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Effects of Long-Chain Molecules on the Population and Orientation of Organic Molecules at the Air/Water Interface

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The effects of penta- and hexadecanoic acids on the population and orientational structure of *p*-nitrophenol, at the air/water interface at a bulk pH of 2, have been studied by using the technique of second-harmonic generation. The results indicate that, with increasing fatty acid at the interface, (1) the population of *p*-nitrophenol at the air/water interface first increases and then decreases, (2) the long axis of *p*-nitrophenol is oriented increasingly toward the surface normal, and (3) the behavior of *p*-nitrophenol is not sensitive to the monolayer liquid-expanded–liquid-condensed phase transition. This indicates that the *p*-nitrophenol is adsorbed near the polar group of the fatty acid and thus is a good probe of the lipid head group region.

Introduction

The effect of spread insoluble long-chain molecules on the adsorption of surface-active solutes, often referred to as "monolayer penetration", has been a subject of interest since 1935.[1] This effect describes thermodynamic and kinetic aspects of the adsorption process of surface-active molecules to an interface containing an insoluble spread film, which may be at full coverage or only partial coverage. Since this topic deals with a two-dimensional structure, it enables scientists to investigate the effects of dimensionality on physical and chemical processes. Furthermore, due to the relation between an insoluble monolayer and a biological membrane, the mechanism of the "penetration" may be of relevance to the understanding of biological interfaces.[2] However, it is difficult to interpret the results of classical surface measurements, such as those of surface tension and surface potential, when more than one species is present at the surface.[3] In this paper, we illustrate how the technique of second-harmonic generation (SHG) can be utilized in the study of a multicomponent system and, in particular, the adsorption of *p*-nitrophenol in the presence of an insoluble fatty acid at surface coverages that are submonolayer to monolayer.

Second-harmonic generation as a surface probe[4] relies on the fact that, under the electric dipole approximation, it is allowed only in a system with no inversion symmetry, such as the air/liquid interface.[5] The nonlinear polarization at 2ω, $\mathbf{P}^{(2)}$, is generated through the nonlinear susceptibility tensor $\chi^{(2)}$

$$\mathbf{P}^{(2)} = \chi^{(2)}\!:\!\mathbf{E}(\omega)\,\mathbf{E}(\omega)$$

This surface susceptibility can be related to the molecular hyperpolarizability, $\alpha^{(2)}$, when local field effects are not of dominant importance. In the case of uniaxial molecules, the relationship is simple:

$$\chi_{zzz} = N_s \langle \cos^3\theta\rangle \alpha_{\zeta\zeta\zeta}$$
$$\chi_{xzx} = \chi_{zxx} = \tfrac{1}{2}N_s \langle \sin^2\theta \cos\theta\rangle \alpha_{\zeta\zeta\zeta} \qquad (1)$$

where N_s is the surface population, θ is the molecular angle with respect to the surface normal, and $\langle\ \rangle$ denotes orientational averaging. (In our notation, z refers to the surface normal, x and y refer to the area on the surface plane, and ζ is the single molecular axis.) From eq 1 we see that the SH method allows both the population and orientation of molecules at the surface to be examined. When there are several species present at the surface, their contribution to the overall susceptibility is additive, provided one takes into account possible differences in their phases. Thus, if the species involved have very different polarizabilities, SHG can be sensitive to a particular one. In this experiment, the small molecule *p*-nitrophenol (PNP) is approximately uniaxial (with the main axis along the dipole moment) and has a large SH signal compared with that of water and the fatty acids. PNP is also very similar to 2,4-dinitrophenol, which is a molecule of biological interest in that it is a proton carrier across membranes. By monitoring the SH signal, we are able to follow the adsorption of PNP, even at low concentrations, into the air/water interface.

Experimental Results on Orientation and Population of *p*-Nitrophenol at the Air/Water Interface

The experimental apparatus, previously described,[5] consists of a synchronously pumped tunable dye laser and single photon counting detection system. Pentadecanoic acid (C15) (99+%) and hexadecanoic acid (C16) (99%) were of highest purity from Aldrich, while PNP from Aldrich (99+%) was purified by recrystallization from water. The insoluble monolayers were spread at constant area[6] with a 5-μL syringe on a subphase of 20 mM PNP in water at pH 2.

The intensity and polarization of the generated second-harmonic radiation were measured at various areas per molecule for both C15 and C16 acids. The results are summarized in Figures 1 and 2. The SH electric field, which is the square root of the intensity, is related to the population of PNP at the surface. Molecular orientation is related to the polarization of $\mathbf{E}_{2\omega}$ through trigonometric functions of the orientation angle θ, e.g., $\langle\cos^3\theta\rangle/\langle\sin^2\theta\cos\theta\rangle$. If a sharp distribution of orientation for PNP molecules at the surface is assumed, the orientation angle θ may be obtained, where θ is measured from the surface normal. We find that the orientation is the same for the pure PNP solution (no monolayer) as for the case of a very large area per fatty acid molecule, i.e., a very low fatty acid surface density. As the area per fatty acid is decreased below 200 Å^2/molecule, the *p*-nitrophenol orientation moves toward the surface normal for both C15 and C16. An approximate correction for this change in orientation on the SH signal, assuming a sharp distribution in orientation, can be obtained. Fortunately, the correction is small compared with the magnitude of the population changes we observed; if such a correction is applied, the behavior of the population as a function of area/molecule is the same as that in Figure 1. At large areas, there is a gradual increase in PNP population as monolayer packing increases. However, at less than 50 Å^2/molecule there is a dramatic decrease in PNP population.

The results of the intensity and polarization measurements of PNP with and without the fatty acids show that there is a considerable effect due to the presence of fatty acid at the interface.

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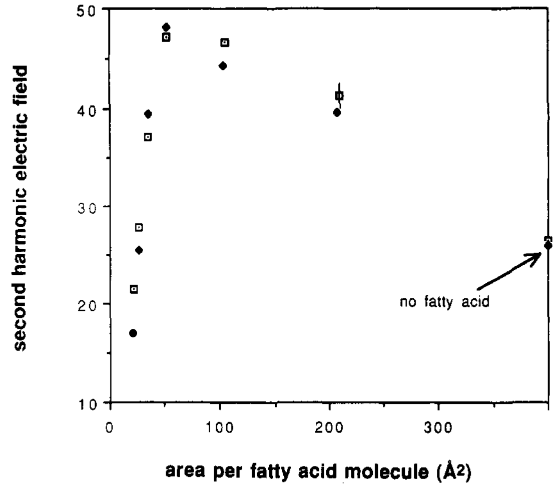

Figure 1. Second-harmonic electric field from fatty acid with 20 mM *p*-nitrophenol subphase at pH 2 as a function of area per fatty acid molecule (Å^2) at the interface: ⧈, pentadecanoic acid; ◆, hexadecanoic acid.

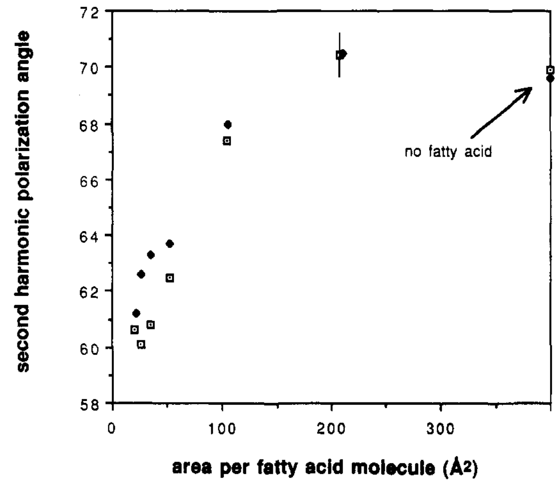

Figure 2. Second-harmonic electric field polarization (deg) from fatty acid with 20 mM *p*-nitrophenol subphase at pH 2 as a function of area per fatty acid molecule (Å^2) at the interface: ⧈, pentadecanoic acid; ◆, hexadecanoic acid.

At large areas per molecule (50–200 Å^2) there is an enhancement in population, possibly due to an attractive interaction between PNP and the carboxyl head group. Thus, as more fatty acid molecules are added to the surface, more PNP molecules are adsorbed. In addition, the PNP molecules alter their orientation toward the surface normal in the presence of the fatty acid, thereby occupying a smaller surface area as the packing gets tighter. Beyond a certain packing, however, PNP molecules cannot be accommodated at the surface any more, and as the fatty acid density further increases, are "squeezed out", causing the surface PNP population to drop.[7]

Probing Monolayer Phase Transitions at the Air/Water Interface

One of the most striking features in these measurements is the similarity in behavior between the C15 and C16 monolayers. It is well-known in the literature that these two monolayer systems have different phase behavior at room temperature,[8] as seen in surface pressure vs area per molecules phase diagrams. Between about 20 and 50 Å^2/molecule, pentadecanoic acid (C15) has a liquid-expanded (LE) to liquid-condensed (LC) phase transition, which is currently believed to be first order in nature and is associated with different orientations of the hydrophobic tails.[9,10]

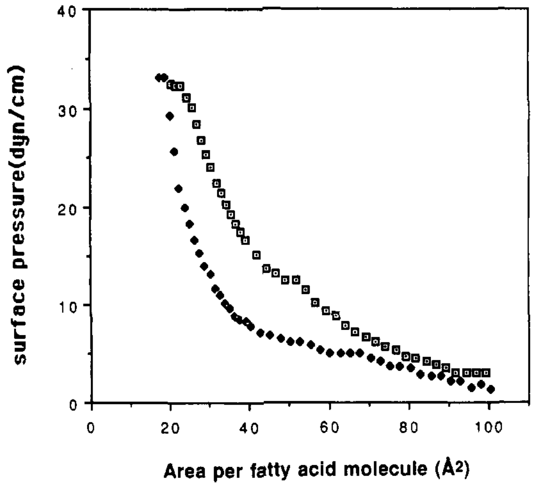

Figure 3. Surface pressure (dyn/cm) from fatty acid with 20 mM *p*-nitrophenol subphase at pH 2 as a function of area per fatty acid molecule (Å^2) at the interface: ⧈, pentadecanoic acid; ◆, hexadecanoic acid.

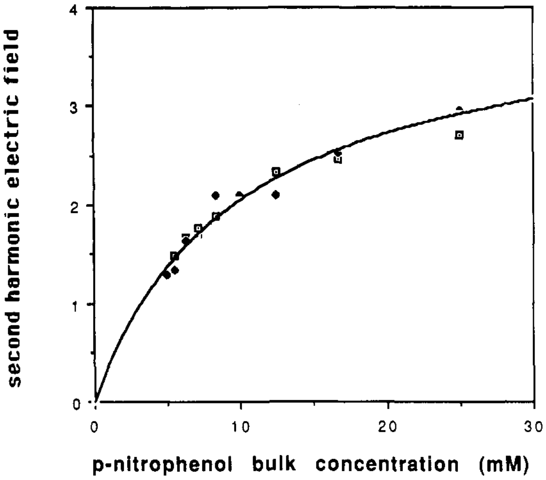

Figure 4. Second-harmonic electric field from *p*-nitrophenol at constant fatty acid surface density (50 Å^2) at pH 2 as a function of *p*-nitrophenol bulk concentration (mM): ⧈, pentadecanoic acid; ◆, hexadecanoic acid. The solid line is the fit to both sets of data using the Langmuir adsorption isotherm.

On the other hand, hexadecanoic acid (C16) shows no such transition and has only one condensed phase. In order to determine the effect of PNP on the π–A phase diagram, we measured the surface pressure vs area of these PNP–fatty acid systems with the use of a Langmuir film balance. The results in Figure 3 show that the difference in the phase diagram of the two acids observed in the absence of PNP persists when PNP is present. To further examine this difference, we measured, using the SH method, the adsorption isotherm of PNP at 50 Å^2/molecule for both fatty acids. The results in Figure 4 show no difference within experimental error between C15 and C16. These two sets of measurements, one surface pressure and the other SHG, seem to be contradictory. However, the π–A phase diagram is mainly due to interactions between the hydrophobic tail parts of the fatty acids. These results can be reconciled upon recognizing that different regions of the interface are probed in these different measurements. The fact that the adsorbing PNP molecule in effect sees the same structure for both C15 and C16 even though the π–A phase diagrams are different implies that PNP is not located in the chain region of the interface but rather is located near the polar head group of the acids. This is consistent with the strongly polar nature of PNP; it is quite likely that it prefers the polar carboxyl region

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rather than the hydrophobic tail part. An interesting result of this work is that the orientation of PNP in the close-packed monolayer that is obtained by assuming a sharp distribution of θ is almost the same as the reported orientation angle of C–OH bond.[9] This might indicate the existence of an orienting interaction between PNP and the C–OH part of the monolayer.

A further interesting result in these SH studies of fatty acids with PNP is our observation of huge fluctuations in the SH signal at low lipid densities, 150, 300, and 600 Å^2. These fluctuations reflect the interfacial inhomogeneity due to aggregates and isolated fatty acid molecule domains and are expected to be present in a gas–liquid coexistence region. Orientational and dynamic information on these aggregates as deduced from the observed time-dependent fluctuations will appear in a separate publication.

Conclusions

In summary, we have shown how SHG may be employed in the study of the structure and population of a solute molecule at an interface containing long-chain molecules. With increasing packing density of fatty acid at the air/water interface, (1) the population of PNP at air/water interface first increases and then decreases, (2) the long axis of PNP is increasingly aligned toward the surface normal, and (3) the behavior of *p*-nitrophenol in pentadecanoic and hexadecanoic acid monolayers is insensitive to the π–A phase diagram in the liquid-expanded–liquid-condensed region. This implies that the coadsorption or "penetration" of PNP happens preferentially in the polar head group of a fatty acid monolayer. Furthermore, huge time-dependent fluctuations in the SH signal were observed at low lipid coverages and are attributed to the inhomogeneity of the interface as expected in the lipid gas–liquid coexistence region.

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Effects of Illumination on the Surface Behavior of CH_3Cl on Clean and K-Dosed Pd(100) Surfaces

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Irradiation of adsorbed CH_3Cl on Pd(100) at 90 K with low-intensity ultraviolet light from a high-pressure Hg lamp induced the cleavage of C–Cl bond to give adsorbed CH_3 and Cl on a clean Pd surface and significantly enhanced the extent of dissociation of CH_3Cl for a K-dosed surface.

Introduction

In previous papers we showed that CH_3Cl adsorbs weakly and molecularly on a clean Pd(100) surface under ultra-high-vacuum conditions.[1,2] However, potassium adatoms markedly influenced its adsorption and caused C–Cl bond cleavage even at around 131 K. The effect of potassium was attributed to enhanced electron donation from the Pd to the adsorbed molecule (at low K coverage) and to a direct interaction between CH_3Cl and K (at and above monolayer). The present work demonstrates that irradiation of the adsorbed layer with UV light produces a profound effect on both surfaces.

Experimental Section

Experiments were carried out in a standard ultra-high-vacuum chamber equipped with facilities for AES, UPS, XPS, TDS, and work function measurements. Sample preparation and cleaning and potassium deposition were described in a previous communication.[3] A coverage of $\Theta_K = 0.5$ (0.5 K atoms per surface Pd atom) was taken for the first saturated layer. The UV light generated from a 700-W Hg arc lamp passed through a high-purity sapphire window in the vacuum chamber. The power density at the sample was estimated to be about 50 mW/cm^2. The incident angle was approximately 30° off the sample normal. The temperature of the sample during irradiation was about 90 K, which includes a $\sim$4 K rise due to radiative heating. The sample was cleaned by Ar$^+$ ion bombardment and high temperature treatment (at $\sim$1200 K) between runs, which are sufficient to remove the surface carbon.

Results and Discussion

Figure 1 shows the effects of illumination at 90 K on the desorption of CH_3Cl below monolayer coverage. In this case the amount of CH_3Cl desorbed with $T_p = 162$ K decreased by about 50%. While no methane formation was observed on the unirradiated surface, an easily detectable methane peak was found at $T_p = 167$–172 K. At monolayer CH_3Cl coverage, a very small additional methane peak appeared at $T_p = 375$–390 K. No other hydrocarbons (ethane, ethylene) were identified in the desorbing gases. Hydrogen desorption occurred above 400 K. After heating of the sample to 400 K (to desorb the molecularly adsorbed CH_3Cl), a Cl Auger signal was found at 181 eV. This signal started to attenuate only at 700 K and was eliminated above 950 K. No residual Cl signal could be seen for the unirradiated surface after desorption of CH_3Cl at 250–280 K. These features clearly indicate that C–Cl bond cleavage occurred following irradiation to give adsorbed CH_3 and Cl. Photoinduced dissociation of a halogen–carbon bond was also observed by White et al.[4–6] in

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