

# Solvent Polarity across Strongly Associating Interfaces

William H. Steel,<sup>†</sup> Carmen L. Beildeck,<sup>†</sup> and Robert A. Walker<sup>\*,†,‡</sup>

Department of Chemistry and Biochemistry and Chemical Physics Program, University of Maryland, College Park, College Park, Maryland 20742

Received: April 22, 2004; In Final Form: July 19, 2004

Solvatochromic surfactants—also referred to as “molecular rulers”—have been used to examine changes in polarity across strongly associating liquid/liquid interfaces. The water/alcohol interfaces were formed between an aqueous subphase and either linear (1-octanol and 1-decanol) or branched (3-octanol and 2,6-dimethyl-4-heptanol) alcohols. Resonance-enhanced second harmonic generation was used to collect effective excitation spectra of species adsorbed to these interfaces. Data suggest that all four water/alcohol interfaces contain a region of reduced polarity between the polar water phase and the bulk alcohol. We attribute this region to the alignment of the alkyl chains of the interfacial alcohol molecules. Polarity across the interfaces formed with linear alcohols changes gradually over the distances spanned by ruler surfactants, and interfacial width scales with the length of the alcohol solvent. In contrast, transitions at the interfaces between water and the two branched alcohols are more abrupt. These differences appear to correlate well with the free volume accessible to the solutes within the alcohol solvents adsorbed to the interface. Results are interpreted on the basis of recent studies examining vibrational structure and order in monolayers of alcohols adsorbed to water and alcohol-vapor interfaces.

## I. Introduction

Strongly associating liquid/liquid interfaces describe boundaries where strong dipolar forces control the structure and dynamics of two immiscible liquids. These surfaces are characterized by low interfacial tensions<sup>1,2</sup> and can contain significant electric potential gradients.<sup>3–5</sup> Accordingly, these interfaces figure prominently in electrochemistry studies as well as in efforts to mimic biophysical systems.<sup>5–9</sup> In particular, strongly associating liquid/liquid interfaces have proven to be valuable systems for determining drug efficacy and have served as effective models of cell membranes.<sup>10</sup> Several experimental and theoretical studies have investigated molecular structure at liquid/liquid interfaces in a variety of manners, including molecular dynamics simulations,<sup>11,12</sup> X-ray scattering experiments,<sup>13</sup> and nonlinear optical spectroscopy.<sup>14–16</sup> Numerous experimental and theoretical studies of weakly associating liquid/liquid interfaces have provided considerable information about the forces controlling the structure and dynamics of the boundaries between two phases with little affinity for one another.<sup>11,17–19</sup> In contrast, fewer studies have investigated how long-range order and interfacial structure are influenced by the strong asymmetric forces inherent to strongly associating interfaces.<sup>20–22</sup> Even less clear is how anisotropic boundaries control interfacial solvation. Here, solvation refers to the noncovalent interactions experienced between a solute and its surroundings. Understanding how interfaces alter solute–solvent interactions from those in bulk solution is essential for formulating quantitative predictive models of solution-phase surface chemistry.

In bulk solution, a solute is subject to isotropic forces, and continuum models of solvation can accurately describe solute behavior.<sup>23</sup> At an interface, however, solutes experience an anisotropic environment, especially if the solute contains both polar and nonpolar functional groups that lead to surface-induced polar ordering. Under these circumstances, short-range interactions between a solute and its interfacial surroundings can lead to dramatic changes in solute energetics, structure, and reactivity. In the studies described below, we use resonance-enhanced second harmonic generation to measure solvent polarity across strongly associating liquid/liquid interfaces. This approach, first developed by Eisenthal and co-workers,<sup>24,25</sup> consists of acquiring effective excitation spectra of solvatochromic probes adsorbed to interfaces and then comparing results to actual excitation wavelengths from the two bulk solution limits. The interfaces discussed below all consist of an aqueous phase in contact with an alcohol, and the solutes are solvatochromic probes that have been integrated into surfactants of varying lengths, i.e., “molecular rulers”.<sup>26,27</sup> Results show that interfacial properties depend sensitively on the structure of the alcohol, with all strongly associating interfaces containing a region of reduced polarity between the adjacent solvent layers. This result is important because it emphasizes how interphase interactions between two solvents can create environments having completely different properties from those of either bulk solution.

On some length scale, interfacial properties must converge to bulk solution limits. Quantifying changes in properties such as density, dielectric constant, and refractive index can lead to the determination of the interfacial width. This distance can be short by molecular standards, leading to abrupt changes in these solvent properties, or the interfacial width can be broad, with properties changing gradually over multiple solvent diameters. Several experimental techniques currently exist for investigating

\* To whom correspondence should be addressed. E-mail: rawalker@umd.edu.

<sup>†</sup> Department of Chemistry and Biochemistry.

<sup>‡</sup> Chemical Physics Program.

the properties of interfaces, each observing a different characteristic feature of these inhomogeneous regions. X-ray<sup>28</sup> and neutron scattering experiments<sup>29</sup> provide the most direct measure of interfacial width by recording profiles of solvent density at liquid/liquid interfaces along the interfacial normal. Such techniques have been used successfully to probe interfacial width at weakly associating water/alkane interfaces and determined these boundaries to be molecularly sharp.<sup>13</sup> This finding is in agreement with molecular dynamics simulations<sup>30–32</sup> and non-linear optical second harmonic generation studies<sup>33</sup> of these interfaces.

Unlike the scattering techniques described above, optical spectroscopy is not a direct measure of changes in solvent properties. Techniques such as total internal reflection fluorescence (TIRF) and second harmonic generation (SHG) probe the interactions between solvent and solute molecules at the interface. These techniques have been broadly applied to interfaces, including air/liquid, solid/liquid, and liquid/liquid boundaries, in attempts to investigate a variety of solvent-sensitive properties of solute probe molecules.<sup>34–40</sup> For example, Kitamura and co-workers have used TIRF to investigate the energy transfer between two fluorescent dyes at weakly associating liquid/liquid interfaces,<sup>36,41</sup> whereas Wirth and co-workers examined the lateral diffusion of Acridine Orange at a variety of weakly associating water/alkane interfaces.<sup>42</sup> Eisenthal and co-workers have used SHG extensively to study solvent polarity and solvation dynamics at liquid/liquid interfaces, producing some of the earliest quantitative models of interfacial polarity.<sup>24,25,43,44</sup> Recent experiments using SHG to probe interfacial excitation of solvatochromic surfactants adsorbed to weakly associating interfaces have shown these boundaries to be molecularly sharp,<sup>33</sup> in agreement with scattering studies and molecular dynamics simulations mentioned above.<sup>30–32,45</sup>

The success of SHG as a probe of solvent polarity at weakly associating liquid/liquid interfaces has led us to believe that it will also be a suitable probe of such behavior at strongly associating interfaces. Although a growing body of work focused on interfacial properties at weakly associating boundaries exists, little has been done to probe solvent properties at interfaces between water and organic solvents capable of interacting through strong dipolar forces.<sup>20,22,46</sup> These strongly associating interfaces play prominent roles in chemistry and warrant thorough investigation. To this point, the majority of work examining strongly associating liquid/liquid interfaces has focused on the vibrational structure of the organic solvent at the interface. For example, sum frequency generation (SFG) has been used to probe the structures of pentadecanoic acid at the water surface,<sup>47</sup> long-chain alcohols at the liquid/vapor interface,<sup>22</sup> and surfactant chains at the air/water interface.<sup>48–50</sup> Emerging from these studies are a variety of conclusions about the structure of the adsorbed surfactants and alkyl chains. Briefly, the presence of gauche defects was determined to be related to the surface coverage<sup>47</sup> and chain length of the adsorbed species.<sup>22,46</sup> Finally, Cramb and Wallace reported using SHG to investigate the orientation of octanol molecules at the water/octanol interface.<sup>9</sup> They determined that the adsorbed octanol molecules exhibited a net tilt away from surface normal.

In addition to the vibrational studies mentioned above, several simulations have been performed that provide information about the structure of strongly associating interfaces. Michael and Benjamin investigated the fluorescence of probes adsorbed to a water/octanol interface and determined that the relaxation times were strongly dependent on the solute's position relative to the interface.<sup>12</sup> Their results also implied that the water/octanol

interface was composed of a low-polarity region that contained no water molecules, a conclusion that is supported by the findings presented in this work.

Experiments described in this work use SHG to investigate the interfacial excitation of surfactants adsorbed to strongly associating liquid/liquid interfaces between water and various alcohols. By observing the solvent-sensitive excitation response, we are able to infer the polarity of the interface. As surfactant length increases, interfacial polarity converges to bulk solution limits, and each family of excitation spectra represents a profile of the changes in solvent polarity across the liquid/liquid interface. These experiments represent the first attempts to probe the dipolar width of water/alcohol interfaces, and as such, some of the interpretation is necessarily speculative.

## II. Experimental Section

Experiments described in this work couple resonance-enhanced SHG spectroscopy with surfactants created specifically to vary the equilibrium distribution of solvatochromic solutes across a liquid/liquid interface. By measuring how the SHG spectra vary with surfactant length, the dipolar width of different strongly associating liquid/liquid interfaces has been measured. The alcohols used to create interfaces with an aqueous subphase include 1-octanol, 1-decanol, 3-octanol, and 2,6-dimethyl-4-heptanol. Whereas similar experiments at interfaces between water and alkanes found such weakly associating interfaces to be sharp,<sup>33</sup> these strongly associating interfaces appear to be broader and to contain a region of reduced polarity between the two phases. These findings are discussed in terms of the molecular structures of the individual solvents themselves and recent simulations that expose the role of interfacial roughness on solvation dynamics and interfacial polarity.

Molecular rulers are surfactants containing an ionic headgroup attached to a hydrophobic nitrobenzene chromophore via an alkoxy spacer whose length can be varied by controlling the number of methylene groups present. They are synthesized via a straightforward, two-step process. A 1,*n*-diol containing *n* methylene groups is combined with *para*-nitrofluorobenzene to produce an intermediate product containing a terminal alcohol. The alcohol is converted to an ionic sulfate group by the addition of chlorosulfonic acid. Surfactants have been produced with spacers ranging from two to eight methylene groups, primarily in even increments. A more complete description of synthetic conditions and characterization of the molecular rulers can be found in ref 27.

Resonance-enhanced SHG was used to acquire effective excitation spectra of molecular rulers adsorbed to different water/alcohol liquid/liquid interfaces. Because of its origins, the resonance-enhanced response is both surface- and molecule-specific, meaning that spectra result only from solutes influenced by interfacial anisotropy.<sup>14,51,52</sup> In a typical experiment, a single coherent optical field of frequency  $\omega$  is incident upon an interface having a submonolayer coverage of a given ruler surfactant. A nonlinear polarization of frequency  $2\omega$  and intensity  $I(2\omega)$  is detected, where the intensity of this second harmonic field is proportional to the square of the second-order susceptibility,  $\chi^{(2)}$

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

and  $\chi^{(2)}$  is a third-rank tensor that, under the electric dipole approximation, is zero in isotropic environments. The  $\chi^{(2)}$  tensor, then, imparts to the technique its inherent surface specificity.

The tensor itself contains both resonant and nonresonant contributions

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

For dielectric systems, such as the water/alcohol interfaces considered here, the resonant term is typically two orders of magnitude larger than the nonresonant contribution and can be related to the microscopic hyperpolarizability

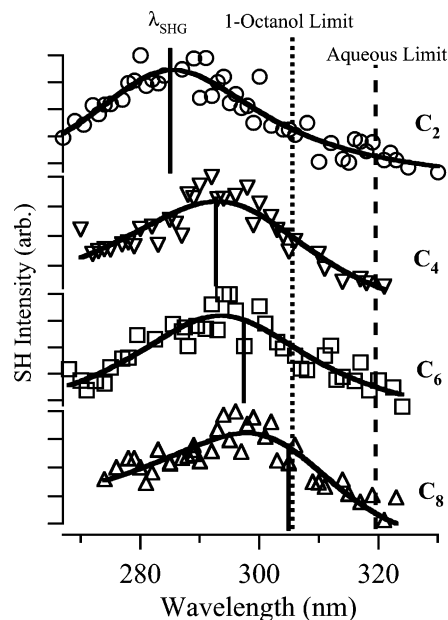
$$\chi_R^{(2)} = \sum_{k,e} \frac{\langle \mu_{gk} \mu_{ke} \mu_{eg} \rangle}{(\omega_{gk} - \omega - i\Gamma)(\omega_{eg} - 2\omega + i\Gamma)} \quad (3)$$

where  $\mu_{ij}$  is the transition matrix element between state  $i$  and state  $j$  (where  $g$  stands for the ground state,  $k$  for an intermediate virtual state, and  $e$  for the first excited state).  $\omega_{ij}$  represents the transition energies between the ground state and states  $k$  and  $e$ , and  $\Gamma$  is the transition's line width. When  $2\omega$  is resonant with  $\omega_{eg}$ ,  $\chi^{(2)}$  becomes large, leading to a strong resonance enhancement in the observed intensity at  $2\omega$ . Thus, measuring the scaled intensity [ $I(2\omega)/I^2(\omega)$ ] as a function of  $2\omega$  records an *effective* excitation spectrum of solutes adsorbed to an interface. With the exception of data recorded to determine solute orientations, spectra in this work were acquired under  $P_{2\omega}P_\omega$  polarization conditions, where  $p$ -polarized light describes light that is polarized in the plane defined by the surface normal and the direction of propagation. Varying the incident and detected polarizations enabled us to determine the average chromophore orientation using methods described previously.<sup>52</sup> Different polarizations did not lead to qualitatively different SHG spectra.

The experimental methods used for acquiring spectra of molecular rulers adsorbed to strongly associating liquid/liquid interfaces are similar to those described in ref 33. One difference between the two systems is the solubility of the molecular rulers in the organic phase. Because of slight surfactant solubility in the alcohol solvents, only one spectrum was usually collected from each prepared sample before the sample was discarded. Over the course of several hours, molecular rulers were able to transfer across the aqueous/organic interface from the water phase into the alcohol. Rulers in the alcohol phase can absorb the second harmonic signal produced by those chromophores adsorbed to the interface; thus, the apparent intensity of the detected SH signal diminishes slightly over time. At weakly associating interfaces, multiple spectra could be recorded from the same system and compared for internal consistency and reproducibility. In the current studies, spectra of surfactants adsorbed to strongly associating interfaces were acquired within 3 h of cell assembly. Spectra acquired during this window demonstrated reproducible behavior, and results were normalized to produce the composite spectra shown in Figures 1–4.

### III. Results

Figure 1 shows the composite SH spectra of four molecular ruler species ( $C_2$ ,  $C_4$ ,  $C_6$ , and  $C_8$  rulers) adsorbed to the water/1-octanol interface, where  $C_n$  refers to the number of methylene groups in the alkyl spacer. The SH data are fit according to eqs 1–3. Overlaid on the plots are dashed and dotted lines to denote the excitation maxima of each species in bulk aqueous and organic solutions, respectively. The solid vertical line on each panel indicates the fitted interfacial maximum of each species (including the nonresonant contribution). Note that interference effects between the resonant and nonresonant contributions to  $\chi^{(2)}$  can lead to calculated SH maxima that do not coincide with the apparent spectral maximum. (For example, see the bottom



**Figure 1.** Resonance-enhanced SHG spectra of (top to bottom)  $C_2$ ,  $C_4$ ,  $C_6$ , and  $C_8$  rulers adsorbed to a water/1-octanol interface. Dotted and dashed vertical lines denote excitation maxima in bulk 1-octanol and water, respectively. Solid vertical lines correspond to SHG maxima ( $\lambda_{SHG}$ ) as determined by fitting the data to eqs 1–3. Note that SHG maxima do not always correspond to the wavelengths with the highest SHG intensity, owing to the nonresonant contribution to  $\chi^{(2)}$  in eq 2.

panel of Figure 1, depicting the SHG spectrum of the  $C_8$  ruler at the water/1-octanol interface.)

The data show that the solvatochromic probe of each solute samples a unique solvation environment. Of greater interest is the local polarity sampled by each probe. The excitation maximum of the  $C_2$  ruler at the water/1-octanol interface is  $285 \pm 3$  nm, compared to maxima of 317 nm in bulk water and 306 nm in 1-octanol. An excitation maximum of 285 nm suggests a solvation environment that is even less polar than that of a bulk alkane having a static dielectric constant of  $\sim 2.0$ . As the alkyl spacer in the molecular rulers lengthens from  $C_2$  to  $C_4$  to  $C_6$  to  $C_8$ , the chromophores can “float” further into the bulk organic phase. The resulting interfacial excitation maxima reflect increasingly polar solvation environments. This change is detected as a red shift in the fitted interfacial excitation maxima from 285 nm for the  $C_2$  ruler to 305 nm for the  $C_8$  ruler. The 305-nm interfacial excitation maximum of the  $C_8$  ruler is similar to the excitation maximum of the  $C_8$  ruler in bulk 1-octanol (306 nm).

Whereas molecular rulers adsorbed to weakly associating interfaces reflected solvation environments that could be described by appropriately weighted additive effects from the two adjacent solvents,<sup>33</sup> here, rulers adsorbed to strongly associating interfaces sample dielectric environments that are considerably less polar than bulk 1-octanol. This result cannot be explained by an additive model of interfacial polarity. The series of spectra implies that the interfacial polarity gradually converges from a nonpolar alkane-like environment to one reflecting a solvation similar to that of bulk 1-octanol. In contrast, when adsorbed to weakly associating interfaces, the same species of probes displayed a monotonic blue shift in interfacial excitation maxima, implying a transition from a more polar to a less polar solvation environment. The length of the alkyl spacer in the  $C_8$  ruler is approximately 1.2 nm, assuming no gauche defects in the chain. This length represents an upper limit to the width of the reduced-polarity region between the



**TABLE 1: Summary of Data Collected for Species Adsorbed to Liquid/Liquid Water/Alcohol Interfaces<sup>a</sup>**

solute	organic solvent	interfacial max <sup>b</sup> (nm)	fwhm <sup>c</sup> (nm)	tilt angle <sup>d</sup> (deg)
C <sub>2</sub> ruler	1-octanol	285	36	34
C <sub>4</sub> ruler	1-octanol	295	36	37
C <sub>6</sub> ruler	1-octanol	297	38	36
C <sub>8</sub> ruler	1-octanol	305	35	37
C <sub>2</sub> ruler	1-decanol	295	40	37
C <sub>4</sub> ruler	1-decanol	295	35	32
C <sub>6</sub> ruler	1-decanol	299	41	
C <sub>8</sub> ruler	1-decanol	300	36	32
C <sub>2</sub> ruler	3-octanol	297	51	
C <sub>4</sub> ruler	3-octanol	294	43	
C <sub>6</sub> ruler	3-octanol	305	48	
C <sub>2</sub> ruler	2,6-dimethyl-4-heptanol	293	42	33
C <sub>4</sub> ruler	2,6-dimethyl-4-heptanol	297	46	
C <sub>6</sub> ruler	2,6-dimethyl-4-heptanol	307	45	32

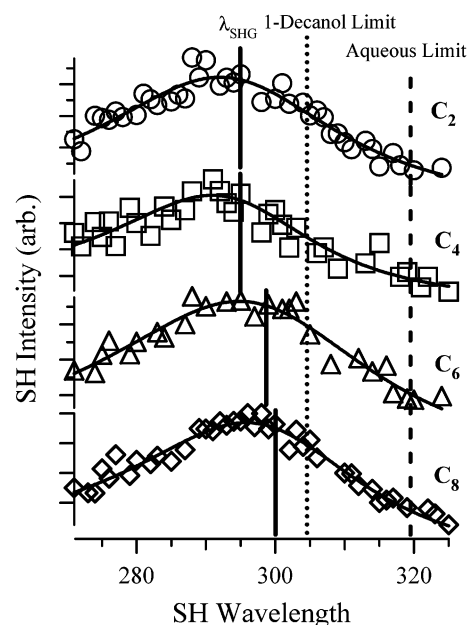
<sup>a</sup> Average excitation wavelength of species is  $\sim 305$  nm in bulk organic solvents and  $\sim 318$  nm in bulk water. <sup>b</sup> Interfacial max refers to the fitted excitation maximum as determined by fitting spectra with eqs 1–3. Reported wavelengths have typical uncertainties of  $\pm 1.5$ – $3.0$  nm. <sup>c</sup> Full width at half-maximum (fwhm) describes the line width of SHG spectra collected at liquid/liquid interfaces. <sup>d</sup> Tilt angle refers to the orientation of the chromophore at liquid/liquid interfaces relative to the surface normal. Reported tilt angles have uncertainties  $\pm 3^\circ$ .

two phases. All weakly associating interfaces were found to converge to bulk organic limits over a distance of less than  $9 \text{ \AA}$ .<sup>33</sup>

Another feature distinguishing this series of spectra from similar series collected at weakly associating interfaces is the relatively constant of the line width of each spectrum as the alkyl spacer lengthens. At weakly associating interfaces, the spectrum of the molecular ruler with the longest alkyl spacer had the narrowest full width at half-maximum (fwhm). Here, there is little change in the line width of the spectra, as they range from 35 nm (C<sub>8</sub>) to 38 nm (C<sub>2</sub> and C<sub>6</sub>). Excitation spectra of molecular rulers in bulk solutions of water and 1-octanol have fwhm of 68 and 56 nm, respectively. A narrower line width for adsorbed species indicates a solvation environment that is more homogeneous than the bulk solution.<sup>53–55</sup> Interestingly, excitation spectra of molecular rulers in bulk alkanes have an average line width of 44 nm. This observation would indicate that ruler species adsorbed to the water/1-octanol interface sample a solvation environment more homogeneous than bulk alkanes.

Polarization-dependent SHG measurements have been used to determine the average orientation of molecular ruler chromophores relative to the surface normal. Varying the polarization of the incident and detected fields samples different elements of the  $\chi^{(2)}$  tensor. Numerous studies have described how these data can be coupled with known properties of the probes and assumptions about interfacial structure to deduce an average orientation of the probe.<sup>35,51,56</sup> Specific details pertaining to the determination of molecular ruler orientations at surfaces can be found in ref 57. The data reported below indicate that all molecular ruler species adsorbed to the water/1-octanol interface adopt similar orientations, ranging from  $34 \pm 3^\circ$  off normal (C<sub>2</sub>) to  $37 \pm 3^\circ$  off normal (C<sub>4</sub> and C<sub>8</sub>). This finding suggests that the chromophores of each ruler species experience similar homogeneous environments at the water/1-octanol interface. Spectral line width and orientation data are discussed in more detail in Section IV. A summary of the data collected at these and other strongly associating interfaces discussed in this work appears in Table 1. The table includes bulk and interfacial maxima, line width values, and orientation data, when available.

The same four molecular ruler surfactants were used to probe interfacial polarity at the water/1-decanol interface. SH spectra

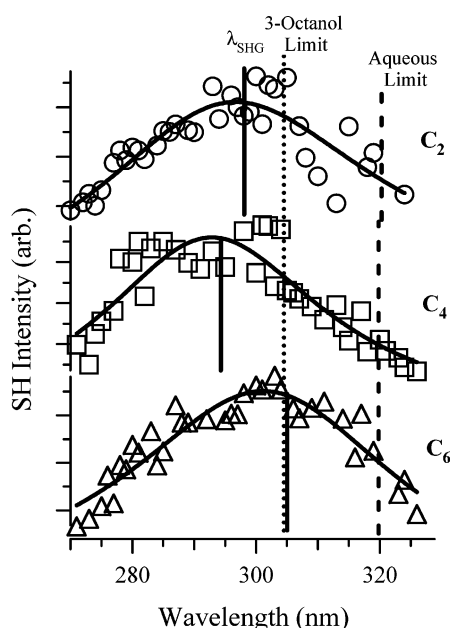


**Figure 2.** Resonance-enhanced SHG spectra of (top to bottom) C<sub>2</sub>, C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> rulers adsorbed to a water/1-decanol interface. Dotted, dashed, and solid vertical lines have the same significance as in Figure 1.

for the water/1-decanol interface are shown in Figure 2, where once again the dashed and dotted lines denote excitation maxima of each species in bulk water and 1-decanol, respectively. Similarly to the water/1-octanol interface, the chromophore of the shortest ruler species, C<sub>2</sub>, experiences the least-polar solvation environment at the water/1-decanol interface. The interfacial maximum of 295 nm for the C<sub>2</sub> ruler is shared by the chromophore of the C<sub>4</sub> ruler before shifting to 300 nm for the chromophore of the C<sub>8</sub> ruler. The C<sub>8</sub> ruler has an excitation maximum of 306 nm in bulk 1-decanol, implying that the interfacial polarity sampled by the C<sub>8</sub> ruler is still less polar than bulk 1-decanol. The difference in water/1-octanol versus water/1-decanol as sampled by the C<sub>2</sub> ruler remains unexplained, but qualitative similarities between the two systems are reassuring. Both linear alcohols create regions of reduced polarity between the bulk water and alcohol phases. That the chromophore of the C<sub>8</sub> ruler does not experience solvation similar to that of the bulk alcohol at the water/1-decanol interface, as it does at the water/1-octanol interface, suggests that the water/1-decanol interface is broader. In general, the data suggest that the width of strongly associating interfaces between water and linear alcohols is related to the length of the alcohol involved.

The line width data for the spectra collected at the water/1-decanol interface are similar to those from the water/1-octanol interface, although the widths cover a slightly broader range: from 35 to 41 nm. Even with this increased range, these data fall within the limits of the uncertainty in the line width calculations ( $\pm 3$  nm), implying that the two interfaces are likely very similar in structure. Orientation measurements also reflect this trend. The tilt of the chromophore of the C<sub>2</sub> ruler is  $37^\circ$  off normal. This value decreases to  $32^\circ$  off normal for the C<sub>8</sub> ruler. Again, given the uncertainty in these values ( $\pm 3^\circ$ ), these can be considered to be equivalent to the tilts observed at the water/1-octanol interface.

Figure 3 shows the SH spectra for three molecular ruler species adsorbed to the water/3-octanol interface: C<sub>2</sub>, C<sub>4</sub>, and C<sub>6</sub>. As was observed at the interfaces between water and the two linear alcohols, the chromophores of the shorter probes

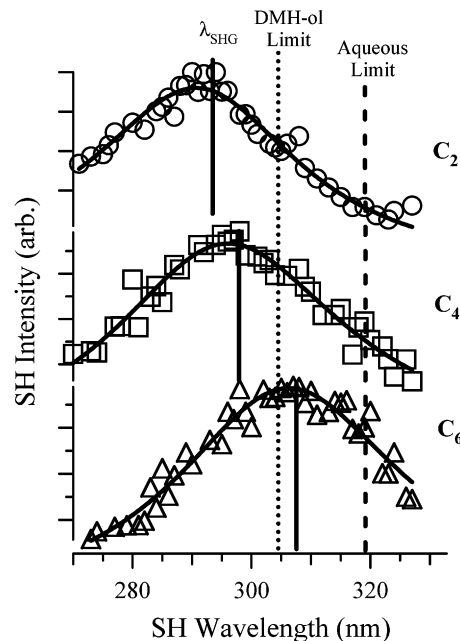


**Figure 3.** Resonance-enhanced SHG spectra of (top to bottom)  $C_2$ ,  $C_4$ , and  $C_6$  rulers adsorbed to a water/3-octanol interface. Dotted, dashed, and solid vertical lines have the same significance as in Figure 1.

experience a solvation that is less polar than that of bulk 3-octanol. The  $C_2$  ruler has an interfacial maximum of 297 nm, whereas the  $C_4$  ruler displays a maximum at 294 nm when adsorbed to the water/3-octanol interface. The slight blue shift observed in the excitation wavelength between the  $C_2$  and  $C_4$  ruler chromophores is a surprising result but does not contradict the picture that emerged from the water/linear alcohol systems. Unlike in the previous (linear alcohol) systems, however, at the water/3-octanol interface, the chromophore of the  $C_6$  ruler has an interfacial excitation maximum equivalent to that of the chromophore in bulk 3-octanol. The chromophore of the  $C_8$  ruler also experiences a polarity similar to that of bulk 3-octanol (see Table 1), although again, the nonresonant contribution is larger than for the shorter species. The conclusion to be drawn from this family of spectra is that the branched 3-octanol has created a more abrupt interface with water than either linear alcohol. The  $C_6$  molecular ruler contains an alkyl spacer that is at most 9 Å long, setting the upper limit of the dipolar width of the water/3-octanol interface.

Additional differences between this system and the two linear alcohol systems can be found when examining the line width data. Here, the line widths of the spectra from the water/3-octanol interface are ~25% broader than from the complementary systems with the linear alcohols. Furthermore, the line width values from the water/3-octanol interface (43–51 nm) are very close to those found in bulk solutions of 3-octanol (49 nm). These observations suggest that the water/3-octanol interface is more heterogeneous than interfaces formed between water and linear alcohols and that interfacial polarity converges to the bulk 3-octanol limit over a shorter length scale than for the linear alcohol systems.

Figure 4 shows the SH spectra of the three shortest molecular rulers adsorbed to the water/2,6-dimethyl-4-heptanol interface. Once again, the interface between water and the branched alcohol appears to be more abrupt than those between water and the linear alcohols. The chromophore of the  $C_2$  ruler experiences the least-polar solvation, as indicated by its interfacial excitation maximum of 293 nm. The  $C_4$  ruler has its



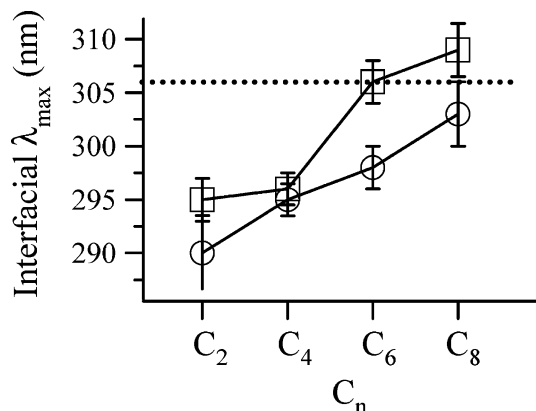
**Figure 4.** Resonance-enhanced SHG spectra of (top to bottom)  $C_2$ ,  $C_4$ , and  $C_6$  rulers adsorbed to a water/2,6-dimethyl-4-heptanol interface. Dotted, dashed, and solid vertical lines have the same significance as in Figure 1.

maximum at 297 nm, implying a local dielectric environment that is less polar than bulk 2,6-dimethyl-4-heptanol. The chromophore of the  $C_6$  ruler absorbs at 307 nm at this interface, a value that is slightly greater than its excitation maximum in bulk 2,6-dimethyl-4-heptanol. The series of spectra is similar to that generated at the water/3-octanol interface and indicates that the interfacial region is no wider than 9 Å, the length of the alkyl spacer in the  $C_6$  ruler.

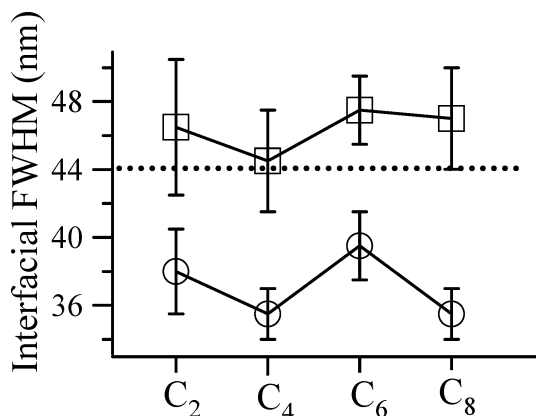
The line widths of the spectra collected at the water/2,6-dimethyl-4-heptanol interface all fall between 42 and 46 nm. These values are slightly larger than those recorded at the water/1-octanol and water/1-decanol interfaces. Although the range is not as wide as that for the line widths of the same species at the water/3-octanol interface, the magnitude of these fwhm data is similar and suggests that the chromophores of the molecular rulers are exposed to interfacial solvation environments that are similar to that of bulk 2,6-dimethyl-4-heptanol (fwhm = 50 nm). Polarization-dependent SHG measurements were again used to calculate the average orientations of the chromophores relative to the surface normal at the water/2,6-dimethyl-4-heptanol interface. The chromophore of the  $C_2$  ruler lies 33° off normal, whereas that of the  $C_6$  ruler lies 32° off normal.

#### IV. Discussion

A feature common to all of the strongly associating interfaces examined in this work is a region of reduced polarity between the water and alcohol phases. This observation emphasizes the nonadditive nature of interfacial properties at strongly associating boundaries. Very recent results from molecular dynamics simulations predict such a low-dielectric region at the water/1-octanol interface, with a minimum in polarity occurring ~6–8 Å into the first 1-octanol layer.<sup>58</sup> In contrast, molecular rulers as well as other solvatochromic probes adsorbed to weakly associating interfaces all sampled polarities that represented weighted contributions from the adjacent solvents.<sup>24,25,33</sup> Results from weakly associating interfaces could be understood in terms of a molecularly sharp interface that is thermally roughened.<sup>30,53</sup>



**Figure 5.** Average fitted interfacial SHG maxima for species adsorbed to strongly associating liquid/liquid water/alcohol interfaces. The dotted horizontal line denotes the average excitation wavelength of the species in bulk organic solvents ( $\sim 305$  nm). The excitation wavelength shifts gradually from a nonpolar limit toward the bulk alcohol limit for the linear alcohols (○), 1-octanol and 1-decanol. The transition from a nonpolar limit to bulk alcohol solvation is more abrupt at the interfaces between water and branched alcohols (□), 3-octanol and 2,6-dimethyl-4-heptanol.



**Figure 6.** Average line width data for SHG spectra of molecular rulers adsorbed to strongly associating liquid/liquid water/alcohol interfaces. The horizontal dashed line denotes the average line width of the excitation spectra of the molecular rulers in bulk alkane solvents ( $\sim 44$  nm). Line widths for molecular rulers adsorbed to interfaces between water and linear alcohols (○) are narrower than those for rulers adsorbed to interfaces between water and branched alcohols (□).

The excitation spectra of molecular rulers adsorbed to strongly associating interfaces indicate that the interfaces between water and linear alcohols are broader than those between water and branched alcohols. Despite the contrasts between weakly and strongly associating interfaces, the relationship between solvent structure and interfacial width at strongly associating interfaces does share a similarity with trends previously observed at weakly associating interfaces. Specifically, free volume considerations based on organic solvent molecular structure appear to control interfacial abruptness.

In this work, two clear patterns emerge in the data from strongly associating interfaces (Figures 5 and 6). Figure 5 shows a plot of the average interfacial maximum observed by each molecular ruler as a function of ruler length for the linear and branched alcohol interfaces. The shifts in excitation wavelength (and thus polarity) are more gradual at interfaces between water and the linear alcohols. Figure 6 shows the averaged line width data, again as a function of ruler length for the linear and branched alcohol interfaces. Overlaid on the plot is a horizontal line denoting the average line width of excitation spectra of

molecular rulers in bulk alkanes (44 nm). As with the excitation wavelength data, the line width data indicate differences between the two types of systems. In general, the spectra recorded at interfaces with branched alcohols have broader fwhm. In this section, we discuss these differences and examine the different factors that can influence interfacial width.

**1. Linear Alcohols.** In the case of the two linear solvents, spectra shown in Figures 1 and 2 indicate that interfacial polarity converges gradually from some nonpolar limit to a dielectric environment reflecting solvation in the bulk alcohol. In earlier work, we attributed this region of reduced polarity to close packing of the alkyl chains of the alcohol molecules at the water/alcohol interface.<sup>59</sup> This picture is consistent with recent X-ray scattering experiments that show the alignment of long-chain surfactants adsorbed to water/hexane interfaces.<sup>13</sup> Furthermore, recent simulations by Benjamin have explicitly modeled the electric field created in a solute cavity located at different positions across a water/1-octanol interface.<sup>58</sup> The results show a distinct minimum in the local polarity  $\sim 6$ – $8$  Å into the 1-octanol phase, supporting the idea that properties across strongly associating interfaces might not reflect those of either bulk phase. In addition, Shen and co-workers conducted vibrational sum frequency generation (VSFG) studies of linear alcohols at the liquid/vapor interface and found that the polar OH groups of these alcohols interact strongly with themselves, and the alkyl chains point away from the liquid.<sup>22</sup> It is likely that a similar orientation occurs at the water/1-octanol interface, with the hydrophilic OH group hydrogen bonding with the adjacent water molecules and the alkyl chains pointing away from the water. Such a picture is supported by recent VSFG studies of monolayers of 1-octanol and 3-octanol at water surfaces.<sup>60</sup> This arrangement could produce a region of reduced polarity between the polar water and bulk alcohol.

Figure 1 shows that, at the water/1-octanol interface, a solvation similar to that of bulk 1-octanol is experienced by the chromophore of the longest ruler used, C<sub>8</sub>. From this series of spectra, we conclude that the width of the water/1-octanol interface is at most 1.2 nm, the length of a fully extended C<sub>8</sub> spacer in the all-trans conformation. Any gauche defects in the alkyl spacer of the ruler surfactant would lead to a shorter projection of the spacer onto the surface normal and reduce the apparent dipolar interfacial width. Molecular dynamics simulations by Berkowitz and co-workers examined the conformational structure of long-chain surfactants (sodium dodecyl sulfate) at the water/vapor and water/carbon tetrachloride interfaces.<sup>61</sup> The simulations predict gauche defects to be present in surfactant chains and indicate that the most defects should occur close to the anionic headgroup of the surfactant. If true, this picture suggests a narrower liquid/liquid interface between water and 1-octanol, and the chromophore of the C<sub>8</sub> molecular ruler should sample a dielectric environment reflecting a reduced polarity. In fact, this is not observed, meaning that other factors should be considered in the analysis of this system. Specifically, factors that reduce the projection of 1-octanol onto the surface normal will limit the interfacial width to only the distance spanned by C<sub>8</sub> rulers containing gauche defects.

At the water/1-octanol interface, the C<sub>8</sub> ruler probe samples a bulk 1-octanol environment even with possible gauche defects in the surfactant chain. If such defects exist, then the solvent molecules cannot be fully extended and parallel to the surface normal. VSFG studies of Shen and co-workers mentioned above found that long-chain alcohols tended to contain such trans-gauche defects at the liquid/vapor interface and also exhibited a net tilt that decreases their projection onto the surface normal.<sup>22</sup>

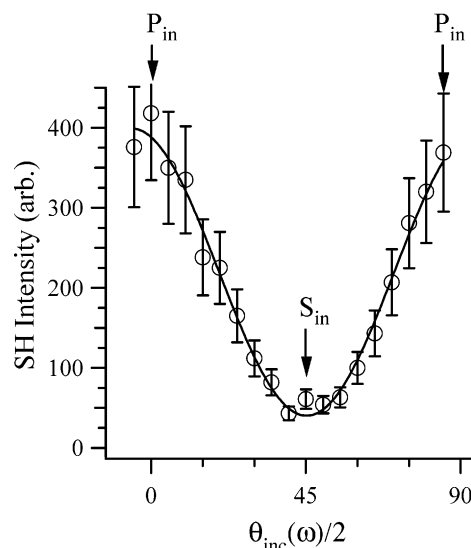


However, alcohol films at the air/water interface show little conformational disorder and a net upright orientation.<sup>20</sup> Our data suggest that, although the C<sub>8</sub> ruler probe might have gauche defects decreasing its length, the long alkyl chains of the 1-octanol molecules are likely tilted off normal at the interface with water, effectively decreasing the width of the nonpolar alkyl region between the water and bulk 1-octanol. The result of these two considerations is that the “shortened” C<sub>8</sub> ruler still spans the water/1-octanol interface, and the chromophore of the longest ruler experiences a surrounding solvation similar to that of bulk 1-octanol.

Geometric considerations of interfacial solvent tilt and conformational disorder within adsorbed surfactants support the findings in this work. The molecular dynamics simulations of sodium dodecyl sulfate at the water/carbon tetrachloride interface predicted the chains of the amphiphile to be oriented approximately 42° off normal.<sup>61</sup> The VSFG studies of alcohols at the liquid/vapor interface determined the average orientation of the long alkyl chains of the alcohols to be approximately 40° off normal.<sup>22</sup> This value agrees well with second harmonic generation studies that found the long axis of the alkyl chains of 1-octanol to be tilted approximately 39° off normal.<sup>9</sup> A gauche defect near the sulfate ion of the molecular ruler would cause the dipole moment of the chromophore to be oriented approximately 7° off the long axis of the alkyl chain. This tilt of 7° relative to the long axis of the alkyl chains of the ruler probes could result in an average chromophore orientation of either approximately 33° or 47° relative to the surface normal, assuming an average chain tilt of approximately 40°. Orientation measurements reveal the chromophore to be tilted approximately 36° off the surface normal for the family of ruler probes at the water/1-octanol interface. This agreement should not be surprising, as we expect excellent registry between the eight-membered alkyl chains of both the 1-octanol and the C<sub>8</sub> ruler probes. The two should pack very efficiently at the water/1-octanol interface, with the chromophore tilting off axis slightly to the observed orientation.

Previous SHG studies performed in our laboratory have examined the excitation of solutes adsorbed to weakly associating liquid/liquid interfaces.<sup>33,59</sup> Orientation measurements included in these studies yielded chromophore orientations ranging from 34° to 51° off the surface normal, depending on the solute and specific system studied. Uncertainties in calculating orientation angles are typically ±3°, assuming that the microscopic hyperpolarizability elements in eq 3 have been calculated accurately.<sup>57</sup> Figure 7 shows a representative plot of SH intensity as a function of incident polarization angle for a molecular ruler surfactant adsorbed to a strongly associating interface. The data have been fit according to procedures described elsewhere to determine the two nonzero hyperpolarizability elements required for determining the orientation angle of the adsorbed chromophores.<sup>35,57</sup>

On average, molecular ruler surfactants adsorbed to weakly associating interfaces adopted orientations between 45° and 50°, whereas, at strongly associating interfaces, the same chromophores have been found to tilt between 32° and 37° off normal. Several years ago, Rowlen and Simpson determined that a SHG “magic angle” of 39° existed.<sup>62,63</sup> They predicted that, given any average orientation and a broad enough distribution about that average, orientation measurements determined by SHG would converge to 39° for a roughened surface. This result contradicts interpretations based on previous SHG studies that assumed distributions described by a single, unique orientation with a delta function distribution. Considering



**Figure 7.** Polarization-dependent SHG spectra of C<sub>4</sub> molecular rulers adsorbed to the water/1-octanol interface. SH intensity is plotted as a function of one-half of the incident polarization angle [ $\theta(\omega)/2$ ]. p and s incident polarizations are denoted on the graph. The data are fit to determine the nonzero elements of the hyperpolarizability found in eq 3. SH intensity for the  $s_{out}p_{in}$  polarization combination necessary for determining the  $\chi_{xxx}^{(2)}$  element was  $31 \pm 5$ . See ref 55 for more details.

the uncertainty in the measurements presented in this work (±3°) the orientations of molecular rulers adsorbed to the water/1-octanol interface are very close to this magic angle. However, as mentioned above, other orientations determined in our laboratory have differed significantly from 39°, including those of *para*-nitrophenol (55°) and 2,6-dimethyl-*para*-nitrophenol (43°) at the water/cyclohexane interface.<sup>16</sup> These two solutes share a similar electronic structure with *p*-nitroanisole (PNAS), the solvatochromic probe used in the molecular ruler surfactants. In our measurements, we assume two nonzero hyperpolarizability elements and a single orientation angle with no distribution.<sup>35</sup> Although these assumptions necessarily introduce uncertainty into our reported measurements, we can state with confidence that molecular ruler surfactants adopt a more upright orientation at strongly associating interfaces than at weakly associating interfaces.

Further support for the proposed water/1-octanol interfacial structure comes from the line width data of the family of spectra recorded at the interface (Table 1). The narrow fwhm (~36 nm) of each spectrum indicates that the chromophore is surrounded by a solvation environment that is much more homogeneous than that of bulk 1-octanol, where broader line widths are observed (~56 nm). The alignment of the alkyl chains of the interfacial 1-octanol molecules could generate such an environment. Spectra of molecular rulers in bulk alkanes have line widths of approximately 44 nm, meaning that probe solvation is more homogeneous at the water/1-octanol interface than in bulk alkanes. This observation is not surprising given that interfacial probes and interfacial solvents all share similar orientations, as well as dipolar interactions.

In the case of the water/1-decanol interface, Figure 2 shows that a polarity indicative of bulk 1-decanol is not experienced by the chromophore of the C<sub>8</sub> ruler. The family of spectra shows the excitation maxima shifting from a nonpolar limit of 295 nm toward 300 nm, which is still ~5 nm away from the average excitation maximum displayed in bulk 1-decanol. We conclude from this result that the water/1-decanol interface is broader than the water/1-octanol interface and that the dipolar

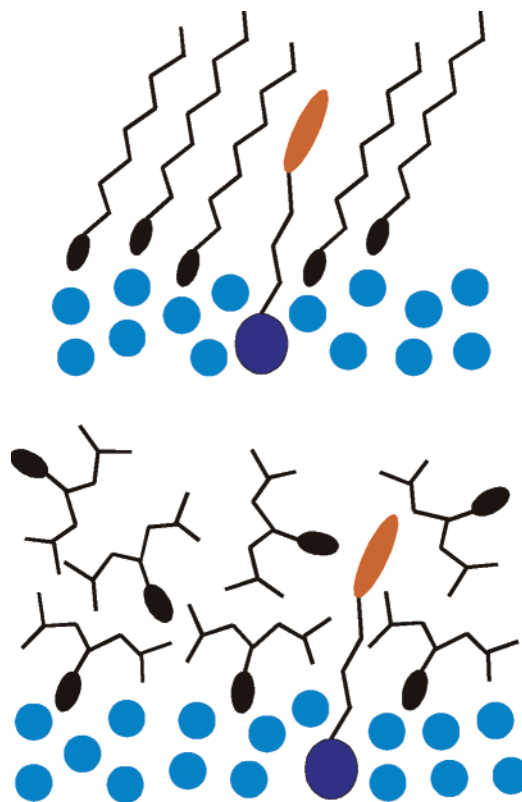
width at interfaces between water and linear alcohols is directly related the length of the alkyl chains on the alcohol.

A fully extended 1-decanol molecule in an all-trans conformation is approximately 1.5 nm. Even with a net molecular tilt at the water/1-decanol interface, the resulting nonpolar region appears to extend beyond the length of the C<sub>8</sub> ruler, as evidenced by the spectra in Figure 2. Adding to the effect of the additional length of the 1-decanol molecules is a finding that the alkyl chains of longer linear alcohols were less likely to tilt off normal at the water/alcohol interface.<sup>9</sup> The longer alkyl chain and a more upright orientation at the water/1-decanol interface could combine to produce a broader interfacial region as sampled by the molecular ruler probes.

Again, orientation measurements support this view. The shortest ruler probe, C<sub>2</sub>, was found to tilt 37° off normal, whereas the longer probes were oriented only 32° off normal. If we were to consider surface roughness as the source of any distribution in orientations, we would not expect any appreciable change in the observed tilt angles, as we see for ruler surfactants at the water/1-decanol interface. The chromophore of the C<sub>2</sub> ruler probe is closest to the interface and more likely to be surrounded by an interfacial structure that is directly susceptible to the interactions between water and the OH groups of the interfacial 1-decanol molecules. As the alkyl spacer of the ruler probes lengthens, the chromophore floats further into the nonpolar region where surfactant chains can more easily adopt the registry of surrounding solvent molecules.

**2. Branched Alcohols.** The spectra shown in Figures 3 and 4 indicate that the interfaces between water and the branched alcohols are more abrupt than those between water and the linear alcohols. In each case, the chromophore of the C<sub>6</sub> ruler probe experiences a solvation similar to that of the bulk alcohol. This finding is not unexpected. Studies of dipolar width at weakly associating water/cyclohexane and water/methylcyclohexane interfaces found the branched alkane interface to be more abrupt.<sup>33</sup> These results were evaluated in terms of solvent packing ability and free molar volumes. Our interpretation of the data from branched alcohol interfaces adopts similar ideas. Unfortunately, few studies of solvents or surfaces have focused on branched alcohols, thus our evaluation of the data is necessarily more speculative.

Although the spectra in Figures 3 and 4 clearly indicate that the interfacial solvation environment converges to that of the bulk alcohol more abruptly than at interfaces with linear alcohols, they also suggest a structure for the nonpolar region between the adjacent bulk solvent layers. The fwhm values of the spectra of molecular rulers adsorbed to interfaces with the branched alcohols are always broader than those at the water/linear alcohol interfaces (Figure 6). The average line widths at the water/3-octanol and water/2,6-dimethyl-4-heptanol interfaces are 47 and 44 nm, respectively. Each of these is larger than the corresponding values at the water/1-octanol (36 nm) and water/1-decanol (38 nm) interfaces and is also closer to the average line width of spectra of molecular rulers in bulk solutions of branched alcohols (~49 nm). We can make two conclusions based on these data. First, because the line widths of spectra recorded at interfaces with branched alcohol are broader, the interfaces between water and the branched alcohols are more heterogeneous than those between water and the linear alcohols. Second, the local polarity experienced by chromophores at these interfaces is very similar to that of the bulk branched alcohols themselves. This observation represents a clear distinction from the trend observed at the interfaces between water and linear alcohols.



**Figure 8.** Schematic representation of the solvation of a molecular ruler probe at two strongly associating interfaces. In the top panel, the probe is surrounded by a homogeneous alkane-like environment at the interface between water and a linear alcohol. In the bottom panel, the same probe is exposed to a more heterogeneous environment with greater free volume and samples a polarity indicative of the bulk alcohol at the water/branched alcohol interface.

In our studies of solvation at weakly associating interfaces, we proposed that the molecular structure of the organic solvent played a large role in the resulting dipolar width of the aqueous/organic boundary.<sup>33</sup> This relationship appears to be a dominant factor at the strongly associating interfaces presented in this work as well. At weakly associating interfaces the amount of free volume present in an organic solvent was directly related to the dipolar width measured at the water/alkane interface. As intermolecular packing ability of the alkane decreased, the ability of the solvent to solvate the chromophore of the molecular ruler probes increased. Consequently, bulk alkane solvation was observed over a shorter length scale at water/branched alkane interfaces than at those interfaces between water and the linear alkanes that packed more efficiently. Figure 8 provides a schematic representation of the differences in structure that arise from these considerations. The chromophore of the probe molecule is surrounded by a more homogeneous environment at the interface with the linear alcohol; thus, it experiences a more alkane-like solvation, and its SH spectrum has a narrower line width.

At strongly associating interfaces, branched alcohols will pack less efficiently than their linear counterparts. The increased free volume among the interfacial branched alcohols can lead to improved solvation of the molecular ruler chromophores. The effect of free volume is likely to be most pronounced at the water/2,6-dimethyl-4-heptanol interface. The molecular volume of 2,6-dimethyl-4-heptanol is 330 Å<sup>3</sup>, the largest of the four solvents in this work. For comparison, the molecular volume of 1-nonanol is 290 Å<sup>3</sup>. The molecular volume of 3-octanol is



significantly less than that of 2,6-dimethyl-4-heptanol, only 264 Å<sup>3</sup>. The spectra in Figure 4 show that the chromophores of both the C<sub>4</sub> and C<sub>6</sub> rulers sample slightly more polar environments at the water/2,6-dimethyl-4-heptanol interface than they do at the water/3-octanol interface. The reduced packing ability of the larger 2,6-dimethyl-4-heptanol molecules appears to allow for better solvation of the chromophores of the longer ruler species than is possible at the water/3-octanol interface. This interpretation necessarily assumes that water plays little or no role in the interfacial solvation of the chromophores.

Free volume considerations do not appear to be a major factor in the results from the water/1-octanol and water/3-octanol interfaces. The molecular volume of 1-octanol, 260 Å<sup>3</sup>, is nearly equal to that of 3-octanol. Whereas this slight difference is not likely to result in a dramatic difference in packing in bulk solution, at an interface, it can result in significant differences between the packing ability of the two solvents. Poor packing of 3-octanol at the water/3-octanol interface is supported by surface tension measurements of the air/3-octanol interface and interfacial tension measurements of a 3-octanol monolayer at the air/water interface.<sup>60</sup> A more likely cause of the reduced dipolar width observed at the water/3-octanol interface is the placement of the OH group on the alcohol solvent. Attaching the OH group to the third carbon in the chain of eight divides the molecule into two shorter segments, one of two carbon groups and one of five. The longer of these is only approximately 7.5 Å in length, a distance easily spanned by the longer molecular ruler species, especially when we consider the net tilt these chains might have.

An additional piece of evidence to consider is the orientation data recorded at the interfaces between water and the branched alcohols. The chromophores adopt, on average, a slightly more upright orientation, approximately 32° off normal, than at the interfaces between water and the linear alcohols (36°). The uncertainty in the orientation calculations (±3°) means that there could be little difference between the two sets of orientations. However, given the additional free volume within branched alcohols, the chromophores of the ruler probes sampling the water/branched alcohol interfaces could very well be oriented closer to the surface normal. At the water/1-octanol interface, for example, there is a strong driving force for the alignment of the alkyl chain of the ruler to adopt the same orientation as the interfacial 1-octanol molecules. The ruler probes are constrained by the surface-induced structure of the surrounding solvent. Assuming that the water/3-octanol interface is much less structured than its water/1-octanol counterpart, this driving force should decrease at the water/3-octanol interface so that the chromophores of the ruler probes could adopt alternative average orientations.

## V. Conclusion

We have used molecular ruler surfactants to probe solute excitation at several strongly associating water/alcohol liquid/liquid interfaces. The data suggest that all of these interfaces contain a region of reduced polarity between the polar water phase and the bulk alcohol. We attribute this region to the alignment of the alkyl chains of the interfacial alcohol molecules. Our findings suggest that some interfaces are sharper than others. Those interfaces comprising water and a branched alcohol converged to bulk alcohol-like solvation over a shorter length scale than those between water and a linear alcohol. These differences correlate well with the solute-accessible free volume within the alcohols. The widths of the interfaces between water and the linear alcohols appear to be directly related to the length

of the alkyl chain on the alcohol. Ongoing studies will continue to explore the relationship between solvent structure and interfacial width.

**Acknowledgment.** This work was supported by the Research Corporation (RI0362) and the National Science Foundation through its CAREER Program (CHE0094246). R.A.W. also gratefully acknowledges fellowship support from the Alfred P. Sloan Foundation.

## References and Notes

- (1) Donahue, D. J.; Bartell, F. E. *J. Phys. Chem.* **1952**, *56*, 480–484.
- (2) Girifalco, L. A.; Good, R. J. *J. Phys. Chem.* **1957**, *61*, 904–9010.
- (3) Dang, L. X. *J. Phys. Chem. B* **1999**, *103*, 8195–8200.
- (4) Josseland, J.; Laguer, G.; Jensen, H.; Ferrigno, R.; Girault, H. H. *J. Electroanal. Chem.* **2003**, *546*, 1–13.
- (5) Pratt, L. R.; Pohorille, A. *Chem. Rev.* **2002**, *102*, 2671–2692.
- (6) Antoine, R.; Bianchi, F.; Brevet, P. F.; Girault, H. H. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3833–3838.
- (7) Cheng, Y.; Corn, R. M. *J. Phys. Chem. B* **1999**, *103*, 8726–8731.
- (8) Conboy, J. C.; Messmer, M. C.; Richmond, G. L. *J. Phys. Chem.* **1996**, *100*, 7617–7622.
- (9) Cramb, D. T.; Wallace, S. C. *J. Phys. Chem. B* **1997**, *101*, 2741–2744.
- (10) Sangster, J. *Octanol–Water Partition Coefficients*; John Wiley and Sons: New York, 1997; Vol. 2.
- (11) Dang, L. X. *J. Phys. Chem. B* **2001**, *105*, 804–809.
- (12) Michael, D.; Benjamin, I. *J. Phys. Chem.* **1995**, *99*, 16810–16813.
- (13) Schlossman, M. L.; Li, M.; Mitrovinic, D. M.; Tikhonov, A. M. *High Perform. Polym.* **2000**, *12*, 551–563.
- (14) Eiseenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343–1360.
- (15) Richmond, G. L. *Annu. Rev. Phys. Chem.* **2001**, *52*, 357–389.
- (16) Steel, W. H.; Walker, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 1132–1133.
- (17) Chipot, C.; Wilson, M. A.; Pohorille, A. *J. Phys. Chem. B* **1997**, *101*, 782–791.
- (18) Mitrovinic, D.; Tikhonov, A. M.; Li, M.; Huang, Z.; Schlossman, M. L. *Phys. Rev. Lett.* **2000**, *85*, 582–585.
- (19) Tikhonov, A. M.; Mitrovinic, D. M.; Li, M.; Huang, Z.; Schlossman, M. L. *J. Phys. Chem. B* **2000**, *104*, 6336–6339.
- (20) Braun, R.; Casson, B. D.; Bain, C. D. *Chem. Phys. Lett.* **1995**, *245*, 326–334.
- (21) Michael, D.; Benjamin, I. *J. Chem. Phys.* **1997**, *107*, 5684–5693.
- (22) Stanners, C. D.; Du, Q.; Chin, R. P.; Cremer, P.; Somorjai, G. A.; Shen, Y. R. *Chem. Phys. Lett.* **1995**, *232*, 407–413.
- (23) *The Chemical Physics of Solvation*; Dogonadze, R. R., Kalman, E., Kornyshev, A. A., Ulstrup, J., Eds.; Elsevier: Amsterdam, 1985; Part A.
- (24) Wang, H.; Borguet, E.; Eiseenthal, K. B. *J. Phys. Chem. A* **1997**, *101*, 713–718.
- (25) Wang, H.; Borguet, E.; Eiseenthal, K. B. *J. Phys. Chem. B* **1998**, *102*, 4927–4932.
- (26) Beildeck, C. L.; Steel, W. H.; Walker, R. A. *Langmuir* **2003**, *19*, 4933–4939.
- (27) Steel, W. H.; Damkaci, F.; Nolan, R.; Walker, R. A. *J. Am. Chem. Soc.* **2002**, *124*, 4824–4831.
- (28) Mitrovinic, D. M.; Zhang, Z.; Williams, S. M.; Huang, Z.; Schlossman, M. L. *J. Phys. Chem. B* **1999**, *103*, 1779–1782.
- (29) Penfold, J.; Richardson, R. M.; Zerbakhsh, A.; Webster, J. R. P. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3899–3917.
- (30) Michael, D.; Benjamin, I. *J. Phys. Chem. B* **1998**, *102*, 5145–5151.
- (31) Michael, D.; Benjamin, I. *J. Chem. Phys.* **2001**, *114*, 2817–2824.
- (32) Squitieri, E.; Benjamin, I. *J. Phys. Chem. B* **2001**, *105*, 6412–6419.
- (33) Steel, W. H.; Lau, Y. Y.; Beildeck, C. L.; Walker, R. A. *J. Phys. Chem. B* **2004**, *108*, 13370–13378.
- (34) Bessho, K.; Uchida, T.; Yamauchi, A.; Shioya, T.; Teramae, N. *Chem. Phys. Lett.* **1997**, *264*, 381–386.
- (35) Higgins, D. A.; Abrams, M. B.; Byerly, S. K.; Corn, R. M. *Langmuir* **1992**, *8*, 1992–2000.
- (36) Ishizaka, S.; Satoshi, H.; Kim, H.; Kitamura, N. *Anal. Chem.* **1999**, *71*, 3382–3389.
- (37) Lagugne-Labarthe, F.; Yu, T.; Barger, W. R.; Shenoy, D. K.; Dalcanele, E.; Shen, Y. R. *Chem. Phys. Lett.* **2003**, *381*, 322–328.
- (38) Naujok, R.; Higgins, D. A.; Hanken, D. G.; Corn, R. M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1411–1420.
- (39) Perrenoud-Rinuy, J.; Brevet, P. F.; Girault, H. H. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4774–4781.

- (40) Uchida, T.; Yamaguchi, A.; Ina, T.; Teramae, N. *J. Phys. Chem. B* **2000**, *104*, 12091–12094.
- (41) Ishizaka, S.; Kim, H.; Kitamura, N. *Anal. Chem.* **2001**, *73*, 2421–2428.
- (42) Kovalski, J. M.; Wirth, M. J. *J. Phys. Chem.* **1995**, *99*, 4091–4095.
- (43) Shang, X. M.; Benderskii, A. V.; Eisinger, K. B. *J. Phys. Chem. B* **2001**, *105*, 11578–11585.
- (44) Shi, X.; Borguet, E.; Tarnovsky, A. N.; Eisinger, K. B. *Chem. Phys.* **1996**, *205*, 167–178.
- (45) Benjamin, I. *Chem. Rev.* **1996**, *96*, 1449–1475.
- (46) Wolfrum, K.; Laubereau, A. *Chem. Phys. Lett.* **1994**, *228*, 83–88.
- (47) Guyot-Sionnest, P.; Hunt, J. H.; Shen, Y. R. *Phys. Rev. Lett.* **1987**, *59*, 1597–1600.
- (48) Bell, G. R.; Bain, C. D.; Ward, R. N. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 515–523.
- (49) Walker, R. A.; Gruetzmacher, J. A.; Richmond, G. L. *J. Am. Chem. Soc.* **1998**, *120*, 6991–7003.
- (50) Watry, M. R.; Richmond, G. L. *J. Am. Chem. Soc.* **2000**, *122*, 875–883.
- (51) Shen, Y. R. *Nature* **1989**, *337*, 519–525.
- (52) Zhang, X.; Cunningham, M. M.; Walker, R. A. *J. Phys. Chem. B* **2003**, *107*, 3183–3195.
- (53) Benjamin, I. *Chem. Phys. Lett.* **1998**, *287*, 480–486.
- (54) Chang, R. *Basic Principles of Spectroscopy*; McGraw-Hill Book Co.: New York, 1971.
- (55) Suppan, P.; Ghoneim, N. *Solvatochromism*; The Royal Society of Chemistry: Cambridge, U.K., 1997.
- (56) Hicks, J. M.; Kemnitz, K.; Eisinger, K. B. *J. Phys. Chem.* **1986**, *90*, 560–562.
- (57) Zhang, X.; Steel, W. H.; Walker, R. A. *J. Phys. Chem. B* **2003**, *107*, 3829–3836.
- (58) Benjamin, I. *Chem. Phys. Lett.* **2004**, *393*, 453–456.
- (59) Steel, W. H.; Walker, R. A. *Nature* **2003**, *424*, 296–299.
- (60) Esenturk, O.; Walker, R. A., manuscript submitted.
- (61) Schweighofer, K.; Essman, U.; Berkowitz, M. L. *J. Phys. Chem. B* **1997**, *101*, 3793–3799.
- (62) Simpson, G. J.; Rowlen, K. L. *J. Am. Chem. Soc.* **1999**, *121*, 2635–2636.
- (63) Simpson, G. J.; Westerbuhr, S. G.; Rowlen, K. L. *Anal. Chem.* **2000**, *72*, 887–898.