurement of the SHG.

It has been shown that the nonlinear polarizability tensor of SDNS is dominated by $\alpha_{\xi\xi\xi}^{(2)}$ arising from the naphthalene chromophore.⁹ Given the structure of the molecule (see Figure 1), the nonlinearity is expected to originate mostly from the asymmetry induced in the π -electron system of the naphthalene by the presence of the SO₃ group on one side and the hydrocarbon chain on the other side. Based on these considerations, we assign the molecular ξ -axis with the naphthalene chromophore in the way as indicated in Figure 1. The angle θ deduced from our SHG experiments, assuming a δ -function orientational distribution, then will correspond to the orientation of this naphthalene portion with respect to the surface normal.

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Table I. Values of the Average Polar Angle from the Surface Normal, θ , for a SDNS Monolayer at Several Interfaces^a

interface	θ	$\epsilon(0)$	σ_B , dyn/cm (without monolayer)	σ_s , dyn/cm (with monolayer)
air/H ₂ O	13	1.0	72	21.5
C ₁₀ H ₂₂ /H ₂ O	21	1.991	50.1	12.3
H ₂ O/CCl ₄	38	2.238	45	7.5

^aThe aqueous phase in all cases is 2 wt % NaCl. σ_B = interfacial tension; σ_s = interfacial tension in presence of SDNS monolayer; $\epsilon(0)$ is the low-frequency dielectric constant of the nonaqueous phase.

(In the following, whenever we mention the experimentally obtained molecular orientation, we are referring to this naphthalene portion.)

Whereas the polar SO₃ group will be in contact with the aqueous phase, the hydrocarbon chains are expected to be more or less normal to the interface. However, given the area per molecule ($A \sim 45 \text{ \AA}^2$), they have a considerable degree of freedom and can be quite disordered.

Table I lists the value of θ obtained for fully condensed monolayers at several interfaces. The results of $\theta = 13^\circ$, 21° , and 38° for air/water,¹⁰ decane/water, and water/carbon tetrachloride, respectively, show that the orientation of SDNS molecules strongly depends on the nature of the materials forming the interface. The orientation of a surfactant molecule is expected to depend on the ratio between the size of the hydrophilic and hydrophobic part (HLB),¹¹ the molecule-molecule interaction, and the molecule-substrate interaction. The HLB of a molecule is mainly determined by its chemical structure.¹²

Recent theoretical studies show that a decrease in the tail-tail interaction will lead to an increase in the molecular tilt angle.¹¹ The tail-tail interaction could be reduced by increasing the low-frequency dielectric constant $\epsilon(0)$ of the nonaqueous phase (see Table I). The tail-tail interaction could also be affected by the interaction between the hydrophobic parts and the nonaqueous phase. Decane easily mixes with the hydrocarbon tails but not with naphthalene. Because carbon tetrachloride is known to interact with naphthalene,¹³ this may affect the interaction between the hydrophobic parts even more. If these interactions of the hydrophobic tails with the nonaqueous phase lead to an effective decrease in the tail-tail interaction, this could qualitatively explain the observed variation in the tilt angle

of SDNS at air/water, decane/water, and water/carbon tetrachloride interfaces.

Molecular dynamics simulations of the structure of monolayers show that the molecules tend to tilt more if the interface is less sharp.¹⁴ The root mean square of the interfacial thickness is inversely proportional to the interfacial tension. It is interesting to note that our observed increase in θ is indeed parallel with a decrease in the interfacial tension σ_B (see Table I).

As has been stated before, our results for θ only refer to the naphthalene portion of the SDNS molecule. A more complete picture could be given if one would also know the structure of the hydrocarbon tails. Due to their negligible contribution of the nonlinearity,⁹ SHG measurements will not be able to address this part of the problem. However, by using another interface-specific $\tilde{\chi}^{(2)}$ process like infrared-visible sum-frequency generation, one could obtain the orientation of the hydrocarbon chains by studying the vibrational spectrum (the C-H modes) of the monolayer.¹⁵

In conclusion, we have demonstrated that the technique of optical second harmonic generation can be used to determine the molecular orientation of monolayers at a liquid-liquid interface. In the case of sodium 1-dodecyl-naphthalene-4-sulfonate at a water/nonaqueous interface, we find that the molecular orientation of surfactants depends strongly on the nature of the nonaqueous phase. Such information is very important for the understanding of the formation of microemulsions¹⁶ and other surfactant-related liquids such as foams. More detailed studies are needed to establish more concrete correlations between the molecular orientation and the zero-frequency dielectric constant, interfacial tension, and solubility. Future investigations will also have to include molecular orientational changes due to changing surface molecular density, aqueous electrolyte concentration, and monolayer phase transitions.^{17,18} By exploiting the intrinsically fast time scale of pulsed lasers, SHG can also be utilized to follow kinetics at a liquid-liquid interface.

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