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Determination of pK_a at the air/water interface by second harmonic generation

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We have used second harmonic generation to directly observe chemical changes in a lipid monolayer. We observed that pK_a of *p*-hexadecyl aniline at the air/water interface is 3.6±0.2 versus 5.3±0.1 in the bulk. This fiftyfold increase in acidity is due to the higher free energy of a charged species at the air/water interface, which favors a shift in the equilibrium towards the neutral form.

1. Introduction

The asymmetry in forces at an interface due to the different bulk media on either side of it results in unique chemical and physical properties. The chemical composition, the orientational structure, the dielectric and transport properties are among the important properties of the interface that differ from that of the bulk media. One would expect properties such as chemical equilibria, pH, molecular motions, the rates of chemical reactions and physical relaxation processes to differ from that of the bulk media. Despite its importance and widespread interest it remains difficult to get a handle on the chemistry and physics of interfaces using traditional spectroscopic techniques. This is due to the overwhelmingly larger number of solute and solvent molecules in the bulk that dominate the signal originating from the much smaller number of molecules in the interface. An important way to circumvent this difficulty is the application of the nonlinear optical processes of second harmonic (SHG) and sum frequency generation (SFG) to study interfaces [1]. The key feature of SHG is its intrinsic sensitivity to the non-centrosymmetric interface between two centrosymmetric media. Research in a variety of areas has shown the wide applicability and power of this method [2–6]. In our laboratory we have focused our attention on equilibrium and dynamic chemical and physical processes at the air/water interface. This includes orientational structure and its energetics, surface potential due to a charged monolayer, chemical equilibria and hydrophobic forces and dynamics of isomerization and energy transfer [7,8]. In this paper we report on the investigation of the pK_a of long chain *p*-hexadecyl aniline at the air/water interface using SHG [#1]. In addition to our interest in understanding how the forces at interfaces affect chemical equilibria we note its relevance to pK_a shifts at protein and membrane interfaces and its consequent effect on biological activity [9,10].

In addition to the SH method, application of surface tension and surface potential measurements have been made in the determination of interfacial pK_a values [11,12]. These latter methods also require the use of the Gouy–Chapman model in the determination of the interfacial pK_a values. The surface potential method requires the additional assumption of neglecting the permanent dipole moment contribution to the measured potential difference, which further complicates the problem. To obtain the surface pK_a by the surface tension method requires the further assumptions that the non-electrostatic interactions, as well as the penetration by counter ions into

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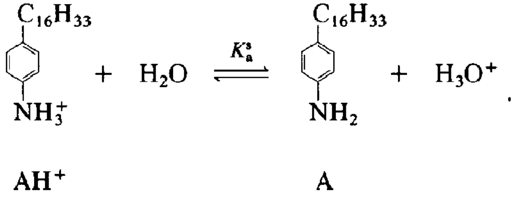
[#1] During the course of this work we have learned that Professor Y.R. Shen's group is also studying pH and pK_a changes at interfaces.

the interface, do not vary with the surface charge density, and thus do not contribute to the change in surface tension with pH. Among the positive features of the SH method is that, as a spectroscopic technique, it can differentiate among the various species by changing the input wavelength(s). This makes it possible to study interfacial equilibria other than equilibria that involve charged species. Aside from the time resolution in pump/probe SH experiments, which permit the measurement of the forward and backward reaction rate constants, the SH technique can be used to study buried surfaces such as liquid/liquid and liquid/solid interfaces, where the use of conventional techniques is not trivial.

2. SH method of surface pK_a measurement

The basic idea of the method used here to obtain the interfacial pK_a is to measure the relative population of the acid and base at the interface using SHG. The remaining quantity that must be obtained to yield surface pK_a is the surface hydronium ion concentration. To do this the surface population of the charged form (acid or base), obtained from the SH measurement is used to calculate the surface potential from the Gouy–Chapman model. This latter model has been shown to be a good model of a charged interface up to high ionic strengths [13,14]. From the surface potential value and the known bulk pH, the surface pH is directly obtained as shown below.

Consider the acid–base equilibrium at the surface for the insoluble material *p*-hexadecyl aniline, a molecule that is insoluble in the bulk in both the acid and base forms;



The equilibrium constant K_a^s for the above process can be expressed as

$$K_a^s = \frac{[A]^s[H_3O^+]^s}{[HA^+]^s} = \frac{[H_3O^+]^s N_A}{N_{HA^+}}, \qquad (1)$$

where s denotes the properties at the surface and N_A and N_{HA^+} are the number densities (molecule/cm^2) of aniline and anilinium at the surface, respectively. Therefore the equation in the logarithmic form can be written as

$$\mathrm{p}K_a^s = \mathrm{pH}^s + \log\frac{N_{HA^+}}{N_A}. \qquad (2)$$

We see from eq. (2) that it is only the ratio of the acid (N_{HA^+}) and base (N_A) forms that are required, not their individual values. If the surface density of the acid plus base forms is a constant at all pH^s values, i.e. $N_0 = N_A + N_{HA^+}$, then the determination of the pK_a^s is greatly simplified. In this latter case the experiments can be carried out using a fixed input wavelength. The signals from the individual species HA$^+$ and A do not have to be obtained, only the total signal is needed. This is the reason why we selected a molecule which was insoluble in the bulk for both the charged acid and neutral base forms. We thus obtain for such a system a total SH electric field

$$E_{tot} = \frac{N_A}{N_0} E_A e^{i\phi} + \frac{N_{HA^+}}{N_0} E_{HA^+}, \qquad (3)$$

where E_A is the SH electric field of aniline at a sufficiently high pH where $N_A = N_0$, similarly E_{HA^+} is the SH electric field of anilinium at sufficiently low pH where $N_{HA^+} = N_0$, and ϕ is the phase difference between SH electric fields of the two species. Using $N_A + N_{HA^+} = N_0$ in eq. (3) we obtain an equation with a single unknown, N_A/N_0 or N_{HA^+}/N_0, since the remaining terms E_{tot}, E_A, E_{HA^+} and ϕ are measured independently using SHG,

$$E_{tot} = \frac{N_A}{N_0} E_A e^{i\phi} + \left(1 - \frac{N_A}{N_0}\right) E_{HA^+}. \qquad (4)$$

We therefore note that the measurement of the SH signal E_{tot} versus bulk pH can be transformed into N_A/N_0 or N_{HA^+}/N_0 versus bulk pH and hence make the measurement of pK_a^s possible.

One last step is required as seen from eq. (2), namely the value of pH^s. The value of pH^s at a charged surface is related to its bulk value, pH^b as follows,

$$\mathrm{pH}^s = \mathrm{pH}^b + \frac{e\Phi}{2.3RT}. \qquad (5)$$

The electric potential Φ is due to the presence of the surface charge density σ which in this case arises from the anilinium ions, $\sigma = eN_{\mathrm{HA}^+}$.

The surface potential Φ can be determined using the Gouy–Chapman model of electrical double layers, which has been found to be a good model of charged interface up to ionic strengths of 2 M [14]. Using this model, the surface potential is given by

$$\Phi = \frac{2kT}{e}\sinh^{-1}\left(eN_{\mathrm{HA}^+}\sqrt{\frac{\pi}{2C\epsilon kT}}\right), \qquad (6)$$

where C is the total number of ions/cm^3 in bulk, ϵ the dielectric constant of the medium, T the temperature in kelvin, k the Boltzmann constant and e the electronic charge.

3. Experimental

An experimental set-up, previously described [3,4], consists of a synchronously pumped dye laser and single photon counting detection system. The fundamental light was at 600 nm and the second harmonic signal at 300 nm was detected.

p-hexadecyl aniline of 97% purity was obtained from Aldrich. It was further purified by recrystallization from ethanol twice. The purity was double checked by NMR and found to be >99%. Hexane of HPLC grade from Aldrich was used to prepare the *p*-hexadecyl aniline solution of known concentration. 1 M HCl solutions were used to make solutions of different pH and 1 M KCl was used to keep the ionic strength constant at 1 M. The water used was double distilled and checked for surface tension. The SHG experiment was performed using a Langmuir trough. A solution of *p*-hexadecyl aniline in hexane was spread over a sub-phase at different pH values. An area of 45 Å^2/molecule was used which corresponds to a surface pressure of 0–7 dyn/cm. The pH of the subphase was measured using a Corning pH meter.

4. Results

As we discussed earlier the experiments require that the acid and base forms of the interfacial molecules be insoluble in the bulk phase. For molecules as large as octadecyl amine, the monolayer dissolves into the subphase when it is ionized as shown by the decrease in surface pressure [15]. To check for the insolubility of *p*-hexadecyl anilinium, *p*-hexadecyl aniline was spread between two barriers in a Langmuir trough and the surface tension both outside and inside was monitored for four hours. The surface tension value remained constant throughout; thus indicating that the hexadecyl anilinium is not soluble in the 1 M HCl subphase.

The surface pressure-area (Π–A) phase diagram of *p*-hexadecyl aniline was obtained at high and low pH corresponding to neutral and positively charged species respectively. The results are displayed in fig. 1. The phase diagram shows that the condensed phase exists below 40 Å^2/molecule at high pH and 60 Å^2/molecule at low pH. The second harmonic electric field as a function of bulk pH showed a sharp change between pH 2–4 and flattens out above pH 4.5 and also below pH 1.0 (fig. 2). The phase difference ϕ between the second harmonic electric field from aniline and the anilinium forms was found to be the same by an interference measurement described in detail elsewhere [4]. The midpoint where the surface number density of aniline and anilinium are equal was determined to be at a bulk pH of 2.6 ± 0.2.

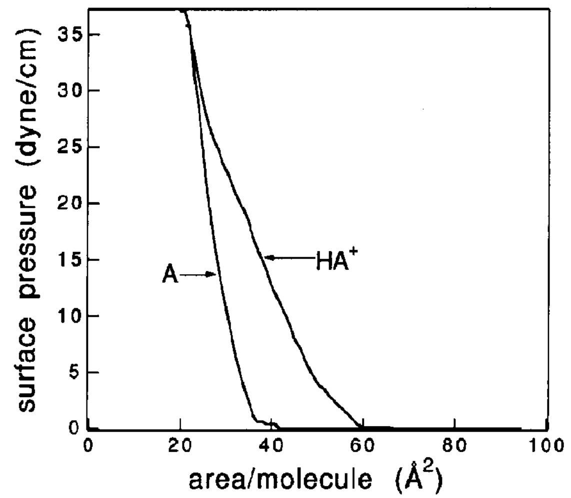


Fig. 1. Surface pressure Π (dyn/cm) versus area (Å^2/molecule) phase diagram of *p*-hexadecyl aniline in acidic and basic solution at constant ionic strength of 1 M.

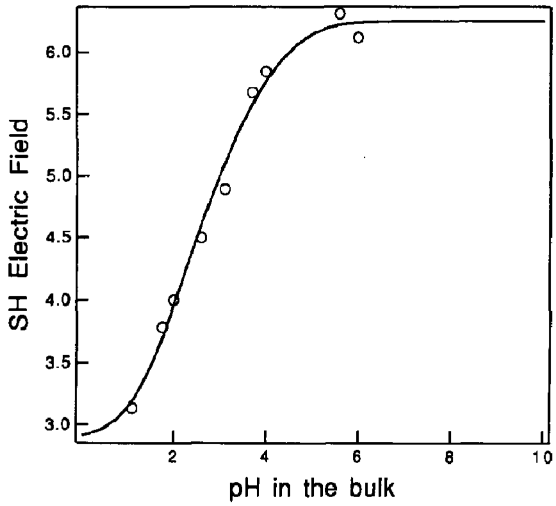


Fig. 2. SH electric field as a function of bulk pH at constant ionic strength of 1 M. Solid curve represents the fit using the Gouy–Chapman model.

To obtain the surface electrostatic potential of the density of anilinium ions N_{HA^+} is required. From the measurement of the SH signal N_{HA^+}/N_0 is obtained. N_0 is known from the amount of hexadecyl aniline spread on the surface to give an area per molecule of 45 Å^2. The surface pH^s value at the midpoint is found to be 3.6±0.2, which using eq. (2) yields a surface pK_a^s of 3.6±0.2. The same value is obtained in an alternative way as outlined in section 5. In the bulk we have determined by potentiometric titration of the pK_a values of ethyl, propyl and butyl aniline at a constant ionic strength of 1 M. The same pK_a value of 5.3±0.1 was found for all the three, indicating that the pK_a is not dependent on the chain length.

5. Discussion

The Π–A phase diagram (fig. 1) of *p*-hexadecyl aniline shows some important features. The curve corresponding to the monolayer on 1 M HCl subphase is in a more expanded state. This is expected since the aniline group is protonated to become anilinium, which exerts an electrostatic repulsion in the monolayer. The phase diagram also shows that the condensed phase exists below 40 and 60 Å^2 for the aniline and anilinium, respectively. The flat region of the phase diagram represents the coexistence of gas and condensed phases. The SH experiment was performed in the condensed phase region of the phase diagram for both the hexadecyl aniline and hexadecyl anilinium forms.

In the SHG experiment as the bulk pH is varied, the relative amounts of hexadecyl aniline and hexadecyl anilinium changes as shown in fig. 2. The species at high pH is neutral aniline and that at low pH is the positively charged anilinium form. The curve of SH electric field as a function of bulk pH shows that the signal from the anilinium is lower than that from neutral aniline. A plausible reason for this is that the lone pair electrons on the nitrogen are not available for delocalization due to the presence of positive charge, which thereby reduces the molecular hyperpolarizability of the hexadecyl anilinium.

An alternative way to obtain the pK_a^s value, other than finding the pH^s at the midpoint as we did earlier, is to fit the data to eqs. (2)–(6) using a least square fitting program. The resulting fit is shown as a solid line in fig. 2. The value of the pK_a obtained in this way is 3.6±0.2. The good fit is also a further indication that the Gouy–Chapman model is a good approximation for these experiments. Since the pK_a in the bulk is the same for ethyl, propyl and butyl aniline, which is consistent with the predictions of the Hammett equation [16], we infer that the pK_a of hexadecyl aniline, if it could be dissolved in the bulk water would also be 5.3. Thus the pK_a at the interface is lower than in the bulk by 1.7, i.e. the acid ionization constant K_a of anilinium at the surface is fifty times as high as the value in bulk. This shows that anilinium is more acidic at the interface. This is not surprising since a charge at an air/water interface increases the surface free energy. The equilibrium at the interface would therefore favor the neutral form which in this case is the basic form of the molecule.

Some early measurements of pK_a of long chain acids and amines using surface pressure and surface potential methods [11,12], show pK_a shifts around 0.5, favoring the neutral species. Our results show a pK_a shift in the same direction but with a larger magnitude. The reason for the larger shift may be related to the difference in molecular structure and solvation energy between the aromatic aniline and the aliphatic acid or base.

6. Conclusion

It has been shown that second harmonic generation is a direct method to observe chemical changes in the *p*-hexadecyl aniline monolayer. We have found that *p*-hexadecyl aniline at the air/water interface has a pK_a value of 3.6 ± 0.2. The pK_a value of alkyl anilinium in bulk water is 5.3 ± 0.1, indicating that the acidity of the anilinium species is fifty times greater at the interface than in the bulk. The increased acidity arises from the higher free energy of a charged species at the air/water interface, which indicates that the anilinium acid–base equilibrium is shifted towards the energetically more favorable neutral form at the interface. This is direct evidence that the chemical properties such as equilibrium constants and pH at the surface can differ significantly from that in the bulk.

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