The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 July 1988 for a fuller description of Letters to the Editor.

COMMUNICATIONS

Studies of neutral and charged molecules at the air/water interface by surface second harmonic generation: Hydrophobic and solvation effects

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Over the last few years, the technique of surface second harmonic generation (SSHG) has developed into a powerful method to investigate selectively the interfacial layer between two centrosymmetric media.[1-13] In our continuing efforts to understand the properties of molecules (e.g., benzene derivatives) at the surfaces of liquid solutions we have earlier focused on their concentration and orientation.[9,10] More recently we observed how the reduced polarity at the surface (due to the low density of molecules on the vapor side) affects a simple chemical reaction, namely the acid–base equilibrium involving neutral nitrophenol and its anion.[11]

We now wish to present preliminary results on the competition between hydrophobic groups that drive molecules to the air/water interface, e.g., CH_2, and hydrophilic groups, in particular charged groups, that drive molecules away from the surface and into the bulk water. By using a molecule that contains both types of groups we have been able to determine how many CH_2 groups must be attached to a phenolate ion ($C_6H_5O^-$) to balance the repulsion of the ion from the interface. We also obtain quantitative information on the respective driving forces for the adsorption of the neutral alkylphenol and the alkylphenolate ion to the air/water interface by measurement of the second harmonic signal as a function of bulk concentrations.

The experimental setup consisted of a cavity-dumped, synchronously pumped dye laser operating at 610 nm, and single photon counting electronics.[9,10] The component of the surface second order nonlinear susceptibility $\chi_s^{(2)}$ perpendicular to the plane of incidence was measured, since it contains only the contribution from the surface region and not the bulk.[14]

At a high pH (~ 13) the alkylphenol deprotonates ($p\mathrm{K} = 9.9$), yielding a predominantly alkylphenolate solution, whose interfacial SH signal is equal to that of neat water when the alkyl chain has $n \leqslant 4$ (Fig. 1). Thus alkylphenolates having chains less than five carbons long are not present at the air/water interface. This translates into less than one tenth of a monolayer based on our sensitivity. We thus conclude for the smaller chain alkylphenolates that the negative charge repels the anion from the interface, despite the hydrophobic effects of both the methylene groups and to some extent the phenyl group. It is at $n = 4$ that the opposing forces are balanced and the phenolate is first detected at the air/H_2O interface. When the alkyl chain contains five or more carbons the hydrophobic effect dominates and the anion is observed in the interface.

To examine adsorption energetics of the neutral and charged species to the air/water interface we measured the dependence of the SH signal on the bulk solute concentration. At low pH, where the bulk solution is predominantly the neutral form, the adsorption of heptylphenol is seen to obey a Langmuir isotherm,[15] Fig. 2. In this model of noninteracting surface sites, the free energy of adsorption ΔG^0 is related to the number of interfacial solute molecules /cm^2 N_s, its maximum number $N_{\max}$, and the bulk concentration C,

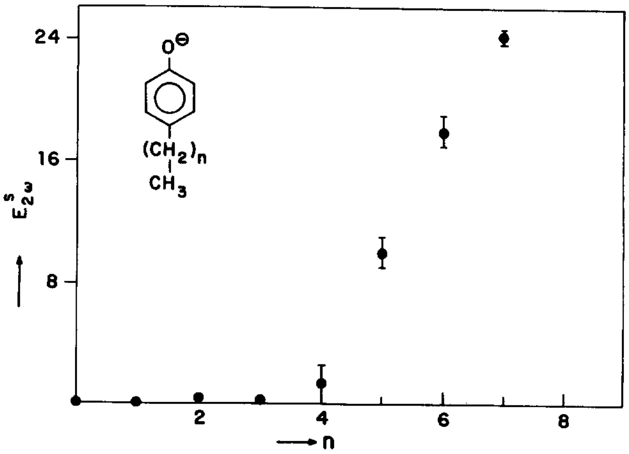

FIG. 1. s-polarized surface second harmonic field as a function of the number of methylene groups in the chain of p-alkylphenolates.

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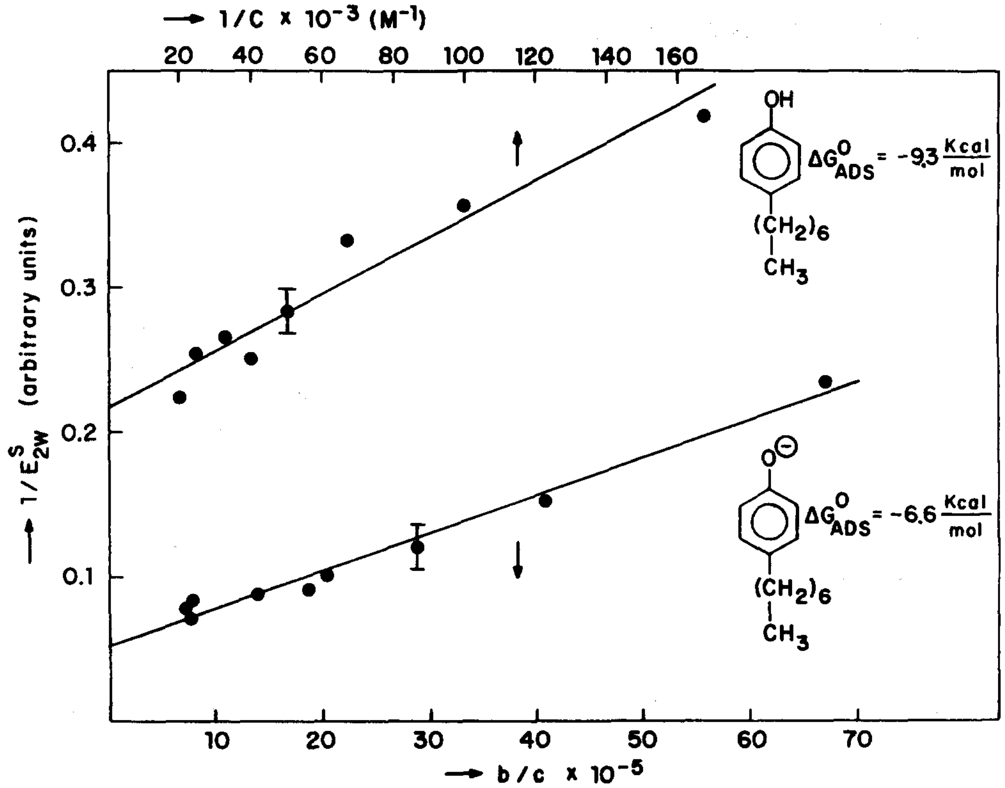

FIG. 2. Plots of $1/E^S_{2\omega}$ against $1/C$ (neutral) and b/C (charged) for the adsorption of *p*-heptylphenol and *p*-heptylphenolate. $b = \exp(e\Psi_0/kT)$. (See the text for definition of Ψ_0.)

$$N_s = \frac{CN_{\max}}{C+a}, \tag{1}$$

where $a = 55.5 \exp(\Delta G^0/RT)$. By measuring both the SH signal $\sim |E_{2\omega}|^2$ and the surface tension of solutions at different solute concentrations, we have found that the SH field $E_{2\omega}$ is linearly proportional to N_s up to a monolayer coverage. Using this we obtain ΔG^0 from Eq. (1) by measuring the SH signal at different bulk concentrations C.

Unlike the free energy of adsorption of neutral molecules to the interface, the adsorption of a charged molecule must include the electrical energy due to the ions in the interfacial region. If we assume a Gouy–Chapman model for the potential Ψ_0 due to the charges we obtain Eq. (1) with ΔG^0 now given by [15]

$$\Delta G^0 = \Delta G^0_c + e\Psi_0 = \Delta G^0_c + e\cdot 52.4 \sinh^{-1}(134\times 10^{-14} N_s/\sqrt{C}), \tag{2}$$

where ΔG^0_c is the nonelectrostatic contribution and $e\Psi_0$ is the electrostatic contribution in mV at 20 °C. We see from Fig. 2 that the free energy ΔG^0 for heptylphenolate is a positive 2.7 kcal/mol larger than that for the neutral heptylphenol molecule. This quantity represents the decreased driving force for adsorption of the charged molecule from the bulk to the air/water interface. These values are comparable to those obtained by surface tension methods for alcohols and alkylsulphates of similar chain length.[16] It should be noted that the SH method has the advantage of being able to cover a wider range of concentrations because of its greater sensitivity, and can be used to differentiate among various chemical species in the interface, unlike surface tension, since the SH technique is a spectroscopic one. Experiments on other charged molecules, and the effects of inorganic electrolytes are in progress.

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