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Optical Surface Second Harmonic Generation Study of the Two Acid/Base Equilibria of Eosin B at the Air/Water Interface

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Surface second harmonic generation (SSHG) has been used to study the two successive acid/base equilibria of eosin B at the air/water interface. Surface tension measurements have shown that the neutral and anionic forms of eosin B are not surface-active. Nevertheless, SSHG was able to follow the appearance and the disappearance, as a function of the aqueous bulk pH, of the three different species at the interface despite the low number of molecules per unit surface present there. The two surface pK_a^s values were measured at $pK_{a1}^s = 4.0$ and $pK_{a2}^s = 4.2$, and both were found to be shifted to larger values as compared to the corresponding ones measured by UV-vis spectroscopy in aqueous bulk solution, at $pK_{a1} = 2.2$ and $pK_{a2} = 3.7$, respectively. These values indicate that the neutral and the monoanionic forms of eosin B are favored at the interface compared to the monoanionic and the dianionic forms, respectively. A wavelength analysis of the SH response of the dianionic form of eosin B at this interface suggests a lower hydration of the molecule at the air/water interface compared to the bulk solution, in agreement with the observed smaller stabilization of the charged species at the interface. The interfacial orientation has been measured for the doubly-charged and neutral forms of eosin B and found at 33° and 31° , respectively.

1. Introduction

Second harmonic generation (SHG) is now a well established surface technique for the study of air/liquid and liquid/liquid interfaces.^{1–5} In the electric dipole approximation, SHG is forbidden in media with inversion symmetry like liquids. Since the inversion symmetry is broken at interfaces, a surface SHG process is allowed there and is surface-specific. However, experiments have shown that in the case of air/bare solvent interfaces, nonlocal contributions from the bulk of the solution could overwhelm the surface terms, leading to a loss of surface specificity.⁶ On the opposite, when the study of chromophores present at an interface is concerned, the signal arising from the chromophores is usually much larger than the signal arising from the solvent molecules, hence yielding again surface specificity. This selectivity to the chromophores is even more pronounced when the fundamental or the harmonic wavelength is tuned to a resonance of the chromophore. In the past, SSHG has mainly been applied to study the surface structure at liquid interfaces, molecular adsorption, and orientation of adsorbates.^{7–18} Chemical reactions like acid/base equi-

libria have also been studied at the air/water^{19–21} and the liquid-liquid^{16,17} interfaces. However, to date, these studies were concerned with water-insoluble monolayers. A comparison with bulk equilibria was therefore not straightforward. Moreover, in these works, the spreading on the surface of charged monolayers yielding a surface excess of charges compensated by a diffuse layer or the applying of an external electrostatic potential difference across the interface was used to electrochemically modify the interfacial acidity.

Eosin B is a diacid which belongs to the xanthene dyes family.²² The two acid-base equilibria are illustrated in Figure 1 along with the equilibrium between the neutral and the lactone forms occurring at low pH. We have also reported the molecular axes x and z for this system. The large π -electron delocalization over the xanthene group of the molecule ensures a high SSHG response, allowing the work at very low surface concentrations. Indeed, this molecule is not surface active and does not specifically adsorb at the air/water interface, that is to say, that its surface excess concentration is negligible. This compound may then be used as a surface probe molecule to study the air/water interface while minimizing any excess surface charge which would be compensated by a diffuse double layer. Consequently, this work aims to show how

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(1) Shen, Y. R. *The principles of nonlinear-optics*; Wiley-Interscience: New York, 1984.

(2) Brevet, P. F. *Surface Second Harmonic Generation Presses*; Polytechniques Universitaires Romandes Lausanne, 1997.

(3) Eienthal, K. B. *Annu. Rev. Phys. Chem.* **1992**, *43*, 627.

(4) Corn, R. M.; Higgins, D. A. *Chem. Rev.* **1994**, *94*, 107.

(5) Brevet, P.-F.; Girault, H. H. *Second Harmonic Generation at Liquid/Liquid Interfaces*; CRC: Boca Raton, FL, 1996.

(6) Tamburello Luca, A. A.; Hébert, P.; Brevet, P. F.; Girault, H. H. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1763.

(7) Heinz, T. F.; Chen, C. K.; Ricard, D.; Shen, Y. R. *Phys. Rev. Lett.* **1982**, *48*, 478.

(8) Hicks, J. M.; Kemnitz, K.; Eienthal, K. B. *J. Phys. Chem.* **1986**, *90*, 560.

(9) Castro, A.; Bhattacharyya, K.; Eienthal, K. B. *J. Chem. Phys.* **1991**, *95*, 1310.

(10) Higgins, D.; Abrams, M. B.; Byerly, S. K.; Corn, R. M. *Langmuir* **1992**, *8*, 1994.

(11) Sarkar, N.; Das, K.; Nath, D.; Bhattacharyya, K. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1769.

(12) Grubb, S. G.; Kim, M. W.; Rasing, T.; Shen, Y. R. *Langmuir* **1988**, *4*, 452.

(13) Bell, A. J.; Frey, J. G.; VanderNoot, T. J. *J. Chem. Soc., Faraday Trans.* **1992**, *84*, 2027.

(14) Higgins, D. A.; Corn, R. M. *J. Phys. Chem.* **1993**, *97*, 489.

(15) Higgins, D. A.; Naujok, R. R.; Corn, R. M. *Chem. Phys. Lett.* **1993**, *213*, 485.

(16) Naujok, R. R.; Higgins, D. A.; Hanken, D. G.; Corn, R. M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1411.

(17) Naujok, R. R.; Paul, H. J.; Corn, R. M. *J. Phys. Chem.* **1996**, *100*, 10497.

(18) Tamburello-Luca, A. A.; Hébert, P.; Brevet, P.-F.; Girault, H. H. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3079.

(19) Zhao, X.; Subrahmanyam, S.; Eienthal, K. B. *Chem. Phys. Lett.* **1990**, *171*, 558.

(20) Xiao, X.-D.; Vogel, V.; Shen, Y. R. *Chem. Phys. Lett.* **1989**, *163*, 555.

(21) Zhao, X.; Ong, S.; Wang, H.; Eienthal, K. B. *Chem. Phys. Lett.* **1993**, *214*, 203.

(22) Drexhage, K. H.; Hänsh, T. W.; Ippen, E. P.; Schäfer, F. P.; Shank, C. V.; Snavely, B. B. In *Topics in applied physics*; Schäfer, F. P., Eds.; Springer-Verlag: Berlin, 1973; Vol. 1.

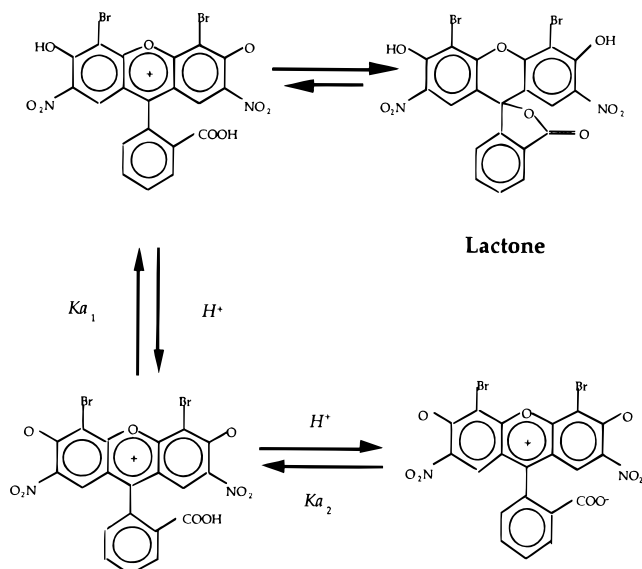


Figure 1. Equilibria for eosin B.

surface hydration directly influences the stability of acids which are not surface active.

2. Experimental Section

The experimental setup for the SSHG measurements has been previously described elsewhere.⁶ The second harmonic output of a Nd³⁺ YAG laser at 532 nm, delivering 35-ps pulses at 20 Hz, is incident on the air/water interface with an angle of 72°. After elimination of the reflected fundamental light and residual harmonic light from optical components with filters, the surface second harmonic signal generated at 266 nm is detected with a photomultiplier through a monochromator and a boxcar averager.

The surface SHG spectrum of eosin B was recorded with a similar setup as presented above. However, in that case, the laser source was a nanosecond Nd³⁺ YAG system pumping an optical parametric oscillator delivering in the signal beam pulses at 10 Hz of 40-mJ energy and 5-ns duration. The detection was performed with a gated photon counter. The intensity stability over the wavelength tuning range was verified using a z-cut quartz crystal in reflection.

In all experiments, eosin B (Aldrich) was used as supplied. Aqueous phases were made with ultrapure Millipore water. UV-Visible absorption measurements were performed using a CARY 1E UV-vis spectrophotometer. Surface tension measurements were carried out using the pendent drop technique which has already been described elsewhere.²³ The pH of the aqueous solution was measured with a Metrohm 654 pH meter. All the experiments were performed immediately after preparation of the solutions to avoid precipitation of the molecular form at low pH.

3. Surface Tension Measurements

Surface tension measurements have been performed at the air/water interface for two different bulk solution pH's, namely, pH = 3 and pH = 6. Measurements at very low pH (pH = 1) were not possible due to the weak solubility at high concentrations of the neutral form of eosin B. This behavior was exhibited by the poor stability of the drop as a function of time. The results for the surface tension as a function of the bulk aqueous concentration for the neutral and the dianionic forms of eosin B are plotted in Figure 2. A mere 2 mN·m⁻¹ decrease of the surface tension is observed as the concentration of both forms of eosin B is increased from zero up to a value of 1.0 × 10⁻² M, which corresponds to the highest concentration of eosin B yielding stable drops over the whole

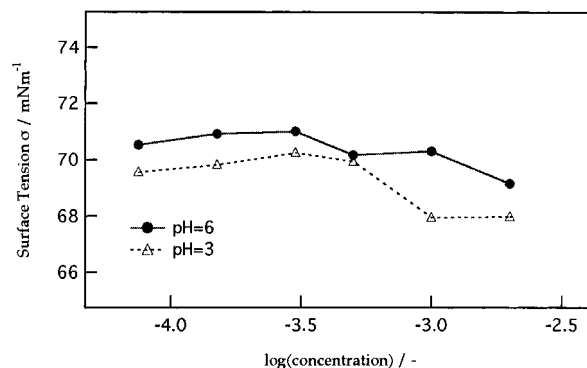


Figure 2. Surface tension vs logarithm of bulk concentration (mol/L) for eosin B at the air/water interface.

range of pH. It is known that xanthene dyes tend to aggregate into dimers and higher oligomers at high concentrations, yielding these drop instabilities. The behavior of eosin B at the air/aqueous solution interface may be described by the laws of the two-dimensional ideal gas, whereby the surface tension is linear with respect to the aqueous bulk concentration. Such an analysis leads to a negligible surface excess concentration for the neutral and the doubly-charged forms of eosin B at the air/aqueous solution interface and subsequently negligible solute-solute interactions there. As a consequence, at pH = 6, we are in the conditions where the formation of a diffuse double layer compensating an excess of surface charge may be neglected. At pH = 3, eosin B is neutral, and therefore, no surface charge excess is present.

The surface tension value measured for the bare air/acid aqueous solution interface is about 70 mN·m⁻¹ and is smaller than the surface tension value of 72.7 mN·m⁻¹ normally obtained for the air/water system. This is caused by the small amount of HCl added to the aqueous solution to define the pH which slightly lowers the surface tension of the free air/water system.²⁴

4. Theoretical Background for SSHG Measurements

The general expression for the second harmonic intensity I^2 at the boundary between two centrosymmetric media may be obtained using the formalism of the sheet of nonlinear polarization. It yields, when applied to the air/water interface in presence of a chromophore,^{2,25-27}

$$I^2 = \frac{1}{2} \frac{\omega^2}{\epsilon_0 c^3} \frac{1}{|\sqrt{\epsilon_m^\Omega} \cos \theta_m^\Omega|} |a_1 \chi_{s,XXZ}^{(2)} \sin 2\gamma \sin \Gamma + (a_2 \chi_{s,XXZ}^{(2)} + a_3 \chi_{s,ZXX}^{(2)} + a_4 \chi_{s,ZZZ}^{(2)}) \cos^2 \gamma \cos \Gamma + a_5 \chi_{s,ZXX}^{(2)} \sin^2 \gamma \cos \Gamma|^2 (I^\omega)^2 \quad (1)$$

where $\chi_{s,XXZ}^{(2)}$, $\chi_{s,ZXX}^{(2)}$ and $\chi_{s,ZZZ}^{(2)}$ are the three nonvanishing and independent components of the surface macroscopic susceptibility tensor, a_i , $i = 1-5$, the usual Fresnel coefficients depending on the experimental geometry. ϵ_m^Ω is the optical dielectric constant of the interfacial region at the harmonic frequency, taken as the mean value between the dielectric constants of the two surrounding media, air and water, in the problem at hand. The angles

(24) Randles, J. E. B. In *Advances in electrochemistry and electrochemical engineering*; Delahay, Paul, T. C. W., Eds.; Interscience: New York, 1963; Vol. 3.

(25) Heinz, T. F. In *Modern Problems in Condensed Matter Sciences*; Ponath, Stegeman, G. I., Eds.; North Holland: Amsterdam, 1991; Vol. 29, p 353.

(26) Mizrahi, V.; Sipe, J. E. *J. Opt. Soc. Am. B* **1988**, 5, 661.

(27) Brevet, P.-F. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 4547.

(23) Girault, H. H.; Shiffrin, D. J.; Smith, B. D. V. *J. Electroanal. Chem.* **1982**, 137, 207.

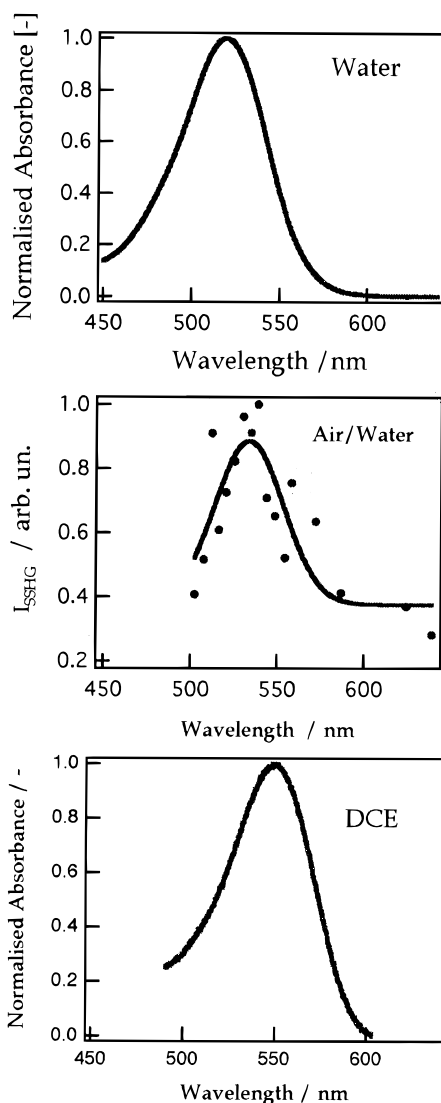


Figure 3. Absorbance UV-vis and surface SHG spectra of the doubly charged form of eosin B (a, top) in water (UV-vis), (b, middle) at the air/water interface (SSHG), and (c, bottom) in 1,2-dichloroethane (UV-vis).

γ and Γ are the polarization angles of the fundamental and harmonic beams, respectively. The three tensor elements $\chi_{s,XXZ}^{(2)}$, $\chi_{s,ZXX}^{(2)}$ and $\chi_{s,ZZZ}^{(2)}$ are directly obtained from the experimental data by fitting eq 1 to the P-polarized and S-polarized output intensities. Neglecting local field effects, the surface macroscopic tensor $\tilde{\chi}_s^{(2)}$ is simply related to the molecular hyperpolarizability tensor $\tilde{\beta}$ of the chromophores by the relation²⁵

$$\tilde{\chi}_s^{(2)} = \frac{N_s}{\epsilon_0} \langle \tilde{\beta} \rangle \quad (2)$$

where N_s denotes the number of molecules per unit surface and $\langle \tilde{\beta} \rangle$ is a short notation for $\langle T(\theta, \phi, \psi) \tilde{\beta} \rangle$, where $\langle T(\theta, \phi, \psi) \rangle$ is the transformation tensor between the molecular and the laboratory frames, the molecular frame being referenced with the Euler's angles θ , ϕ , and ψ . Assuming that eosin B has a C_{2v} symmetry, therefore underestimating the effect of the carboxylic group, the hyperpolarizability tensor $\tilde{\beta}$ has only three independent elements, β_{ZZZ} , β_{ZZX} and β_{XXZ} , where the z coordinate is taken along the C_2 axis; see Figure 1. With a random distribution for the averaging over the angles ϕ and ψ , eq 2 reduces to the following system:²⁵

$$\begin{aligned} \chi_{s,XXZ}^{(2)} &= \frac{1}{2} \frac{N_s}{\epsilon_0} \left[\langle \cos \theta \sin^2 \theta \rangle \beta_{ZZZ} - \frac{1}{2} \langle \cos \theta \sin^2 \theta \rangle \times \right. \\ &\quad \left. (\beta_{ZZX} + 2\beta_{XXZ}) + \langle \cos \theta \rangle \beta_{XXZ} \right] \\ \chi_{s,ZXX}^{(2)} &= \frac{1}{2} \frac{N_s}{\epsilon_0} \left[\langle \cos \theta \sin^2 \theta \rangle \beta_{ZZZ} - \frac{1}{2} \langle \cos \theta \sin^2 \theta \rangle \times \right. \\ &\quad \left. (\beta_{ZZX} + 2\beta_{XXZ}) + \langle \cos \theta \rangle \beta_{ZZX} \right] \\ \chi_{s,ZZZ}^{(2)} &= \frac{N_s}{\epsilon_0} \left[\langle \cos^3 \theta \rangle \beta_{ZZZ} + \frac{1}{2} \langle \cos \theta \sin^2 \theta \rangle (\beta_{ZZX} + 2\beta_{XXZ}) \right] \end{aligned} \quad (3)$$

In order to deduce the molecular orientation angle θ , the number of unknowns in eq 3 has to be reduced down to three. This is achieved considering the symmetry of the transitions involved in the resonant SSHG process. Eosin B is a molecule which is very similar to the rhodamine dye family. Since the optical properties of such molecules are governed by the π electrons in the three rings of the xanthene group, these molecules may be considered as being planar with a mirror plane perpendicular to the plane of the molecule, passing through the oxygen atom and the opposite carbon atom in the central phenyl ring.²⁸ Thus, the transition dipole matrix elements lie in the plane of the molecule, either along the x or the z direction. It has been shown that the singlet states S_0 and S_2 are even under the reflection operation, while the singlet state S_1 is odd in these compounds.^{7,28,29} The $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transition dipole moments are therefore parallel to the x axis, and the $S_0 \rightarrow S_2$ moment is parallel to the z axis. In our experiments, the fundamental wavelength at 532 nm is resonant with the $S_0 \rightarrow S_1$ transition. We therefore neglect the β_{ZZZ} component of the molecular hyperpolarizability tensor and only keep the β_{ZZX} and the β_{XXZ} components in the calculations. It is now possible to determine the orientation parameter D given by

$$D = \frac{\langle \cos^3 \theta \rangle}{\langle \cos \theta \rangle} = \frac{\chi_{s,ZZZ}^{(2)} + 4\chi_{s,XXZ}^{(2)} + 2\chi_{s,ZXX}^{(2)}}{3\chi_{s,ZZZ}^{(2)} + 4\chi_{s,XXZ}^{(2)} + 2\chi_{s,ZXX}^{(2)}} \quad (4)$$

yielding the angle of orientation θ . In this work, we use a Dirac delta function to extract the angle θ from eq 4.

5. Surface SHG Spectrum

As seen in the previous section, the SSHG response of eosin B arises from the second-order nonlinear response of the delocalized π electrons of the xanthene group. This optical nonlinearity is large and allows the recording of an SSHG spectrum despite the very low surface concentration of eosin B. For these measurements, the bulk aqueous concentration of eosin B is 3.0×10^{-5} M. The surface SHG spectrum of eosin B given in Figure 3b has been recorded at the air/water interface for the E^{2-} form, that is, at high pH values. The maximum of the resonance is observed at 533 nm. This spectrum is compared with the two UV-vis spectra recorded for the same form E^{2-} of eosin B, in bulk water, Figure 3a, and bulk 1,2-dichloroethane, Figure 3c.³⁰ In bulk water, the maximum of the absorption band is found at 520 nm, whereas in 1,2-dichloroethane, this maximum wavelength is found

(28) Hermann, J. P.; Ducuing, J. *Opt. Commun.* **1972**, *6*, 101.

(29) Di Lazzaro, P.; Mataloni, P.; De Martini, F. *Chem. Phys. Lett.* **1985**, *114*, 103.

(30) Ding, Z.; Wellington, R. G.; Brevet, P.-F.; Girault, H. H. J. *Electroanal. Chem.*, in press.

at 555 nm. For xanthene derivatives, the shift of the $\pi-\pi^*$ absorption band to shorter wavelengths with the increasing hydrogen-bonding power of the solvent is due to the better stabilization of the ground state of the molecule rather than the excited state.³¹ At the interface, the maximum of the absorption band, measured at 533 nm, is found halfway between the value obtained for 1,2-dichloroethane and the value obtained in water. At the air/water interface, hydration of the xanthene ring of the dianionic form of eosin B is therefore found to be different from the one encountered in highly hydrogen-bonding solvents, like water, and non-hydrogen-bonding solvents, like 1,2-dichloroethane. The position of the maximum of the absorption band of the air/water surface spectrum is thus indicative of a loss in the hydrogen-bonding power of water with the solute at the interface.

6. Surface pK_a Measurements

Depending on the bulk aqueous pH, eosin B is present in three different forms at the interface, EH^2 , EH^- , or E^{2-} . Hence, the elements of the macroscopic susceptibility tensor $\tilde{\chi}_s^{(2)}$ are the sum of the three corresponding elements:

$$\chi_{s,ijk}^{(2)} = \chi_{s,ijk,\text{E}^{2-}}^{(2)} + \chi_{s,ijk,\text{EH}^-}^{(2)} + \chi_{s,ijk,\text{EH}_2}^{(2)} \quad (5)$$

which, using eq 4, becomes

$$\chi_{s,ijk}^{(2)} = \frac{N_{\text{E}^{2-}}^s}{\epsilon_0} \langle \beta_{\text{E}^{2-}} \rangle_{ijk} + \frac{N_{\text{EH}^-}^s}{\epsilon_0} \langle \beta_{\text{EH}^-} \rangle_{ijk} + \frac{N_{\text{EH}_2}^s}{\epsilon_0} \langle \beta_{\text{EH}_2} \rangle_{ijk} \quad (6)$$

Here, we have neglected the local and the nonlocal contributions from the solvent, since the optical response from eosin B is overwhelming. Also, contributions from intermolecular interactions are neglected owing to the low surface concentrations. These surface concentrations, $N_{\text{E}^{2-}}^s$, $N_{\text{EH}^-}^s$, and $N_{\text{EH}_2}^s$, expressed in molecules $\cdot \text{m}^{-2}$, are proportional to the molar surface concentrations and are related to the surface pH^s and the two surface pK_a 's. Hence, eq 6 may be rewritten as

$$\chi_{s,ijk}^{(2)} = \frac{N^s}{\epsilon_0 A^s} [\langle \beta_{\text{E}^{2-}} \rangle_{ijk} 10^{2pH^s - pK_{a1} - pK_{a2}} + \langle \beta_{\text{EH}^-} \rangle_{ijk} 10^{pH^s - pK_{a1}} + \langle \beta_{\text{EH}_2} \rangle_{ijk}] \quad (7)$$

with

$$A^s = 1 + 10^{pH^s - pK_{a1}} + 10^{2pH^s - pK_{a1} - pK_{a2}} \quad (8)$$

which yields the magnitude of the resulting surface susceptibility as a function of the two surface pK_a 's, the surface pH^s , and the hyperpolarizabilities of the three forms of eosin B. In eq 7, the total surface eosin B concentration N^s is used.

The experiment was performed at a bulk concentration of $c = 3 \times 10^{-5}$ M of eosin B. In order to determine the two surface pK_a 's and the nonlinear response of the three forms of eosin B, the evolution of the three elements of the tensor $\tilde{\chi}_s^{(2)}$ as a function of the aqueous bulk pH has been recorded. The evolution of the tensor element $\chi_{s,\text{ZZX}}^{(2)}$ as a function of the bulk pH is shown on Figure 4. Three different harmonic responses are observed corresponding to the three different forms of eosin B: the neutral, the monoanionic, and the dianionic forms. However, the determination of the surface pK_a 's requires the knowledge

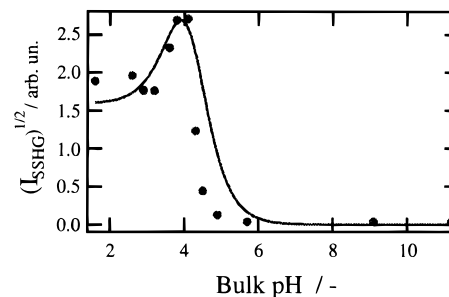


Figure 4. Square root of the SSHG intensity of eosin B as a function of the bulk aqueous pH in the case of *S*-in and *P*-out polarization combination.

Table 1. Bulk and Surface pK_a 's of Eosin B in Water Solution and at the Air/Water Interface and the Corresponding Energy W as Calculated from Equation 9

eosin B	pK_{a1}	pK_{a2}
bulk water ³²	2.2	3.7
air/water interface	4.0	4.2
W , kJ mol ⁻¹	10.3	13.1

of the true surface pH^s . As discussed above for the surface tension results, the surface excess concentration of eosin B may be neglected at all aqueous bulk pH values. As a direct consequence, no double layer is present to counterbalance the surface charge excess, as would have been the case if a nonnegligible surface excess concentration of eosin B had been measured. We therefore assume a uniform proton concentration from the bulk aqueous solution up to the interface and take the surface pH^s to be equal to the bulk aqueous pH. To reduce the number of free parameters in eq 7 used to determine the surface pK_a 's from the experimental curve, two limiting cases may be devised. At low pH, we assume that only the neutral form of eosin B is present at the interface, hence unambiguously determining the hyperpolarizability for this form. In a similar manner, we assume that at high pH, only the doubly charged species are present, thus unambiguously determining the hyperpolarizability of the doubly charged species. Finally, the two pK_a and the hyperpolarizability of the singly charged species are obtained from fit of the experimental data to eq 7. The surface pK_a 's values determined with this procedure are reported in Table 1 along with the bulk aqueous values reported by Levillain and Fompeydie.³² These values were confirmed by UV-vis spectrophotometry in the course of this work. The measured surface pK_a 's values are larger than the bulk pK_a 's values reported in the literature, indicating that the forms of eosin B holding a smaller charge are favored at the interface. For the first deprotonation corresponding to the OH acid function, the pK_a shift is of the order of 1.8 ± 0.2 units, whereas for the second deprotonation corresponding to the COOH acid function, the pK_a shift is of only 0.5 ± 0.2 unit. The observation of a different shift for the two pK_a values indicates a different solvation experienced by the two anionic forms (singly and double charged) of eosin B.

Molecules at surfaces have, in principle, a different Gibbs energy of hydration at an interface as compared to the bulk solution. We may split this Gibbs energy of hydration into an electrostatic contribution, taking into account the stabilization of ions in polar solvent, and a nonelectrostatic contribution. This latter part may be taken to be equal to the Gibbs energy of hydration of the neutral form. The difference in the Gibbs energy of hydration for the three forms of eosin B is thus given by

(31) Martin, M. M. *Chem. Phys. Lett.* **1975**, *35*, 105.

(32) Levillain, P.; Fompeydie, D. *Anal. Chem.* **1985**, *57*, 2561.

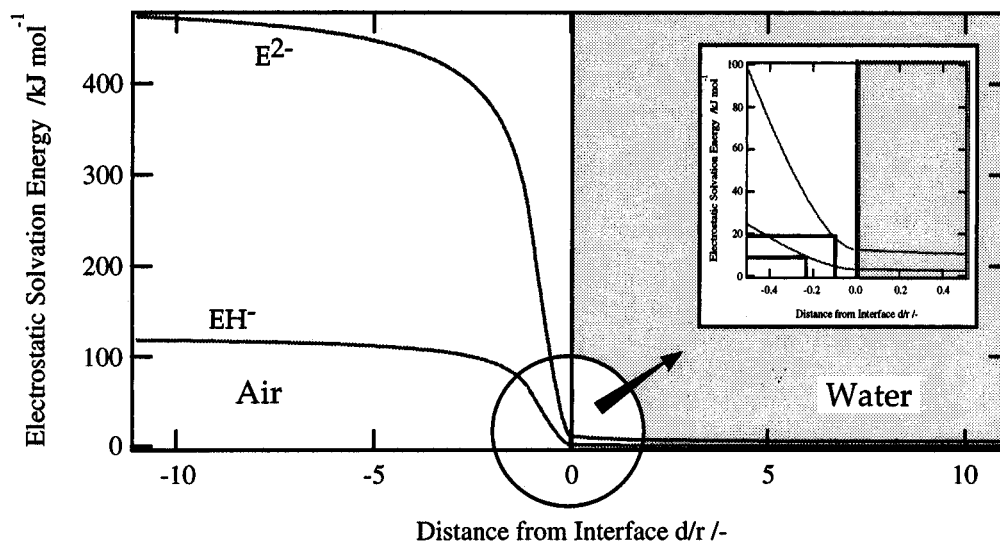


Figure 5. Born electrostatic contribution for a doubly charged moiety and a single charged moiety at the air/water interface as a function of the distance d to the interface. The interface is situated at $d = 0$. Distance is expressed in eosin B radius units (0.56 nm). A zoom of the interfacial region is given in the insert and shows the solvation of the two anionic forms of eosin B. This curve is calculated from eq 10 and the asymptotic expression far from the interface.

the electrostatic contribution. It is equal to the electrostatic work to transfer the molecules from the bulk solution to the surface. We labeled this work W . Hence, using a simple Boltzmann distribution for the partition of eosin B between the interface and the bulk solution, the difference between the pK_a 's at the interface and in the bulk solution is given by the two following relations:

$$\begin{aligned} pK_{a1}^s - pK_{a1} &= \frac{1}{2.3RT} [W_{EH^-}] \\ pK_{a2}^s - pK_{a2} &= \frac{1}{2.3RT} [W_{E^{2-}} - W_{EH^-}] \end{aligned} \quad (9)$$

The measure of the shift of the two surface pK_a 's of eosin B from their bulk solution values allows an evaluation of the electrostatic work W and, therefore, of the solvation environment of the two forms E^{2-} and EH^- of eosin B. Once W is obtained, two physical interpretations may be discussed:

(a) We can first consider a continuous model where the interface is a plane boundary between two continuous homogeneous dielectric media. Hydration of the eosin B molecule at the surface depends on the degree of penetration of the molecule into the vapor side of the interface. Using the continuous approach based on electrostatic considerations, Kharkats and Ulstrup have analytically calculated the electrostatic Gibbs energy, W , for the transfer of an ion between two dielectric phases separated by a sharp planar boundary.³³ Their calculations, incorporating a finite ionic size and the image charge interaction, yield

$$\begin{aligned} W = & \frac{Z^2 e^2 N_{Av}}{32\pi\epsilon_0\epsilon_1 r} \left[\left(2 + 2\frac{d}{r} \right) + \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right) \left(4 - 2\frac{d}{r} \right) \right] + \\ & \frac{Z^2 e^2 N_{Av}}{32\pi\epsilon_0\epsilon_1 r} \left[\left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^2 \left(\frac{(1 + d/r)(1 - 2d/r)}{1 + 2d/r} + \frac{r}{2d} \ln(1 + \right. \right. \\ & \left. \left. 2d/r) \right) \right] + \frac{Z^2 e^2 N_{Av}}{16\pi\epsilon_0\epsilon_2 r} \left(\frac{2\epsilon_2}{\epsilon_1 + \epsilon_2} \right)^2 \left(1 - \frac{d}{r} \right) \end{aligned} \quad (10)$$

The static dielectric constants of the two phases are ϵ_1

and ϵ_2 . The ion is assumed to be a sphere of radius r . The parameter d defines the distance between the interface and the center of the sphere. Equation 10, expressed for the ion in medium 1, is valid in the region $0 \leq d \leq r$, that is, when the ion is close to the interface. Exchanging ϵ_1 and ϵ_2 in eq 10 leads to the same result for the ion in medium 2. Figure 5 shows the electrostatic solvation Gibbs energy profile at the air/water interface for the singly EH^- and doubly E^{2-} deprotonated forms of eosin B. The distance d to the interface is expressed in radius units of E^{2-} , whose value is 0.56 nm. The radius has been estimated from the aqueous diffusion coefficient of the moiety measured by cyclic voltammetry and the Stokes–Einstein relation.²⁹ The positive work to move the two anions from the bulk aqueous solution to the interface region is a function of the distance to the boundary as well as to the charge of the species. The case of the doubly deprotonated form, though, requires 4 times more energy than the singly charged species if the two forms are taken to the same position at the interface. As represented in the insert in Figure 5, the experimental shifts of the pK_a 's correspond to the dianionic E^{2-} form being more hydrated by water molecules than the monoanionic form EH^- , a smaller pK_a^s shift yielding a smaller change in solvation energy. It is to be noted here that the quantities $W_{E^{2-}}$, W_{EH^-} , and $W_{E^{2-}} - W_{EH^-}$ are actually the difference between the corresponding value obtained from eq 9 and the hydration energy in bulk aqueous water. The hydration of the form EH^- is therefore weaker at the interface than the one of the dianionic form. The strong shift observed for the pK_{a1}^s corresponding to the alcoholate function is due to the lower water stabilization experienced by EH^- at the interface. At higher surface pH's, for which the second deprotonation occurs, E^{2-} is found to be closer to the water phase. There, lower changes in hydration are experienced by the moiety, inducing a smaller shift of pK_{a2}^s corresponding to the carboxylate function. However, as confirmed by the surface absorption SHG spectrum recorded for the E^{2-} form, the moiety, and its xanthene ring in particular, still remains in a region where the hydrogen-bonding power of the solvent is weakened. Finally, although the model presented above only takes into account the electrostatic contributions, it eventually yields the same conclusions as the computer simulations on

(33) Kharkats, Y.; Ulstrup, J. *J. Electroanal. Chem.* **1991**, 308, 17.

Table 2. Orientation Angle for the Neutral and Doubly Deprotonated Forms of Eosin B at the Air/Water Interface^a

eosin B form	θ
EH ₂	31
E ²⁻	33

^a The experimental error on the angle is ca. 2°.

solvation including Lennard-Jones and Coulomb interactions between water molecules and ions.^{34,35}

(b) A second approach is to consider the interfacial region as a medium having a dielectric constant different than the bulk one. Eosin B p*K*_a's therefore directly depend on the polarity of the environment, which varies along the direction normal to the interface as one goes from the water phase to the vapor phase. Determination of the apparent interfacial dielectric constant may be obtained from a continuum model such as Born's model. The electrostatic contribution W_{Born} for the transfer of an ion from the bulk solution to the interface is given by

$$W_{\text{Born}} = \frac{z^2 e^2 N_{\text{Av}}}{8\pi\epsilon_0 r} \left(\frac{1}{\epsilon_{\text{m}}} - \frac{1}{\epsilon_1} \right) \quad (11)$$

where ϵ_1 is the bulk water dielectric constant ($\epsilon_1 = 78$) and ϵ_{m} the apparent interfacial dielectric constant. By combining eqs 9 and 11, the interfacial dielectric constant ϵ_{m} is calculated to be 10 for the environment around EH⁻ and 26 around E²⁻, indicating that the localization of the EH⁻ form is closer to the vapor side than those of the E²⁻ form.

Thus, it appears that the lower hydration of the xanthene ring at the interface and the reduced polarity of the interfacial region on aqueous side favor the acid-base equilibria of eosin B toward the forms of the molecule holding a weaker charge.

7. Molecular Orientation

The values of the three independent tensor elements $\chi_{s,XX}^{(2)}$, $\chi_{s,ZZ}^{(2)}$ and $\chi_{s,ZZZ}^{(2)}$ have been obtained from the SSHG measurements at different polarization configurations for both the neutral EH₂ and the doubly charged E²⁻ forms of eosin B and are given in Table 2. These experiments were done at pH = 1.3 and 9.5 to ensure the predominance of only one form at the interface, EH₂ or E²⁻, respectively. The average orientation angle θ has then been calculated using eq 4. The value of θ determined in this manner is the minimum value taken by the angle between the molecular *z* axis and the normal to the interface. However, it does not give the absolute position of the substituent carboxyphenyl ring at the interface, that is, up vs down. From a computational description of the lipophilicity of the neutral form of eosin B obtained from the molecular lipophilicity potential (MLP),³⁶ it may be shown that the distribution of the hydrophilic and hydrophobic parts of the moiety are rather symmetric, precluding a clear determination of the carboxyphenyl group localization at the interface. The two nitro groups on both ends of the xanthene ring are the hydrophilic parts, the two hydrophobic regions being at the halogen atoms position and on the neutral carboxyphenyl ring. Interference patterns between a reference system, a *z*-cut quartz plate for instance, and the sample should in

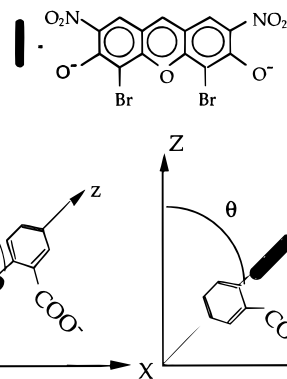


Figure 6. Two possible orientations, up vs down, of eosin B at the air/water interface. The carboxyphenyl group does not lie in the same plane as the xanthene group.

principle answer the question.³⁷ Since the xanthene and the carboxyphenyl groups are not coplanar, two configurations may thus be allowed at the interface for the neutral form of eosin B as seen on Figure 6. For the E²⁻ form of the molecule, since the carboxylic group is deprotonated, the down position may be more favored, the carboxylic group being closer to the aqueous phase.

From the data in Table 2, eosin B is found to be more tilted toward the water phase when present at the interface in the doubly charged E²⁻ form, its angle being $\theta = 33^\circ \pm 2^\circ$, whereas in the neutral form EH₂, its angle is $\theta = 31^\circ \pm 2^\circ$. Also, no significant variation of θ is observed for the E²⁻ moiety as the bulk concentration is increased from $c = 3 \times 10^{-5}$ to 3×10^{-4} M, thus indicating that the orientation angle is independent of solute-solute interactions. This latter behavior is expected since the area per molecule is large compared to the eosin B molecular dimensions owing to the negligible surface excess. Orientation at the interface is therefore essentially driven by the solute-solvent interactions. The same observation has been made for phenol derivative monolayers at the air/water and the hexane/water interfaces.¹⁷ These values are close to the one found for several other related compounds of the xanthene family at the air/water interface.^{6,28} The values of the angle θ measured suggest that the doubly charged form E²⁻ of eosin B lies more tilted toward the water phase than the neutral form EH₂. This behavior may reflect the tendency of eosin B to optimize its hydration, depending on its charge distribution. This change in orientation, however, remains small.

8. Conclusion

We have performed a comparative study of the two acid/base equilibria of eosin B in bulk aqueous solution and at the air/water interface as well as surface tension measurements and SSHG wavelength dependence experiments. From all these results, a molecular picture of the environment of eosin B at the air/water interface may be obtained. Surface tension measurements at two different bulk pH's showed that a negligible surface excess of eosin B was present at the air/water interface. From the bulk pH dependence of the second harmonic signal, the two surface p*K*_a's corresponding to the two acid/base equilibria were deduced and an increase of the p*K*_a's was observed at the interface, indicating that the forms of eosin B holding a weaker charge were favored. This observation is related to the lower hydration experienced by the two anionic

(34) Benjamin, I. *J. Chem. Phys.* **1991**, *95*, 3698.

(35) Benjamin, I. *Acc. Chem. Res.* **1991**, *28*, 233.

(36) Carrupt, P. A.; Gaillard, P.; Billois, F.; Weber, P.; Testa, B.; Meyer, C.; Pérez, S. In *Methods and principles in medicinal chemistry*; Pliska, V., Testa, B., van de Waterbeemd, H., Eds.; VCH: Weinheim 1996; Vol. 4, p 195.

(37) Kemnitz, K.; Bhattacharyya, K.; Hicks, J. M. *Chem. Phys. Lett.* **1986**, *131*, 286.

forms at the interface. Two approaches may be devised to describe the loss of polarity of the interfacial region as compared to the aqueous bulk solution. A wavelength dependence analysis of the SSHG response of the doubly charged form of eosin B has also shown that the hydrogen-bonding power of the interfacial environment of the molecule was weakened. Finally, from orientation measurements, it has been found that the doubly charged form of eosin B lies flatter at the air/water interface than the neutral form.

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