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Th. Rasing, T. Stehlin, Y.R. Shen, M.W. Kim, and P. Valint, Jr.

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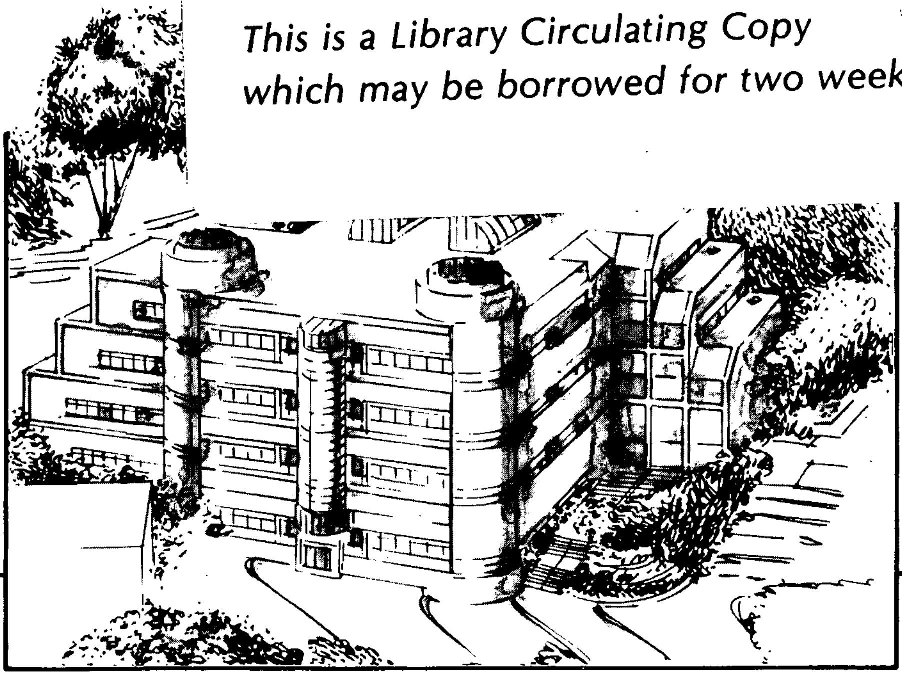

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Submitted to Journal of Chemical Physics

ADSORPTION KINETICS OF SURFACTANT MOLECULES AT A LIQUID-AIR INTERFACE

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ABSTRACT

The adsorption of the surfactant sodium-dodecyl naphthalenesulfonate from the bulk to the water-air interface was studied by optical second harmonic generation. An initial rapid Langmuir type of adsorption to about 80% of a monolayer is observed, followed by a much slower adsorption until a full monolayer is formed.

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Surface active molecules are important for lubrication, friction, wetting, evaporation control, detergency, micellar structure, Langmuir-Blodgett films, and as model membranes. The combination of a hydrophilic part, which prevents evaporation, and a hydrophobic part that strongly reduces the solubility in the water subphase causes these surfactants to form stable monolayers at the water-air interface. For many practical applications, one uses slightly soluble surfactants where the solubility is determined by the relative contributions of the hydrophilic and hydrophobic parts. In those situations it is of interest to determine the kinetics of the monolayer formation from the bulk and the final composition of the surface layer. Traditionally, one uses surface tension and calorimetric measurements to study this. However, it is difficult to determine the surface concentration from these methods.[1]

We have recently shown how the newly developed technique of optical second harmonic generation (SHG) can be exploited to study molecular monolayers at liquid-air,[2] liquid-liquid,[3] and various other interfaces.[4] In this paper we show that we also can use SHG in combination with surface tension measurements to obtain in-situ both the adsorption kinetics and the final composition of a surfactant system. The molecules under investigation are sodium-dodecylnaphthalene-sulfonate [SDNS; $CH_3(CH_2)_{11}$-$C_{10}H_6$-SO_3Na]. Using a 2% NaCℓ water solution as the subphase, we find that after a fast initial adsorption to approximately 80% of a monolayer, the adsorption of SDNS follows Langmuir kinetics to a final coverage of $\theta = 1$.

The effectiveness of SHG as a surface probe stems from the fact that in the electric dipole approximation SHG is forbidden in centrosymmetric media but necessarily allowed at a symmetry breaking interface or surface.[5] As an optical probe it has the advantage of a high spectral and time resolution and of being applicable to any interface accessible by light.

Second harmonic generation arises from the induced nonlinear polarization $\vec{P}(2\omega)$ by

$$\vec{P}(2\omega) = \overleftrightarrow{\chi}^{(2)}\vec{E}(\omega)\vec{E}(\omega) \quad , \tag{1}$$

where $\overleftrightarrow{\chi}^{(2)}$ is a second order nonlinear susceptibility and $\vec{E}(\omega)$ the incident laser field. The surface nonlinear susceptibility $\overleftrightarrow{\chi}_s$ which is responsible for the SHG from an interface can be written as

$$\overleftrightarrow{\chi}_s^{(2)} = \overleftrightarrow{\chi}_w^{(2)} + \overleftrightarrow{\chi}_m^{(2)} \quad , \tag{2}$$

where $\overleftrightarrow{\chi}_w^{(2)}$ and $\overleftrightarrow{\chi}_m^{(2)}$ are the susceptibilities of the substrate (here water) and the adsorbate monolayer, respectively, the latter including contribution from adsorbate-substrate interaction. Although zero under the electric dipole approximation, a weak quadrupole effect causes $\overleftrightarrow{\chi}_w^{(2)}$ to be non-zero. For adsorbates of moderate nonlinearity the SHG signal from an adsorbate covered surface far exceeds that of the bare surface, and in those cases we may approximate $\overleftrightarrow{\chi}_s^{(2)} = \overleftrightarrow{\chi}_m^{(2)}$. When $\overleftrightarrow{\chi}_m^{(2)}$ is small, the substrate background cannot be neglected and in order to subtract it, one has to know the phase difference between $\overleftrightarrow{\chi}_s^{(2)}$ and $\overleftrightarrow{\chi}_m^{(2)}$. This is obtained by interference of both the bare and covered substrate signals with that from a quartz place excited by the same pump beam.

For a surface density of adsorbates N_s and neglecting local field corrections, $\overleftrightarrow{\chi}_m^{(2)}$ can be written as

$$\overleftrightarrow{\chi}_m^{(2)} = N_s \langle \overleftrightarrow{\alpha}^{(2)} \rangle \ , \qquad (3)$$

where $\overleftrightarrow{\alpha}^{(2)}$ is the molecular nonlinear polarizability and the angular brackets < > denote an average over all molecular orientations.

We have shown in an earlier publication that the molecular orientation of SDNS on a water surface is only weakly dependent on the surface concentration.[2] Therefore, if N_s is varied, the SH signal should be directly proportional to N_s^2. Thus, for the study of adsorption dynamics of SDNS on water, we can use SHG to monitor the change in surface density as a function of time.

A saturated solution of SDNS in water was made from 3 mg SDNS in one liter of distilled water which was heated to 70°C when all SDNS dissolved. After adding 2% NaCℓ and cooling down, this mixture became slightly cloudy because of precipitation, insuring that a saturated solution was obtained. A Langmuir trough was used to contain the solution. It was made out of glass with the edges wrapped with teflon tape. The surface tension was measured by a Wilhelmy plate.[6]

For the SHG measurements we used the frequency doubled output of a Q-switched Nd:YAG laser at 532 nm as the pump beam. Figure 1 shows a schematic picture of the experiment and the structure of SDNS. With a pump energy of about 5 mJ per 10 nsec pulse focused to .03 cm^2 we observed a SH signal of about .6 photons per pulse from the bare water surface and about 4 photons per pulse from the surface covered with a full monolayer of SDNS at $N_s = 2.2 \times 10^{14}\ cm^{-2}$ and a surface pressure $\pi = 31$ dynes/cm. As we shall see, a full monolayer of SDNS on water was obtained in equilibrium with the saturated solution of SDNS. This was calibrated against the full monolayer of SDNS prepared by spreading the molecules on water in the usual way.

The measurement of SDNS adsorption kinetics (SDNS molecules emerging from water) were carried out by first cleaning the surface with a Teflon barrier and then immediately proceeding with data taking. Figure 2 shows the results of the SHG and surface tension measurements as a function of time. If the adsorption barrier for the surfactant molecules is independent of the coverage θ, then the change in θ is expected to follow Langmuir kinetics as

$$d\theta/dt = K(1 - \theta/\theta_o) , \qquad (4)$$

where θ_o is the final coverage and K a constant. Using $\chi_m = \chi_o\theta$, where χ_o is the susceptibility for the final coverage, we can fit the time dependence of θ from our SHG data as

$$\theta/\theta_o = 1 - ae^{-Kt} . \qquad (5)$$

For $t_o < t < 80$ min, we find $a = 1.0$ and $1/K = 48$ min, while for $t > 80$ we get $a = 0.22$ and $1/K = 150$ min. Here, the starting point t_o is used as an adjustable parameter. For the adsorption process, $t = 0$ is defined from the moment that the surface is swept clean by the movable barrier. To attach the float for the surface tension measurements and for the water surface to become stable, a few minutes will pass before the actual data taking can start.

By comparing the signal for $t \to \infty$ with that of a full spread monolayer of SDNS ($N_s = N_o = 2.22 \times 10^{12}$ cm^{-2}, $\pi = 31$ dynes/cm) we find that $\theta_o = 1$, i.e., the molecules eventually form a full monolayer. This is also consistent with the observed pressure, which saturates at $\pi = 28$ dynes/cm. Because for SDNS, as for many other surfactants, π only varies very slowly with N_s for small N_s (see ref. 1), its time-dependence cannot very well be used to study the adsorption kinetics, though it does indicate that a full monolayer is formed eventually.

One can make an estimate for the observed time constant by looking at the bulk concentration $c = 4.52 \times 10^{15}$ cm^{-3}. With $N_o = 2.22 \times 10^{14}$ cm^{-2} a full monolayer can be obtained by the depletion of a layer of thickness $d = 4.91 \times 10^{-2}$ cm. The bulk diffusion constant $D = k_BT/6\pi\eta r$ (where η = viscosity and r = size of the molecule) can be estimated to be $D \cong 10^{-6}$ cm^2 s^{-1}. With $D = d^2/t$ one gets t = 40 min, which is very similar to the observed time constant 1/K = 48 min. Recent studies of polymer adsorption an an air-water interface also show a time constant that is identical to the bulk diffusion constant.[7]

The observation that for t > 80, the time constant increases to 1/K = 150 min indicates that the adsorption process is not completely independent of the coverage. Because this takes place for $\theta > .8$ this is not so surprising: at such high concentrations each new arriving surfactant molecule has to find room to adsorb at the interface. This will cause the effective time constant to increase. The fact that there are two different time regimes in the adsorption process has also been observed in other systems.[1]

In conclusion, by using the technique of optical second harmonic generation we have been able to follow the kinetics of the adsorption of the SDNS surfactant molecules from the bulk to the water-air interface. We have observed two different time regimes, where the initial faster adsorption time is consistent with the bulk diffusion constant. By comparing the adsorbed layer with a full spread monolayer we have been able to make an absolute calibration of the final coverage and found it to be 100%.

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Figure Captions

Fig. 1 Schematic diagram of experiment and structure of SDNS molecule.

Fig. 2 Observed surface pressure π (open circles, right hand scale) and nonlinear susceptibility χ_m at an air-water interface of a 2% NaCℓ water solution saturated with SDNS surfactant. The dashed line is a Langmuir-type fit for the change in surface coverage.

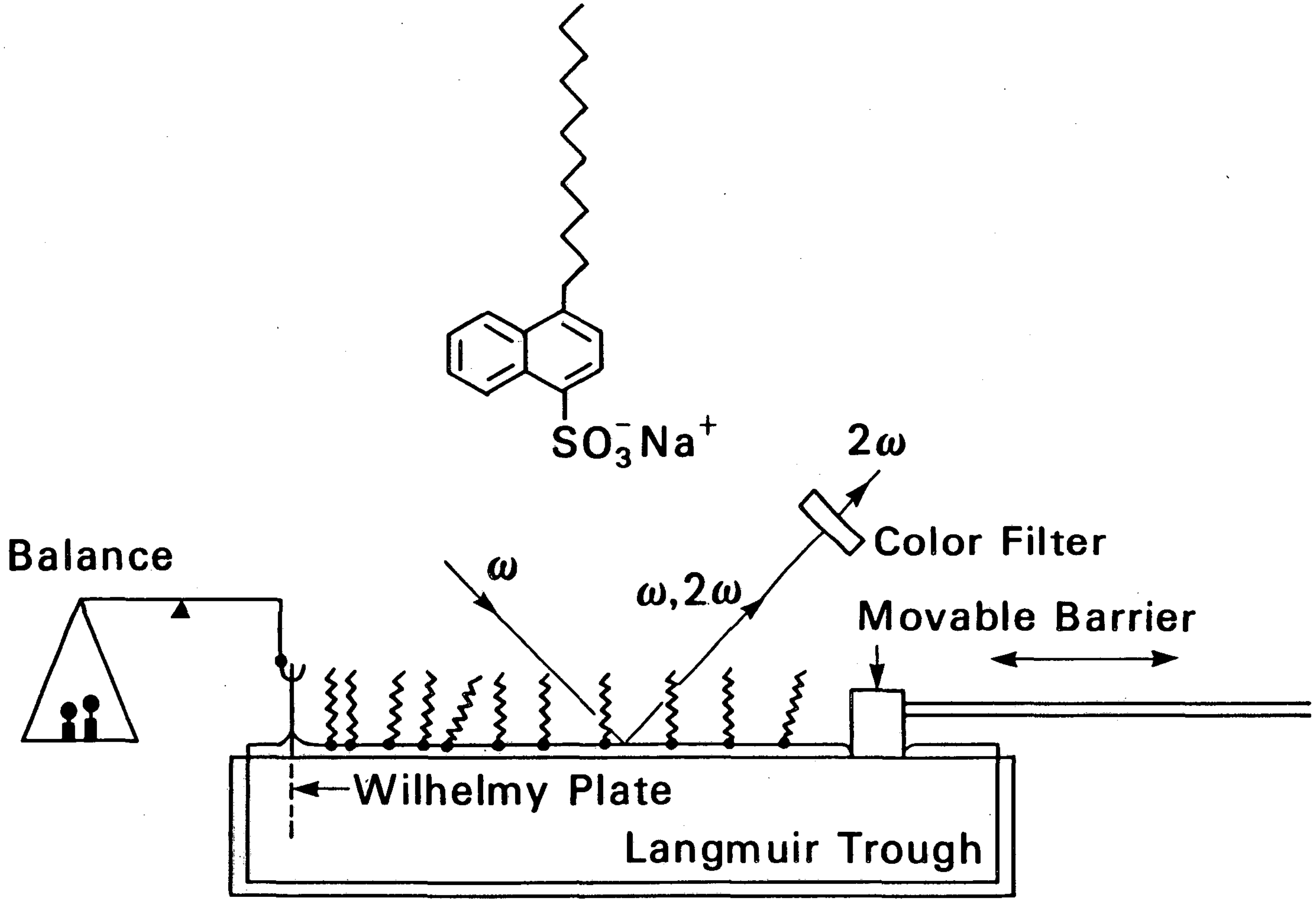

Fig. 1

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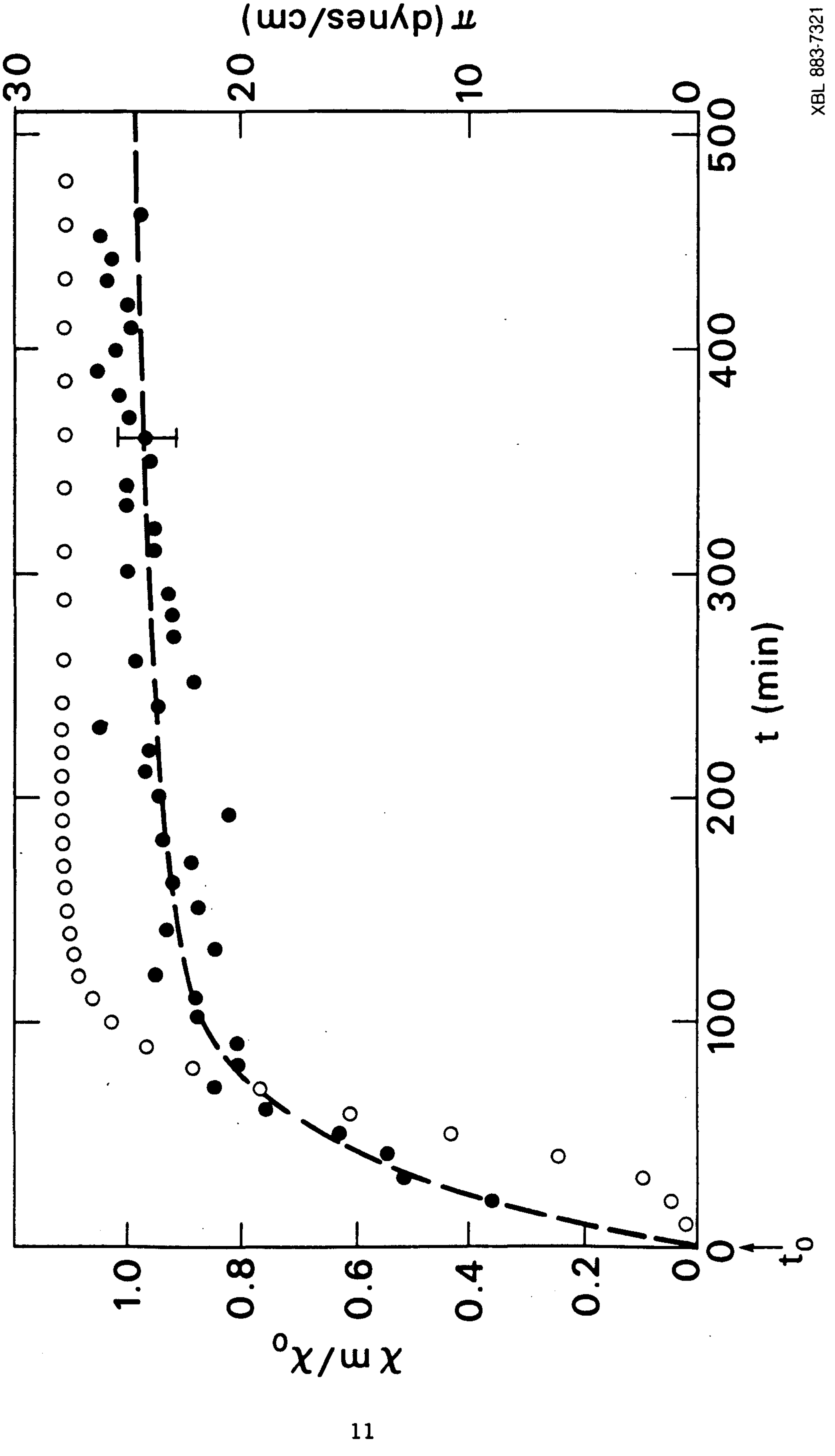
χ m/χ$_o$
0
0.2
0.4
0.6
0.8
1.0
t (min)
0
100
200
300
400
500
t$_0$
π (dynes/cm)
0
10
20
30
XBL 883-7321

Fig. 2

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