Orientation of surfactant molecules at a liquid-air interface measured by optical second-harmonic generation

Th. Rasing and Y. R. Shen

Department of Physics, University of California, Berkeley, California 94720 and
Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720

Mahn Won Kim, P. Valint, Jr., and J. Bock

Exxon Research and Engineering Company, Annandale, New Jersey 08801
(Received 4 October 1984)

The average molecular orientation of a monolayer of sodium-dodecylnapthalene-sulfonate on a water-air interface has been determined by use of optical second-harmonic generation. The molecular orientation is shown to vary smoothly with increasing surface density of the molecules.

Insoluble molecular monolayers at gas-liquid or liquid-liquid interfaces are interesting from a fundamental as well as a practical point of view. They are rather ideal for studies of the rich world of two-dimensional phase transitions[1,2] and provide an insight to the understanding of surfactants, wetting, microemulsions, and membrane structures.[3] In the interpretation of the observed properties of these systems, various assumptions about the molecular orientation are often made,[1] but so far, few clear experimental data are available.

In this paper we present the first measurement of the molecular orientation of a monolayer of surfactant molecules at a water-air interface using the newly developed optical second-harmonic-generation (SHG) technique.[4] The molecules under investigation are sodium-dodecylnaph-thalene-sulfonate (SDNS) [$CH_3(CH_2)_{11}-C_{10}H_6-SO_3Na$, where $C_{10}H_6$ is a double benzene structure]. We found, along with the measurement of surface pressure versus surface molecular area indicating the absence of a transition between an expanded and a condensed liquid phase, the orientation of these surfactant molecules changing continuously as a function of the surface pressure, and approaching a limiting inclination angle $\sim 30°$ for a saturated monolayer.

That optical SHG is an effective surface probe has been demonstrated recently in a number of cases.[4-7] It is based on the idea that SHG is forbidden in centrosymmetric media but allowed at the interfaces where the inversion symmetry is necessarily broken. The surface nonlinear susceptibility $\overleftrightarrow{\chi}_S^{(2)}$ which is responsible for the SHG at an interface generally reflects the properties of the surface layer. If $\overleftrightarrow{\chi}_S^{(2)}$ arises mainly from a monolayer of molecular adsorbates, and takes the form

$$\overleftrightarrow{\chi}_S^{(2)} = N_S \langle \overleftrightarrow{\alpha}^{(2)} \rangle , \qquad (1)$$

where N_S is the surface density of the molecules, and $\langle \overleftrightarrow{\alpha}^{(2)} \rangle$ is the nonlinear polarizability averaged over the molecular orientational distribution, then a measurement of $\overleftrightarrow{\chi}_S^{(2)}$ should enable us to obtain information about the orientation of the adsorbates. This is particularly true for rodlike molecules whose $\overleftrightarrow{\alpha}^{(2)}$ is dominated by a single element $\alpha_{\xi\xi\xi}^{(2)}$ along the molecular axis $\hat{\xi}$. For example, when the orientational distribution of the molecules in the azimuthal plane is random, the nonvanishing components of $\overleftrightarrow{\chi}_S^{(2)}$

can be written as[5]

$$\chi_{S,\perp\perp\perp}^{(2)} = N_S \langle \cos^3\theta \rangle \alpha_{\xi\xi\xi}^{(2)} ,$$

$$\chi_{S,\perp\|\|}^{(2)} = \chi_{S,\|\perp\|}^{(2)} = \chi_{S,\|\|\perp}^{(2)} = \frac{1}{2} N_s \langle \cos\theta \sin^2\theta \rangle \alpha_{\xi\xi\xi}^{(2)} , \qquad (2)$$

where θ is the polar angle between the molecular axis and the surface normal, and the subindices $\perp$ and $\|$ refer to directions perpendicular and parallel to the surface, respectively. We see from Eq. (2) that a measurement of the ratio of any two linear combinations of $\chi_{S,\perp\perp\perp}^{(2)}$ and $\chi_{S,\perp\|\|}^{(2)}$ can yield a weighted average of θ. The average value or the most probable value of θ can then be deduced by assuming a certain orientational distribution function.

We have applied this technique to the study of the orientation of a monolayer of SDNS molecules floating on a water surface. This surfactant consists of a hydrophilic polar functional group (SO_3Na) and a hydrophobic hydrocarbon chain [$CH_3(CH_2)_{11}-C_{10}H_6$]. The latter prevents the molecules from dissolving into the water. This is further helped by adding 2% NaCl to the water.

The molecules were first dissolved in methanol and then spread on the water surface by a μl pipette. Evaporation of the methanol left the SDNS molecules uniformly distributed on the surface. The water trough was made out of glass and the edges of it were coated with paraffine. The thermal agitation of the SDNS molecules on the water surface produces a two-dimensional surface pressure π, which is equal to the reduction of the surface tension of the water. The latter was determined by measuring the force acting on a thin Pt float which was hung half in the water on a balance.[8] Figure 1 shows the measured π as a function of the surface area per molecule (A) for SDNS on water containing 2% NaCl. The π-A diagram does not exhibit any discontinuous phase transition usually observed in this pressure range for this type of molecular monolayer.[1]

For the SHG measurement, we used the frequency doubled output of a Q-switched Nd^{3+}:YAG laser at 532 nm with a ~ 7-nsec pulse duration as the pump beam. Using a pulse energy ~ 20 mJ incident on the SDNS covered water surface with a beam cross section ~ 0.6 cm^2, we found a SH signal ~ 0.1 photon/pulse at $\pi \sim 5$ mNm^{-1}. Each data point was obtained by averaging over $3000-6000$ pulses. There was also a detectable SH signal from the water (~ 0.025 photon/pulse), which constituted the background.
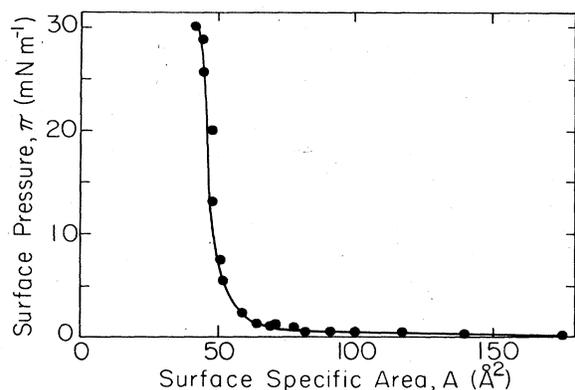
FIG. 1. Surface pressure π of SDNS as a function of the area per molecule A on a water surface containing 2% NaCl.

FIG. 2. Tilt angle θ between the molecular axis and the surface normal as a function of the surface pressure π for SDNS on water containing 2% NaCl.

The signal from the surfactant-covered surface was proportional to $|\vec{\chi}_S^{(2)}+\vec{\chi}_W^{(2)}|^2$, while that from a bare water surface was proportional to $|\vec{\chi}_W^{(2)}|^2$, where $\vec{\chi}_W^{(2)}$ is the effective surface nonlinear susceptibility of the water. Both could be measured separately. However, in order to deduce the value of $\vec{\chi}_S^{(2)}$, we need to know the phase difference between $\vec{\chi}_S^{(2)}$ and $\vec{\chi}_W^{(2)}$. This was measured by interfering both signals with that from a quartz plate excited by the same pump beam.[5] We found that the phase difference $\phi_S - \phi_W$ was $\sim 10°$. It was positive and different from zero because the second-harmonic frequency 2ω was on the shoulder of the absorption band at 290 nm associated with the phenyl ring of SDNS. Since both ω and 2ω were far away from resonances in water, we expect $\phi_W = 0$. Thus, from the measured $|\vec{\chi}_S^{(2)}+\vec{\chi}_W^{(2)}|^2$ and $|\vec{\chi}_W^{(2)}|^2$, the value of $\vec{\chi}_S^{(2)}$ could be obtained. If the distribution of SDNS was random in the azimuthal plane, then a weighted average of θ could be deduced from Eq. (2). The azimuthal isotropy was actually confirmed by noting that the observed SH output was independent of the sample rotation about the surface normal.

In analyzing the data, we assumed a δ function for the orientational distribution in θ. This means that the orientation of SDNS would be specified by a single value of θ. Figure 2 then gives the result on how θ of SDNS on water varies with the surface pressure π. It appears that at high pressures towards a saturated monolayer, the molecules tilted at $\sim 30°$ from the surface normal, while at low pressures, they inclined more towards the surface plane.

The result supports the commonly accepted picture that compressing molecules on a liquid surface would tend to make them stand up. The data show that the orientation of SDNS on water varied smoothly with π down to 0.1 mNm^{-1} without exhibiting any discontinuity. Below $\pi = 0.1$ mNm^{-1}, the signal-to-noise ratio was too small to be meaningful. Thus, we conclude that in the present case there is no observable orientational phase transition in this range of surface pressures. This agrees with the π-A measurement shown in Fig. 1, which also does not display any phase-transitional discontinuity. Usually, in other surfactant monolayer systems, the π-A curve in this pressure range does exhibit a discontinuity attributed to an orientational phase transition between an expanded and a condensed
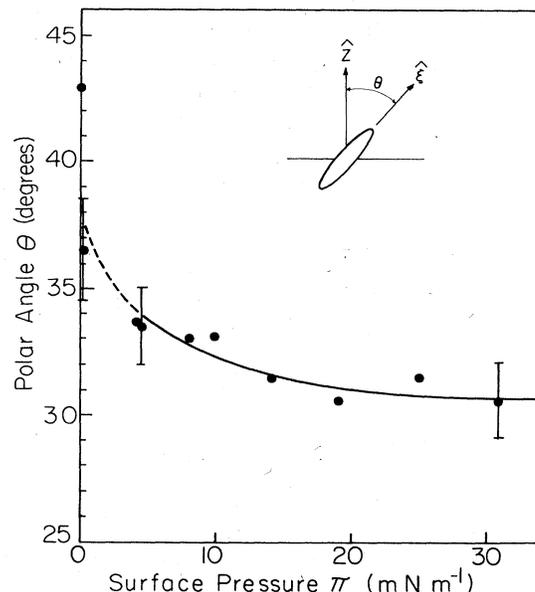
liquid phase. SDNS is obviously an exception. That SDNS tilts at $\sim 30°$ from the surface normal in the high-pressure limit is also different from the usual assumption that they should align normal to the surface. This is presumably the result of the steric effect of the molecular structure.

We should note that the results here do not depend very critically on the assumption of a δ-function orientational distribution. If, instead, we assume a Lorentzian distribution with a spread of 10° FWHM (full width at half maximum), then corresponding to $\theta = 30°$ in the δ-function case, we would find the center of the Lorentzian distribution at $\theta \sim 27°$.

In the above analysis, by assuming the validity of Eq. (1), we have neglected interactions between the molecules and between the molecules and the substrate. This may seem to be contrary to the fact that the surface pressure exists because of the intermolecular interaction and adsorption occurs only through the molecule-substrate interaction. However, it is well known that in molecular fluid, the molecules more or less preserve their individual electronic properties. Then, if the local-field correction is negligible, Eq. (1) should be a good approximation. The local-field correction arising from the induced dipole-induced dipole interaction is indeed negligible if the molecules are big. For a system of molecules with linear polarizabilities $\alpha_\parallel^{(1)} = \alpha_\perp^{(1)} = 10$ Å, it follows from Ref. 9 that at $N_S = 2.2 \times 10^{14}/\text{cm}^2$ ($\pi \sim 20$ mN/cm), the average local-field correction factors $L_\parallel$ and $L_\perp$ are 1.03 and 0.95, respectively. This shows that the local-field effects can actually be neglected in the present case. As a further check, we have also found that $|\chi_{S,\perp\perp}^{(2)}|^2/\langle\cos^3\theta\rangle^2$ and $|\chi_{S,\perp\parallel\parallel}^{(2)}|^2/\langle\sin^2\theta\cos\theta\rangle^2$ obtained from measurements are closely proportional to N_S^2, indicating that Eq. (1) is valid.

In conclusion, we have shown for the first time how opti-

cal second-harmonic generation can be used to measure the average molecular orientation of a molecular monolayer at a water-air interface. The orientation of the SDNS molecules appears to vary continuously and tilt more towards the surface normal with increasing surface pressure. It shows no discontinuity in the variation and approaches a limiting inclination angle $\sim 30°$.

[1]For a review, see, e.g., G. M. Bell, L. L. Coombs, and L. J. Dunne, Chem. Rev. **81**, 15 (1981), and references therein.

[2]D. A. Lavis, B. W. Southern, and G. M. Bell, J. Phys. C **15**, 1077 (1982).

[3]*Micellization, Solubilization and Microemulsions,* edited by K. L. Mittal (Plenum, New York, 1977); J. S. Huang and M. W. Kim, Phys. Rev. Lett. **47**, 1463 (1981).

[4]C. K. Chen, T. F. Heinz, D. Ricard, and Y. R. Shen, Phys. Rev. Lett. **46**, 15 (1981).

[5]T. F. Heinz, H. W. K. Tom, and Y. R. Shen, Phys. Rev. A **28**, 1883 (1983).

[6]H. W. K. Tom, T. F. Heinz, and Y. R. Shen, Phys. Rev. Lett. **51**, 1983 (1983).

[7]H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, T. F. Heinz, G. A. Somorjai, and Y. R. Shen, Phys. Rev. Lett. **52**, 348 (1984).

[8]G. F. Graines, Jr., *Insoluble Monolayers at Liquid-Gas Interfaces* (Wiley, New York, 1966).

[9]P. Ye and Y. R. Shen, Phys. Rev. B **28**, 4288 (1983).