

Solvent Polarity at an Aqueous/Alkane Interface: The Effect of Solute Identity

William H. Steel and Robert A. Walker*

Department of Chemistry and Biochemistry, University of Maryland, College Park, College Park, Maryland 20742

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Aqueous/alkane interfaces figure prominently in a host of phenomena ranging from solvent extraction to membrane modeling to emulsification.¹ Molecular dynamics simulations have provided detailed pictures of how interfaces alter solvent properties, such as density, relaxation dynamics, and long range order.² However, many predictions from these studies have not been verified due to experimental difficulties associated with noninvasively accessing buried interfaces. In this report, we show that different solutes sample markedly different environments *at the same interface*. While this result may seem intuitive, it does represent the first direct evidence that interfacial properties depend on more than simply the bulk properties of two adjacent phases.

One property of liquid/liquid interfaces that can be probed is solvent polarity.³ Solvent polarity is a measure of the electric field induced inside a solute cavity and depends on the size of the solute and solvent dipoles, as well as solvent polarizability. Given the importance of solvent polarity in solution-phase chemistry, this property should play a leading role in controlling interfacial solute concentration, conformation, and reactivity.

Several years ago, Eisenthal and co-workers used resonance-enhanced second harmonic generation (SHG) to measure effective excitation spectra of known solvatochromic chromophores adsorbed to different liquid/liquid interfaces as well as the air/water interface.^{3a,b} Data revealed that the interfacial polarity could be described by averaged contributions from the two adjacent phases. Molecular dynamics simulations showed this result to be consistent with an interface that was molecularly sharp but thermally roughened, although simulations also suggested that this result should also be very sensitive to probe position relative to the sharp interface.^{2a} Kitamura and co-workers used total internal reflection fluorometry (TIRF) to study liquid/liquid interfaces and found that the average-polarity model breaks down as the polarity of the organic phase increases.^{3c} However, the TIRF technique is not surface specific, and results could represent a convolution of surface and bulk behavior.

We have chosen to examine the interfacial polarity of the aqueous/cyclohexane interface using solvatochromic probes that differ slightly in their functionality. Of the two probes used, *para*-nitrophenol (PNP) is considerably more polar than its hydrophobic analogue 2,6-dimethyl-*para*-nitrophenol (dmPNP). By taking advantage of PNP's enhanced aqueous solubility, we hope to alter slightly the equilibrium distribution of chromophores across the aqueous/cyclohexane interface. In doing so, we can test how subtle variations in solute structure affect solute solvation at the same interface.

Both PNP and dmPNP are negatively solvatochromic chromophores, meaning that first excited-state excitation energies red-shift with increasing solvent polarity.⁴ The origin of this red shift is due to preferential solvation of each solute's more polar excited state relative to their respective ground states. Figure 1 shows the solvatochromic behavior of both PNP and dmPNP plotted as excitation wavelength versus solvent polarity. Solvent polarity has

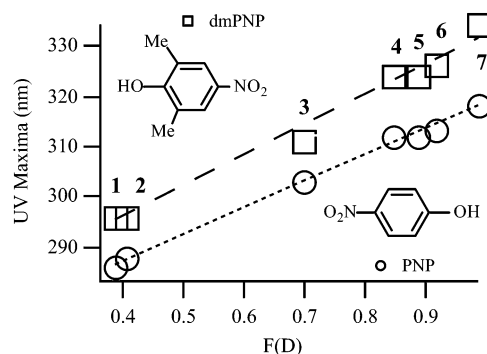


Figure 1. UV excitation maxima of dmPNP (□) and PNP (○) in bulk solvents: (1) octane, (2) cyclohexane, (3) diethyl ether, (4) octanol, (5) hexanol, (6) ethanol, and (7) water. Maxima are plotted against the Onsager polarity function, $F(D)$.

been characterized by the Onsager function, $F(D)$:

$$F(D) = \frac{2(D - 1)}{2D + 1} \quad (1)$$

where D is a solvent's static dielectric constant.

The monotonic solvatochromic behavior of both PNP and dmPNP as a function of solvent polarity indicates that these solutes are sensitive primarily to long-range, nonspecific dipolar forces such as those used in dielectric continuum models.^{4,5} The entire excitation window of dmPNP is red-shifted slightly from that of PNP due to the electron-donating properties of the two methyl substituents. The larger excitation maxima window for dmPNP relative to PNP (38 vs 30 nm) suggests that the dmPNP undergoes a larger change in dipole upon excitation.

To probe the solvatochromic behavior of these solutes at the aqueous/cyclohexane interface, we have used SHG to measure effective excitation spectra of adsorbed species in a manner first employed by Eisenthal and co-workers.^{3a,b} This surface-specific method is sensitive to the energetics and orientation of electronic transition moments.⁶ The intensity of the detected SH signal scales quadratically with the second-order susceptibility, $\chi^{(2)}$:

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

where $I(\omega)$ is the intensity of the incident field, and $\chi^{(2)}$ is a third rank tensor that under the dipole approximation is zero in isotropic environments. The $\chi^{(2)}$ tensor is responsible for the technique's inherent surface specificity and contains both resonant and non-resonant contributions. The resonant contribution to $\chi^{(2)}$ is typically much larger than that from the nonresonant piece and can be related to the molecular hyperpolarizability:

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

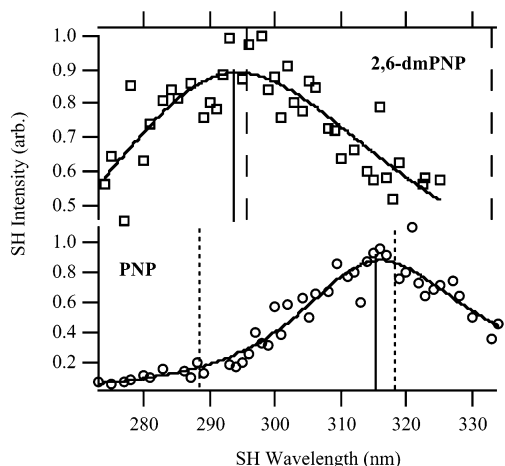


Figure 2. SH spectra of dmPNP (\square) and PNP (\circ) at the aqueous/cyclohexane interface. Fits to eqs 2 and 3 (including a nonresonant term) lead to band positions of 293 and 315 nm, respectively. Dashed lines represent excitation maxima of dmPNP in bulk cyclohexane (296 nm) and water (334 nm). Dotted lines denote excitation maxima of PNP in cyclohexane (288 nm) and water (318 nm).

where μ_{ij} is the transition matrix element between states i and j . (Here, g refers to the ground state, k refers to an intermediate, virtual state, and e refers to contributing excited states.) Brackets denote an orientational average over all contributing states. When 2ω is resonant with ω_{eg} , $\chi_R^{(2)}$ becomes large, leading to a strong enhancement in the observed intensity at 2ω . Thus, measuring the scaled intensity $[I(2\omega)/I^2(\omega)]$ as a function of 2ω records *effective* excitation spectra of solutes adsorbed to liquid/liquid interfaces. Previous SHG experiments of solid/liquid interfaces have shown that interfacial solvent polarity depends sensitively on the intermolecular forces between the two phases.^{6b}

Figure 2 shows SH spectra of dmPNP and PNP adsorbed to an aqueous/cyclohexane interface. Overlaid on each spectrum are lines denoting the excitation maxima of each species in bulk water and cyclohexane. The data clearly indicate that these two solutes experience different polarities *at the same interface*. The more polar solute, PNP, samples a polar environment, similar to that of bulk water as evidenced by a $\lambda_{\max,SHG}$ of 315 nm. In contrast, the interfacial polarity probed by dmPNP is the same as that in bulk cyclohexane ($\lambda_{\max,SHG} = 293$ nm).

The dramatic change in solvent polarity accompanying the addition of the two methyl groups to PNP appeals to intuition. The two methyl groups increase the hydrophobic character of the solute, causing the dmPNP to be preferentially solvated in the organic phase as compared to PNP. Quantitative measurements of polarization-dependent, SH intensities support this picture. Different polarization combinations (of ω and 2ω) sample different elements of the $\chi^{(2)}$ tensor.⁷ Provided that the (ground and excited state) electronic structure of the probe is well characterized, these experiments enable average molecular orientations to be calculated.^{6c,7} The average orientation of PNP adsorbed to the aqueous/cyclohexane interface has the pseudo- C_2 symmetry axis 55° away from the surface normal, whereas the dmPNP solutes are oriented only 43° from the surface

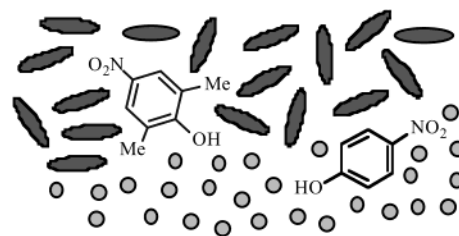


Figure 3. A schematic representation of dmPNP and PNP orientations at the aqueous/cyclohexane interface. The two methyl groups in dmPNP lead to a more upright orientation, suggesting preferential solvation by the nonpolar cyclohexane phase. The polar PNP solute adopts an in-plane orientation, consistent with strong associations with water.

normal. While the difference in orientations is small, it is consistent with a picture that has both functional groups of PNP interacting with the aqueous phase and the two methyl groups of dmPNP “pulling” the solute into the organic phase (Figure 3). We note that the dmPNP orientation of 43° lies close to the SH “magic angle” of 39° predicted by Simpson et al. This result could be attributed to a broad distribution of dmPNP orientations or a (thermally) roughened surface.^{7b} If either effect causes the dmPNP result, then PNP would appear to enjoy either a narrower distribution or be less susceptible to the effects of surface roughness.

To summarize, data show that subtle alterations of solute structure can alter significantly the solute’s local solvation environment at *the same* interface. This finding implies that interfacial solvation is determined as much by solute structure as by gradients in solvent properties across the interfacial boundary and supports predictions that dramatic changes in solvation should accompany small changes in solute position relative to a sharp boundary.^{2a} Furthermore, this result strongly motivates the need to accurately profile the length-scales on which solvation changes across different liquid interfaces.⁸

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