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MEASUREMENT OF ORIENTATION OF SURFACTANT MOLECULES AT A LIQUID-AIR INTERFACE BY OPTICAL SECOND-HARMONIC GENERATION

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ABSTRACT: 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 provide an insight to the understanding of surfactants, wetting, microemulsions, and membrane structures.[1] In the interpretation of the observed properties of these systems, various assumptions about the molecular orientations are often made,[2] but so far, few clear experimental data are available.

In this paper we present a 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.[3] The molecules under investigation are sodium-dodecylnaphthalene-sulfonate (SDNS) [$CH_3(CH_2)_{11}$-$C_{10}H_6$-SO_3Na, where $C_{10}H_6$ is a double benzene structure]. Figure 1 shows the measured surface pressure 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.[2]

That optical SHG is an effective surface probe has been demonstrated recently in a number of cases.[3-6] 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

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

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[4]

$$\begin{aligned} \chi_{S,\perp\perp\perp}^{(2)} &= N_S\langle\cos^3\theta\rangle\alpha_{\xi\xi\xi}^{(2)}, \\ \chi_{S,\perp\parallel\parallel}^{(2)} &= \chi_{S,\parallel\perp\parallel}^{(2)} = \chi_{S,\parallel\parallel\perp}^{(2)} = \frac{1}{2}N_S\langle\cos\theta\sin^2\theta\rangle\alpha_{\xi\xi\xi}^{(2)}, \end{aligned} \tag{2}$$

where θ is the polar angle between the molecular axis and the surface normal, and the subindices $\perp$ and $\parallel$ 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 $\chi_{S,\perp\parallel\parallel}^{(2)}$ 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.

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 ~ 30° from the surface normal, while at low pressures, they inclined more towards the surface plane (see also Ref. 7).

In conclusion, we have shown for the first time how optical 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 ~ 30°.

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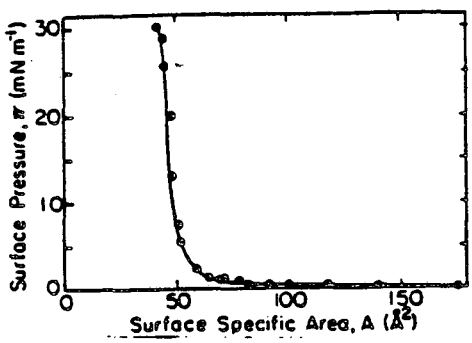

Fig. 1 Surface pressure π of SDNS as a function of the area per molecule A on a water surface contain- 2% NaCℓ.

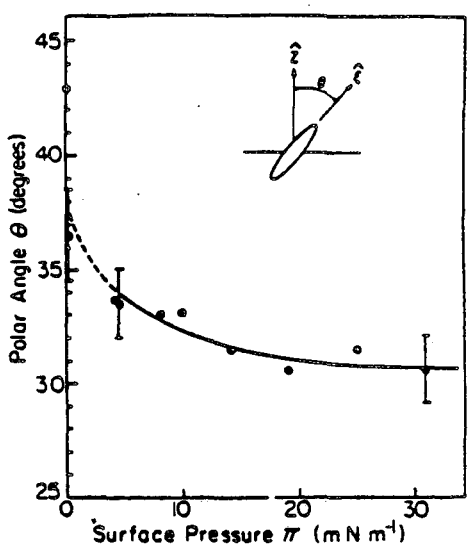

Fig. 2 Tilt angle θ between the molecular axis and the surface normal as a function of the surface pressure π for SDNS on water containing 2% NaCℓ.

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