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STUDIES OF MOLECULAR MONOLAYERS AT AIR-LIQUID INTERFACES BY SECOND HARMONIC GENERATION: QUESTION OF ORIENTATIONAL PHASE TRANSITION

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Studies of Molecular Monolayers at Air-Liquid Interfaces by Seccnd Harmonic Generation: Question of Orientational Phase Transition

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Insoluble molecular monolayers at gas-liquid interfaces provide an insight to the understanding of surfactants, wetting, micromulsions and membrane structures and offer a possibility to study the rich world of 2-dimensional phase transitions. In the interpretation of the observed properties of these systems various assumptions about the molecular orientation are often made, but so far few clear experimental data exist [1]. In this paper we will show how optical second harmonic generation (SHG) can be used to measure the molecular orientation of monolayers of surfactant molecules at water-air interfaces. By simultaneously measuring the surface pressure versus surface molecular area we can show for the first time that the observed liquid condensed-liquid expanded transition is an orientational phase transition.

The SHG radiation from a medium arises from the induced second-order polarization

$$P(2\omega) = \chi^{(2)}(2\omega):E(\omega)E(\omega) \tag{1}$$

in the medium. When the latter has inversion symmetry $\chi^{(2)}$ vanishes in the electric-dipole approximation. This makes SHG an effective surface probe at any interface between two centrosymmetric media, because there the inversion symmetry is necessarily broken. Apart from the intrinsic high spectral and time resolution, optical SHG is a unique surface probe because of its versatility: it can be used at solid-vacuum, solid-solid, solid-air, solid-liquid and liquid-air interfaces, as has been shown recently [2-6].

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

$$\chi_s^{(2)} = N_s\langle\alpha^{(2)}\rangle \tag{2}$$

where N_s is the surface density of the molecules and $\langle\alpha^{(2)}\rangle$ is the nonlinear polarizability averaged over the molecular orientational distribution. If $\alpha^{(2)}$ is dominated by a single component $\alpha_{\xi\xi\xi}$ along the molecular axis ξ and the latter is randomly distributed in the azimuthal plane, the nonvanishing components of $\chi_s^{(2)}$ can be written as:[3]

$$\chi^{(2)}_{s,\perp\perp\perp} = N_s\langle\cos^3\theta\rangle\alpha_{\xi\xi\xi}$$

$$\chi_{s,\parallel\perp\parallel} = \chi_{s,\perp\parallel\parallel} = 1/2(N_s)\langle\sin^2\theta\ \cos\theta\rangle\alpha_{\xi\xi\xi} \tag{3}$$

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. From (3) it follows that a measurement of the ratio of any two linear combinations of $\chi_{s,\perp\perp\perp}$ and $\chi_{s,\parallel\perp\parallel}$ can yield a weighted average of θ.

The monolayers were prepared by spreading a solution on a thoroughly cleaned water surface. The trough was made out of glass with the edges coated with paraffin. The density of molecules was controlled by a teflon barrier and the surface tension was measured by a Wilhelmy plate [7]. For the SHG measurements we used the frequency doubled output of a Q-switched Nd^{3+}:YAG laser at 532 nm with a 7 nsec pulsewidth as the pump beam.

Due to higher order contributions, there was a non-negligible signal arising from the bare water proportional to $|\chi_w^{(2)}|^2$, while the signal from the surfactant covered surface was proportional to $|\chi_s^{(2)} + \chi_w^{(2)}|^2$. Both were measured separately, so that $\chi_s^{(2)}$ could be deduced.

Using a pump energy of ~ 50 mJ/cm^2/pulse, we found a SHG signal of 2-3 photon/pulse for the bare water and typically 0.1-0.5 photon/pulse for the adsorbates.

As a first example, we have applied this technique to a monolayer of sodium-dodecylnaphthalene-sulfonate (SDNS) floating on a water surface [6]. Figure 1 shows the measured surface pressure π as a function of the surface area per molecule (A). The π-A diagram does not exhibit any discontinuous phase transition (the rapid increase in π close to 50 Å^2 indicates the formation of a full close packed monolayer). Figure 2 gives the result of θ as a function of π, showing a smoothly decreasing θ with a limiting inclination angle of ~ 30°

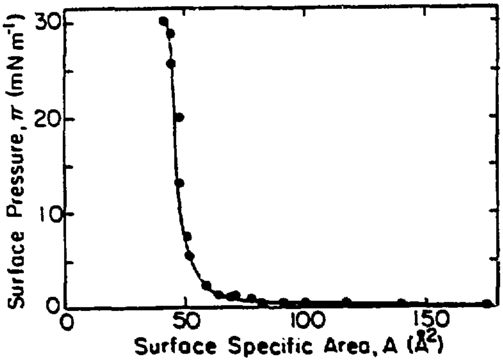

Fig. 1. Surface pressure π of SDNS as a function of the area per molecule A on a water surface

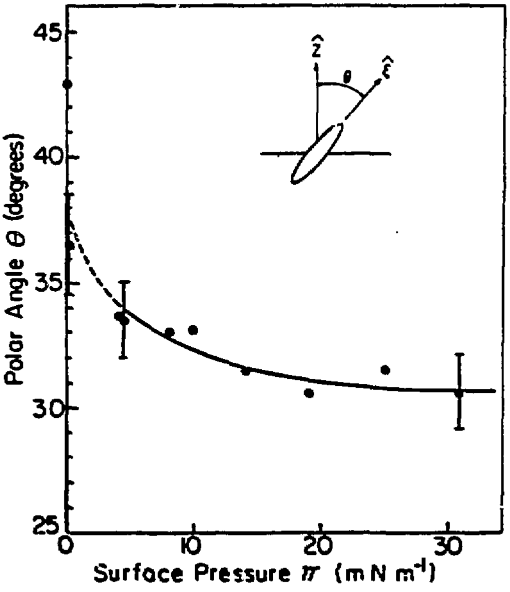

Fig. 2. Tilt angle θ between the molecular axis and the surface normal as a function of the surface pressure π for SDNS on water

at a full monolayer. The nonlinear polarizability of SDNS is dominated by the naphthalene part which is tilted at ~ 30° from the alkyl chain. The final value of θ = 30° then supports the commonly accepted, but never verified, picture that compressing molecules on a liquid surface would force them to stand up.

As a second example, we have studied pentadecanoic acid (PDA) on water. Figure 3 shows the π-A diagram of PDA at various temperatures. The sharp kinks in the middle of the π-A diagrams indicate the transition between the so-called liquid-expanded (LE) and liquid-condensed (LC) phases, which appears to be strongly temperature dependent. Though known for a long time, the nature of this liquid-liquid transition is still controversial and little understood [1].

It is suspected that the transition is governed by the molecular orientation. Figure 4 shows the results of our orientational measurements for PDA at 25°C. In the LE phase, θ rapidly increases with increasing density until the LE-LC transition is reached, where after it changes more slowly and linearly with N_s.

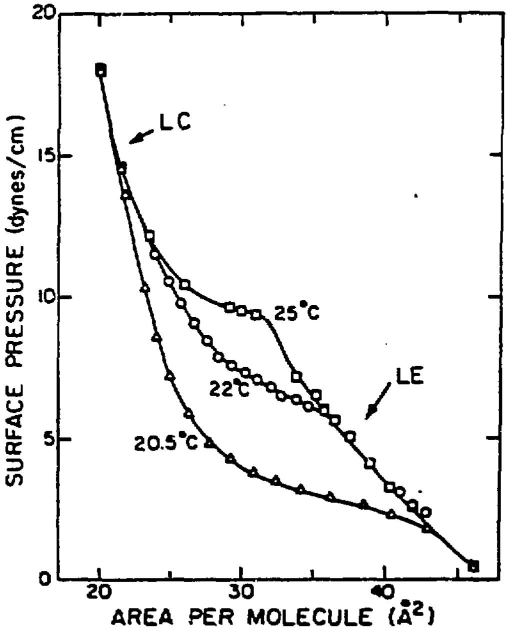

Fig. 3. π-A diagram for PDA at various temperatures. The sharp kink in each curve signals the onset of the LE-LC transition

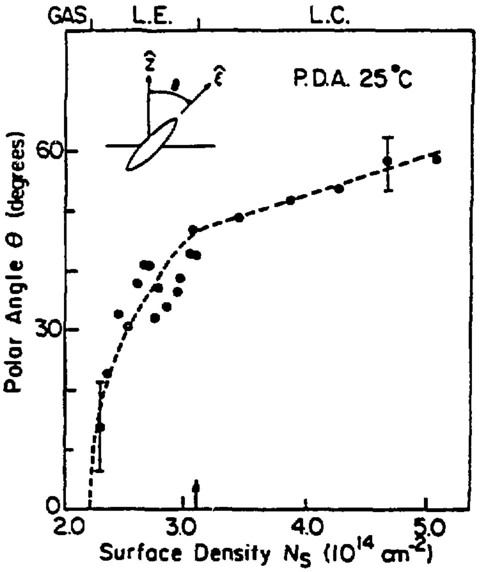

Fig. 4. Tilt angle θ between the molecular axis and the surface normal as a function of the surface density for PDA on water at 25°C

In order to relate θ to the molecular orientation we must determine the dominant SHG contributor on the molecule. We found that the nonlinear polarizability of PDA is dominated by the C-OH bond. Then Fig. 4 shows the C-OH orientation as a function of the molecular density. Physically, we expect that this polar bond would like to stick normally into the water, and hence the molecules would tilt away from the surface normal. Indeed, when we extrapolate the experimental results to lower densities, we find θ approaching 0° at $N_s = 2.2 \times 10^{14}$ cm^{-2} = gas-liquid (LE) transition point. In the LE phase, with increasing N_s, the steric interaction of the hydrocarbon chains of neighboring molecules tends to align the molecules towards, and consequently forces the C-OH orientation away from, the surface normal. At $N_s = 3.1 \times 10^{14}$ cm^{-2} a phase transition to an oriented liquid occurs.

By measuring the orientation just below the LE-LC transition (in the LE phase) we found $\theta = 45° \pm 3°$ for all temperatures, though the transition point itself is very temperature-dependent (see Fig. 3). This supports the observation that the LE-LC transition is indeed an orientational phase transition.

In conclusion, we have shown how optical SHG can be used as a very effective and versatile surface probe. Using this technique we have been able for the first time to follow the molecular orientation of monolayers of molecules on a water-air interface as a function of their surface density and have shown that the observed LE-LC transition is an orientational phase transition.

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