

Solvation of *p*-Nitrophenol at a Water/Alkane Interface: The Role of Ionic Strength and Salt Identity

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Second harmonic generation (SHG), a surface specific, nonlinear optical spectroscopy, was used to study the interfacial solvation of a neutral surfactant, *p*-nitrophenol (PNP), adsorbed to the water/cyclohexane interface in the presence of simple salts at varying salt concentrations. The purpose of this work was to determine what relationship (if any) exists between interfacial polarity and bulk solution ionic strength. Data show an apparent red shift in SHG spectra with an increase in salt anion size from fluoride to chloride to bromide at 1 M salt concentrations. A spectral red shift of the PNP electronic excitation implies an increase in local polarity. Within experimental limits, however, these observed interfacial spectral shifts mimic shifts in absorbance spectra observed for PNP in bulk electrolyte solutions. Given the similarities between bulk and surface behavior, we conclude that observed shifts in SHG spectra may be attributed to effects similar to those found in bulk solution. Additionally, the surface adsorption of PNP to the water/cyclohexane interface was studied to determine the surface distribution of PNP and the conjugate base, *p*-nitrophenoxide (PNP[−]), for a 10 mM PNP solution. PNP adsorption is favored over PNP[−] adsorption by a factor of 10, giving rise to an equilibrium surface distribution that is an order of magnitude greater than that found in bulk solution. These findings indicate that the amount of PNP[−] at the surface in an aqueous solution of 10 mM PNP is negligible.

Introduction

The surface activity of simple salt ions in electrolyte solutions has been debated for decades^{1–4} and continues to be an area of active interest.^{5–9} Typically, ionic surfactants adsorb to a liquid surface to reduce the surface free energy leading to a decrease in the surface tension of the solution relative to that of the neat liquid. However, early surface tension measurements of aqueous salt solutions at the air/water interface showed a prominent *increase* in surface tension relative to that of neat water.^{4,10} This observation was interpreted as a negative surface activity and a depletion of simple salt ions at the air/water interface.^{3,11–13} Simple thermodynamic considerations suggest that this view of ion depletion at the surface is reasonable given the unfavorable enthalpic change required to desolvate surface ions.

In contrast to this traditional picture of simple ion surface depletion, recent molecular dynamics simulations suggest that some simple ions will, in fact, migrate to a liquid surface, and the degree to which an ion will partition to the surface depends on the ion's polarizability.⁵ Ab initio quantum calculations, Car–Parrinello molecular dynamics simulations, and molecular dynamics simulations based on polarizable force fields were used to examine aqueous slabs doped with sodium fluoride, chloride, bromide, and iodide at effective concentrations of ~1 M. Density profiles of the ions and water oxygen atoms indicate that highly polarizable iodide and bromide ions exhibit positive excess surface concentrations. Results show that such surface accumulation is possible because the nonzero net dipole of water molecules asymmetrically solvating the surface ions polarizes the ions leading to a stabilization that balances the energy penalty of incomplete solvation. Because chloride ions are not as polarizable as bromide and iodide ions, their surface

concentration is predicted to be slightly less than bulk concentration. Very small, nonpolarizable, strongly hydrated fluoride ions are depleted from the surface region.⁵ Very recent results from XPS measurements support these predictions.⁹

The studies described above focus on ion activity at the air/water interface. Few studies have explored the effects of charge on liquid/liquid interfacial environments, although measurements have shown that the surface tension of a water/organic interface increases with the addition of alkali halide salts by almost the same amount as the air/water surface tension.¹⁴ Given that simple ions in aqueous solutions influence interfacial properties, one may wonder how these altered properties change the local environment experienced by molecular solutes adsorbed to liquid/liquid interfaces. The following study probes the impact that ions have on the local polarity about a solute at a water/alkane interface.

Motivation and Background

Motivation for this work stems from the aforementioned conflicting observations of simple ion surface activity as well as the observation that interfacial polarity appears to depend on the charge of ionic surfactant headgroups.^{15,16} In previous work,^{15,17–20} we described the use of variable length, ionic surfactants — “molecular rulers” — to assess quantitatively the interfacial widths of various liquid/liquid interfaces. Molecular rulers consist of a hydrophobic, solvatochromic surfactant and an ionic headgroup connected by a variable-length alkyl chain spacer. The ionic headgroup “anchors” the ruler to the aqueous phase, allowing the hydrophobic chromophore to “float” into the organic phase. Figure 1 shows structures of anionic and cationic molecular ruler surfactants.

Resonance-enhanced second harmonic generation (SHG) is a surface-specific, nonlinear optical spectroscopy used to

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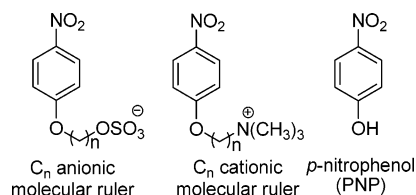


Figure 1. Surfactant molecular structures. Anionic molecular ruler surfactants contain a sulfate headgroup while cationic rulers contain a trimethylammonium headgroup. Also, the molecular structure of *p*-nitrophenol (PNP), a neutral surfactant, is shown.

measure the effective excitation energy of a chromophore within the interfacial region and thus infer the interfacial polarity. Observing changes in the solvatochromic probe response as a function of alkyl chain length provides a means to measure the interfacial dipolar width, the distance required for solvent polarity to converge to the bulk organic limit. When the probe samples a polarity corresponding to that of the bulk organic solvent, the headgroup–probe separation sets an upper limit to the interfacial dipolar width.

The interfacial polarity sampled by an anionic ruler adsorbed to the water/cyclohexane interface approaches the bulk cyclohexane limit from an environment of intermediate polarity between that of bulk water and bulk cyclohexane.¹⁷ However, when cationic surfactants are used, the observed behavior is quite different.¹⁵ The SHG spectrum for the shortest cationic ruler surfactant lies at a wavelength shorter than the wavelength maximum of the chromophore's absorbance spectrum in bulk cyclohexane. For the *p*-nitroanisole-based probe in molecular ruler surfactants, a blue shift in the absorbance spectrum typically corresponds to solvation in a less polar environment suggesting that the interfacial polarity sampled by the shortest cationic ruler appears to be *even* less polar than that of the adjoining bulk cyclohexane phase. This result could arise from several different sources,¹⁵ although the most likely cause is a change in the electronic structure of the chromophore rather than a decrease in interfacial polarity.¹⁶ Specifically, coupling between the cationic headgroup and the electron-rich aromatic ring would reduce the change in dipole moment accompanying electronic excitation of the molecule and would result in a shift to shorter wavelength in the electronic absorbance spectrum relative to a neutral analogue with no intramolecular association.¹⁵

Evidence for such intramolecular association in bulk solution stems from nuclear Overhauser enhancement (NOE) NMR experiments where cationic molecular ruler solutions in D₂O were irradiated at the chemical shift corresponding to the methyl groups of the quaternary trimethylammonium headgroup.¹⁵ A small but significant enhancement in the integrated intensity of peaks corresponding to the protons situated “meta” to the nitro group indicates a through-space interaction between these protons and those of the methyl protons in the headgroup as depicted in Figure 2. This intramolecular coupling between the cationic headgroup and the aromatic ring is most pronounced for the shortest surfactants and is not observable in NMR experiments for surfactants having four methylene spacers or more.¹⁵ No such intramolecular interaction is observed for anionic molecular ruler surfactants of any length.

To examine whether simple anions could prohibit the intramolecular interactions described above, SHG spectra were collected for cationic molecular ruler surfactants adsorbed to the liquid/vapor interface of aqueous solutions saturated with 1-octanol in the presence of simple salts.¹⁶ Such an interface captures the solvation properties of a weakly associating

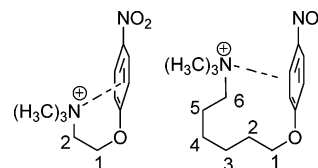


Figure 2. Intramolecular charge–dipole interaction for cationic molecular ruler surfactants. The cationic charge on the headgroup interacts with the aromatic ring of the chromophore in cationic molecular ruler surfactants containing two or three carbons in the alkyl chain. One possible configuration for a molecular ruler containing six carbons in the alkyl chain is shown. Note that in this configuration, the methyl protons are not as close to the aromatic ring as they are in the configuration shown for a cationic molecular ruler containing two carbons in the alkyl chain.

water/organic interface due to the self-assembly of an alkyl monolayer at the liquid/vapor boundary.^{16,18,20–22} This 1-octanol in water system has been used as a convenient mimic of the water/alkane boundary.¹⁶ When short cationic molecular rulers are adsorbed to this liquid/vapor surface, the SHG spectra again shift to shorter wavelengths relative to the spectra of anionic rulers, similar to the behavior of cationic rulers adsorbed to the water/cyclohexane interface. However, the addition of sodium iodide to the aqueous solution leads to a spectral red shift in the SHG spectrum, and at iodide concentrations greater than 1 mM, the cationic and anionic surface spectra are indistinguishable. The spectral shift to anionic ruler behavior is attributed to a weakening of the charge–dipole interactions proposed for cationic molecular rulers. Screening of this association occurs due to Coulombic interactions between the iodide anion and the trimethylammonium cationic headgroup of the surfactant. Inhibition of the intramolecular association would inhibit the reduction of the change in dipole moment associated with electronic excitation. Consequently, the cationic surfactant would exhibit behavior similar to that of the anionic molecular ruler.¹⁶

To explore further surface charge–probe coupling, experiments described in this work attempt to decouple the probe from the charge by using a neutral surfactant, *p*-nitrophenol (PNP) (Figure 1), and adding simple salts at various concentrations to the solutions. The use of a neutral surfactant also allows us to control closely the ionic strength of each system, a condition that is difficult to manage when using molecular rulers due to ionic contaminants. On the basis of the results presented below, we conclude that, in the absence of direct correlation between the charged species and a probe molecule, charges have a similar influence on interfacial solvation of neutral organic species such as PNP as they do in bulk solution. The following section describes experimental conditions for collecting SHG spectra, UV/vis spectra, and surface pressure isotherms for PNP at the water/cyclohexane interface. A discussion of SHG results, a comparison to bulk solution limits, and an analysis of the surface distribution of PNP and the conjugate base, *p*-nitrophenoxide (PNP[−]), are found in the Results and Discussion section.

Experimental Section

All chemicals were purchased from either Fisher Scientific or J. T. Baker with the exception of PNP, which was purchased from Aldrich. All compounds were used without further purification. Salt purity was confirmed by IR absorbance spectroscopy and surface tension measurements. Salts were stored in open containers in an oven set to ~100 °C and cooled to room temperature in closed containers immediately before use to keep them dry. All glassware was immersed in an acid bath containing a 50/50 mixture of nitric and sulfuric acids for

at least 1 h and rinsed copiously with distilled, deionized water prior to use. All aqueous solutions were made with distilled, deionized water from a Millipore system and, unless specifically stated, are at a pH of 5.7 ± 0.2 .

SHG spectra in this work were acquired under either $P_{\omega}P_{2\omega}$ or $P_{\omega}A_{2\omega}$ polarization conditions, where P polarized light describes light that is polarized in the plane defined by the direction of propagation and the surface normal and A indicates no discrimination of polarization. Varying the incident and detected polarizations enables us to determine the average chromophore orientation using methods described previously.²³ Different polarizations did not lead to qualitatively different SHG spectra. The SHG apparatus is built around a Ti:sapphire regeneratively amplified, femtosecond laser (Clark-MXR CPA 2001) that produces 130 fs pulses with energies of $700 \mu\text{J}$ at a wavelength of 775 nm and a repetition rate of 1 kHz. The output of the Ti:sapphire laser pumps a commercial optical parametric amplifier (OPA, Clark-MXR). The visible output of the OPA is tunable from 550 to 700 nm, with a bandwidth of 2.5–0.5 nm. The polarization of the incident beam is controlled with a Glan-Taylor polarizer and a half-wave plate. A series of filters block the fundamental 775 nm and any second harmonic light generated from the preceding optical components. Second harmonic photons are detected in the reflected direction by photon-counting electronics. Typical signal levels average 0.01–0.1 photon per shot. A second polarizer selects the polarization of the SH signal, and a short pass filter and monochromator serve to separate the second harmonic signal from background radiation.

Because the visible OPA cannot be synchronously tuned, acquisition of a complete SHG spectrum requires multiple hours. A typical procedure entails allowing the sample to equilibrate and manually tuning the incident light to each desired wavelength. System alignment is reoptimized at every wavelength to account for the wavelength-dependent changes in the angle of the reflected SH signal. At each wavelength, SH data are collected for four 10-s intervals and normalized for incident power. Although tedious, this procedure ensures that spectra are reproducible. A single wavelength might be sampled three separate times several hours apart (beginning, middle, and end of an acquisition sequence). If the normalized SH signal from each of these three samplings does not fall within experimental uncertainty (typically $\sim 15\%$), data acquisition is halted and the spectrum is discarded. In addition, data at the same wavelength were often acquired by using several different incident powers and then normalized to confirm quadratic dependence of the SH signal intensity on the incident field intensity predicted by equation 1 below. To within limits of experimental precision, the predicted quadratic behavior was always observed.

In this study SHG samples contain a solution of PNP that has been allowed to equilibrate with an adjacent cyclohexane phase for at least 1 h. A prism used to focus the light onto the liquid/liquid interface keeps the organic phase from evaporating over time. The PNP solutions have a concentration of 10 mM, corresponding to $\sim 80\%$ of full monolayer coverage (full monolayer coverage is 1.05×10^{14} molecules/cm²). Aqueous solutions may also contain simple salts (NaF, NaCl, or NaBr) at various concentrations. Solutions containing NaI were omitted from this study since any results attributed to the presence of anionic species cannot be assigned solely to the effects of I[−], but must also consider the presence of I₃[−].

The electronic excitation energies of PNP in bulk electrolyte solutions were determined by UV/vis absorbance spectrophotometry with a double-beam Hitachi U-3010 instrument. Aque-

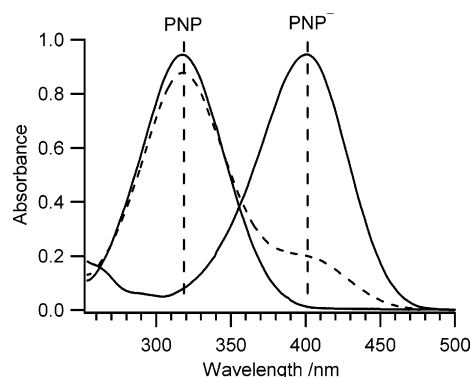


Figure 3. Bulk aqueous solution spectra of PNP under acidic, neutral, and basic conditions. At neutral pH (dashed line), the band contains contributions from both PNP and PNP[−]. Under acidic and basic conditions, the solution contains entirely PNP ($\lambda_{\text{max}} = 318 \text{ nm}$) and PNP[−] ($\lambda_{\text{max}} = 400 \text{ nm}$), respectively.

ous solutions were prepared with PNP concentrations of 0.1 mM or less to keep the absorbance < 1 . As described in the Results and Discussion section, the pK_a of PNP is 7.15.²⁴ Therefore an equilibrium distribution of PNP and the conjugate base, *p*-nitrophenoxide (PNP[−]), exists in bulk solution at neutral pH. Salt-free, UV/vis spectra of neutral, acidic, and basic PNP solutions are shown in Figure 3. Acidic and basic solutions give rise to PNP and PNP[−] spectra, respectively. Both bands have relatively Gaussian distributions and are separated from one another by $\sim 80 \text{ nm}$. For UV/vis absorbance studies, the solute was kept in its neutral state by ensuring that all solutions were at a pH of ~ 3 .

The surface activities of PNP and sodium *p*-nitrophenoxide (NaPNP) at the water/cyclohexane interface were determined by using the Wilhelmy plate method to acquire surface pressure isotherms. The solubilities of PNP and NaPNP dictate that the concentrations ranged from 0 to 20 mM for PNP solutions and 0 to 500 mM for NaPNP solutions. Aqueous solutions were allowed to equilibrate for at least 1 h with an adjoining cyclohexane phase. Acidic solutions were prepared by adding HCl to lower the pH to 2–3. The total ion concentration for these solutions comes from hydronium and chloride ions in the case of acidic PNP measurements and the Na⁺ counterion in the NaPNP solutions. The concentrations of H₃O⁺ and Cl[−] are small compared to the total PNP concentration ($\sim 10\%$). The Na⁺ concentration is equal to the PNP[−] concentration, but the sodium ions are small and positively charged and therefore have a tightly bound hydration shell. We assume that, compared to the aromatic PNP[−], Na⁺ ions are less likely to adsorb to the surface and will have a negligible effect on PNP[−] adsorption. Also, surface tension measurements of PNP at the water/cyclohexane interface in the presence of 1 M sodium salts show little deviation in surface pressure compared to measurements in the absence of the sodium salts ($\sim 7\%$). After fitting the data to a Gibbs isotherm (eq 4), the terminal surface coverage for each system was determined by using eq 5 as explained in the following section.

Results and Discussion

To observe the solvation environment of a solute adsorbed to a liquid/liquid interface, we utilize resonance-enhanced second harmonic generation (SHG). SHG is a nonlinear optical spectroscopic method that allows for the measurement of an effective excitation spectrum at an interface.^{25,26} This technique is both surface specific and molecularly specific, making it a very powerful means of probing buried interfaces.^{27–29} Experi-

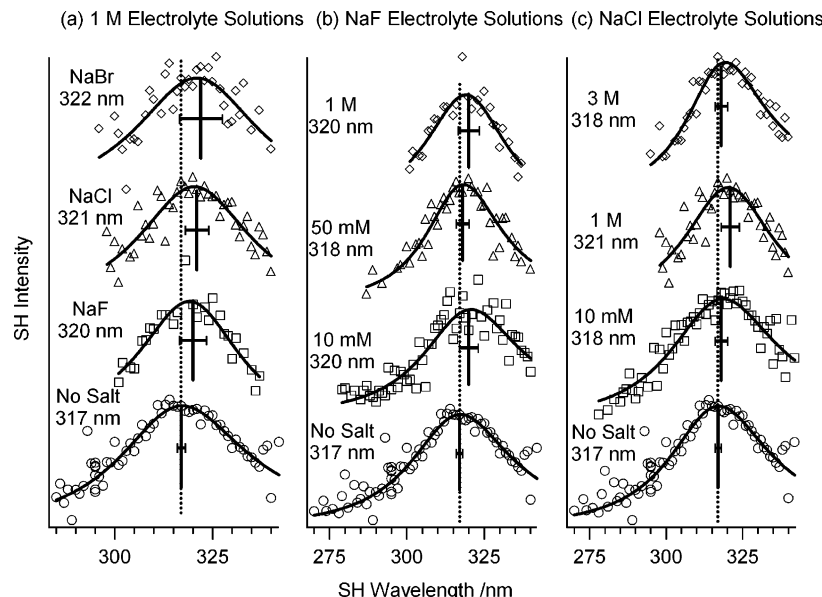


Figure 4. SHG spectra of PNP at the aqueous/cyclohexane interface where the electrolyte solutions are (a) 1 M NaF, 1 M NaCl, and 1 M NaBr, (b) 10 mM NaF, 50 mM NaF, and 1 M NaF, and (c) 10 mM NaCl, 1 M NaCl, and 3 M NaCl. The spectra have been fit according to eqs 1–3. The solid vertical lines correspond to the interfacial excitation wavelength maxima of PNP in the presence of the indicated salt while the dashed vertical line in each panel corresponds to the interfacial wavelength maximum, λ_{SH} , of PNP at the *neat* water/cyclohexane interface. Note that in some cases, the solid line does not coincide with the spectral fit due to small nonresonant contributions to $\chi^{(2)}$. The uncertainty in λ_{SH} is indicated by horizontal error bars and ranges from ± 1 (salt-free PNP solution) to ± 5.5 nm (1 M NaBr system) with an average uncertainty of ± 3 nm.

mentally, light with frequency ω is focused onto an interface, and a signal with frequency 2ω is detected. The intensity of the detected signal is proportional to the square of the second-order susceptibility tensor, $\chi^{(2)}$:

$$I(2\omega) \propto |\chi^{(2)}|^2 I(\omega)^2 \quad (1)$$

where $I(2\omega)$ and $I(\omega)$ are the intensities of the detected and incident light, respectively. Within the dipole approximation, $\chi^{(2)}$ is zero in isotropic environments meaning that any detected second harmonic signal necessarily arises from the anisotropic boundary between the aqueous and organic phases. The $\chi^{(2)}$ tensor is composed of both nonresonant and resonant contributions:³⁰

$$\chi^{(2)} = \chi_{NR}^{(2)} + \chi_R^{(2)} \quad (2)$$

The resonant contribution is typically quite large relative to the nonresonant contribution. $\chi_R^{(2)}$ is related to the microscopic hyperpolarizability through the following relationship:

$$\chi_R^{(2)} = \sum_{k,e} \frac{\langle \mu_{gk} \mu_{ke} \mu_{eg} \rangle}{(\omega_{gk} - \omega - i\Gamma)(\omega_{eg} - 2\omega + i\Gamma)} \quad (3)$$

where Γ is the line strength, and μ_{ij} represents the transition matrix element between states i and j (g is the ground state, e is the first excited state, and k is some virtual intermediate state).³⁰ According to this relation, when 2ω is resonant with ω_{eg} , $\chi^{(2)}$ becomes large yielding a strong resonance enhancement in the intensity of the detected signal, $I(2\omega)$. An *effective* excitation spectrum of a surfactant adsorbed to an interface can therefore be determined by measuring $I(2\omega)/I(\omega)^2$ as a function of 2ω .

Figure 4 shows SHG spectra for PNP at the water/cyclohexane interface where the aqueous phase contains different salts and a variety of bulk salt concentrations. With the exception of the spectrum for the salt-free system, each spectrum shown

TABLE 1: Comparisons of Wavelength Maxima for Bulk and Interface Electrolyte Solution Spectra

sample	$\lambda_{\max}(\text{SHG})$, nm	$\lambda_{\max}(\text{bulk})$, ^a nm	$\Delta\lambda_{\max}$, ^b nm	$\delta\lambda_{\max}(\text{SHG})$, ^c nm
no salt	317	317.3	0	± 1
1 M NaF	320	320.1	0	± 3.5
1 M NaCl	321	318.4	3	± 3
1 M NaBr	322	318.5	4	± 5.5
3 M NaCl	318	319.6	2	± 2

^a Reported values are averages of several measurements. Bulk solution measurements were made with 0.5 nm resolution. Therefore, uncertainty in these measurements is ± 0.5 nm. ^b $\Delta\lambda_{\max} = \lambda_{\max}(\text{SHG}) - \lambda_{\max}(\text{bulk})$. ^c $\delta\lambda_{\max}(\text{SHG})$ represents the uncertainty in the wavelength maximum of the SHG measurement with use of a 95% confidence interval.

reflects a composite of at least three and up to nine individual spectra that have been normalized and averaged together. The salt-free sample was used as a benchmark to assess the consistency of the experimental setup. Consequently, the corresponding spectrum shown in Figure 4 is a composite of 17 spectra. Since increasing the number of spectra incorporated into a composite reduces the uncertainty in the SHG wavelength maximum, the spectrum for the salt-free system is much less noisy than the other spectra shown in Figure 4. Data for each spectrum were fit by using eqs 1–3. With constant salt concentrations of 1 M, the SHG spectra appear to shift to longer wavelength as the salt's anion size increases from fluoride to chloride to bromide (Figure 4a). In the absence of salt, the SHG spectrum for PNP lies at 317 nm, but the spectrum shifts as much as +5 nm when NaBr is added, the most extreme case. However, such a large shift is within the window of uncertainty, $\delta\lambda_{\max}(\text{SHG})$, as shown in Table 1. Therefore, such a shift may not be significant. Additionally, a closer inspection of spectral trends shows no dependence on bulk salt concentration for either the NaF or NaCl systems (Figure 4b,c). The SH wavelength maximum shifts anywhere from 1–4 nm to the red, independently of salt concentration, a shift that remains within our windows of uncertainty.

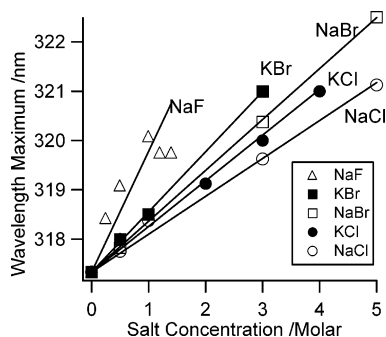


Figure 5. Wavelength maxima for electronic absorbance spectra of PNP in bulk electrolyte solutions. The resolution of the spectrophotometer yields an uncertainty in each data point of ± 0.5 nm. Measurements for NaF deviate from linearity as salt concentration approaches the solubility limit. Therefore the fit for these data includes only the first four data points.

To interpret the apparent spectral red shift observed for changes in ion identity at 1 M concentrations, we compared SHG spectra to bulk aqueous electrolyte solution absorbance spectra. As shown in Figure 5, the solute's electronic excitation shifts to longer wavelength as bulk salt concentration increases, and the magnitude of the observed red shift correlates to ion size and hydration energy. With the exception of the fluoride ion, the red shift is more dramatic for larger ions, both cationic and anionic. For both potassium and sodium salts, the red shift is greater for a bromide counterion than a chloride counterion. If anion identity is maintained, the red shift is greater for a potassium counterion than a sodium counterion.

This shift in bulk electrolyte solution spectra could arise from either a change in the solvent's bulk dielectric properties or specific ion–solute interactions. However, the static dielectric constant of a solvent generally *diminishes* upon the addition of electrolytes due to excluded volume effects and the screening of solvent dipoles by ions, which lead to a decrease of dipole–dipole correlations.^{31–35} For PNP, a decrease in the solvent's dielectric constant would lead to a *blue* shift in the absorbance spectrum. Consequently, the observed *red* shift must be attributed to specific ion–solute interactions that increase the solute's ground-state dipole moment relative to the dipole moment of the excited state. A previous report has suggested that the arrangement of water molecules around a PNP molecule is similar to that of water around cations.³⁶ The authors claim that the competition for hydration between PNP and cations weakens the solvation of PNP. The solvation of PNP is weakened even further by cations with more negative enthalpies of hydration. The solvatochromic behavior of PNP indicates that a more strongly bound solvation shell around the solute causes a red shift in the electronic absorbance spectrum. Consequently, PNP in electrolyte solutions containing larger cations (K^+ vs Na^+ in this case) will show a larger positive deviation (= red shift) from the salt-free absorbance wavelength maximum.³⁷

Conversely, anions will tend to enhance the solvation of PNP molecules in solution. Enhanced solvation of PNP is most pronounced for weakly hydrated anions. Therefore, one expects to see a more prominent red shift from the salt-free absorbance wavelength for larger, less solvated anions. The expected results are consistent with data presented in this work, although we are as yet unable to explain the behavior of fluoride-containing solutions. (Fluoride salts were not used in the work cited above.³⁷)

As summarized in Table 1, the observed spectral shifts of PNP adsorbed to aqueous electrolyte/cyclohexane interfaces

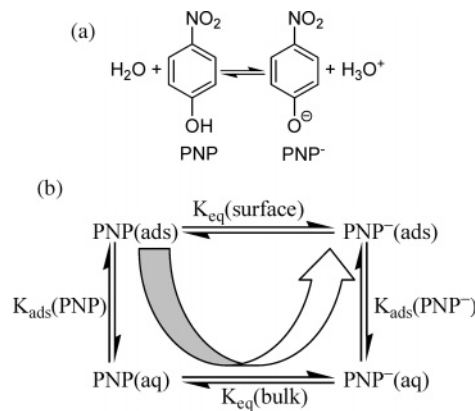


Figure 6. Equilibrium equations governing the distribution of PNP and PNP^- molecules in bulk solution (a) and at the water/cyclohexane interface (b).

closely track changes in the solute's electronic structure in bulk aqueous electrolyte solutions as a function of salt concentration and identity. For 1 M NaF measurements, the SHG maximum is identical with the bulk solution absorbance maximum. The slight red shift from bulk solution measurements for 1 M NaCl and 1 M NaBr (+3 and +4 nm, respectively) lies within the uncertainty associated with the SHG measurements (see Table 1). Even if the apparent spectral red shift observed for adsorbed PNP as a function of ion identity is real, given the small magnitude of the shift from bulk electrolyte solution limits and the absence of any systematic spectral shift as a function of salt concentration (Figure 4b,c), we can attribute the observed red shift in surface spectra entirely to effects similar to those in bulk electrolyte solutions rather than specific, surface charge effects. However, given the magnitude of the uncertainty in $\lambda_{max}(SHG)$, any effects of ions on surface solvation cannot differ significantly from bulk solution interactions.

This conclusion that simple salts affect both water/cyclohexane interfacial polarity and bulk solution solvation of PNP in the same way is somewhat surprising given the previously discussed results for cationic and anionic molecular ruler surfactants. Probe–headgroup interactions for cationic surfactants were thought to significantly perturb the response of the solvatochromic chromophore whereas anionic headgroups showed no evidence of such interaction.^{15,16} Furthermore, given recent molecular dynamics simulations⁵ that indicate a significantly higher surface activity for bromide ions than fluoride ions, we would expect a marked difference in SHG spectra for NaF and NaBr systems. However, surface spectra of both systems are indistinguishable from their respective bulk solution limits. To reconcile previous findings^{5,15,16} with the results presented above, we suggest that the effects of charge on surface solvation are important only when the charge and the solute are closely coupled (as they are in cationic surfactants).

In our efforts to study effects of electrolytes on surface solvation, we carefully controlled the aqueous phase ionic strength. Using a neutral surfactant, PNP, as opposed to the charged molecular ruler surfactants helps minimize the amount of unwanted charged species in solution. However, PNP presents a unique source of ions through its equilibrium with the conjugate base, PNP^- ($pK_a = 7.15$,²⁴ Figure 6a). To ensure that the liquid/liquid interface was not “contaminated” by this ionic solute, the surface distribution of PNP and PNP^- in a solution containing 10 mM PNP was determined.

Since the change in Gibbs free energy is a state function and is related to the equilibrium constant describing PNP/PNP^- partitioning, we can determine the surface distribution of these

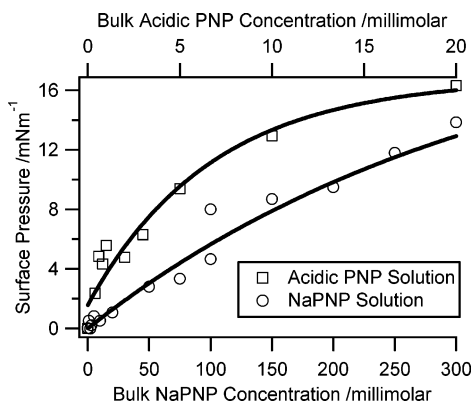


Figure 7. Surface pressure isotherms for PNP and PNP^- . Surface pressure data were fit by using the Gibbs isotherm (eq 4). Uncertainty (2σ) ranges from 1 to 6 mN m^{-1} for acidic PNP measurements (squares, top axis) and 0.1 to 0.8 mN m^{-1} for NaPNP measurements (circles, bottom axis). Data from acidic PNP solutions indicate PNP adsorption while data from NaPNP correspond to PNP^- adsorption.

two species by taking a stepwise path as shown in Figure 6b. The equilibrium distribution for PNP and PNP^- in bulk solution ($K_{\text{eq}}(\text{bulk})$) is known, and the equilibrium constants for the adsorption of PNP ($K_{\text{ads}}(\text{PNP})$) and PNP^- ($K_{\text{ads}}(\text{PNP}^-)$) in 10 mM solutions were calculated from adsorption isotherms at the water/cyclohexane interface of PNP under acidic conditions and NaPNP, respectively.

Figure 7 shows the surface pressure isotherms for these two systems acquired by using the Wilhelmy plate method.³⁸ Excess surface concentration was determined by fitting the data to the Gibbs equation:³⁸

$$A\pi = A(\gamma_o - \gamma) = \Gamma RT \ln(a) \quad (4)$$

where A is the interfacial area (cm^2), π the interfacial pressure (the difference between the surface tensions of the neat interface, γ_o , and that of the interface containing surfactants, γ (J/cm^2)), Γ is the surface excess (mol), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature ($298 \pm 2 \text{ K}$), and a is the activity of the surfactant in bulk solution. Since measurements are taken at millimolar concentrations, we approximate the solute activity with the bulk concentration, c (mol L^{-1}). The slope at any given point on a plot of π vs $\ln(c)$ gives rise to the excess surface concentration of the surfactant, Γ/A (mol/cm^2), for the given bulk concentration.

$$\frac{\partial \pi}{\partial \ln(c)} = \frac{\Gamma}{A} RT \quad (5)$$

The surface excess concentrations of PNP and PNP^- from 10 mM solutions of acidic PNP and NaPNP are 2.04×10^{-10} and $2.06 \times 10^{-11} \text{ mol}/\text{cm}^2$, respectively, a difference of 1 order of magnitude.

Determining the equilibrium constant for an adsorption process is difficult because there exists no well-defined standard state for the surface excess concentration. In these calculations, a mole fraction of 1 was used as the standard state for each species at the surface and in bulk solution. Given that the surface orientation of PNP is 55° off normal³⁹ and the volume occupied by one PNP molecule is $\sim 57 \text{ \AA}^3$, we estimate that, using the room-temperature density of water, each surface molecule of PNP or PNP^- replaces about two water molecules. Defining the depth of the adsorbed monolayer to be $\sim 3.3 \text{ \AA}$ (according to the size of a PNP molecule with such an orientation) allows us to calculate the mole fraction of adsorbed surfactant, X_i^{ads} ,

where i represents either PNP or PNP^- . The mole fraction of adsorbed PNP was calculated to be 0.12 by using the isotherm for PNP under acidic conditions ($\text{pH} \sim 3$) and that of PNP^- was determined to be 0.01 by using the isotherm for NaPNP, assuming total dissociation of NaPNP into Na^+ and PNP^- . We then calculate the mole fraction of the solute in bulk solution X_i by multiplying the molar concentration (0.01 M) by the molar volume of water, 0.018 L mol^{-1} . (This calculation assumes that there is no change in the molar volume of water from that of pure water for such dilute solutions.) For a 10 mM solution, X_i is 1.8×10^{-4} . The equilibrium constant for adsorption of species i , $K_{\text{ads}}(i)$, is simply $[X_i^{\text{ads}}/X_i]$. Given the surface excess concentrations of PNP and PNP^- (stated above), the equilibrium constants are calculated to be 680 for $K_{\text{ads}}(\text{PNP})$ and 61 for $K_{\text{ads}}(\text{PNP}^-)$.

The surface distribution of PNP and PNP^- in a 10 mM solution, $K_{\text{eq}}(\text{surface})$, can now be determined according to the following equation

$$K_{\text{eq}}(\text{surface}) = K_{\text{eq}}(\text{bulk}) K_{\text{ads}}(\text{PNP}^-) / K_{\text{ads}}(\text{PNP}) \quad (6)$$

where $K_{\text{eq}}(\text{bulk})$ represents the equilibrium distribution of PNP and PNP^- in bulk solution. Here, we have neglected any contributions from the hydronium ion. The bulk solution dissociation reaction is defined simply as $\text{PNP}(\text{aq}) \leftrightarrow \text{PNP}^-(\text{aq})$, and the equilibrium constant, $K_{\text{eq}}(\text{bulk})$, is defined accordingly for a 10 mM solution. Under these conditions, $K_{\text{eq}}(\text{bulk})$ is 2.6×10^{-3} . The equilibrium surface distribution, $K_{\text{eq}}(\text{surface})$, of PNP and PNP^- is $\sim 2.4 \times 10^{-4}$. Compared to the amount in bulk solution, there is even less PNP^- at the surface of a 10 mM solution of PNP. We conclude that since only about 0.02% of the surface molecules are PNP^- , there is very little "contamination" of the surface by this ionic species, and therefore, any spectral changes produced by ions come from simple salts rather than the equilibrium between PNP and PNP^- .

Conclusions

Previous experiments using SHG to examine surfactants adsorbed to the water/cyclohexane interface suggested that cationic molecular ruler surfactants are solvated by a less polar interfacial environment than analogous anionic surfactants at the same interface. SHG studies of a neutral surfactant, PNP, adsorbed to the water/cyclohexane interface were performed to further explore the role of charges in interfacial solvation. Results indicate that, compared to bulk solution absorbance spectra, there is no dependence of SHG spectra on charge identity or concentration when the simple salts NaF, NaCl, and NaBr are added to the aqueous phase. These seemingly contradictory results are resolved by the following conclusions: (1) charges at the water/cyclohexane interface influence the interfacial solvation of a solute in the same way that bulk solution solvation is affected by the addition of electrolytes and (2) the spectral shift of adsorbed cationic molecular rulers (relative to anionic molecular rulers) suggests a nonpolar interfacial environment but is actually a result of a change in the solute's electronic structure due to an unshielded probe-headgroup interaction. Additionally, a surface tension study of a 10 mM PNP solution in equilibrium with an organic cyclohexane phase was carried out. Results indicate that the partitioning of PNP and PNP^- at the surface favors PNP adsorption over PNP^- adsorption by a factor of 10. This equilibrium distribution is 1 order of magnitude greater than that found in bulk solution, demonstrating that the amount of PNP^- present at the water/cyclohexane interface of a 10 mM PNP solution is negligible.

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References and Notes

- (1) Gouy *J. Phys.* **IV** **1910**, 9, 457.
- (2) Stern, O. Z. *Elektrochem.* **1924**, 30, 508.
- (3) Randles, J. E. B. *Phys. Chem. Liq.* **1977**, 7, 107.
- (4) Weissenborn, P. K.; Pugh, R. J. *J. Colloid Interface Sci.* **1996**, 184, 550.
- (5) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2002**, 106, 6361.
- (6) Petersen, P. B.; Saykally, R. J. *Chem. Phys. Lett.* **2004**, 397, 51.
- (7) Raymond, E. A.; Richmond, G. L. *J. Phys. Chem. B* **2004**, 108, 5051.
- (8) Liu, D.; Ma, G.; Levering, L. M.; Allen, H. C. *J. Phys. Chem. B* **2004**, 108, 2252.
- (9) Ghosal, S.; Hemminger, J. C.; Bluhm, H.; Mun, B. S.; Hebenstreit, E. L. D.; Ketteler, G.; Ogletree, D. F.; Requejo, F. G.; Salmeron, M. *Science* **2005**, 307, 563.
- (10) Onsager, L.; Samaras, N. N. T. *J. Chem. Phys.* **1934**, 2, 528.
- (11) Adam, N. K. *The Physics and Chemistry of Surfaces*; Oxford University Press: London, UK, 1941.
- (12) Bickerman, J. J. *Surface Chemistry: Theory and Applications*; Academic Press: New York, 1958.
- (13) Chatteraj, D. K.; Birdi, K. S. *Adsorption and the Gibbs Surface Excess*; Plenum: New York, 1984.
- (14) Aveyard, R.; Saleem, S. M. *J. Chem. Soc., Faraday Trans. 1* **1976**, 72, 1609.
- (15) Beildeck, C. L.; Steel, W. H.; Walker, R. A. *Langmuir* **2003**, 19, 4933.
- (16) Beildeck, C. L.; Steel, W. H.; Walker, R. A. *Faraday Discuss.* **2005**, 129, 69.
- (17) Steel, W. H.; Damkaci, F.; Nolan, R.; Walker, R. A. *J. Am. Chem. Soc.* **2002**, 124, 4824.
- (18) Steel, W. H.; Walker, R. A. *Nature* **2003**, 424, 296.
- (19) Steel, W. H.; Lau, Y. Y.; Beildeck, C. L.; Walker, R. A. *J. Phys. Chem. B* **2004**, 108, 13370.
- (20) Steel, W. H.; Beildeck, C. L.; Walker, R. A. *J. Phys. Chem. B* **2004**, 108, 16107.
- (21) Esenturk, O.; Walker, R. A. *Vibrational Studies of Alcohol Films: Molecular Structure Vs. Long-Range Order*; 227th National Meeting of the American Chemical Society, Anaheim, CA, 2004; American Chemical Society: Washington, DC, 2004.
- (22) Esenturk, O.; Mago, D.; Walker, R. A. In preparation.
- (23) Zhang, X.; Steel, W. H.; Walker, R. A. *J. Phys. Chem. B* **2003**, 107, 3829.
- (24) *CRC Handbook of Chemistry and Physics*, 77th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1996.
- (25) Eisenthal, K. B. *J. Phys. Chem.* **1996**, 100, 12997.
- (26) Richmond, G. L. *Annu. Rev. Phys. Chem.* **2001**, 52, 357.
- (27) Wang, H.; Borguet, E.; Eisenthal, K. B. *J. Phys. Chem. A* **1997**, 101, 713.
- (28) Zhang, X.; Esenturk, O.; Walker, R. A. *J. Am. Chem. Soc.* **2001**, 123, 10768.
- (29) Zhang, X.; Walker, R. A. *Langmuir* **2001**, 17, 4486.
- (30) Shen, Y. R. *Nature* **1989**, 337, 519.
- (31) Levesque, D.; Weis, J. J.; Patey, G. N. *J. Chem. Phys.* **1980**, 72, 1887.
- (32) Patey, G. N.; Carnie, S. L. *J. Chem. Phys.* **1983**, 78, 5183.
- (33) Kusalik, P. G.; Patey, G. N. *J. Chem. Phys.* **1988**, 88, 7715.
- (34) Barthel, J. M. G.; Krienke, H.; Kunz, W. *Top. Phys. Chem.* **1998**, 5, 1.
- (35) Bockris, J. O. M.; Reddy, A. K. N. *Modern Electrochemistry*, 2nd ed.; Plenum: New York, 1998; Vol. 1.
- (36) Nikol'skii, B. P.; Yudovich, E. E.; Pal'chevskii, V. V.; Spevak, V. N. *Zh. Obshch. Khim.* **1969**, 39, 1673.
- (37) Nikol'skii, B. P.; Yudovich, E. E.; Pal'chevskii, V. V.; Spevak, V. N. *Zh. Fiz. Khim.* **1970**, 44, 709.
- (38) Adamson, A. W. *Physical Chemistry of Surfaces*; John Wiley & Sons: New York, 1990.
- (39) Steel, W. H.; Walker, R. A. *J. Am. Chem. Soc.* **2003**, 125, 1132.