New method for determination of surface pK_a using second harmonic generation

Xiaolin Zhao, Shaowei Ong, Hongfei Wang and Kenneth B. Eisenthal [1]
Department of Chemistry, Columbia University, New York, NY 10027, USA

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A new method to determine the pK_a of chemical species at aqueous insulating interfaces is based on the discovery that the interface potential is linearly proportional to the measured second harmonic electric field. The proportionality constant is the effective third-order susceptibility and is the same for all aqueous interfaces studied, which has its origin in the polarization of bulk water induced by the charged form of the acid or base at the interface. We have determined that $CH_3(CH_2)_{21}NH_3^+$ at the air/water interface has a pK_a of 9.9 ± 0.2 versus 10.6 in bulk water.

1. Introduction

The asymmetry in forces at an interface due to the different bulk media on either side of it results in its unique chemical and physical properties. One would expect equilibrium properties such as chemical equilibrium constants, pH, and dynamic properties such as molecular motions, energy relaxation and chemical reactions 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. The reason is that the overwhelmingly large number of solute and solvent molecules in the bulk most often dominates the signal originating from the surface. One way to circumvent this difficulty is the application of the interface selective nonlinear optical processes of second harmonic generation (SHG) and sum frequency generation (SFG) [1]. The key feature of these nonlinear techniques is their intrinsic sensitivity to the noncentrosymmetric interface between two centrosymmetric media [2–5].

2. Method based on the nonlinear susceptibility $\chi^{(2)}$

In past studies we have used SHG to determine the surface pK_a of long chain *p*-hexadecyl aniline $[CH_3(CH_2)_{15}C_6H_4NH_2]$ at the air/water interface [6]. The basic idea of the method used in these surface pK_a studies was to measure the relative population of the acid to base forms at the interface using SHG, and to obtain the surface hydronium ion concentration by combining the interface charge density (acid or base forms) with a model of the charged interface region [6,7]. These quantities are related to the interface pK_a for the acid–base reaction,

$$HA^+ + H_2O \rightleftharpoons A + H_3O^+ \qquad (1)$$

by

$$pK_a = pH_s + \log\left(\frac{[HA^+]}{[A]}\right). \qquad (2)$$

The SH measurements yield the ratio of HA^+ to A, i.e. the ratio of acid to base populations at the interface. From the population of the charged form at the surface the surface potential is calculated using the Gouy–Chapman model of the diffuse double layer. This model has shown to be valid in the range of these experimental studies [8,9]. From the surface potential value and the known bulk pH_b, the surface pH_s is directly obtained using the Boltzmann relation,

$$pH_s = pH_b + \frac{e\Phi(0)}{2.3\,kT}. \qquad (3)$$

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[1] To whom correspondence should be addressed.

The pK_a was then readily found using eq. (2). We will refer to the above method as the $\chi^{(2)}$ method because the source of the SH signal is the interface nonlinear susceptibility $\chi^{(2)}$, which is proportional to the population of the acid and base forms of the monolayer.

3. New method based on $\chi^{(3)}$ due to the polarization of the bulk water molecules by the charged interface

Although the $\chi^{(2)}$ method has been successfully used to determine the pK_a of long chain molecules at air/water interfaces, it requires that the acid–base moieties have $\chi^{(2)}$ values greater than that of the background water $\chi^{(2)}$. For many aromatic acids and bases this is not a problem since their large nonlinear polarizabilities yield large signals, especially when compared with the weak SH signal from a neat water/air interface. However for many saturated organic and inorganic acids and bases the magnitude of their $\chi^{(2)}$ values are only comparable to or smaller than that of the interfacial water. For this reason we propose a different method for measuring the pK_a of interfacial species that have small $\chi^{(2)}$ nonlinearities. The idea for this model is based on our discovery that the electric field of various charged interfaces polarizes the bulk water molecules and generates a significant SH signal by a third-order process, $\chi^{(3)}$ [10,11]. We find that the magnitude of the signal from the $\chi^{(3)}$ process is comparable to or larger than the total $\chi^{(2)}$ contributions in the nonaromatic water interfaces studied. This has been found to be the case for the solid silica (quartz)/water interface which becomes negatively charged at intermediate and high pH values, ($-SiO^-$), the negatively charged monolayer $CH_3(CH_2)_{21}SO_3^-K^+$ and the positively charged monolayer $CH_3(CH_2)_{21}N^+(CH_3)_3Br^-$ at the air/water interface [10,11]. We found in these studies that the SH electric field can be expressed as

$$E_{2\omega}=A+B\Phi(0)\,, \tag{4}$$

where A is the total effective $\chi^{(2)}$ contribution from water and the acid and base species, B is the effective $\chi^{(3)}$ due to the polarized water, and $\Phi(0)$ is the electric potential at the interface. It is to be noted that the relative sign of A and $B\Phi(0)$, i.e. whether the phase is 0° or 180°, affects the magnitude of $E_{2\omega}$. We shall discuss the molecular basis of their phases at a later point. The SH field $E_{2\omega}$ is a normalized quantity having been divided by the SH field obtained from an air/neat water interface. The key discovery was that the SH field was not only linearly proportional to the interface potential $\Phi(0)$ as shown in eq. (4) but that the proportionality constant B has the same value for all of the water interfaces that we have studied. This constant is therefore proposed to be characteristic of liquid water interfaces. From eq. (4) we see that the interface potential can be obtained from a determination of the value of A, use of the universal water constant B and measurement of $E_{2\omega}$. This provides an alternative way to measure interface pK_a values as illustrated in the following discussion. The equilibrium constant K_a for the acid–base reaction given in eq. (1) can be written as

$$\begin{aligned} K_a &= \frac{f}{1-f}[H_3O^+]_s \\ &= \frac{f}{1-f}[H_3O^+]_b \exp\left(\frac{-e\Phi(0)}{kT}\right), \end{aligned} \tag{5}$$

where f is the molar fraction of the neutral form A, $[H_3O^+]_b$ is the bulk hydronium ion concentration and $\Phi(0)$ is the electric potential at the charge plane. From eq. (5) we see that to obtain the surface pK_a it is necessary to measure f and $\Phi(0)$. According to eq. (4), we can use SHG to measure $\Phi(0)$ if A and B can be evaluated. Since the B value is universal for aqueous interfaces [10,11] and is obtained from any aqueous interface, we have to determine only A and $\Phi(0)$. The value of A is given by

$$A=(1-f)A_{\mathrm{acid}}+fA_{\mathrm{base}}+A_{\mathrm{water}}\,, \tag{6}$$

where A_{water}, A_{acid} and A_{base} are the effective $\chi^{(2)}$ values of water, acid and base species, respectively. The summed quantities $A_{\mathrm{acid}}+A_{\mathrm{water}}$ and $A_{\mathrm{base}}+A_{\mathrm{water}}$ are obtained from SH measurements on the completely charged monolayer ($f=0$) and the neutral monolayer ($f=1$), respectively. From eq. (6) we see that A can then be expressed in terms of the single unknown quantity f. It is then possible to fit the whole $E_{2\omega}$ versus bulk pH curve with the surface pK_a as the fitting parameter. It is interesting to note that for the nonresonant monolayers we have found that the total $\chi^{(2)}$ is comparable to that of neat water, thus indicating the dominant contribution of water molecules to $\chi^{(2)}$. We have seen that this is the case for the positively charged monolayer $CH_3(CH_2)_{21}N^+(CH_3)_3Br^-$ and the negatively charged monolayer $CH_3(CH_2)_{21}SO_3^-K^+$ at air/water interfaces.

At the air/water interface it has been demonstrated that the Gouy–Chapman electric double layer model is valid up to a 2M total 1:1 electrolyte concentration [9]. For this model, the electric potential at the charge plane $\Phi(0)$ is related to the interfacial charge density and total electrolyte concentration,

$$\Phi(0)=\frac{2kT}{ze}\sinh^{-1}\left(\sigma\sqrt{\frac{\pi}{2C\epsilon kT}}\right), \qquad (7)$$

where σ is the charge density at the interface, e is the electronic charge, ϵ is the bulk dielectric constant, C is the total bulk electrolyte concentration in units of number/cm^3, and z is the sign of the charged monolayer. In the case of an ionizable HA^+ insoluble monolayer, the surface charge density σ is directly related to the ionization degree f by $\sigma=(1-f)\sigma_{max}$, where σ_{max} is the surface charge when the monolayer is completely ionized. This later quantity is known for a given spread monolayer density. The determination of $\Phi(0)$ from SH measurements is used to obtain the ionization degree f from eq. (7). The pK_a is then readily found using eq. (5). We will refer to the above method for surface pK_a determination as the $\chi^{(3)}$ method.

4. Interface pK_a of $CH_3(CH_2)_{21}NH_2$

In this Letter, we report on the use of the $\chi^{(3)}$ method to determine the surface pK_a of the insoluble monolayer docosyl amine $CH_3(CH_2)_{21}NH_2$, which we refer to as $C_{22}NH_2$.

4.1. Experimental

The $C_{22}NH_2$ was synthesized from $CH_3(CH_2)_{20}CN$ by reduction with $LiAlH_4$ in anhydrous ether. The product was then passed through a silica column and the main component was identified using mass spectra and NMR. It was then re-crystallized from ethanol at least four times before being used. The $C_{22}NH_2$ was spread at a fixed area per molecule of 30 Å^2 on an aqueous solution containing KCl, KOH and HCl. The pH of the aqueous solution was measured with a Corning pH meter. The SH signal from the sample was normalized to the SH signal from an air/neat water interface. A fixed total electrolyte concentration of 10 mM was used in all of the systems studied.

4.2. Results and discussion

Fig. 1 shows the SH electric field for the ionizable monolayer C22 amine as a function of the bulk pH at 30 Å^2 at a total electrolyte concentration of 10 mM. It is seen that the SH electric field increases as the bulk pH decreases. The ionizable monolayer C22 amine becomes progressively charged as the bulk pH is decreased, which therefore increases the surface potential. If the signs of the A and $B\Phi$ terms appearing in eq. (4) are the same then the SH signal should increase as the potential increases, i.e. as the bulk pH decreases. This is the observed dependence as seen in fig. 1. The molecular basis for A and $B\Phi(0)$ having the same sign follows from the interference

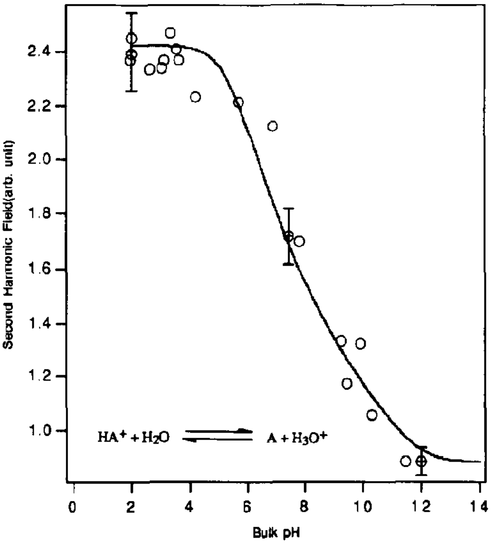

Fig. 1. SH electric field which is a function of the neutral and charged interface population of $CH_3(CH_2)_{21}NH_2$ versus bulk pH at a 30 Å^2 monolayer coverage and a constant 10 mM electrolyte concentration. The dots are the experimental points and the solid line is the theoretical fit to the $\chi^{(3)}$ mechanism. The surface pK_a is found to be 9.9 ± 0.2 compared with the bulk amine pK_a value of 10.6.

that the preferred alignment of the water molecules at the interface, due to forces other than that of the electrostatic field, is one where the permanent water dipole moments point toward the bulk, i.e. oxygen is up [12]. Thus the field-independent term A (the effective $\chi^{(2)}$) can be viewed as resulting from this preferred orientation of water at the interface. For the positively charged monolayer $C_{22}NH_3^+$ the $B\Phi(0)$ term favors an alignment of the bulk water molecules with the oxygen directed towards the positively charged interface. Thus the $\chi^{(2)}$ contribution from the interface water molecules and the $\chi^{(3)}$ contribution which is electric field dependent and constructively. Support for this interpretation is found in our results on a negatively charged monolayer at the air/water interface [10], where the prediction one would make based on this model of the $\chi^{(3)}$ contribution is that the water molecules would prefer to be oriented with the protons pointing up toward the negatively charged monolayer. Hence the water molecules would have their oxygens pointing down (permanent dipole moments up) for the negatively charged monolayer, which is opposite to their preferred orientation for the positively charged monolayer. Since $\chi^{(2)}$ comes from water having their oxygens preferentially up and $\chi^{(3)}$ from the oxygens preferentially down for the negative monolayer we predict and find that the SH signal decreases as the negative charge density increases [11]. This molecular interpretation is consistent with eq. (4), where it is seen that the A and $B\Phi(0)$ terms have the same sign when $\Phi(0)$ is positive, i.e. for the positively charged monolayer, and have the opposite sign when $\Phi(0)$ is negative, i.e. for the negatively charged monolayer.

The surface pK_a of the ionizable monolayer C22 amine was determined by the above $\chi^{(3)}$ method to be 9.9 ± 0.2. It is satisfying that this value is the same as the pK_a value of C19 amine obtained from surface potential measurements [13]. This assures us of the effectiveness of this new spectroscopic method to measure the surface pK_a not only at air/water interfaces but also at buried interfaces such as insulating solid/aqueous interfaces [10]. In the bulk solution hexyl, octyl and other small chain alkyl amines have a bulk pK_a of 10.6 [14]. Assuming that the bulk pK_a of shorter chain amines and docosyl amine are the same we conclude that the pK_a of C22 amine at the interface is lower than in the bulk by 0.7 units, indicating that $C_{22}NH_3^+$ is more acidic by a factor of five at the interface. The increased acidity is due to the higher interface free energy of the charged $C_{22}NH_3^+$ acid relative to the neutral $C_{22}NH_2$ base. The increased acidity is consistent with the studies of the long chain aniline [15], hexadecyl aniline [7], where it was found that the pK_a at the air/water interface is 3.6, compared to a pK_a of 5.3 in the bulk.

5. Conclusions

In conclusion we have demonstrated the feasibility of determining the pK_a at aqueous insulating interfaces by a new and versatile method that is based on the determination of the interface electric potential by SH measurements. The origin of the electric potential is the charged form of the monolayer (acid or base) which polarizes the bulk water molecules and thereby generates a second harmonic signal. The second harmonic field is proportional to the surface potential, which in turn depends on the charge population, i.e. the degree of acid–base ionization. This method can be used to measure the interface pK_a for any insulating aqueous interface since the proportionality constant (the effective $\chi^{(3)}$) between the measured second harmonic field and the surface potential is universal for aqueous interfaces. Using the $\chi^{(3)}$ method to determine the surface pK_a, we have found that $CH_3(CH_2)_{21}NH_3^+$ at the air/water interface has a pK_a of 9.9 ± 0.2, while the pK_a of alkyl amine in bulk water is 10.6. This result shows that the acidity of $C_{22}NH_3^+$ is five 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 acid–base equilibrium in eq. (1) is shifted towards the energetically more favorable neutral form at the interface. This result is consistent with our previous studies on hexadecyl aniline. An examination of the pK_a dependence of the ionic strength and surface density is in progress and will appear in a separate publication.

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