

Molecular Rotation at Negatively Charged Surfactant/Aqueous Interfaces[†]

Kim T. Nguyen, Xiaoming Shang, and Kenneth B. Eisenthal*

Department of Chemistry, Columbia University, New York, New York 10027

Received: May 23, 2005; In Final Form: January 10, 2006

The effect of charge on the rotational dynamics of the molecular probe coumarin 314 (C314) at air/water interfaces covered with the negatively charged surfactant sodium dodecyl sulfate (SDS) was investigated using femtosecond time-resolved second harmonic spectroscopy. The out-of-plane orientational time constant at the highest SDS surface coverage of 100 Å² per molecule is 383 ± 9 ps. The rotational dynamics is slower than at the air/water interface where the out-of-plane reorientational time constant is 336 ± 6 ps. At the air/water interface the rotational dynamics is over three times slower than the bulk orientational diffusion time of 100 ps. The relatively small effect of the surfactant charge density on the C314 rotation time constant is surprising, considering the marked dependence of the C314 orientation, spectra, and surfactant phase diagram on surfactant density.

Introduction

The asymmetric environment at an interface presents a unique chemical milieu for molecular adsorbates. Molecular interactions and motions at the interface are different from those of the bulk liquid due to both the change of solvent properties at the interface and the inherent anisotropy of the interfacial environment.^{1–6} The time varying torques exerted by solvent molecules, which are responsible for the solute molecule's rotational motions, are anticipated to be different at an interface compared with the bulk liquid. The origin of these differences is the change in density and the orientational dependence of the intermolecular potential at the interface. These factors effect an anisotropic orientation and a preferred alignment (up vs down) of adsorbed molecules and a solvent structure unlike that of the bulk liquid.⁷

Second harmonic generation (SHG) is a well-established and powerful method to study interfaces, and of special value for systems where the molecules of interest are present in the bulk media bounding the interface as well as at the interface itself.^{8–10} For such systems the contribution of the bulk species to whatever spectroscopic signal is being detected will generally overwhelm the signal from the much lower interface population of the species being investigated. There are cases where the molecules of interest are so strongly interface selective that linear spectroscopies can be used successfully.¹¹ Previous femtosecond pump–probe studies in this laboratory have reported a significantly slower reorientation time of the dye molecule coumarin 314 (C314) at the air/water interface than the value of 100 ps in bulk water using a closely related coumarin molecule.^{7,12} The slower rotational relaxation time of C314 at the air/water interface than in bulk water indicates that the rotational friction is larger at the interface. At the water surface, the water molecules form more ordered hydrogen bonding networks than in the bulk water.^{13,14} This more highly ordered water structure hinders the rotation of C314 at the interface. It has been shown that the structure of water is further altered at charged interfaces.^{3,5,15–19} Because of this charge induced change in the

interfacial water structure, experiments were initiated to determine the effect of charged interfaces on molecular orientational dynamics.

Charged interfaces are ubiquitous, ranging from aqueous/mineral oxide interfaces to aqueous/cell membrane interfaces, as two examples. It is found that biological membrane/aqueous interfaces usually contain negatively charged phospholipids in the lipid bilayer that constitute the membrane. To mimic negatively charged biointerfaces, we have chosen to investigate monolayers of anionic surfactants at the air/water interface, because of their simplicity. In the present study the rotational motions of C314 at the anionic sodium dodecyl sulfate (SDS) [CH₃(CH₂)₁₁OSO⁻Na⁺]/aqueous interface were measured. SDS dissolved in water forms a monolayer at the air/water interface with the negatively charged sulfate groups immersed in the water phase and the hydrophobic dodecane tails extended into the air.²⁰ It should be noted that the simplicity of such a system has certain advantages. For example, one can easily vary the surface charge density by changing the bulk SDS concentration as well as by changing the charged headgroup and alkane tail. In this way information regarding the effects of the lipid structure and lipid density on interfacial dynamics can be realized. Using such a model system, we have studied the ultrafast solvation dynamics of C314 at negatively charged air/water interfaces at various charge densities.⁶ The studies of rotational dynamics of probe molecules at the SDS/water interface is a continuation of our studies on molecular motions at liquid interfaces.^{6,7,21–27}

In this paper we report the first measurements of the out-of-plane rotation dynamics of C314 at negatively charged surfactant/water interfaces. The introduction of a charged monolayer changes the ordering of water molecules at the interface,^{5,6,13,27} which in turn can affect the orientational motion of the adsorbate C314 at the interface. The three surface coverages of SDS used in these experiments were 500, 250, and 100 Å²/molecule. The 2D phase diagram of SDS in a 15 μM C314 solution is shown in Figure 1. We note also that the bulk SDS concentrations are well below the critical micellar concentration (8 mM).²⁰

Isolation of the out-of-plane orientational component of the C314 molecular interfacial rotation is achieved in the following way. A circularly polarized laser pump pulse, incident along

[†] Part of the special issue "Charles B. Harris Festschrift".

* Author to whom correspondence should be addressed. Tel: 212-854-3175. Fax: 212-932-1289. E-mail: eisenth@chem.columbia.edu.

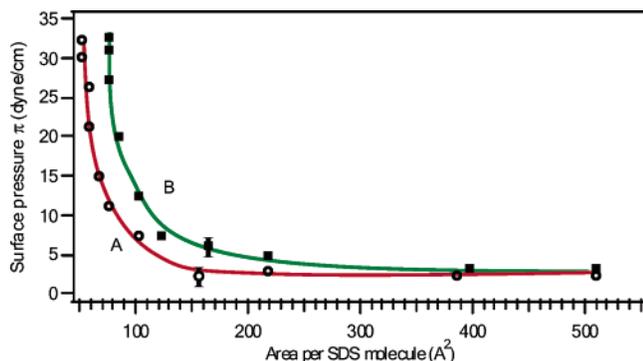


Figure 1. 2D phase diagram of SDS monolayers (A) without coumarin, and (B) with 15 μM coumarin 314.

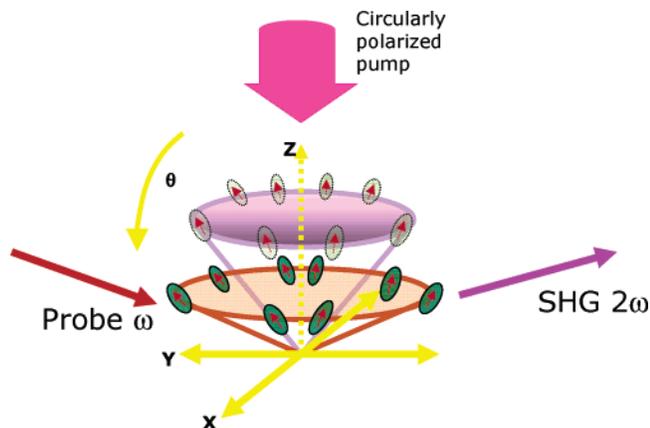


Figure 2. Schematic showing the effect of normal incident circularly polarized pumping on the excitation of interfacial C314 molecules. Darkened C314 molecules are preferentially excited by the pump light.

the interfacial normal, excites C314 molecules to their lowest excited singlet state (Figure 2). The orientational equilibrium distribution at the interface is perturbed by the pump pulse because the molecules whose transition moments have larger components along the polarized light field are preferentially excited. Initially the ground state molecules are isotropically distributed in the interfacial plane because of the inherent in-plane isotropy of liquid/air interfaces. Thus for normal incidence the equal intensities of the circularly polarized pump light along all in-plane directions, yields an in-plane isotropic distribution of excited and ground state molecules. There is therefore no time-dependent change in the in-plane orientational distribution because the in-plane (angle φ) distribution of molecules, both excited and ground state, is isotropic in the plane of the interface. Thus the kinetics observed are only due to out-of-plane motions of the C314 molecules because the circular polarized pump perturbs only the equilibrium orientational distribution in the polar angle θ , favoring absorption transition orientations having large θ values.

Experimental Section

The pump–probe time-resolved second harmonic generation setup is built around a regeneratively amplified Ti:sapphire femtosecond laser system (Clark MXR) that produces 130 fs pulses with energies of ~ 1 mJ at 842 nm and a repetition rate of 1 kHz. Frequency doubling a small portion of the fundamental in a BBO crystal is used to obtain the pump excitation light of 421 nm with energies of 0.7 μJ per pulse. The remainder of the Ti:sapphire laser output pumps an optical parametric amplifier (OPA, Clark MXR). The idler output of the OPA is frequency doubled in a phase matched 0.5 mm thick BBO crystal to

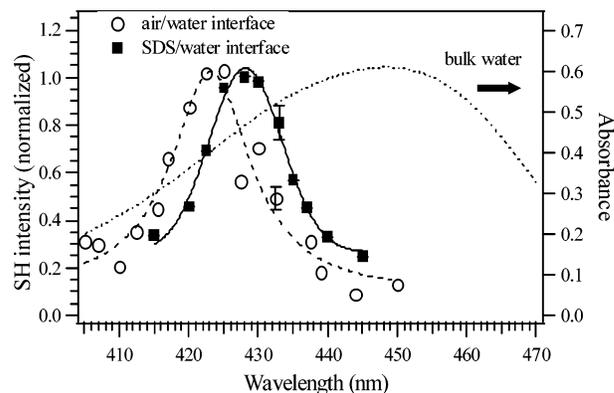


Figure 3. SHG spectra of C314 at the (■) SDS air/water interface (surface coverage of 100 $\text{\AA}^2/\text{SDS}$ molecule) and at the (○) neat air/water interface. The linear absorption spectrum of C314 in bulk water is also shown.

produce tunable probe beam output with energies of 13 μJ per pulse. The probe wavelength is 836 nm for the air/water measurements and 858 nm for the SDS/water measurements. We note that the probe beam is two photon resonant with the coumarin 314 dye molecules at their respective interfaces. The polarization of the circularly polarized pump beam is controlled using a quarter wave plate. The pump beam is incident normal to the sample surface. The probe beam is polarized at 45° with respect to the incident plane and incident at 70° to the interface normal. The sample is contained in a shallow Teflon beaker mounted on a stage rotating at 2.5 rpm to minimize heating and degradation effects. The $\chi^{(2)}_{xx}$ element of the resultant second harmonic signal is selected by an S-oriented Glan-Taylor polarizer with a short wave pass glass filter and several apertures used to block the fundamental prior to the collection optics. The x -axis is in the plane of the interface and perpendicular to the plane of incidence with the z -axis defined as normal to the interface. The first subscript of $\chi^{(2)}_{xx}$ indicates the polarization of the SH light; the next two subscripts indicate the polarization components of the incident probe light. The generated SH signal is focused into a $1/4$ m monochromator (Jarell Ash) and detected by a photomultiplier tube (Hamamatsu). Laser-grade coumarin 314 (Acros) was recrystallized from ethanol and sublimed in vacuo at 40 °C. A 15 μM solution was made using ultrapure water (resistivity = 18.2 $\text{M}\Omega\cdot\text{cm}$, Millipore Corp). The GC-grade SDS (Fluka) was purified by dissolving in hot 95% EtOH (14 mL/g) followed by filtering and cooling. This process was repeated five times followed by drying overnight in a vacuum desiccator. Three SDS concentrations, 0.05 mM, 0.125 mM, and 0.6 mM corresponding to the surface coverage of 500, 250, and 100 $\text{\AA}^2/\text{molecule}$, were used to form the monolayers under study. The monolayers were prepared by dissolving SDS in 12.5 mL of the coumarin 314 solution, transferring the solution to a shallow Teflon beaker, and allowing the solution to stand for 30 min prior to the start of laser experimentation in order to allow for complete monolayer formation. The Teflon beakers were cleaned prior to use by immersion in freshly prepared piranha solution for 20 min and then rinsed with copious amounts of ultrapure water in order to remove any trace organics.

Results and Discussion

Figure 3 shows both the surface absorption spectrum of C314 at the SDS air/water interface for an SDS surface coverage of 100 $\text{\AA}^2/\text{molecule}$, and at the neat air/water interface obtained from SHG measurements using tunable incident probe light

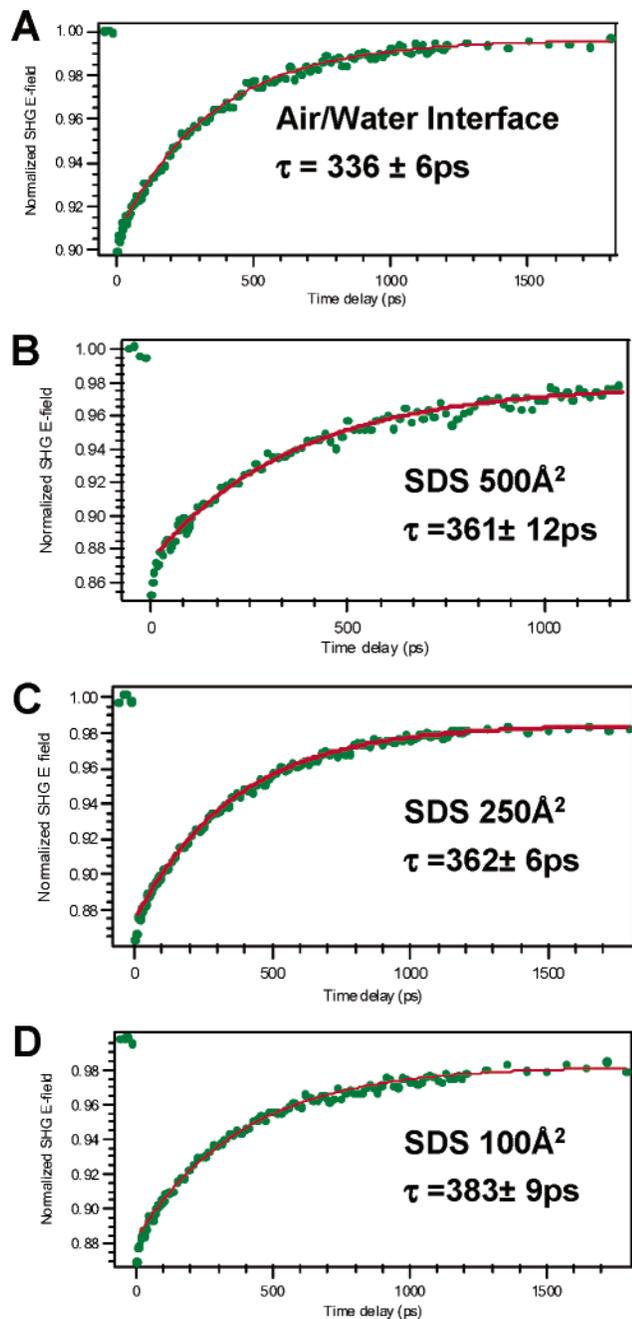


Figure 4. Out-of-plane orientational relaxation of C314 at (A) the air/water interface, (B) the SDS 500 Å² per molecule/water interface, (C) the SDS 250 Å² per molecule/water interface, and (D) the SDS 100 Å² per molecule/water interface. The solid curves are single exponential plus baseline fits of the normalized second harmonic electric field vs picosecond delay time. At the air/water interface $\tau = 336 \pm 6$ ps, at the SDS 500 Å² per molecule/water interface $\tau = 361 \pm 12$ ps, at the SDS 250 Å² per molecule/water interface $\tau = 362 \pm 6$ ps, and at the SDS 100 Å² per molecule/water interface $\tau = 383 \pm 9$ ps.

wavelengths. We measured the time dependence of the $\chi^{(2)}_{zzx}$ second-order susceptibility element of the surfactant free C314 air/water interface, and C314 at the air/water interfaces at three different SDS surface coverages. The kinetics of the out-of-plane orientational motion of coumarin 314 at air/water interfaces containing SDS at a density of 500 Å² per SDS molecule, 250 Å², and 100 Å² are shown in Figure 4. The normalized SHG electric field (square root of the SHG intensity) is plotted vs the pump delay. At negative times, i.e., before the pump pulse has arrived, only ground state molecules are being probed,

yielding a constant SHG signal. Immediately following photoexcitation there is a sharp decrease in signal due to ground state bleaching and the opposing SHG contributions of the newly excited molecules with respect to the remaining ground state molecules. This cancellation is due to the opposite phases of the $\chi^{(2)}$ elements for the ground and excited molecules treating the C314 as a two state system. The subsequent dynamics is due to the out-of-plane reorientational relaxation of the non-equilibrium anisotropy created by the pump pulse. More specifically, the excitation pulse, which is polarized at $\theta = \pi/2$, i.e., in the interface plane, generates more C314 excited molecules with their transition moments at larger θ values, leaving more of the remaining ground state C314 molecules oriented with their transition moments at smaller θ angles. Following the induced orientational anisotropy there will be a net rotation of excited molecules from larger to smaller θ values, whereas for the ground state molecules there will be a net motion to larger θ values. Both excited state and ground state molecules contribute to the SHG dynamics. However the contribution of the excited molecules is decreased from its initial value (at the time of excitation) because of ultrafast interfacial solvation dynamics (<10 ps) that brings the excited molecules to an energy of decreased resonance with the probe light at ω .^{6,26–28} The $\sim 10\%$ baseline bleach remaining after $t = 1.2$ ns represents the electronic ground state population that will recover on the time scale of the interface excited state lifetime, determined to be 4.5 ns.⁷ The solid lines in Figure 4 are fits to a single exponential plus baseline, giving an out-of-plane decay time of 336 ± 6 ps for the air/water interface, 361 ± 12 ps for the SDS 500 Å² coverage, 362 ± 6 ps for the SDS 250 Å² coverage, and 383 ± 9 ps for the SDS 100 Å² coverage. It is evident that there is an increase in rotation time in going from air/water to 500 Å² per molecule SDS/water, whereas in going from 500 Å² to 250 Å² there is no observable change in the rotation time constant. Considering the phase diagram we see that there is a small change in the surface pressure, 1–2 dyn/cm in going from 500 Å² to 250 Å², which indicates that there is a small change in the interfacial forces and structure that is sampled by the C314 molecule. At 250 Å² and 500 Å² the system is in a “liquid–gas” coexistence region, which at these densities consists of surfactant molecules located chiefly in “liquid” droplets.²⁹ The density of surfactant in the droplet remains the same until the “phase transition” to the liquid region at ~ 150 Å², after which a sharp rise in surface pressure is seen (Figure 1). The C314 adsorbed to the surfactant “droplets” would experience the same local density of surfactants at both 250 Å² and 500 Å². Thus it is not surprising that the rotation times are the same within experimental error. On the other hand the surface pressure changes by a factor of 2, from 7 dyn/cm to 15 dyn/cm, in going from 250 Å² to 100 Å², which results in the increase in rotation time at the 100 Å² coverage. We find that the C314 rotation time at the air/water interface is more than a factor of 3 slower than the rotational time of 100 ps for a comparable coumarin molecule, C153, in bulk water.¹² A similar slowing of the rotational dynamics was observed for rhodamine 6G at the air/water interface.²² These results suggest that the interfacial friction for the C314 adsorbates is significantly larger than in the bulk aqueous solution. In contrast to the slower rotation times observed for C314 at the air/water interface, simulations of the orientational relaxation of *N,N'*-diethyl-*p*-nitroaniline at the air/water interface yielded rotational relaxation times that are faster than in bulk water.³⁰ The decrease was attributed to the lower density of water molecules at the interface. The disagreement with the experimental results

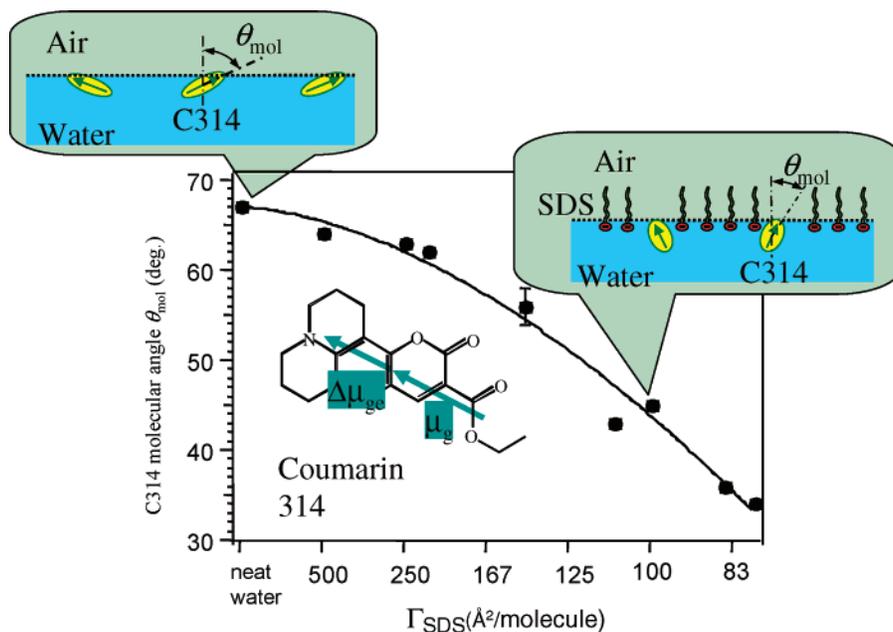


Figure 5. The molecular angle with respect to the interface normal of coumarin 314 at the negatively charged SDS/water interface as a function of SDS density.

reported here could be due to differences in the structure of the probe molecule and its interface location. It is to be noted that unlike the coumarin and rhodamine 6G molecules, for which an increase in the orientational diffusion time at the air/water interface relative to the bulk was observed, the orientational relaxation of doubly charged eosin B at the air/water interface was observed to undergo a decrease of the orientational relaxation time from 350 to 90 ps.³¹ The decreased relaxation time was not attributed to the lower density at the interface but rather to reduced hydrogen bonding with water at the interface. It is to be noted as well that the effects of hydrogen bonding on the eosin B dianion rotation are not present in C314 because there are no ionized carboxyl chromophores available for hydrogen bonding. Another factor that could cause the different behavior of C314 and rhodamine 6G vs eosin B is the double charge of eosin B. The repulsive image forces exerted against interfacial eosin B could restrict its interfacial orientation. In other words the orientational distribution of eosin B is significantly narrower than for C314 and rhodamine 6G. Because of this the deviations in the interfacial orientations of the excited and ground state molecules are reduced. Thus the orientational motions required to achieve orientational equilibrium after photoexcitation is small. In contrast the initial orientations of eosin B are the same in all directions in the bulk solution. The deviation from bulk isotropy induced by the polarized excitation pulse is greater than the deviation induced in the narrow orientational distribution of interfacial molecules. The narrowness of the eosin B orientational distribution implies that a smaller change in the orientation angles is required to achieve equilibrium. This could result in faster orientational dynamics in the interface vs the bulk solution.

In the discussion up to this we have not included the effect of SDS on the orientational distribution of the ground state C314 molecules. This distribution of angles is relevant to the solid angle available to the C314 rotational motions. Although the orientation of C314, assuming a sharp distribution, changes markedly in going from the air/aqueous interface to the 100 \AA^2 SDS/aqueous interface (Figure 5), we cannot infer how the solid angle available to the C314 rotation is affected. Knowledge of the orientational distribution would be of value to both the work

reported here on C314 and the eosin B studies. In order to estimate the mean and angular distribution of the adsorbed molecules it is necessary to combine the SHG results with other orientational sensitive measurements such as angle resolved absorbance by photoacoustic detection.³²

Early structural studies using X-ray scattering and surface enhanced IR spectroscopy have shown that there is a polar alignment of water molecules at charged metal electrode interfaces.^{33,34} Vibrational sum frequency generation (SFG) measurements of water vibrations at a charged quartz/water interface^{2,13,35} and at a charged surfactant/water interface^{3,5,36} showed that there were changes in the water structure at charged interfaces compared with the neat air/water interface. At a high density of charges, whether SiO^- at the quartz/water interface or charged surfactants at the air/water interface, there is a large electrostatic field ($\sim 10^8$ V/m), which aligns interfacial water molecules and bulk molecules extending to a distance dependent on the solution electrolyte concentration.^{37–39} SFG studies of the higher O–H symmetric stretch (3100–3300 cm^{-1}) of interfacial water suggest that the water, in the presence of the negatively charged SDS, experiences higher H bond ordering, yielding some “icelike” structures at the interface.⁵ Previous studies in this laboratory have shown that negatively charged surfactants, SDS and ionized stearic acid, slow the solvation dynamics of C314 compared with the surfactant free air/water interface.^{6,27} These results were attributed to the more highly ordered hydrogen bond structures which can cause a decrease in the water diffusional mobility, i.e., a change in the breaking and forming of water–water hydrogen bonds. These disparate studies of equilibrium and dynamic properties at negatively charged water interfaces point to an enhanced ordering of interfacial water molecules.

It is of interest to note that SFG studies have found that the maximum alignment of interfacial water molecules, as measured by changes in the SFG vibrational spectra, is achieved at a SDS surface coverage of 250 $\text{\AA}^2/\text{molecule}$.⁵ The further increase of SDS surface coverage appears to have only a minimal effect on alignment of interfacial water molecules as detected by SFG measurements.^{3,5,6} Therefore the observed slowing of rotational dynamics, though small, for the SDS surface coverages from

250 Å²/molecule to 100 Å²/molecule cannot be solely due to the ordering of interfacial water molecules. A possible factor that could be responsible for the increase in rotational relaxation time in going from 250 Å² to 100 Å², without any change in water structure, is the strong electrostatic interaction of the negatively charged SDS headgroup with the large dipole moments of both ground (6 D) and excited (8 D) C314 molecules. Direct evidence of increasing C314–SDS interactions in changing the SDS density from 250 Å² to 100 Å² is seen in the marked change in surface pressure when C314 is present at the interface (Figure 1). Similarly, evidence of strong interactions is reflected in the large change in the C314 orientation as the SDS surface density is increased. The orientational change of ~20° in going from 250 Å² to 100 Å² per SDS molecule is shown in Figure 5. The marked changes in orientation and surface pressure on changes in the density of SDS indicate the sensitivity of a probe molecule to detect interfacial changes that are not evident in changes in water structure. Considering the evidence of strong C314–SDS interactions, it is perhaps surprising that the effect of SDS on C314 rotational dynamics is not larger. The out-of-plane rotational time changes from 336 ± 6 ps at the surfactant free air/water interface to 383 ± 9 ps at the 100 Å² SDS/water interface. The relatively small effect of the charged surfactant on C314 rotations raises the question of whether the out-of-plane rotational motions of molecules at the phospholipid membrane/water interface of biological cells would also be relatively insensitive to the phospholipid composition of the membrane. This issue is being investigated.

Conclusion

The effects of a negatively charged interface on the out-of-plane rotational dynamics of an organic dye molecule coumarin 314 (C314) at the anionic sodium dodecyl sulfate (SDS) surfactant/water interface were investigated using femtosecond pump–second harmonic probe spectroscopy. At the highest SDS coverages of 100 Å² per surfactant molecule the out-of-plane rotation time is 383 ± 9 ps, which is to be compared with the out-of-plane rotation time of 336 ± 6 ps at the air/water interface and 100 ps in bulk water. It is surprising perhaps that the effect of SDS on the rotation time of C314 relative to the surfactant free air/water interface is small considering the marked effect of C314 on the surface pressure as seen in the SDS–C314 phase diagram, and manifested also in the large shift of 40° in the polar orientation of C314 at the highest SDS surface coverage relative to the C314 orientation at the neat C314 air/water interface. An implication of this result is that the out-of-plane rotational motion of organic molecules similar to C314 might not be sensitive to the phospholipid composition of biological membranes.

Acknowledgment. The authors gratefully acknowledge the financial support of the National Science Foundation and the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science of the United States Department of Energy.

References and Notes

- (1) Wang, H. F.; Borguet, E.; Eiseenthal, K. B. *J. Phys. Chem. A* **1997**, *101*, 713.
- (2) Du, Q.; Freysz, E.; Shen, Y. R. *Science* **1994**, *264*, 826.
- (3) Gragson, D. E.; Richmond, G. L. *J. Am. Chem. Soc.* **1998**, *120*, 366.
- (4) Gragson, D. E.; McCarty, B. M.; Raymond, E. A.; Richmond, G. L. *Abstracts of Papers*, 213th National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington, DC, 1997; p 51.
- (5) Gragson, D. E.; McCarty, B. M.; Richmond, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 6144.
- (6) Benderskii, A. V.; Eiseenthal, K. B. *J. Phys. Chem. A* **2002**, *106*, 7482.
- (7) Zimdars, D.; Dadap, J. I.; Eiseenthal, K. B.; Heinz, T. F. *J. Phys. Chem. B* **1999**, *103*, 3425.
- (8) Eiseenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343.
- (9) Richmond, G. L.; Robinson, J. M.; Shannon, V. L. *Prog. Surf. Sci.* **1988**, *28*, 1.
- (10) Shen, Y. R. *Annu. Rev. Phys. Chem.* **1989**, *40*, 327.
- (11) Wirth, M. J.; Burbage, J. D. *J. Phys. Chem.* **1992**, *96*, 9022.
- (12) Horng, M. L.; Gardecki, J. A.; Maroncelli, M. *J. Phys. Chem. A* **1997**, *101*, 1030.
- (13) Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1993**, *70*, 2313.
- (14) Raymond, E. A.; Tarbuck, T. L.; Brown, M. G.; Richmond, G. L. *J. Phys. Chem. B* **2003**, *107*, 546.
- (15) Allen, H. C.; Raymond, E. A.; Richmond, G. L. *J. Phys. Chem. A* **2001**, *105*, 1649.
- (16) Vieceli, J.; Benjamin, I. *J. Phys. Chem. B* **2003**, *107*, 4801.
- (17) Watry, M. R.; Tarbuck, T. L.; Richmond, G. I. *J. Phys. Chem. B* **2003**, *107*, 512.
- (18) Gurau, M. C.; Kim, G.; Lim, S. M.; Albertorio, F.; Fleisher, H. C.; Cremer, P. S. *ChemPhysChem* **2003**, *4*, 1231.
- (19) Miranda, P. B.; Du, Q.; Shen, Y. R. *Chem. Phys. Lett.* **1998**, *286*, 1.
- (20) Chatteraj, D. K.; Birdi, K. S. *Adsorption and the Gibbs Surface Excess*; Plenum: New York, 1984.
- (21) Zhao, X. L.; Goh, M. C.; Subrahmanyam, S.; Eiseenthal, K. B. *J. Phys. Chem.* **1990**, *94*, 3370.
- (22) Castro, A.; Sitzmann, E. V.; Zhang, D.; Eiseenthal, K. B. *J. Phys. Chem.* **1991**, *95*, 6752.
- (23) Zhao, X. L.; Eiseenthal, K. B. *J. Chem. Phys.* **1995**, *102*, 5818.
- (24) Zimdars, D.; Eiseenthal, K. B. *J. Phys. Chem. B* **2001**, *105*, 3993.
- (25) Zimdars, D.; Eiseenthal, K. B. *J. Phys. Chem. A* **1999**, *103*, 10567.
- (26) Benderskii, A. V.; Eiseenthal, K. B. *J. Phys. Chem. B* **2000**, *104*, 11723.
- (27) Benderskii, A. V.; Eiseenthal, K. B. *J. Phys. Chem. B* **2001**, *105*, 6698.
- (28) Zimdars, D.; Dadap, J. I.; Eiseenthal, K. B.; Heinz, T. F. *Chem. Phys. Lett.* **1999**, *301*, 112.
- (29) Gaines, G. L. *Insoluble monolayers at liquid-gas interfaces*; Interscience Publishers: New York, 1966.
- (30) Michael, D.; Benjamin, I. *J. Phys. Chem. B* **1998**, *102*, 5145.
- (31) Antoine, R.; Tamburello-Luca, A. A.; Hebert, P.; Brevet, P. F.; Girault, H. H. *Chem. Phys. Lett.* **1998**, *288*, 138.
- (32) Simpson, G. J.; Westerbuhr, S. G.; Rowlen, K. L. *Anal. Chem.* **2000**, *72*, 887.
- (33) Habib, M. A.; Bockris, J. O. *Langmuir* **1986**, *2*, 388.
- (34) Ataka, K.; Yotsuyanagi, T.; Osawa, M. *J. Phys. Chem.* **1996**, *100*, 10664.
- (35) Du, Q.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1994**, *72*, 238.
- (36) Gragson, D. E.; Richmond, G. L. *J. Phys. Chem. B* **1998**, *102*, 3847.
- (37) Ong, S. W.; Zhao, X. L.; Eiseenthal, K. B. *Chem. Phys. Lett.* **1992**, *191*, 327.
- (38) Zhao, X. L.; Ong, S. W.; Eiseenthal, K. B. *Chem. Phys. Lett.* **1993**, *202*, 513.
- (39) Wang, H. F.; Zhao, X. L.; Eiseenthal, K. B. *J. Phys. Chem. B* **2000**, *104*, 8855.