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Reduced Polarity in Protic Solvents near Hydrophobic Solid Surfaces

Xiaoyi Zhang, Okan Esenturk, and Robert A. Walker*

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

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Solvent polarity impacts solution-phase chemistry by controlling solute solubility, conformation, and reactivity.[1] Surfaces, however, can alter solvent properties considerably from bulk solution limits.[2] Identifying how surfaces and solvents conspire to create solvating environments having distinct dielectric properties is essential for accurately modeling broad classes of interfacial phenomena, including electron transfer,[3] self-assembly,[4] and molecular recognition.[5] This communication reports that hydrophobic solid surfaces produce regions of significantly reduced polarity in protic solvents, although these same surfaces impact the polarity of polar, aprotic solvents in an opposite fashion. Results demonstrate how solvents having similar dielectric properties can behave quite differently near surfaces due to disparities in local, short-range intermolecular forces.

Interfacial polarity is inferred from measured solvatochromic shifts in the first $\pi-\pi^*$ transition wavelength of *p*-nitrophenol (pNP). The difference in dipole moments between ground state and excited-state pNP is ~10 D.[6] Differential solvation of these two states leads to a solvent-sensitive excitation wavelength that monotonically red-shifts ~30 nm as solvent polarity increases from that of isooctane ($\epsilon = 1.9$ at 20 °C, $\lambda_{\max} = 285$ nm) to that of water ($\epsilon = 80.4$, $\lambda_{\max} = 318$ nm). (Figure 1).

Experiments probing interfacial solvent polarity employ second harmonic generation (SHG), a surface specific spectroscopy that is sensitive to the energetics and orientation of electronic transition moments.[8] The intensity of the detected SH signal (at 2ω) scales quadratically with the second-order susceptibility, $\chi^{(2)}$:

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

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 nonresonant and resonant contributions. The resonant contribution to $\chi^{(2)}$ can be related to the molecular hyperpolarizability:[8b,c]

$$\chi^{(2)}_{\text{res}} = \sum_{\text{k,e}} \frac{\mu_{\text{gk}}\mu_{\text{ke}}\mu_{\text{eg}}}{(\omega_{\text{gk}} - \omega - i\Gamma)(\omega_{\text{eg}} - 2\omega + i\Gamma)} \tag{2}$$

where μ_{ij} is the transition matrix element between state *i* and *j*. (Here, g refers to the ground state, k to an intermediate, virtual state, and e to a contributing excited state.) When 2ω is resonant with ω_{eg}, $\chi^{(2)}_{\text{res}}$ 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 an *effective* excitation spectrum of solutes adsorbed to the solid−liquid interface. For solid−liquid systems described below, the nonresonant signal measured from the silica surface−neat solvent interface is always more than 50× smaller than the solid−liquid systems containing the adsorbed chromophores.

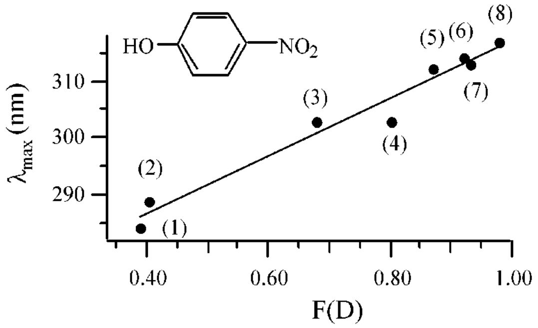

Figure 1. Solvatochromic behavior of pNP in different solvents. $\lambda_{\max}$ is the pNP absorption maximum in different solvents, and $F(D)$ is the Onsager polarity function[7] and is equal to $2(D-1)/(2D+1)$ where D is a solvent's static dielectric constant. Solvents shown are (1) isooctane, (2) cyclohexane, (3) ethyl ether, (4) 1,1,2-trichloroethane, (5) 1-octanol, (6) acetonitrile, (7) ethanol, and (8) water.

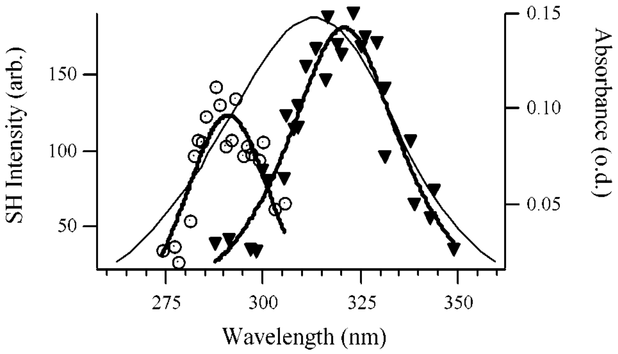

Figure 2. SH spectra of pNP adsorbed to hydrophilic (triangles) and hydrophobic (circles) surfaces from 10 mM solution of pNP in 1-octanol. Fits to data were generated according to eqs 1−2. Superimposed on the spectra is the UV absorption in 1-octanol.

Figure 2 shows the SH spectra of pNP adsorbed to hydrophilic and hydrophobic substrates from a 10 mM 1-octanol solution. Superimposed on the two SH spectra is the UV−vis spectrum of pNP in bulk 1-octanol. Hydrophilic surfaces are hydroxylated silica. Hydrophobic surfaces are created by treating hydrophilic surfaces with dichlorodimethylsilane dissolved in THF. Contact angles at the aqueous−hydrophobic surface measure 77 ± 3°, consistent with previous reports of methyl-terminated quartz.[9]

Fits of the SH spectra calculate that the pNP transition wavelength shifts +7 nm (to longer wavelengths) and −20 nm (to shorter wavelengths) for the hydrophilic and hydrophobic systems, respectively. Such behavior suggests that the hydrophilic−octanol interface presents pNP with a more polar environment than bulk octanol while the hydrophobic−octanol interface is less polar. These results appeal to intuition. A high density of surface and solvent dipoles across the hydrophilic−1-octanol interface can create strong electric fields around adsorbed pNP

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solutes. A diminished dipole density in the hydrophobic−octanol system should reduce interfacial polarity relative to the bulk solution limit.

Three possible models can be invoked to explain the reduction in solvent polarity across the hydrophobic−1-octanol interface: an additive model of interfacial polarity,[2a] surface-induced changes in solvent structure,[10] or dry-layer formation.[11] The additive model of interfacial polarity has been successfully applied to weakly associating air−liquid and liquid−liquid interfaces.[2a] This model quantifies interfacial polarity as the arithmetic mean of the polarities of the two adjacent phases. Applying this model to solid−liquid systems requires assigning a contribution to the observed transition wavelength from the hydrophobic surface. Given a solute transition wavelength of 290 nm at the hydrophobic−octanol surface and a transition wavelength of 314 nm in bulk octanol, one deduces a transition wavelength of 269 nm for pNP at the bare hydrophobic surface. While this result seems inconsistent with data presented in Figure 1, the predicted absorption compares favorably with an anticipated vapor-phase absorption of ~265−270 nm.[12]

Alternatively, if the hydrophobic surface induces the interfacial octanol solvent molecules to arrange themselves with their alkyl chains lying parallel to the surface,[10] then adsorbed solute species would experience solvation forces similar to those in bulk alkane solutions. Based on the solvatochromic data in Figure 1, an "alkane-like" interfacial environment would lead to pNP excitation wavelengths between 285 and 290 nm.

The third model—dry layer formation—describes a region of reduced solvent density that arises from the imbalance between strong solvent−solvent interactions and comparatively weak solvent−substrate interactions.[11] Experimentally, a region of reduced solvent density would affect the solvatochromic behavior of adsorbed solutes by reducing the differential solvation of solute electronic states. In the limit that solvent−solute and substrate−solute interactions disappear, a solute's transition wavelength would approach its gas-phase value.

To test these models we acquired SH spectra of pNP adsorbed to different hydrophobic−solvent, solid−liquid interfaces. Figure 3 shows SH spectra of pNP adsorbed to interfaces formed between hydrophobic surfaces and 1-butanol and 1,1,2-trichloroethane (TCE). The SH spectrum for the butanol system shifts −36 nm relative to the corresponding bulk solution excitation spectrum. In contrast, the TCE SH spectrum shifts +12 nm to longer wavelengths. In other words, the region across a hydrophobic−butanol, solid−liquid interface is less polar than bulk solution. Replacing the protic solvent with a polar, aprotic solvent, however, creates an interfacial environment that is more polar than bulk solution.

The spectrum from the hydrophobic−butanol system is significant. The pNP transition wavelength is calculated to be 276 nm—well below the shortest transition wavelength in any organic solvent and inconsistent with the additive model of interfacial polarity.[12] Surface-induced changes in interfacial solvent structure also fail to account for the hydrophobic−1-butanol data. Given the relative sizes of 1-butanol and 1-octanol, any reduction in interfacial polarity due to solvent reorientation should be more extreme for the less polar, 1-octanol system, not vice versa. Hence, the pNP spectrum at the hydrophobic−1-butanol interface supports the idea that the reduction in solvent polarity is due to a diminished solvation around the solute.

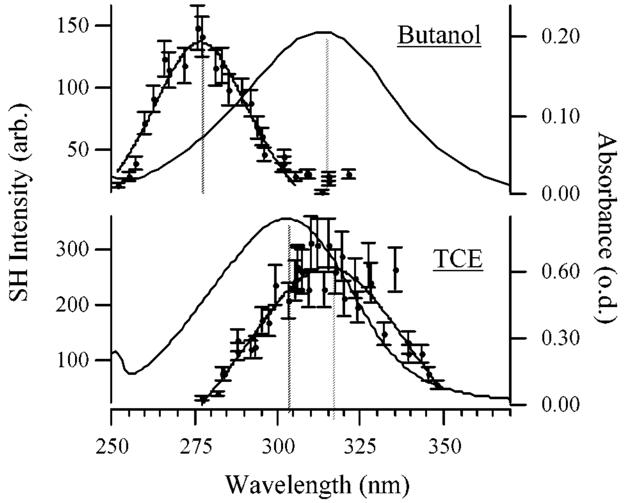

Figure 3. SH spectra of pNP adsorbed to hydrophobic−butanol (top) and −1,1,2-trichloroethane (bottom) interfaces. Superimposed on each SH spectrum is the UV absorption spectrum of pNP in the corresponding solvent. Dashed lines correspond to transition maxima.

TCE is the least polar solvent used in these studies. (See Figure 1.) Based simply on solvent property considerations, one might naively assume the region across a hydrophobic−TCE, solid−liquid interface to be the least polar of those presented. The SH spectra show just the opposite to be true. The origins of this effect remain uncertain, although surface-induced anisotropy in this nonassociating solvent may enhance reaction fields inside of interfacial solute cavities.[7]

We believe these results are significant for several reasons. First, data show that solvent polarity across weakly associating solid−liquid interfaces depends sensitively upon solvent identity rather than bulk solvent dielectric properties. Second, experiments suggest that a strong imbalance between solvent−solvent and solvent−substrate forces can create regions of significantly diminished solvent polarity consistent with predictions of dry layer formation at hydrophobic surfaces. Finally, shifts in solute transition wavelengths indicate that experiments are sensitive to the extent of solvation across the interfacial region. Such data should serve as benchmarks for developing models of solvation near solid−liquid boundaries.[2b,11b]

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