Second Harmonic Generation Studies of Adsorption at a Liquid–Liquid Electrochemical Interface

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The technique of optical second harmonic generation (SHG) is applied to the measurement of molecular adsorption at the interface between two immiscible electrolyte solutions (ITIES). The resonant second harmonic response from 2-(n-octadecylamino)naphthalene-6-sulfonate (ONS) is used in conjunction with interfacial tension measurements to optically determine the relative surface coverage of the anionic surfactant molecule at a charged water–dichloroethane interface. At a pH of 9, ONS adsorption occurs at all potentials positive of the potential of zero charge. The potential-dependent adsorption of ONS can be described by a Frumkin isotherm with a free energy of adsorption that varies linearly with applied potential. The potential dependence of the SHG from the interface provides important information on the position of the adsorbed ONS molecules with respect to the ITIES. At a pH of 3, both the anionic form of ONS and the protonated zwitterionic form of ONS are present at the liquid–liquid interface. At very positive potentials, the anionic ONS at the interface undergoes a field-dependent conversion to the zwitterionic form.

Introduction

The transport of chemical species across liquid–liquid interfaces is central to the functioning of many complex heterogeneous chemical systems, both biological and synthetic. The mechanism of this macroscopic transport is primarily controlled by the detailed molecular structure of the interface. Whether dealing with elaborate biological molecular architectures or with simple two-phase systems, a complete understanding of the adsorption, orientation, and organization of both solute and solvent molecules within the interfacial region is the first step in the elucidation of the mechanism for the movement of molecules through the interface. One type of liquid–liquid interface which has been of interest since the turn of the century is the interface between two immiscible electrolyte solutions (ITIES).[1] In the past 20 years a great deal of improvement has been made in the measurement of molecular adsorption and organization at the ITIES.[1–4] The double-layer structure of the ITIES is similar (but not identical) to the much-studied case of the solid–electrolyte surface and has been inferred from a number of elegant interfacial tension and electrochemical measurements of the interface.[1–8] However, to date there have been a limited number of spectroscopic studies on the adsorption of both soluble and insoluble monolayers at liquid–liquid interfaces[9–11] and exceedingly few spectroscopic studies of molecular adsorption at the ITIES.

A major problem in the spectroscopic study of the liquid–liquid interface is the separation of the optical response of the interface from the optical response of the adjacent bulk media. This problem is particularly difficult given the fact that the light employed in spectroscopic studies normally possesses a wavelength hundreds or thousands of times greater than typical interfacial distances. Optical second harmonic generation (SHG) is an inherently surface-sensitive technique for studying the interface between two centrosymmetric media that overcomes this distance disparity.[12] The second harmonic process converts two photons of frequency ω to a single photon of frequency 2ω. In the electric dipole approximation, this process requires a noncentrosymmetric medium. For the interface between two centrosymmetric media, such as the interface between two liquids, only the molecules which participate in the asymmetry of the interface will contribute to the SHG. For systems where the SHG from the interface is dominated by resonant molecular contributions to the surface nonlinear susceptibility, the SHG response can be directly related to the relative surface coverage of an adsorbed molecule. With a demonstrated submonolayer sensitivity, a nearly instantaneous

optical response time, and the ability to easily discriminate between surface species and species in the adjacent bulk media, SHG has been employed extensively at a wide variety of surfaces.[10,13–20]

In this paper we report the first application of surface SHG measurements to the study of an electrochemical liquid–liquid interface. Resonant SHG measurements are used to monitor the adsorption of the surfactant molecule 2-(n-octadecylamino)-naphthalene-6-sulfonate (ONS) at a water/1,2-dichloroethane interface. The relative surface coverage of the anionic surfactant molecule as a function of applied potential is determined from the surface SHG signal. The results of these SHG experiments are used to provide new information complementary to that obtained from measurements of the interfacial tension of the ITIES. At a pH of 9, anionic ONS adsorption is found to occur at all potentials positive of the potential of zero charge (pzc). The adsorption of ONS can be described by a Frumkin isotherm with a free energy of adsorption that increases with the applied potential and with the surface coverage of ONS. At a pH of 3, the combination of SHG and interfacial tension measurements is used to determine that both the anionic and the zwitterionic forms of ONS are present at the water–dichloroethane interface. At potentials very positive of the pzc, the anionic ONS at the interface undergoes a field-dependent protonation of its amino group to form the zwitterion.

Experimental Considerations

Millipore-filtered water and SpectrAR grade (Mallinckrodt) 1,2-dichloroethane obtained from Baxter Scientific were used for the aqueous and organic electrolyte solutions. Both 0.1 M potassium chloride and 25 mM tetrabutylammonium chloride (TBACl) were employed as supporting electrolytes in the two aqueous phases, and 1 mM tetrabutylammonium tetraphenyl-borate (TBATPB) was used as a supporting electrolyte in the dichloroethane. For the pH-dependent experiments, 25 mM Na_2-HPO_4 and H_3PO_4 were used to control the pH of the aqueous phase. All of the salts used here were obtained from Fluka Chemical Corp. (puriss grade) and were used as received. The surfactant ONS was obtained from Molecular Probes and was stored desiccated at −20 °C. The aqueous and organic phases were preequilibrated prior to use by shaking in a separatory funnel. For the surfactant adsorption measurements, 25 mL of a 20 μm ONS aqueous solution was preequilibrated with 25 mL of the dichloroethane solution. The ONS partitions between the aqueous and organic phases during the preequilibration process. From

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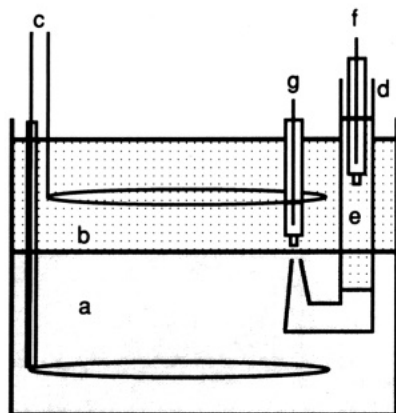
Figure 1. Electrochemical cell used for interfacial tension measurements and SHG measurements of the ITIES. The components of the cell are labeled as follows: (a) dichloroethane solution, (b) aqueous solution, (c) platinum counter electrode loops, (d) Luggin capillary for the organic-phase reference electrode, (e) aqueous-phase filling solution for the organic-phase Luggin capillary, (f) and (g) Ag/AgCl reference electrodes.

UV–vis absorption experiments, the organic-phase ONS concentration was determined to be approximately 2 μM. All of the glassware used in these experiments, including the electrochemical cell, was thoroughly cleaned in 10% Microcleaner solution, Millipore-filtered water, and Nochromix/concentrated H_2SO_4 solution and was finally rinsed with Millipore-filtered water.

A four-electrode potentiostat was used to control the potential and measure the current across the liquid–liquid interface. The potentiostat was constructed in house following the design of Samec.[21] Two platinum (DF Goldsmith) loops were used as the counter electrodes in the aqueous and organic phases, and two Ag/AgCl electrodes were used as reference electrodes and were placed in Luggin capillaries positioned near the ITIES to minimize *IR* drop problems. As in previous ITIES measurements,[22] the Luggin capillary in the organic phase was half-filled with dichloroethane solution and topped off with a 25 mM TBACl aqueous solution in which the organic-phase Ag/AgCl electrode resided. The electrochemical system can be described as follows:

Ag|AgCl|25 mM TBACl in H_2O|1 mM TBATPB in

$C_2H_4Cl_2$|0.1 M KCl in H_2O|AgCl|Ag
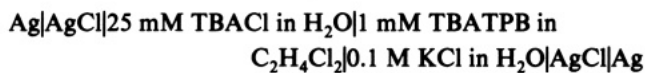
The third interface from the right is the liquid–liquid interface of interest. This cell is shown pictorially in Figure 1. The potential applied between the aqueous (w) and organic (o) phases will be denoted as $E_w - E_o$, following the conventions of previous authors.[23]

Interfacial tension measurements were made by the Wilhelmy method using a NIMA Technologies electronic balance and a Teflon plate.[11a] Potential-dependent interfacial tension measurements from the bare (no ONS present in solution) interface were obtained in real time with the Wilhelmy plate. For the surfactant solutions, the entire electrochemical system was allowed to sit at the open circuit potential for at least 1 h prior to the start of an experiment in order to permit the ONS adsorbed at the ITIES to reach equilibrium. The interfacial tension measurements were then made with the Wilhelmy plate detachment method. The applied potential was varied slowly between 0.2 and 0.5 V in 10-mV increments at 6-min intervals. This nominally slow potential variation was selected in order to permit sufficient time for the adsorbed surfactant molecules to reach equilibrium while preventing significant contamination of the interface from the passage of small currents. Interfacial tension measurements made in this manner can be assumed to have a precision of 0.1 dyn/cm and an accuracy of 0.4 dyn/cm.

The SHG measurements of ONS adsorption were made with the 605-nm output of a synchronously-pumped, cavity-dumped dye laser/mode-locked Nd:YAG laser system (Coherent Model 702) with a 3-ps pulse width and 3.8-MHz repetition rate. The
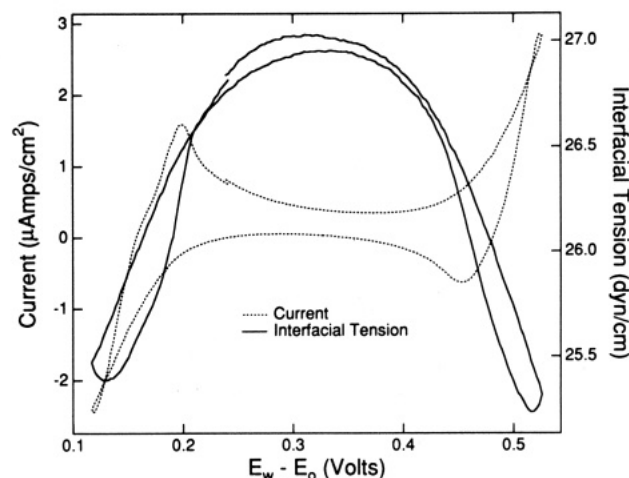
Figure 2. Interfacial tension (—) and cyclic voltammogram (⋯) for the bare interface between water and 1,2-dichloroethane as a function of the applied potential, $E_w - E_o$. The aqueous phase contained 0.1 M KCl and the 1,2-dichloroethane contained 1 mM TBATPB. The scan rate was 1 mV/s.

laser light was focused onto the water–dichloroethane interface at an incident angle of 45°. The laser system, optics, and detection electronics were identical to those used previously,[17,24] except that gated single-photon counting electronics were used in the experiments reported here to reduce the dark count level to below 1 count/s. The SHG originating at the water–air interface can be neglected since the incident laser light was not focused onto this interface; in addition, the reflectivity of the water–dichloroethane interface for both the fundamental and second harmonic wavelengths is extremely low ($\approx$0.3%). The SHG measurements were obtained with a fundamental input polarization of 45° and a second harmonic output polarization of 90° (s-polarized light). This polarization combination resulted in the largest SHG signal from the interface. SHG data were also obtained with p-polarized input/p-polarized output and s-polarized input/p-polarized output combinations. These additional experiments yielded the same potential-dependent curves to within 15–20%.

Results and Discussion

The cyclic voltammogram (CV) showing the cell current versus applied potential for a water–dichloroethane interface with no surfactant present in solution is shown in Figure 2 (dashed line). Ion transfer across the interface limits the potential window from approximately 0.200 to 0.500 V. Interfacial tension measurements at the ITIES were made concurrently with the CV; these results are also shown in Figure 2 (solid line). The change in interfacial tension (dγ) with applied potential and surfactant activity in the organic phase (a_{ONS}) is governed by the following simplified form of the Gibbs equation[23]

$$-d\gamma = q_w\, d(E_w - E_o) + \Gamma_{ONS}RT\, d\ln(a_{ONS}) \qquad (1)$$

where q_w is the excess surface charge density on the water side of the interface and Γ_{ONS} is the surface concentration of the adsorbed ONS. As seen in Figure 2, the interfacial tension in the absence of adsorption varies in a parabolic fashion. The hysteresis in the interfacial tension measurements is due to ion transfer across the interface. At an applied potential of approximately 0.320 V, the slope $-d\gamma/dE$ is zero and there is no excess surface charge on the interface, as described by eq 1. This potential of zero charge (pzc) has been measured previously to be 0.300 V.[25] Capacitance measurements have shown that at this potential there is virtually no oriented dipole layer at the interface, and therefore the inner or Galvani potentials of the water and organic phases (ϕ_w and ϕ_o respectively) are equal.[26] The SHG measured from the bare ITIES (no ONS present in solution) was less than 5 counts/s at all potentials.
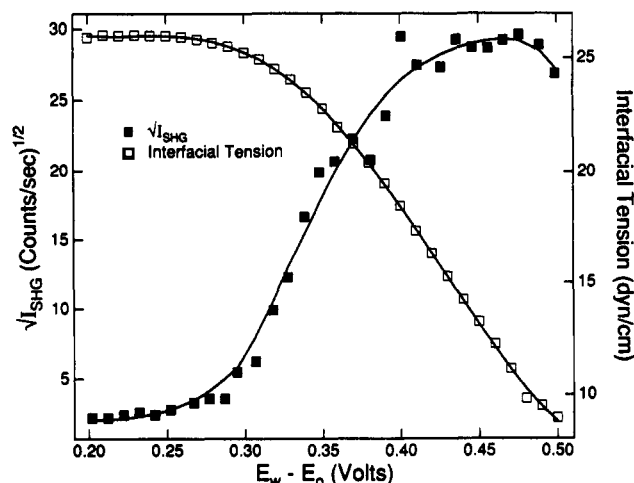
Figure 3. Interfacial tension (open squares) and the square root of the SHG intensity, $\sqrt{I_{SHG}}$ (filled squares), as a function of the applied potential, $E_w - E_o$, for 20 μM ONS, 50 mM KCl, and 25 mM Na$_2$HPO$_4$ in water (pH = 9) and 1 mM TBATPB in 1,2-dichloroethane. The data points were collected from 0.2 to 0.5 V at 6-min intervals.

When the 20 μM solution of ONS was used with the aqueous pH fixed at 9, the CV was virtually unchanged but the interfacial tension was altered significantly, as shown in Figure 3 (open squares). The changes observed in the interfacial tension are similar to those observed previously for charged surfactants at the ITIES.[23] For the ONS system reported here, the pzc is shifted to approximately 0.250 V. At potentials positive of the pzc, the interfacial tension decreases monotonically to 9.0 dyn/cm. Both effects are indicative of the adsorption of an anionic surfactant from the organic phase at positive potentials.

Concurrently with the large drop in interfacial tension at the ITIES, a large increase in the surface SHG signal at 302.5 nm is observed. The square root of the SHG signal, $\sqrt{I_{SHG}}$, is plotted in Figure 3 (filled squares) along with the interfacial tension measurements. The SHG signal is almost zero at potentials negative of the pzc and reaches a maximum level of 900 counts/s above 0.450 V. This surface SHG signal is a molecular SHG signal due to the presence of an oriented monolayer of ONS at the interface. Information on the average orientation of the molecules at the interface can be obtained from the polarization dependence of the surface SHG signal[17,20,27] and will be described in detail in a subsequent paper. For the purposes of this paper, it is only important to note that the polarization dependence of the surface SHG signal did not change significantly as a function of applied potential or pH. Since the surface SHG signal is proportional to the square of the surface concentration of ONS,[12] the square root of the SHG intensity, $\sqrt{I_{SHG}}$, can be used as an optical measurement of the relative surface coverage θ by assuming $\theta = 1$ at 0.470 V and $\theta = 0$ at 0.200 V. The surface density of ONS at 0.470 V can be estimated from the observed interfacial tension via the Gibbs equation (eq 1) and is approximately 1 × 10^{14} molecules/cm^2.

Both the interfacial tension measurements and the SHG signal from the ITIES demonstrate that there is a potential-dependent adsorption of ONS anions to the interface as depicted in Figure 4. The relative surface coverage, θ, determined from the SHG data in Figure 3 can be used to quantify the relation between the applied potential and the extent of ONS adsorption. This relation is written in the general form

$$\ln\left(\frac{\theta}{1-\theta}\right) = \ln\left(\frac{a_{ONS}}{a_{org}}\right) - \frac{\Delta G^0}{RT} + \frac{bF}{RT}(\phi_w - \phi_o) - \frac{c\theta}{RT} \quad (2)$$

Equation 2 is a Frumkin isotherm where the free energy of adsorption depends upon the potential difference across the interface $\phi_w - \phi_o$. In eq 2, a_{ONS} is the activity of ONS in the organic phase (2 μM), a_{org} is the activity of the organic solvent
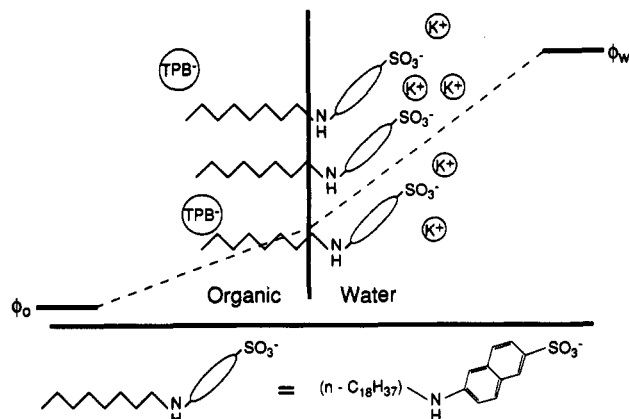
**Figure 4.** Proposed model for ONS adsorption at the ITIES at potentials positive of the pzc ($\phi_w > \phi_o$). The naphthalene head group of ONS is found to lie near the aqueous side of the interface as described in the text. A simple diagram of the potential drop across the liquid–liquid interface is also presented with the Galvani potentials in the organic and aqueous phases shown as ϕ_o and ϕ_w, respectively.
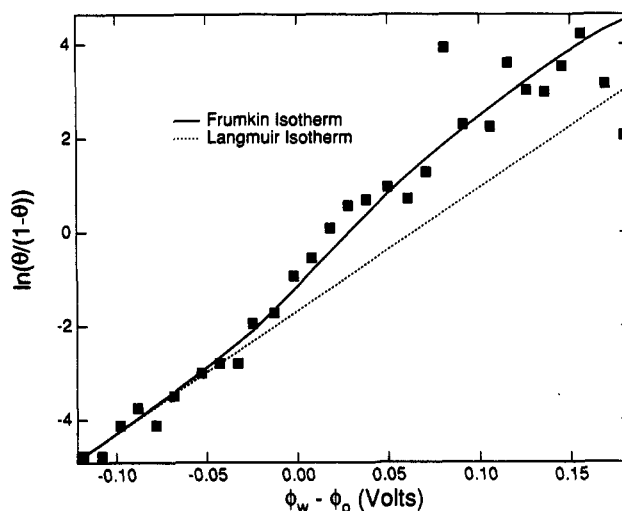
Figure 5. Plot of ln ($\theta/(1-\theta)$) (filled squares) vs applied potential, where θ is the optically determined relative surface coverage of ONS at pH = 9. The x-axis ($\phi_w - \phi_o$) was obtained by subtracting 0.320 V (the point at which $\phi_w = \phi_o$) from $E_w - E_o$. The dashed line corresponds to a Langmuir isotherm with a free energy of adsorption that varies linearly with $E_w - E_o$. The solid line is a fit of the data to a Frumkin isotherm as described by eq 2 in the text.

(12.6 M), ΔG^0 is the free energy of adsorption from the organic phase to the interface at the potential where $\phi_w = \phi_o$ (0.320 V), b is the portion of the applied potential felt by the ONS, and c is a Frumkin interaction parameter. (c/RT is equivalent to g' in the notation of Bard and Faulkner.[28]) If $c = 0$, the Frumkin isotherm reduces to a simple Langmuir isotherm.

A plot of ln ($\theta/(1-\theta)$) versus $\phi_w - \phi_o$ is shown in Figure 5. These data can be fit to eq 2 (the solid line in Figure 5). At low surface coverages the last term in eq 2 becomes negligible, and ln ($\theta/(1-\theta)$) becomes linear with potential as predicted from a Langmuir adsorption isotherm (the dotted line). The slope and intercept of this line yield values of 0.67 ± 0.05 for b and a value of −35 ± 1 kJ/mol for ΔG^0. The strength of adsorption for ONS at the water–dichloroethane interface reported here is comparable to that observed previously for similar anionic surfactants at similar interfaces[11,18b] and is comparable to the measured free energy of transfer across the water–dichloroethane interface for other large organic anions.[1,29] The value of b provides information as to where the naphthalene head group of ONS is positioned in relation to the interface. If the ONS head group protrudes far into the aqueous phase, then b will be close to a value of one. If, on the other hand, the ONS does not penetrate into the aqueous layer but remains at the outer Helmholtz plane of the organic
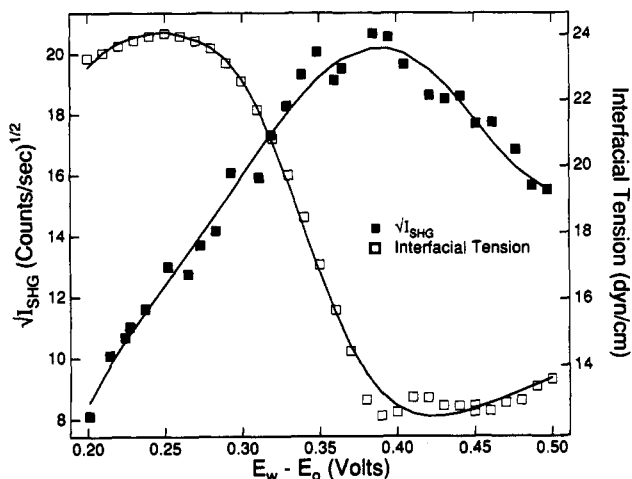
Figure 6. Interfacial tension (open squares) and $\sqrt{I_{SHG}}$ (filled squares) as a function of the applied potential, $E_w - E_o$, for 20 μM ONS, 50 mM KCl, and 25 mM Na_2HPO_4 in water (adjusted to pH = 3 with H_3PO_4) and 1 mM TBATPB in 1,2-dichloroethane. The data points were collected from 0.2 to 0.5 V at 6-min intervals.

side of the interface, then b will be approximately 0.24, as calculated from Gouy–Chapman theory.[5b] The observed value for b of 0.67 indicates a somewhat intermediate position for the adsorbed surfactant at the ITIES.

At higher potentials, assuming negligible changes in molecular orientation, the surface coverage is observed to be larger than that predicted by a Langmuir isotherm, suggesting that the presence of ONS at the interface enhances its adsorption. This enhancement requires a value of c in the Frumkin isotherm of –4 ± 1 kJ/mol (g'= –1.4 ± 0.4) in order to properly fit the experimental results. The enhancement of adsorption strength with increasing surface coverage is not expected for simple anions such as chloride or nitrate and may be attributed to the chain–chain interactions of the ONS molecules which lead eventually to aggregation. In addition, the presence of the counterions in the interfacial region may reduce the net effects of electrostatic repulsion.

At a pH of 3, protonation of the amine group of ONS (pK_a = 3.74[30]) will make the zwitterion the majority species in aqueous solution. The molecular SHG response of the ONS zwitterion is expected to be much smaller than that of the ONS anion since the protonation of the amine prevents the amine from behaving as an electron-donating ring substituent. It is well-known that the presence of such an electron-donating substituent greatly enhances (by nearly 2 orders of magnitude) the SHG response of similar molecules.[31,32] Thus, to a very good approximation, the SHG from the interface at a pH of 3 will depend only on the surface coverage of the anionic ONS species while the interfacial tension measurements will vary in a more complicated fashion with the surface coverages of both the anionic and zwitterionic forms of ONS.

The potential dependence of the interfacial tension for the water–dichloroethane interface with 20 μM ONS present at a pH of 3 is plotted in Figure 6 (open squares). The interfacial tension measurements indicate the presence of both the anionic and zwitterionic form of ONS at the interface. As in the pH 9 case, the pzc is shifted to 0.250 V, indicating the adsorption of the anionic ONS. However, the interfacial tension at the pzc is 24.1 dyn/cm, a 2.9 dyn/cm decrease from the 27.0 dyn/cm value observed at the bare ITIES (see Figure 2). This decrease indicates that the ONS zwitterion may also be adsorbed to the interface at the pzc. As the applied potential is moved positive of the pzc, the interfacial tension decreases, which can again be interpreted as a result of the increase in adsorption of anionic ONS.

At a potential of 0.400 V the interfacial tension in the pH 3 system levels out at a value of 12.8 dyn/cm. A similar behavior

has been observed for interfacial tension measurements of the adsorption of phosphatidylcholine at the water–dichloroethane interface.[23] This behavior has been attributed to the potential-dependent conversion of the charged phosphatidylcholine at the interface to a zwitterionic form. In the case of ONS, the potential dependence of the interfacial tension suggests that the anionic species is being converted to the zwitterionic ONS form at applied potentials above 0.390 V. This conversion occurs due to the modification of the hydrogen ion activity at the interface

$$a_{H^+}^{NH} = a_{H^+}^{w} \exp\left[-\frac{F}{RT}(\phi_{NH} - \phi_w)\right] \qquad (3)$$

where $a_{H^+}^{w}$ is the hydrogen ion activity in the aqueous phase, $a_{H^+}^{NH}$ is the hydrogen ion activity at the amine site of the adsorbed ONS molecules, and ϕ_{NH} is the microscopic potential at that site (see Figure 4).[23] If the structure of the interface is altered as the adsorbed ONS is converted to the zwitterionic form, ϕ_{NH} need not be a simple function of the applied potential.

The interpretation of the interfacial tension measurements in terms of the coadsorption of both zwitterionic and anionic forms of ONS to the ITIES is verified by the surface SHG measurements. The square root of the SHG signal from the interface at a pH of 3 as a function of applied potential is plotted along with the interfacial tension in Figure 6 (filled squares). As mentioned above, the molecular SHG from the interface is expected to only come from the anionic form of the ONS, and hence $\sqrt{I_{SHG}}$ will be an optical measure of its surface concentration. $\sqrt{I_{SHG}}$ increases from the pzc up to an applied potential of 0.390 V, indicating an increase in the surface concentration of anionic ONS at the interface. At potentials positive of 0.400 V, $\sqrt{I_{SHG}}$ begins to decrease due to the field-induced conversion of the adsorbed anionic surfactant to the zwitterion. Note that, unlike the pH 9 system, $\sqrt{I_{SHG}}$ is not zero at the pzc. This suggests that a small amount of anionic ONS is present at the interface at this potential. Anionic ONS adsorption at the pzc requires the presence of additional cations at the interface and implies that the presence of the zwitterionic ONS at the interface has enhanced the adsorption of the anionic ONS.

The potential dependence of the SHG from the interface can provide information on the changes in $a_{H^+}^{NH}$ and ϕ_{NH} through eq 3 and thus can be used to determine the approximate location of the naphthalene head group with respect to the ITIES. The surface concentration of anionic ONS at 0.5 V is about 75% of the surface concentration at 0.4 V (see Figure 6). From a simple acid–base equilibrium this change corresponds to a decrease in the interfacial pH of 0.12 at the amine position. If the anionic ONS were positioned entirely in the organic phase, ϕ_{NH} would be approximately equal to ϕ_o and a pH change of 1.7 would be expected. Alternatively, if the anionic ONS were positioned entirely on the aqueous side of the interface, the pH at the amine position would not depend on potential at all. The value of 0.12 therefore suggests that the naphthalene head group is adsorbed at an intermediate position close to the aqueous phase (see Figure 4), in agreement with the conclusions of the pH 9 experiments.

Summary and Conclusions

We have demonstrated that adsorption of molecular species to the ITIES can be easily monitored in situ with the molecular SHG from the interface. The SHG technique provides a selective and highly sensitive probe of the species at the liquid–liquid interface. For the specific case of ONS at the water–dichloroethane interface, the adsorption of the anionic form of ONS at a pH of 9 was monitored as a function of applied potential. From quantitative analysis of the optically measured surface coverage, the strength and character of the surfactant adsorption were elucidated. For a pH of 3, the SHG experiments verified that the adsorbed anionic ONS was converted to the neutral zwitterionic form at potentials positive of the pzc by the field-induced

protonation of the ONS amine moiety. The use of SHG measurements in conjunction with traditional interfacial tension measurements provides a powerful combination of tools for the study of adsorption at the ITIES. A future paper will deal with the determination of the average molecular orientation from SHG measurements at the ITIES.

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