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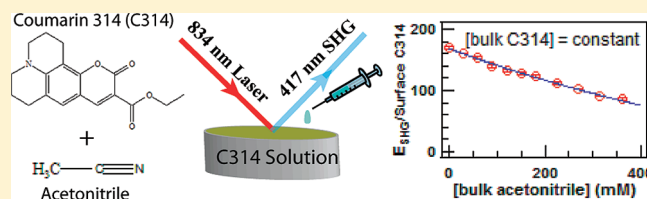
Competitive Adsorption at the Air–Water Interface: A Second Harmonic Generation Study

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S Supporting Information

ABSTRACT: Competitive adsorption between coumarin 314 (C314) and acetonitrile at the air–water interface was studied using second harmonic generation, taking advantage of both the surface specificity and molecule selectivity of the technique. The surface concentration of C314 was selectively probed at the air–aqueous interface. As acetonitrile was added to the solution it was observed that acetonitrile displaces C314 at the interface.

The experimental results are well-represented by a competitive Frumkin–Fowler–Guggenheim (cFFG) adsorption model.



INTRODUCTION

The coexistence of surface-active organics at the air–aqueous interface changes the chemical and physical properties of the interface. This is critical for such varied processes as charge-transfer reactions in environmental systems,^{1–3} personal care product design,^{4–6} gas retention in bread dough,^{7,8} and proper lung function.^{9–11} In a complex aqueous mixture, the population of species at the interface is determined by a variety of factors including the adsorption thermodynamics for each molecule, their relative concentrations, and intermolecular interactions at the surface. Measurement of the adsorption isotherm of one component selectively in the presence of others is not straightforward. Conventional techniques like surface tension^{4–12} will measure the surface excess of all components but cannot probe the surface concentration of individual components in a mixture. Interactions among molecules at the air–water interface can confound the results of such measurements.^{4–6} In many cases the competitive adsorption processes are kinetically controlled and thus describe a nonequilibrium situation where the surface–bulk partitioning depends on additional factors such as the order of addition of the components.^{10,13} Detection of single components is essential to understand such processes in more detail.^{14–18} The second-order nonlinear optical techniques, second harmonic generation (SHG) and vibrational sum-frequency generation (VSFG), are monolayer-sensitive and provide details of molecular adsorption geometry.^{19,20} They are surface-specific because second-order nonlinear processes are allowed in the asymmetric interface regions only and are forbidden in bulk. Molecular selectivity is achieved by adjusting the frequency of the incident light to match an electronic resonance (for SHG) or a vibrational resonance (for SFG). In this way, an enhancement of 3–5 orders of magnitude is obtained.^{19,20}

We used second harmonic generation to study competitive adsorption between coumarin 314 (C314) and acetonitrile (Scheme 1) at the air–water interface. C314 is a slightly soluble, surface-active dye. It is an aromatic molecule containing

carbonyl, ethyl ester, lactone groups, and C–N bonds that can be viewed as a model for environmental humic-like substances (HULIS).²¹ The second harmonic absorption peak of C314 at the air–water interface is 419 nm.²² The SHG signal can be strongly enhanced if the wavelength is close to a two-photon resonant with an electronic transition, in this case the $S_0 \rightarrow S_1$ transition of C314.²² Acetonitrile is a soluble surface-active organic liquid which does not have any resonance at this wavelength. As a result, in a mixture of C314 and acetonitrile we can selectively probe the SHG response from C314 molecules in the presence of acetonitrile at the air–water interface. In this way we monitor the effect of acetonitrile on the adsorption behavior of C314 at the air–water interface. Another reason for choosing these two molecules for study is that both are nonionic and do not show strong acid–base properties in water and, hence, the ionic strength or pH of the solution is not expected to change upon varying concentration of any of the components.

The aim of this work is 2-fold: (1) to study competitive adsorption of two species with considerable affinity for the air–aqueous interface, of which C314 is slightly soluble, and acetonitrile is soluble in bulk water; (2) to demonstrate the applicability of SHG to the detailed study of surface processes in complex aqueous organic mixtures.

EXPERIMENTAL SECTION

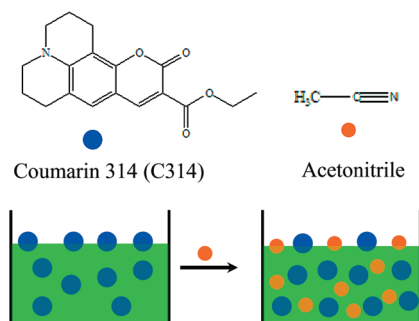
Coumarin 314 (C314, 97%) and acetonitrile were purchased from Sigma-Aldrich and used as received. Neutral water (pH 7) of 18 MΩ/cm was used in the experiments to prepare all solutions. No additional salt or buffer was added. Experiments were done at a room temperature of 22 °C. The surface tension of the water used in these experiments was 72.1 ± 0.3 dyn/cm at that temperature.

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Scheme 1. Competitive Adsorption at the Air–Water Interface between Two Organic Molecules, Coumarin 314 (C314) and Acetonitrile^a



^a Acetonitrile displaces C314 from the interface.

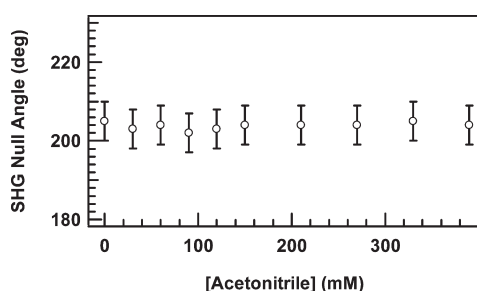


Figure 1. SHG Null angle of 14 μM C314 solution at different concentrations of acetonitrile.

C314 stock solutions were prepared by adding approximately 30 mg of C314 to 250 mL of water. The resulting mixture was sonicated for 2 h with occasional stirring and then stirred for another hour to ensure homogeneity. The excess C314 was then removed using a membrane filter with 0.45 μM diameter pores. Concentration of the stock solutions was calculated from the molar extinction coefficient ($46000 \text{ M}^{-1} \text{ cm}^{-1}$) at the absorption maxima (449 nm). Absorption spectra were measured using a Cary 5000 spectrophotometer. Concentration of the solution was checked to be stable for over 6 h by optical density measurements. A wait time of ~ 45 min was allowed for the aqueous C314 solution to reach equilibrium before collection of the SHG signal. To prepare C314–acetonitrile mixtures, the required amount of acetonitrile was injected into the C314 solution. A mixing time of ~ 8 min was given after each addition of acetonitrile before collecting the SHG signal. Note that subsaturation concentrations were used for both species. The C314 concentration ($7\text{--}14 \mu\text{M}$) is less than the saturation concentration ($\sim 30 \mu\text{M}$). The surface excess of acetonitrile at the air–water interface reaches its maximum value at a bulk mole fraction of $\sim 0.1(4.7)$.²³ In this study, the maximum concentration of acetonitrile used is 0.5 M.

The laser setup for SHG experiments consisted of a Nd:YVO₄ solid state laser (Spectra-physics, Millennia Vs) pumped Ti:sapphire laser (KMLab) which provides 50 fs pulses at 834 nm. The fundamental beam with energy of 2 nJ per pulse was focused to the sample interface at 70° from the surface normal. Polarization of the beam was controlled by a half-wave plate and a polarizer. A red filter is used before the sample to cut off any possible second harmonic from the fundamental laser

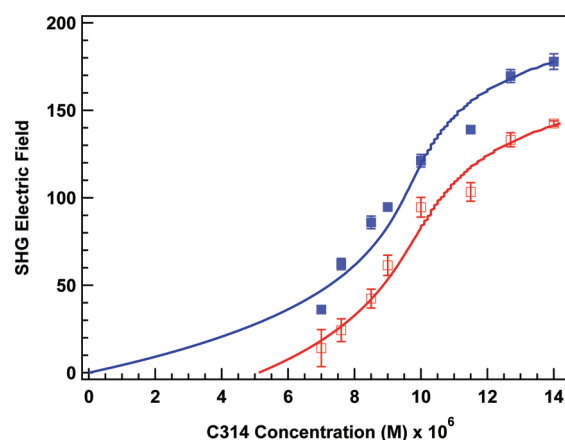


Figure 2. Adsorption isotherm of C314 in the absence (blue solid box), and in the presence (red open box) of 120 mM acetonitrile. Curves shown are from a fit using eqs 2 and 6 respectively.

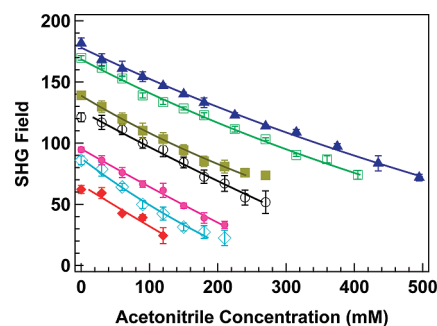


Figure 3. SHG electric field as a function of concentration of acetonitrile added to C314 solutions at varying bulk concentrations: 7.6 μM (red solid diamond), 8.5 μM (blue open diamond), 9 μM (dark red solid box), 10 μM (black open circle), 11.5 μM (dark green solid box), 12.7 μM (green open box) and 14 μM (dark blue solid triangle). Curves shown are the fit using eq 5.

impinging on optical components before it reaches the interface. From the beam reflected off the sample surface, the fundamental beam was removed with a blue pass filter and the signal at the second harmonic wavelength (417 nm) is selected by a monochromator (CVI Digikrom 240). An analyzer was placed to select the s-polarization of the signal. Our detector was composed of a PMT (Hamamatsu R4220P) and a single photon counter. For the SHG isotherm measurements, input polarization was fixed at 45° with respect to the incident plane and the s-polarized signal was detected. To measure the null angle, the analyzer was rotated to obtain the lowest signal, keeping the input polarization at 45° (Figure 1). The sample dish was on a rotating stage (Newport ESP 100 Universal motion controller/driver) to minimize local heating of the sample. SHG measurements were done at 22°C .

RESULTS

The surface second harmonic signal from an aqueous C314 solution at a given bulk concentration of C314 decreases with addition of acetonitrile into the solution. This is clear from Figure 2 which shows a second harmonic field (square root of second harmonic signal) both in the absence and in the presence of 120 mM acetonitrile at different bulk concentrations of C314. The second harmonic field (square root of second harmonic

signal) is proportional to the number of resonant surface species (in this case, C314) weighted by the orientation average. From null-angle measurements of the SHG light, it was found that the orientation of C314 does not change with increasing acetonitrile concentration, as expected at the low acetonitrile concentrations used here (Figure 1). Hence, SHG field is directly proportional to the number of C314 molecules present at the interface and, consequently, the plots in Figure 3 may be considered as adsorption isotherms of C314 at the air–water interface in the absence and the presence of 120 mM acetonitrile. It is clear that in the presence of acetonitrile, less C314 resides at the interface for a given bulk concentration of C314 (Scheme 1). Moreover, Figure 3 shows, in the range of conditions studied, the decrease in SH field is roughly linear with increasing acetonitrile concentration.

DISCUSSION

Modeling of Single Species Adsorption. The adsorption behavior for single adsorbed species can be modeled by Frumkin–Fowler–Guggenheim (FFG) isotherm which is a modification of the Langmuir isotherm incorporating lateral interaction between adsorbed molecules.^{24–31} The FFG equation is

$$\frac{\theta}{1-\theta}e^{-g\theta} = bc \quad (1)$$

where θ is the fractional surface coverage of the adsorbed species, b is the binding constant (adsorption equilibrium constant), c is bulk concentration, and g is a parameter representing the lateral interaction between the adsorbed species at the air–water interface. In the absence of lateral interaction ($g = 0$), the model reduces to the Langmuir equation.

The adsorption isotherm for acetonitrile was obtained from the surface tension data of aqueous acetonitrile mixtures reported by Cheong and Carr (see Supporting Information).³² In this case, the surface coverage of acetonitrile (θ_a) is replaced by $\Gamma_a/\Gamma_{a,\max}$ where Γ_a and $\Gamma_{a,\max}$ are the surface excess and limiting surface excess of acetonitrile. The isotherm can be fitted with $g = 0$ (i.e., Langmuir adsorption model with no lateral interactions) and the binding constant of acetonitrile (b_a) was found to be 1.1 ± 0.3 (see Supporting Information).

For the C314, E_{SHG} is proportional to the surface coverage of C314 and, hence, we can replace θ_{C314} ($N_{\text{C314}}/N_{\text{C314,max}}$) by αE_{SHG} , where α is a constant. Rewriting eq 1 we get

$$C_{\text{C314}} = \frac{1}{b_{\text{C314}}} \frac{\alpha E_{\text{SHG}}}{1 - \alpha E_{\text{SHG}}} e^{-g_{\text{C314}} \alpha E_{\text{SHG}}} \quad (2)$$

A fit of eq 2 to the C314 adsorption isotherm (Figure 2) gives $\alpha = (4.5 \pm 0.2) \times 10^{-3}$, $b_{\text{C314}} = (1.86 \pm 0.16) \times 10^4$ and $g_{\text{C314}} = 3.4 \pm 0.2$. A positive value of g implies that attractive interactions exist between C314 molecules; however, the origin of such an interaction is not understood at this moment.

Modeling Adsorption of the Mixture of C314–Acetonitrile. A competitive Frumkin–Fowler–Guggenheim (cFFG) model is obtained from a simplified form of the generalized Frumkin–Damaskin adsorption isotherm, neglecting the size effect of the adsorbed species.^{27,28} Applying it to the C314–acetonitrile system, we get

$$b_a c_a = \frac{\theta_a}{1 - \theta_{\text{C314}} - \theta_a} e^{-g_a \theta_a - g_{\text{C314},a} \theta_{\text{C314}}} \quad (3)$$

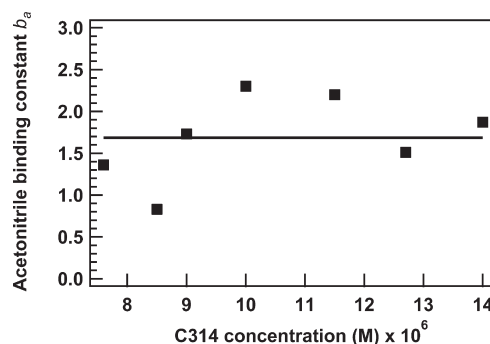


Figure 4. Dependence of acetonitrile binding constant on the C314 concentration in the C314–acetonitrile aqueous mixture. Line indicates the average binding constant of acetonitrile.

$$b_{\text{C314}} c_{\text{C314}} = \frac{\theta_{\text{C314}}}{1 - \theta_{\text{C314}} - \theta_a} e^{-g_{\text{C314}} \theta_{\text{C314}} - g_{\text{C314},a} \theta_a} \quad (4)$$

where b_i , c_i , θ_i , g_i are equilibrium constant, bulk concentration, surface coverage, and lateral interaction, respectively, of species i (C314 or acetonitrile). The parameter $g_{\text{C314},a}$ quantifies the lateral interaction between C314 and acetonitrile molecules at the air–water interface.

For a fixed initial C314 concentration with amount of acetonitrile varying, we can substitute: $\theta_{\text{C314}} = \alpha E_{\text{SHG}}^0$ and $\theta_a = \beta(E_{\text{SHG}}^0 - E_{\text{SHG}})$ where E_{SHG}^0 and E_{SHG} are the SHG field in the absence and in the presence of acetonitrile, respectively. Rewriting eq 3, we get

$$b_a c_a = \frac{\beta(E_{\text{SHG}}^0 - E_{\text{SHG}})}{1 - \alpha E_{\text{SHG}}^0 - \beta(E_{\text{SHG}}^0 - E_{\text{SHG}})} e^{-g_a \beta(E_{\text{SHG}}^0 - E_{\text{SHG}}) - g_{\text{C314},a} \alpha E_{\text{SHG}}^0} \quad (5)$$

For 14 μM C314 bulk concentration and varying acetonitrile, using $g_a = g_{\text{C314},a} = 0$ yields $\beta = (5 \pm 1) \times 10^{-4}$, $b_a = 1.9 \pm 0.5$, and $E_{\text{SHG}}^0 = 177.72 \pm 1.63$. Changing the g values does not improve the fit. This equation describes the data for all C314 concentrations shown in Figure 3. The resulting binding constants of acetonitrile are similar (Figure 4) and nearly independent of C314 concentration. The average value of the acetonitrile binding constant was found to be 1.7 ± 0.2 , similar to that calculated for solutions containing acetonitrile alone.

For a fixed acetonitrile concentration with varying C314, we may write $\theta_a = \beta(E_{\text{SHG}}^0 - E_{\text{SHG}}) = \beta\Delta$ and $\theta_{\text{C314}} = \alpha(E_{\text{SHG}} + \Delta)$. Here, Δ is the decrease in SHG field due to a fraction of the surface being occupied by the acetonitrile molecules. This value is assumed to be the same for all C314 concentrations. Rewriting eq 4, we get

$$b_{\text{C314}} c_{\text{C314}} = \frac{\alpha(E_{\text{SHG}} + \Delta)}{1 - \alpha(E_{\text{SHG}} + \Delta) - \beta\Delta} e^{-g_{\text{C314}} \alpha(E_{\text{SHG}} + \Delta) - g_{\text{C314},a} \beta\Delta} \quad (6)$$

For 120 mM acetonitrile and concentration of C314 varying using the values $g_{\text{C314},a} = 0$, $\alpha = 4.5 \times 10^{-3}$, and $\beta = 5 \times 10^{-4}$, fit of eq 6 to the C314 desorption data in Figure 3 results $b_{\text{C314}} = (1.95 \pm 0.1) \times 10^4$, $\Delta = 33 \pm 4$, and $g_{\text{C314}} = 3.35 \pm 0.08$. This implies that addition of acetonitrile does not change the lateral interaction between the C314 molecules and no lateral interaction is found between adsorbed C314 and acetonitrile molecules.

In summary, all the experimental results are well-described by the FFG model using a similar set of fit parameters which describe the surface–bulk partitioning of each species in isolation. This suggests that the presence of acetonitrile at the surface does not affect the adsorption free energy of C314, and vice versa, under the conditions studied. This is consistent with a lack of strong intermolecular interactions between C314 and acetonitrile molecules ($g = 0$) at the surface and invariance of molecular reorientation of C314 with acetonitrile addition.

SUMMARY

We have shown that the competitive adsorption of C314 and acetonitrile at the air–aqueous interface is well-described by the FFG adsorption model. This work demonstrates the applicability of second harmonic generation to study the adsorption behavior of individual components to the air–water interface in the presence of other surface-active agents. This capability will be particularly valuable for studying the surface–bulk partitioning of organic species in complex environmentally and biologically relevant aqueous systems. For example, measurement of the surface partitioning and interface-specific properties of polycyclic aromatic hydrocarbons, humic and fulvic acids, and HULIS in complex mixtures typical of natural waters and aqueous atmospheric aerosols can elucidate the mechanisms and efficiency (and thus environmental significance) of photosensitized reactions at the air–aqueous interface.^{1–3}

ASSOCIATED CONTENT

S Supporting Information. Calculation of surface equilibrium constant of acetonitrile and waiting time selection for SHG signal from aqueous C314 solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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