

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

Alonso Castro, Kankan Bhattacharyya,^{a)} and Kenneth B. Eisenthal
Department of Chemistry, Columbia University, New York, New York 10027

(Received 31 January 1991; accepted 12 April 1991)

Surface second harmonic generation has been used to study the adsorption of alkyl phenols and anilines and their respective ions to the air/water interface. The free energies of adsorption of the neutral molecules were obtained using a simple Langmuir model. The quantitative effects of the opposing hydrophobic and solvation forces on molecular adsorption were investigated by varying the chain length of alkylphenolate and alkylanilinium ions. An alkyl chain of at least five carbons was found to be necessary to balance the bulk ionic solvation and thereby bring the ion interface population to a level above the water background. The adsorption of the ions can be described quantitatively by using a modified Langmuir model that includes the electrostatic free energy of the electric double layer as given by the Gouy–Chapmann theory. From the excellent fit of the second harmonic data to this treatment, the chemical and electrostatic free energies of adsorption, interface electric potential, and interface pH were obtained.

I. INTRODUCTION

Continuing our efforts to understand the behavior of organic molecules at interfaces, we now present a detailed study of the energetics of adsorption of small benzene derivatives (e.g., phenols and anilines) at the surface of aqueous solutions, using the nonlinear optical technique of surface second harmonic generation (SHG).¹ This technique is recognized as a very powerful and sensitive method for investigating structural aspects for a variety of interfaces.^{2–13} Since SHG is electric dipole forbidden in the bulk, this technique can be used to probe selectively the interfacial layer between two centrosymmetric media. Information about the relative populations of adsorbates at the air/water interface can be obtained readily, because the observed s -polarized reflected SH field amplitude $E_{2\omega}^s$ is proportional to the number of adsorbed molecules.

The purpose of the present work is threefold. In the first place, we examine what kind of adsorption isotherm explains the interfacial populations of the successive members of the homologous series of p - n -alkylphenols and p - n -alkylanilines and their respective ions at the air/solution interface. The second aim is to investigate the effect of the size of the alkyl chain attached to these molecules on the adsorption energetics. Finally, we studied the competition between the hydrophobicity of the hydrocarbon part of the molecule and the solvation effect of the O^- or NH_3^+ groups for phenolate and anilinium ions, respectively, on the interface population. The hydrophobicity tends to drive the species away from the bulk and keep them at the surface, while the solvation pulls them towards the bulk. Specifically, we have tried to find out the minimum size of the pendent p - n -alkyl chain which will keep the charged molecules at the surface. Our preliminary results⁵ showed for the phenolate ion that five or more carbons are needed for the hydrophobicity to overcome solvation. We now extend these studies to the anilinium case.

^{a)} Present address: Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 32, India.

II. EXPERIMENTAL

A cavity-dumped synchronously pumped picosecond dye laser operating at 610 nm and 4.1 MHz repetition rate, producing pulses of 5 ps duration was used. For some of the experiments, the dye laser was amplified to 10–15 μ J pulse energy at 10 KHz repetition rate by means of a 20 W copper vapor laser. The input beam was focused into the liquid sample at an angle of 70° from the normal to the surface. The reflected surface second harmonic signal was directed through an analyzer, filters, and monochromator, and detected with a cooled photomultiplier tube and single-photon counting equipment. The output polarization analyzer was set perpendicular to the plane of incidence such that only the s -polarized component of the SH signal was measured. To subtract the background signal due to water, the relative phase of the water and the sample signal were determined in a manner discussed in our earlier publication.¹⁴

All organic samples were obtained from Aldrich Chemical Co. or Fisher Scientific and purified by vacuum distillation or vacuum sublimation. HPLC grade water (Aldrich) was used as a solvent without further purification. The phenolate and anilinium ions were obtained by increasing and decreasing the solution pH with NaOH and HCl, respectively. All solutions containing charged species were held at 0.1 M total electrolyte concentration.

III. RESULTS AND DISCUSSION

A. Neutral phenols and anilines

Since the SH electric field $E_{2\omega}^s$ is proportional to the number of adsorbed molecules, the adsorption isotherm can be determined from measurements of the SH intensity $I_{2\omega}^s = |E_{2\omega}^s|^2$ at various bulk concentrations. Adsorption isotherms were obtained in this manner for p - n -alkylphenols with zero to seven carbons and for p - n -alkylanilines with zero to six, and ten carbons in the hydrocarbon chain. These neutral phenols and anilines are nonresonant at the wavelength used (610 nm) and the second harmonic has the same

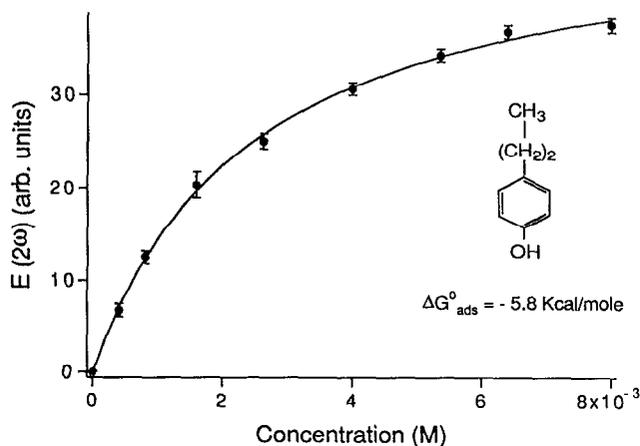


FIG. 1. *p*-propylphenol adsorption isotherm. The line represents the best fit to the Langmuir equation.

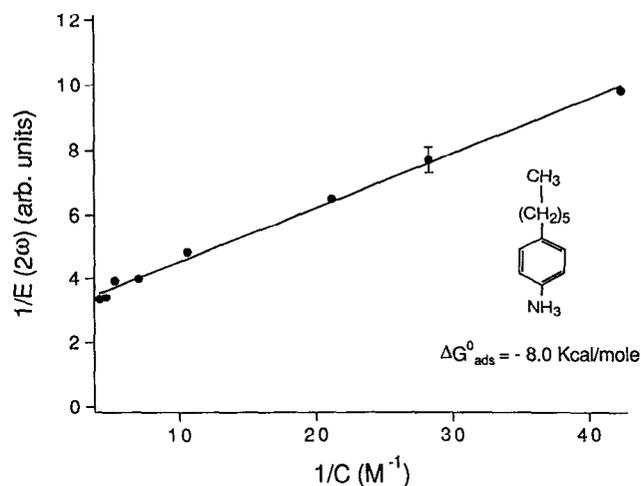


FIG. 2. Reciprocal fit to the Langmuir equation for *p*-hexylaniline. $\Delta G_{\text{ads}}^{\circ} = RT \ln(a/55.5)$ [see Eq. (4)] $\Delta G_{\text{ads}}^{\circ} = -8.01 \pm 0.04$ kcal/mol in this case.

phase as water. Thus, the correct second harmonic field in this case is the difference of the square roots of the signal intensities for phenol or aniline solution and that of neat water. The corrections due to water background were of minor importance for the various molecules studied. In all cases, the adsorption was found to obey the Langmuir isotherm¹⁵ (see below) over all ranges of concentrations. As an example, the experimental points along with the Langmuir fit are shown in Fig. 1 for *p*-propylphenol. Similar plots were obtained for the other phenols and anilines. The Langmuir model assumes that the surface can be treated as a lattice of noninteracting sites and thus a monolayer is formed when the number of adsorbed molecules is maximum. The adsorption process can be described by the "reaction" between bulk molecules (*M*) and empty surface sites (*ES*) to give filled sites (*FS*):



The kinetic equation is

$$\frac{dN}{dt} = k_1 \frac{C}{55.5} (N_{\text{max}} - N) - k_2 N, \quad (2)$$

where *N* is the number of adsorbed molecules/cm², *N*_{max} its maximum number, *k*₁ and *k*₂ the rate constants for adsorption and desorption, respectively, *C* the bulk concentration, and 55.5 the molarity of water. At equilibrium, *dN/dt* = 0,

and one obtains the usual form of the Langmuir adsorption equation

$$\frac{N}{N_{\text{max}}} = \frac{C}{(C + a)}, \quad (3)$$

where $a = 55.5 k_2/k_1 = 55.5 \exp(\Delta G_{\text{ads}}^{\circ}/RT)$. By rewriting Eq. (3) as

$$\frac{1}{N} = \frac{a}{N_{\text{max}}} \frac{1}{C} + \frac{1}{N_{\text{max}}}, \quad (4)$$

we note that 1/*N* is inversely proportional to the bulk concentration *C*. Since the second harmonic field *E*_{2ω}^s is proportional to *N*, we find that by plotting the inverse of the second harmonic electric field vs the inverse of the solute bulk concentration, we obtain a straight line from which $\Delta G_{\text{ads}}^{\circ}$ can be obtained, as Eq. (4) indicates. This is shown in Fig. 2 for *p*-hexylaniline. Similar plots were obtained for the other molecules studied. Experimental free energies of adsorption for a number of neutral *p*-*n*-alkylphenols and anilines have been measured in this way. The results are presented in Table I and in Fig. 3 as a plot of $\Delta G_{\text{ads}}^{\circ}$ vs hydrocarbon chain length. Our previous results on the investigation of the kinetics of adsorption of a similar molecule *p*-nitrophenol to the air/water interface,⁶ showed excellent agreement with Eq.

TABLE I. Chemical free energies of adsorption $\Delta G_{\text{chem}}^{\circ}$ for neutral anilines and phenols and their respective ions.

Carbon chain length	Anilines	Aniliniums	Phenols	Phenolates
0	-3.5 ± 0.4		-3.80 ± 0.03	
1	-4.3 ± 0.3		-4.4 ± 0.1	
2	-4.7 ± 0.2		-5.0 ± 0.1	
3	-5.8 ± 0.1		-5.78 ± 0.04	
4	-6.4 ± 0.3		-6.7 ± 0.1	
5	-7.2 ± 0.2		-7.29 ± 0.04	
6	-8.01 ± 0.04	-5.25 ± 0.05	-8.2 ± 0.3	-5.08 ± 0.14
7		-6.05 ± 0.07	-9.3 ± 0.1	-5.77 ± 0.08
8		-6.73 ± 0.07		-6.74 ± 0.07
10	-11.3 ± 0.1			

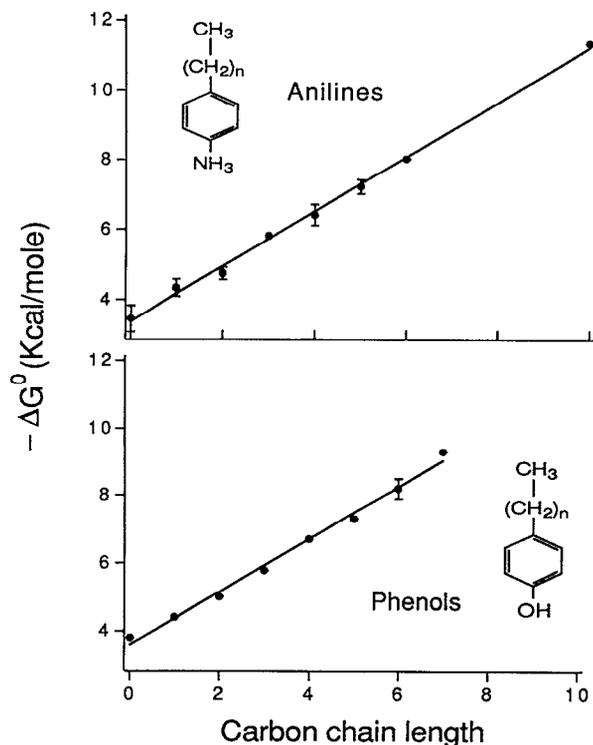


FIG. 3. $\Delta G_{\text{ads}}^{\circ}$ vs the number of carbons in the alkyl chain of neutral phenols and anilines.

(2). This further supports the Langmuir model for describing the experimental adsorption isotherms. Rigorously, Eqs. (2)–(4) should be expressed in terms of bulk activities instead of concentrations. However, we found that the use of concentrations introduced a negligible error, less than 2% for the most concentrated solutions, in our calculations of $\Delta G_{\text{ads}}^{\circ}$.

Free energies of adsorption are more negative for the higher members of the series, because an increase in the alkyl chain length increases the hydrophobicity, and thus the increased bulk repulsion causes a higher free energy release upon adsorption. It is interesting to note that, in both cases anilines and phenols, a straight line with slope = 780 cal/mol (± 20 and 30, respectively) was obtained. This quantity is the difference in free energies between two successive members of the homologous series and corresponds to the free energy of adsorption of a methylene (CH_2) group. This value is in good agreement with those obtained by surface tension methods,^{16–18} which are in the range 0.6–0.8 kcal/mol.

B. Phenolates and aniliniums

In an earlier study, we investigated how the reduced polarity at the surface of a solution (due to the low density of molecules in the vapor side) affects a simple acid-base equilibrium involving neutral nitrophenol and its anion.⁴ Our results indicated that in the interfacial region, the population of the anion decreased due to its decreased stability in the interface. This causes a shift in the equilibrium at the surface that overwhelmingly favors the neutral undissociated nitrophenol. In the case of *p*-*n*-alkylphenolate and anilinium ions,

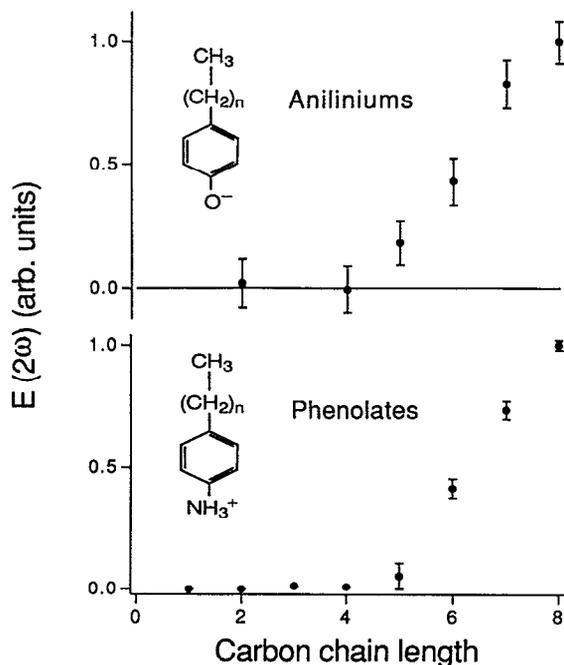


FIG. 4. *s*-polarized second harmonic field as a function of carbon chain length for phenolate and anilinium ions.

the shorter chain members behave in the same way and, hence, do not show surface second harmonic generation. This happens because the strong solvation of the O^- and NH_3^+ strongly favors the bulk phase. For longer alkyl chains, however, the hydrophobic interactions dominate the solvation effects, and the anion is driven to the surface. From measurement of the SH intensity of the different members of the series, we can determine how many methylene (CH_2) groups are required to balance solvation of the charged group. Figure 4 shows the surface SH signal for a series of *p*-*n*-alkyl phenolate and anilinium ions at a fixed bulk concentration. In both cases, it can be seen that when the alkyl chain has five or more carbons, hydrophobicity overcomes solvation.

Adsorption isotherms for phenolates and aniliniums with six, seven, and eight carbons in the alkyl chain were obtained by measuring $|E_{2\omega}^s|^2$ vs bulk concentration. It is important to mention at this point that when an alkylphenol is deprotonated, the absorption spectrum shifts to the red and as a result the corresponding phenolates are two-photon resonant at 305 nm. Thus, the phase of the SH signal becomes different by 90° from that of water. Then, the corrected SH electric field can be obtained by first subtracting the signal intensities for the phenolate solution and that of neat water, and then taking the square root. This is not the case for anilinium ions. After protonation, the spectrum shifts to the blue and there is no absorption at 305 nm. Consequently, the corrected SH electric field is obtained in the same way as for the neutral case.

To describe the adsorption isotherm of these charged molecules, we must include the electrostatic repulsion effect due to the interfacial double layer created upon adsorption. In other words, $\Delta G_{\text{ads}}^{\circ}$ is the sum of an electrostatic contribution ($\Delta G_{\text{elec}}^{\circ}$) and a nonelectrostatic one ($\Delta G_{\text{chem}}^{\circ}$),

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{chem}}^{\circ} + \Delta G_{\text{elec}}^{\circ} \quad (5)$$

where $\Delta G_{\text{elec}}^{\circ}$ is related to Ψ_0 , the electrostatic interfacial double-layer potential¹⁹

$$\Delta G_{\text{elec}}^{\circ} = N_A z e \Psi_0 \quad (6)$$

where N_A is Avogadro's number, z the ion valency, and e the elementary charge. The calculation of Ψ_0 can be accomplished by means of the Gouy–Chapmann double-layer model,^{20,21} which yields the following expression:

$$\Psi_0 = \frac{2kT}{ze} \sinh^{-1} \frac{(1.36 \times 10^{-14} N)}{\sqrt{C_t}} \quad (7)$$

where C_t is the total electrolyte concentration, which is constant and equal to 0.1 M for the present experiments. Combining Eqs. (3) and (5)–(7), the Langmuir equation can be written as

$$N = \frac{CN_{\text{max}}}{C + a \cdot b} \quad (8)$$

with $a = 55.5 \exp(\Delta G_{\text{chem}}^{\circ}/RT)$ and $b = \exp(\Delta G_{\text{elec}}^{\circ}/RT)$. Since $E_{2\omega}^s$ is proportional to N , we can rewrite Eq. (8) as

$$E_{2\omega}^s = \frac{CE_{2\omega}^s(\text{max})}{C + a \cdot b} \quad (9)$$

as we did for the neutral species case. Since N appears explicitly in the expression for b [Eq. (7)], we substitute the following expression for N :

$$N = \frac{E_{2\omega}^s}{E_{2\omega}^s(\text{max})} \cdot N_{\text{max}} \quad (10)$$

where N_{max} is the maximum number of molecules for the saturated monolayer. By measuring the dependence of surface tension on concentration, N_{max} can be obtained by application of the Gibbs surface equation. However, for the molecules studied, saturation in the bulk occurs before a close-packed monolayer is formed at the surface. Since N_{max} is independent of chain length for the molecules studied,²² we measured instead the surface tension of *p*-dodecylphenolate and *p*-dodecylanilinium. The values for N_{max} were

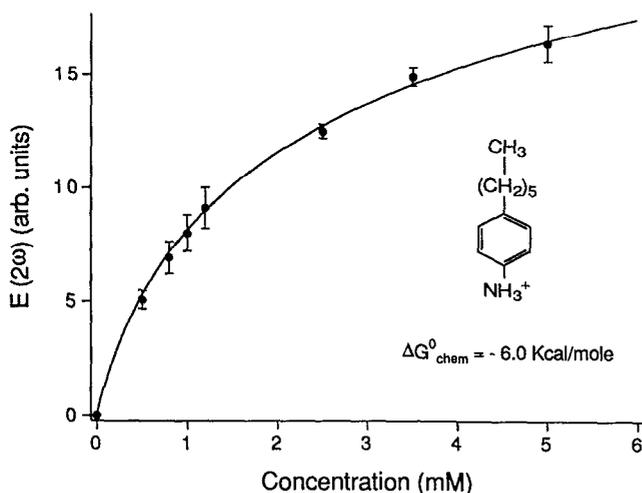


FIG. 5. *p*-hexylanilinium adsorption isotherm. The line represents the best fit to the Langmuir equation including the electrostatic term [Eq. (9)].

$(2.3 \pm 0.2) \times 10^{14}$ for aniliniums and $(2.4 \pm 0.2) \times 10^{14}$ for phenolates. Then, ΔG° can be obtained from a two-parameter [a and $E_{2\omega}^s(\text{max})$] least-squares fit to Eq. (9). Figure 5 shows the experimental isotherm for *p*-hexylanilinium along with the theoretical fit. Similar plots were obtained for the other members of the phenolate and anilinium series, and all of them were found to agree very well with the model. The obtained $\Delta G_{\text{chem}}^{\circ}$ values are shown in Table I.

Again, the difference on $\Delta G_{\text{chem}}^{\circ}$ between two consecutive members of the series of phenolates and aniliniums corresponds to the free energy of adsorption of a CH_2 group. The values obtained are 750 ± 40 cal/mol for aniliniums and 830 ± 80 cal/mol for phenolates. Both values, although obtained from only three chain lengths, are within experimental error of the values obtained for the neutral molecules.

It is interesting to note that the $\Delta G_{\text{chem}}^{\circ}$ values for the charged species are smaller in magnitude than those for the neutral species (Table I). The presence of a charge in the molecule has two effects on $\Delta G_{\text{ads}}^{\circ}$. First, there is an extra work required to bring a charge up to an already charged interface, namely, $\Delta G_{\text{elec}}^{\circ}$, which has already been taken into account. Besides, there is extra work required to remove the charged molecule from its solvated state in the bulk, including hydrogen bonding, which is not included in the double layer $\Delta G_{\text{elec}}^{\circ}$ term. This effect decreases the magnitude of $\Delta G_{\text{chem}}^{\circ}$ for a charged molecule, making it less negative than that of a neutral molecule.

The electrostatic part of the free energy was calculated using Eq. (6). The values of $\Delta G_{\text{elec}}^{\circ}$ are positive because it

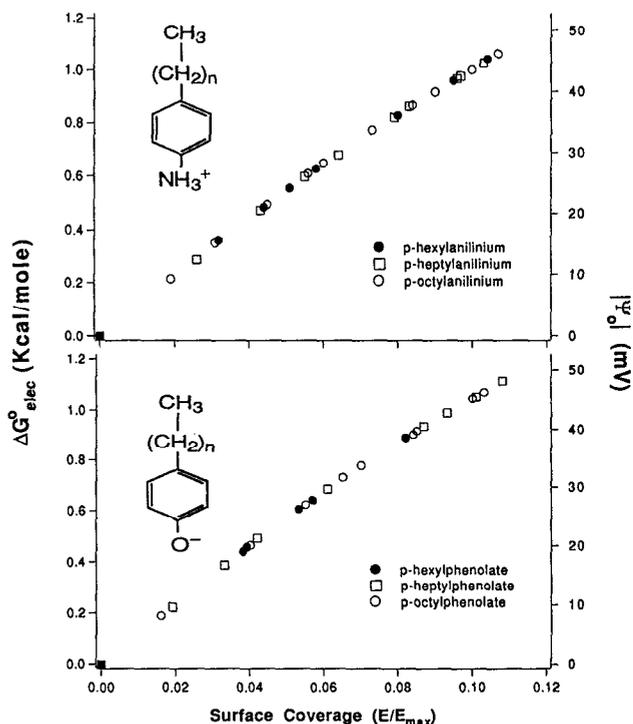


FIG. 6. Electrostatic contribution to the total free energy of adsorption for phenolate and anilinium ions, plotted as a function of surface coverage θ . The corresponding values of the double-layer potential Ψ_0 can be obtained from Eq. (7) in the text.

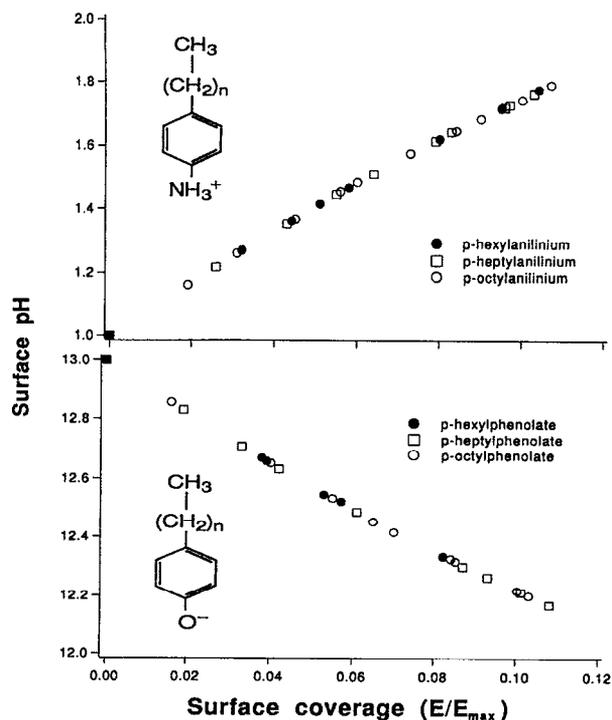


FIG. 7. Surface pH as a function of surface coverage θ for phenolate and anilinium ions. The bulk pH is equal to 13.0 for phenolates and 1.0 for aniliniums.

represents the work done by the system to bring an ion to an already charged interface. The plots of ΔG_{elec}^0 and $|\Psi_0|$ vs θ , where $\theta \equiv N/N_{max} = E_{2\omega}^s/E_{2\omega}^s(max)$, are shown in Fig. 6. As the surface population increases, the absolute value of Ψ_0 , i.e., $z\Psi_0$, increases as indicated by Eq. (7). Under the conditions of the experiments reported here, Ψ_0 is almost linear in N , and therefore the monotonic increase of the $\Delta G_{elec}^0 = N_A z e \Psi_0$ with θ .

Another interesting point can be made regarding the surface population of H_3O^+ ions^{23,24} and, consequently, the surface pH . According to the Boltzmann equation, bulk and surface (H_3O^+) are related by

$$(H_3O^+)_s = (H_3O^+)_b \exp\left(\frac{-e\Psi_0}{kT}\right), \quad (11)$$

the subscripts s and b referring to surface and bulk phases, respectively. In logarithmic form, Eq. (11) becomes

$$pH_s = pH_b + \left(\frac{e\Psi_0}{2.3kT}\right) \quad (12)$$

where pH_b is equal to 13.0 for phenolates and 1.0 for aniliniums. Figure 7 presents the pH_s vs θ plots. For the negatively charged phenolates, Ψ_0 is negative and the surface pH is smaller than the bulk pH , as expected since a negatively charged interface will attract hydrogen ions to it, effectively decreasing the surface pH with respect to the bulk. The opposite argument applies to a positively charged interface; pH_s is greater than pH_b .

For many years, several studies regarding free energies of adsorption have been made, mainly by means of the surface tension technique.²⁵ Although no specific work on p - n -alkyl phenols and anilines has been done, our results for free

energies of adsorption are comparable in magnitude to those of fatty acids, alcohols, and alkylsulfonates of similar chain length.^{26–28} However, as we have demonstrated earlier,⁴ SHG is much more sensitive than surface tension measurements. In fact, under the conditions of our experiments, when the intensity of the SHG signal changed by a factor of 80, the surface tension changed by less than 10%. Thus, the SH method can be used to cover a wider range of concentrations because of its greater sensitivity. Moreover, SHG has the advantage of being able to differentiate among the adsorbed species, since it is a spectroscopic method, whereas surface tension methods cannot.

IV. CONCLUSIONS

We have shown the applicability of the SHG technique for the study of adsorption energetics of neutral and charged molecules at the air/solution interface. The adsorption of various members of the p - n -alkyl phenol and aniline series have been found to obey the Langmuir isotherm over all ranges of concentrations. Free energies of adsorption for a series of molecules have been obtained, and ΔG_{ads}^0 for a CH_2 group was found to be -780 ± 20 cal/mol. The adsorption isotherm for the charged species, i.e., phenolates and aniliniums, can be described by including the Gouy-Chapmann theory of the electric double layer into the Langmuir model. This demonstrates the applicability of the Gouy-Chapmann model to the adsorption of the ions studied. The electrostatic contribution to the free energy of adsorption, the double-layer potential, and the surface pH , have been obtained. We have also found that the minimum number of carbons in the alkyl chain of both the phenolates and aniliniums required to bring the molecules to the surface is equal to five. This corresponds to the number necessary to bring the hydrophobic forces into balance with the opposing ionic solvation forces that drive the molecule into the bulk, away from the interface.

ACKNOWLEDGMENTS

We wish to acknowledge the National Science Foundation, the Air Force Office of Scientific Research, and the Petroleum Research Fund administered by the American Chemical Society for financial support of this research.

- ¹N. Bloembergen and P. S. Persham, Phys. Rev. **128**, 606 (1962).
- ²Y. R. Shen, Nature **337**, 519 (1989).
- ³J. M. Hicks, K. Kemnitz, K. B. Eisenthal, and T. F. Heinz, J. Phys. Chem. **90**, 560 (1986).
- ⁴K. Bhattacharyya, E. V. Sitzmann, and K. B. Eisenthal, J. Chem. Phys. **87**, 1442 (1987).
- ⁵K. Bhattacharyya, A. Castro, E. V. Sitzmann, and K. B. Eisenthal, J. Chem. Phys. **89**, 3376 (1988).
- ⁶A. Castro, S. Ong, and K. B. Eisenthal, Chem. Phys. Lett. **163**, 412 (1989).
- ⁷E. V. Sitzmann and K. B. Eisenthal, J. Chem. Phys. **90**, 2831 (1989).
- ⁸G. L. Richmond, J. M. Robinson, and V. L. Shannon, Prog. Surf. Sci. **28**, 1 (1988).
- ⁹B. Dick, A. Gierulsky, and G. Marowsky, Appl. Phys. B **38**, 107 (1985).
- ¹⁰A. L. Harris, C. E. D. Chidsey, N. J. Levinos, and D. N. Loiacono, Chem. Phys. Lett. **141**, 350 (1987).
- ¹¹J. Y. Huang and A. Lewis, Biophys. J. **55**, 835 (1989).
- ¹²E. S. Peterson and C. B. Harris, J. Chem. Phys. **91**, 2683 (1989).
- ¹³D. J. Campbell, D. A. Higgins, and R. M. Corn, J. Phys. Chem. **94**, 3681 (1990).

- ¹⁴K. Kemnitz, K. Bhattacharyya, J. M. Hicks, G. R. Pinto, K. B. Eisenthal, and T. F. Heinz, *Chem. Phys. Lett.* **131**, 285 (1986).
- ¹⁵D. K. Chattoraj and K. S. Birdi, *Adsorption and the Gibbs Surface Excess* (Plenum, New York, 1984), pp. 165–169.
- ¹⁶A. F. H. Ward and L. Tordai, *Nature* **158**, 416 (1946).
- ¹⁷F. Tokiwa and K. Ohki, *J. Colloid Interface Sci.* **26**, 457 (1968).
- ¹⁸I. J. Lin and P. Somasundaran, *J. Colloid Interface Sci.* **37**, 731 (1971).
- ¹⁹D. A. Haydon and F. H. Taylor, *Philos. Trans. R. Soc. London Ser. A* **253**, 255 (1960).
- ²⁰G. Gouy, *Ann. Phys. (Leipzig)* **7**, 129 (1917).
- ²¹D. T. Chapmann, *Philos. Mag.* **25**, 475 (1913).
- ²²Our surface tension measurements of C₁₂ and C₁₆ phenolates at the air/water interface yielded the same values for N_{\max} . See also, M. J. Rosen, *Surfactants and Interfacial Phenomena* (Wiley, New York, 1978), p. 60.
- ²³X. Zhao, S. Subrahmanyam, and K. B. Eisenthal, *Chem. Phys. Lett.* **171**, 558 (1990).
- ²⁴X. Xiao, V. Vogel, and Y. R. Shen, *Chem. Phys. Lett.* **163**, 555 (1989).
- ²⁵A. F. H. Ward, *Trans. Faraday Soc.* **42**, 399 (1946).
- ²⁶R. Perea-Carpio, F. Gonzalez-Caballero, J. M. Bruque, and G. Pardo, *J. Colloid Interface Sci.* **95**, 513 (1983).
- ²⁷M. J. Rosen and S. Aronson, *Colloids Surf.* **3**, 201 (1981).
- ²⁸A. M. Posner, J. R. Anderson, and A. E. Alexander, *J. Colloid Sci.* **7**, 623 (1952).