J|A|C|S
ARTICLES

Probing Molecular Structure at Interfaces for Comparison with Bulk Solution Behavior: Water/2-Propanol Mixtures Monitored by Vibrational Sum Frequency Spectroscopy

Sho Kataoka and Paul S. Cremer*

Contribution from the Department of Chemistry, Texas A&M University, 3255 TAMU,
College Station, Texas 77842-3012

Received January 9, 2006; E-mail: cremer@mail.chem.tamu.edu

Abstract: The orientation of the isopropyl group at the liquid/vapor interface in 2-propanol/water binary mixtures was studied by vibrational sum frequency spectroscopy. The CH_3 stretch modes of the two methyl groups were used to determine the molecule's orientation by employing a novel united atom approach to model the $(CH_3)_2X$ moiety. For this purpose, the changes in the molecular susceptibility of the isopropyl group stretches were derived in the laboratory frame as a function of the tilt and twist angles. The results indicated that the methyl groups lay down on the surface at low alcohol mole fraction and gradually twisted with increasing mole fraction. At the azeotrope, $x_{\mathrm{iso}} = 0.68$, one of the methyl groups aligned approximately parallel to the surface normal, whereas the other was nearly parallel with the liquid/vapor interface. When the mole fraction of 2-propanol was higher than 0.68, the orientation of 2-propanol remained almost constant. The change in the alcohol's orientation with 2-propanol mole fraction closely tracked changes in its bulk activity coefficient. Such results lead to a picture in which the surface structure and bulk properties of the system are closely linked.

Introduction

At low mole fraction, an amphiphilic organic component in an aqueous mixture tends to partition to the liquid/vapor interface to form a Gibbs monolayer.[1] This decreases the surface tension and relieves some of the unfavorable interactions between the nonpolar portion of the molecule and the surrounding aqueous solution. The Gibbs adsorption equation provides the surface excess of the organic solute, Γ_{org}, using the values of the surface tension, γ, and bulk activity coefficient, a:[1]

$$\Gamma_{\mathrm{org}} = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln a_{\mathrm{org}}}\right)_{\mathrm{T}} \qquad (1)$$

The surface excess reaches its maximum value exactly where the partial molar volume of the solvent obtains its minimum value for many miscible organic/aqueous mixtures including 2-propanol/water.[2] This is strong macroscopic evidence that the bulk properties and surface properties of aqueous two-component mixtures are linked and that it should be possible to relate the bulk properties to the molecular structure at interfaces.

A deeper understanding of the relationship between bulk and surface behavior would be of particular interest for azeotropic mixtures. An azeotropic mixture consists of two or more chemical components at the specific mole ratio where the vapor and liquid-phase compositions are identical for a given pressure and temperature.[3] Industrial processes for obtaining pure compounds from azeotropic mixtures require extra steps, which can include the addition of entrainers and dehydration salts[4] or the use of a reactive azeotrope.[5] Currently, these separation processes cost a considerable amount of energy,[4] and a better understanding of azeotropes might be of significance for the development of more efficient methods for obtaining neat compounds.

The 2-propanol/water azeotrope occurs at 80.2 °C with a 0.68 mole fraction ($x_{\mathrm{iso}} = 0.68$) of 2-propanol at 1 atm (Figure 1).[4,6,7] As can be seen from the graph, the gas phase mole fraction of the alcohol deviates most strongly from the reference line when $x_{\mathrm{iso}} < 0.1$. The mole fraction of the alcohol in the gas phase changes only modestly between $x_{\mathrm{iso}} = 0.1$ and $x_{\mathrm{iso}} = 0.68$. Finally, the gas-phase mole fraction crosses below the reference line at the azeotropic composition and does not return to it until $x_{\mathrm{iso}} = 1.0$. Therefore, this liquid mixture cannot be distilled beyond the azeotropic point.

To gain insight into the molecular structure at the liquid/vapor interface of the 2-propanol/water system, we have employed vibrational sum frequency spectroscopy (VSFS). VSFS is a surface-specific vibrational technique and is particu-

---

(1) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley: New York, 1997.

(2) Yano, Y. F. *J. Colloid Interface Sci.* **2005**, *284*, 255−259.

(3) Hilmen, E. K. Ph.D. Thesis, Norwegian University of Science and Technology, 2000.

(4) Petlyuk, F. B. *Distillation Theory and Its Application to Optimal Design of Separation Units*; Cambridge University Press: Cambridge, UK, New York, 2004.

(5) Song, W.; Huss, R. S.; Doherty, M. F.; Malone, M. F. *Nature* **1997**, *388*, 561−563.

(6) De Nevers, N. *Physical and Chemical Equilibrium for Chemical Engineers*; Wiley: New York, 2002.

(7) Gmehling, J.; Onken, U.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection*; Dechema; Distributed by Scholium International: Frankfurt/Main Flushing, NY, 1977.

10.1021/ja060156k CCC: $33.50

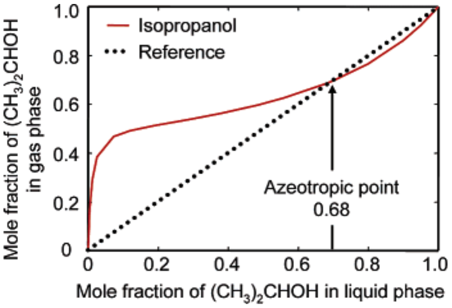

Figure 1. Liquid/vapor equilibrium phase diagram for the 2-propanol/water system (after ref 7).

larly well suited for providing orientational information on the detected molecules.[8−15] Among other applications, it has been employed for probing Langmuir monolayers[12,16,17] and is also useful for studying the orientation of Gibbs monolayers.[18−32] Herein, VSFS spectra at the liquid/vapor interface have been collected at alcohol mole fractions ranging from 0.005 to 1. The purpose of these studies was to monitor the CH_3 symmetric and asymmetric stretch modes of the isopropyl moiety. Because this species has two methyl groups, a novel procedure is introduced to treat the entire $(CH_3)_2X$ unit as a single entity.[33] The results indicate that 2-propanol reorients from a conformation where the two methyl groups are lying down to one in which they twist to allow one of them to face toward the vapor phase as the mole fraction of alcohol is increased. The reorientation occurs rapidly at low mole fraction and slows down as the azeotrope is approached. Changes in orientation nearly cease to occur above the azeotropic point. These changes map quite well to changes in the bulk activity coefficient of 2-propanol as a function of mole fraction and, hence, provide a nexus between a molecular-level surface property and the macroscopic behavior of the bulk solution.

Theory

VSFS. VSFS[8,12,34−36] is a second-order nonlinear optical spectroscopy whereby two incident laser beams (tunable frequency infrared and fixed frequency visible) are overlapped at an interface to generate an output at the sum of the two frequencies. The intensity of the sum frequency signal can be expressed as follows:

$$I_{\mathrm{SFG}} \propto |\chi_{\mathrm{eff}}{}^{(2)}|^2 \cdot I_{\mathrm{vis}} \cdot I_{\mathrm{IR}} \tag{2}$$

where I_{vis} and I_{IR} are the intensities of the two input lasers (visible and infrared, respectively), and $\chi_{\mathrm{eff}}{}^{(2)}$ is the effective nonlinear susceptibility, which can be expressed in the form:

$$\chi_{\mathrm{eff}}{}^{(2)} = \chi_{\mathrm{NR}}^{(2)} + \chi_{\mathrm{R}}^{(2)} = \chi_{\mathrm{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\mathrm{IR}} - \omega_q + i\Gamma_q} \tag{3}$$

where $\chi_{\mathrm{NR}}^{(2)}$ is the frequency independent nonresonant term and $\chi_{\mathrm{R}}^{(2)}$ is the resonant contribution. $\chi_{\mathrm{R}}^{(2)}$ consists of A_q, ω_{IR}, ω_q, and Γ_q, which are the oscillator strength, the frequency of the incoming IR beam, the resonant frequency, and the peak width of qth resonant mode, respectively. Hence, by fitting VSFS spectra using eqs 2 and 3, A_q and ω_q can be obtained. VSFS experiments can be performed with both the s and p polarizations of the sum frequency, visible, and IR beams. For example, ssp denotes S_{SF}, S_{Vis}, and P_{IR}. Two other critical polarization combinations are sps, and ppp.

Assuming an isotropic xy plane, A_q can be related to the susceptibilities of the detected molecules in laboratory-fixed coordinates as follows:

$$A_{q,\mathrm{ssp}} = L_{yy}(\omega_{\mathrm{SF}})L_{yy}(\omega_{\mathrm{vis}})L_{zz}(\omega_{\mathrm{IR}})\sin\Theta_{i,\mathrm{IR}} \cdot \chi_{yyz} \tag{4}$$

$$A_{q,\mathrm{sps}} = L_{yy}(\omega_{\mathrm{SF}})L_{zz}(\omega_{\mathrm{vis}})L_{yy}(\omega_{\mathrm{IR}})\sin\Theta_{i,\mathrm{vis}} \cdot \chi_{yzy} \tag{5}$$

$$\begin{aligned} A_{q,\mathrm{ppp}} = &-L_{xx}(\omega_{\mathrm{SF}})L_{xx}(\omega_{\mathrm{vis}})L_{zz}(\omega_{\mathrm{IR}})\cos\Theta_{r,\mathrm{SF}}\cos\Theta_{i,\mathrm{vis}}\sin\Theta_{i,\mathrm{IR}} \cdot \chi_{xxz} - \\ &L_{xx}(\omega_{\mathrm{SF}})L_{zz}(\omega_{\mathrm{vis}})L_{xx}(\omega_{\mathrm{IR}})\cos\Theta_{r,\mathrm{SF}}\sin\Theta_{i,\mathrm{vis}}\cos\Theta_{i,\mathrm{IR}} \cdot \chi_{xzx} + \\ &L_{zz}(\omega_{\mathrm{SF}})L_{xx}(\omega_{\mathrm{vis}})L_{xx}(\omega_{\mathrm{IR}})\sin\Theta_{r,\mathrm{SF}}\cos\Theta_{i,\mathrm{vis}}\cos\Theta_{i,\mathrm{IR}} \cdot \chi_{zxx} + \\ &L_{zz}(\omega_{\mathrm{SF}})L_{zz}(\omega_{\mathrm{vis}})L_{zz}(\omega_{\mathrm{IR}})\sin\Theta_{r,\mathrm{SF}}\sin\Theta_{i,\mathrm{vis}}\sin\Theta_{i,\mathrm{IR}} \cdot \chi_{zzz} \end{aligned} \tag{6}$$

where $\Theta_{r,\mathrm{SF}}$, $\Theta_{i,\mathrm{vis}}$, and $\Theta_{i,\mathrm{IR}}$ are the reflection, r, and incident, i, angles of the sum frequency, visible, and IR radiation, respectively. L_{ii} ($i = x, y,$ or z) are the Fresnel coefficients, which are well-defined functions of the refractive indices of the media and incident angles of the three beams.[36] The refractive indices used to determine the Fresnel coefficients were 1.31 in the infrared and 1.34 in the visible for water. The refractive indices for 2-propanol and air were taken to be 1.38 and 1.00, respectively, at all frequencies. For the z-component of the Fresnel coefficient, it is necessary to make a thin film approximation to determine the appropriate index of refraction.

---

(8) Shen, Y. R. *The Principles of Nonlinear Optics*; J. Wiley: New York, 1984.
(9) Shen, Y. R. *Nature* **1989**, *337*, 519−525.
(10) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281−1296.
(11) Lambert, A. G.; Davies, P. B.; Neivandt, D. J. *Appl. Spectrosc. Rev.* **2005**, *40*, 103−145.
(12) Richmond, G. L. *Chem. Rev.* **2002**, *102*, 2693−2724.
(13) Wang, J.; Paszti, Z.; Even, M. A.; Chen, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7016−7023.
(14) Wang, J.; Chen, X. Y.; Clarke, M. L.; Chen, Z. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 4978−4983.
(15) Hommel, E. L.; Merle, J. K.; Ma, G.; Hadad, C. M.; Allen, H. C. *J. Phys. Chem. B* **2005**, *109*, 811−818.
(16) Gurau, M. C.; Kim, G.; Lim, S. M.; Albertorio, F.; Fleisher, H. C.; Cremer, P. S. *ChemPhysChem* **2003**, *4*, 1231−1233.
(17) Gurau, M. C.; Lim, S. M.; Castellana, E. T.; Albertorio, F.; Kataoka, S.; Cremer, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 10522−10523.
(18) Conboy, J. C.; Messmer, M. C.; Richmond, G. L. *J. Phys. Chem. B* **1997**, *101*, 6724−6733.
(19) Bell, G. R.; Bain, C. D.; Ward, R. N. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 515−523.
(20) Zhang, D.; Gutow, J. H.; Eisenthal, K. B.; Heinz, T. F. *J. Chem. Phys.* **1993**, *98*, 5099−5101.
(21) Kim, J.; Chou, K. C.; Somorjai, G. A. *J. Phys. Chem. B* **2003**, *107*, 1592−1596.
(22) Johnson, C. M.; Tyrode, E.; Baldelli, S.; Rutland, M. W.; Leygraf, C. *J. Phys. Chem. B* **2005**, *109*, 321−328.
(23) Tyrode, E.; Johnson, C. M.; Baldelli, S.; Leygraf, C.; Rutland, M. W. *J. Phys. Chem. B* **2005**, *109*, 329−341.
(24) Wolfrum, K.; Graener, H.; Laubereau, A. *Chem. Phys. Lett.* **1993**, *213*, 41−46.
(25) Huang, J. Y.; Wu, M. H. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1994**, *50*, 3737−3746.
(26) Ma, G.; Allen, H. C. *J. Phys. Chem. B* **2003**, *107*, 6343−6349.
(27) Chen, H.; Gan, W.; Lu, R.; Guo, Y.; Wang, H. F. *J. Phys. Chem. B* **2005**, *109*, 8064−8075.
(28) Chen, H.; Gan, W.; Wu, B. H.; Wu, D.; Guo, Y.; Wang, H. F. *J. Phys. Chem. B* **2005**, *109*, 8053−8063.
(29) Yeh, Y. L.; Zhang, C.; Held, H.; Mebel, A. M.; Wei, X.; Lin, S. H.; Shen, Y. R. *J. Chem. Phys.* **2001**, *114*, 1837−1843.
(30) Ju, S. S.; Wu, T. D.; Yeh, Y. L.; Wei, T. H.; Huang, J. Y.; Lin, S. H. *J. Chin. Chem. Soc.* **2001**, *48*, 625−629.
(31) Sung, J.; Park, K.; Kim, D. *J. Phys. Chem. B* **2005**, *109*, 18507−18514.
(32) Sung, J.; Park, K.; Kim, D. *J. Korean Phys. Soc.* **2004**, *44*, 1394−1398.
(33) Hirose, C. Personal communication.
(34) Hirose, C.; Akamatsu, N.; Domen, K. *J. Chem. Phys.* **1992**, *96*, 997−1004.
(35) Hirose, C.; Akamatsu, N.; Domen, K. *Appl. Spectrosc.* **1992**, *46*, 1051−1072.
(36) Zhuang, X.; Miranda, P. B.; Kim, D.; Shen, Y. R. *Phys. Rev. B* **1999**, *59*, 12632−12640.

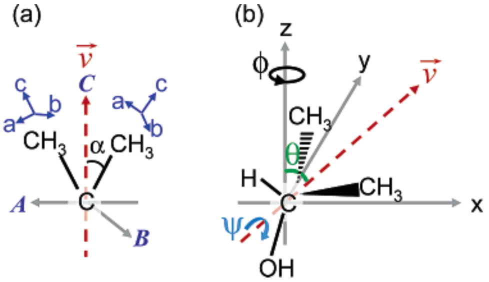

Figure 2. (a) Coordinates in the molecular frame: the (*a*,*b*,*c*) axis is for methyl group fixed coordinates and the (*A*,*B*,*C*) axis is for isopropyl group fixed coordinates.[34] The *C* axis bisects the two methyl groups, and the *A* axis is set in the plane of the two methyl groups. (b) The geometry of 2-propanol in laboratory frame coordinates. The vector, $\vec{v}$, bisects the two methyl groups. The symbols θ, ψ, and ϕ represent the tilt angle, the twist angle about $\vec{v}$, and the azimuthal angle about the *z*-axis for the isopropyl group as described in the text, respectively.

In this case, the average value between air and the liquid was employed. For example, in the case of pure 2-propanol: $(1.38 + 1.00)/2 = 1.19$.

Coordinate of the Isopropyl Group. To perform orientational analysis, we employed a novel method in which the nonlinear susceptibility of the isopropyl group in the laboratory frame was derived by combining the hyperpolarizabilities of the two individual methyl groups in the molecular frame.[33] The transformation between the molecular and laboratory frames was performed by using a united atom model for each methyl group. Such transformations have typically been performed for smaller moieties, such as CH_3 and CH_2 groups.[34] Previously, the $(CH_3)_2X$ group has been treated by dividing it into individual moieties as in work done on acetone.[29] Such an approach, however, requires the use of six coordinates to define the position of this group. However, if we treat each methyl group as a united atom, a coordinate system for $(CH_3)_2X$ with only three separate coordinates can be introduced.

To perform the coordinate transformation, it is necessary to combine the individual methyl groups in (*a*, *b*, *c*) coordinates into united atoms in (*A*, *B*, *C*) coordinates and then transfer this system into the laboratory frame with coordinates (*x*, *y*, *z*).[33,37] A picture of the relevant coordinate systems is shown in Figure 2. A vector, $\vec{v}$, which bisects the two methyl groups, is first defined in the molecular coordinate frame and then transformed onto the laboratory coordinate system. In the molecular frame, $\vec{v}$ is set to be coincident with the *C*-axis (Figure 2a). The angle each methyl group makes with the *C*-axis is defined as α. The angle between the methyl groups (i.e., the angle of the $(CH_3)-C-(CH_3)$ moiety) is therefore 2α. In the laboratory frame, the orientation of the isopropyl group can be expressed with three Euler angles: θ, ψ, and ϕ (Figure 2b),[37] where θ is the angle between the surface normal and $\vec{v}$. ψ is the azimuthal angle about $\vec{v}$. When $\psi = 0$, the plane of the isopropyl groups is perpendicular to the *xy* plane. On the other hand, when $\psi = 90°$ the two methyl groups are equidistant from the *xy* plane. The angle ϕ is the azimuthal angle of $\vec{v}$ about the *z*-axis. It is assumed in all the data analysis that the isopropyl moiety is isotropically oriented with respect to the ϕ coordinate.

Angle Analysis of the Isopropyl Group. χ_{ijk} (i, j, or $k = x$, y, or z) is a component of the second-order nonlinear susceptibility, $\chi^{(2)}$, in laboratory coordinates. The value of χ_{ijk} varies as a function of the number density of the detected molecules, their molecular hyperpolarizability, and their orientational average. This section is devoted to transforming the hyperpolarizability, β_{ijk}, in molecular coordinates to susceptibilities χ_{ijk} (i, j, or $k = x$, y, or z) in laboratory coordinates.

The hyperpolarizabilities of the two methyl groups, β_{ijk} (i, j, or $k = a$, b, or c), need to be transformed from methyl group fixed coordinates (*a*, *b*, *c*) to isopropyl group fixed coordinates (*A*, *B*, *C*) within the molecular frame (Figure 2a).[35] Each CH_3 group has C_{3v} symmetry; therefore, the only nonvanishing components for the symmetric stretch are $\beta_{aac} = \beta_{bbc}$ and β_{ccc}. The nonvanishing components for the asymmetric stretch are $\beta_{caa} = \beta_{cbb} = \beta_{aca} = \beta_{bcb}$.[34] The angle of internal rotation of the two methyl groups would affect the transformation of the hyperpolarizability to the isopropyl group, but it is hereby assumed that both methyl groups can rotate freely. Therefore, the isopropyl group has quasi-C_{2v} symmetry with nonvanishing components β_{AAC}, β_{BBC}, and β_{CCC}, for the a1 vibrations.[34] For the b1 vibrations, the nonvanishing components are $\beta_{ACA} = \beta_{CAA}$ and for the b2 vibrations they are $\beta_{BCB} = \beta_{CBB}$.[34] In this description "a" and "b" designate symmetric and asymmetric modes with respect to the *C*-axis, whereas "1" and "2" denote in-plane and out-of-plane modes. Using this transformation,[35] the hyperpolarizability, β_{ijk}, for the vibrational modes of the isopropyl moiety in terms of the angle, α, between the two methyl groups can be written as:

Symmetric Stretch

$$\begin{aligned}
&\text{(a1)} && \beta_{AAC} = -2(\beta_{aac} - \beta_{ccc})(\cos\alpha - \cos^3\alpha) + 2\beta_{aac}\cos\alpha \\
& && \beta_{BBC} = 2\beta_{aac}\cos\alpha \\
& && \beta_{CCC} = 2(\beta_{aac} - \beta_{ccc})(\cos\alpha - \cos^3\alpha) + 2\beta_{ccc}\cos\alpha \\
&\text{(b1)} && \beta_{CAA} = -\,2(\beta_{aac} - \beta_{ccc})(\cos\alpha - \cos^3\alpha) \\
& && \beta_{ACA} = -2(\beta_{aac} - \beta_{ccc})(\cos\alpha - \cos^3\alpha)
\end{aligned} \tag{7}$$

Asymmetric Stretch

$$\begin{aligned}
&\text{(a1)} && \beta_{AAC} = -4\beta_{caa}(\cos\alpha - \cos^3\alpha) \\
& && \beta_{CCC} = 4\beta_{caa}(\cos\alpha - \cos^3\alpha) \\
&\text{(b1)} && \beta_{CAA} = -2\beta_{caa}(\cos\alpha - 2\cos^3\alpha) \\
& && \beta_{ACA} = -2\beta_{caa}(\cos\alpha - 2\cos^3\alpha) \\
&\text{(b2)} && \beta_{CBB} = 2\beta_{caa}\cos\alpha \\
& && \beta_{BCB} = 2\beta_{caa}\cos\alpha
\end{aligned} \tag{8}$$

Note that β_{BBC} is 0 and is omitted from the lists. In this study, the bond angle for the $(CH_3)-C-(CH_3)$ moiety is assumed to be fixed at 112° (or $\alpha = 56°$).

Finally, all hyperpolarizability components, β_{ijk}, need to be transformed to the laboratory coordinate frame for consideration of the ssp, sps, and ppp polarization combinations.[35] As noted above, 2-propanol molecules at the liquid/vapor interface should be azimuthally isotropic on the macroscopic scale; therefore, ϕ is uniformly distributed from 0 to 2π. In this case, the

---

(37) Ji, N.; Shen, Y. R. *J. Chem. Phys.* **2004**, *120*, 7107−7112.

nonvanishing macroscopic hyperpolarizabilities should be χ_{yyz} for ssp, χ_{xxz}, $\chi_{zxx} = \chi_{xzx}$, and χ_{zzz} for ppp, and χ_{yzy} for sps. Each component in eqn. 7 and eqn. 8 is now substituted into the transformation table of ref 35[38] to obtain the relationship of the macroscopic hyperpolarizability tensor elements with the angles θ and ψ. The transformations are as follows:

Symmetric Stretch

$$\chi_{yyz} = \chi_{xxz} = (N/2\epsilon_0)(\beta_{aac} - \beta_{ccc})[\{(\cos\alpha - \cos^3\alpha) \times (5 + 3\cos 2\psi) - 2\cos\alpha\}(\cos\theta - \cos^3\theta) - 2(\cos\alpha - \cos^3\alpha)\cos\theta] + (2N/\epsilon_0)\beta_{aac}\cos\alpha\cos\theta \quad (9)$$

$$\chi_{yzy} = \chi_{xzx} = \chi_{zxx} = (N/2\epsilon_0)(\beta_{aac} - \beta_{ccc})\{(\cos\alpha - \cos^3\alpha) \times (5 + 3\cos 2\psi)(\cos\theta - \cos^3\theta) + 2\cos\alpha\cos\theta(\cos^2\alpha + \cos^2\theta - 2)\} \quad (10)$$

$$\chi_{zzz} = (N/\epsilon_0)(\beta_{aac} - \beta_{ccc})[(\cos\alpha - \cos^3\alpha)\{2\cos^3\theta - 3(1 + \cos 2\psi)(\cos\theta - \cos^3\theta)\} - 2\cos\alpha\cos{}^3\theta] + (2N/\epsilon_0)\beta_{aac}\cos\alpha\cos\theta \quad (11)$$

Asymmetric Stretch

$$\chi_{yyz} = \chi_{xxz} = (N/\epsilon_0)\beta_{caa}[(\cos\alpha - \cos^3\alpha)\{-2\cos\theta + 3(\cos\theta - \cos^3\theta)(1 + \cos 2\psi)\} - 2\cos^3\alpha(\cos\theta - \cos^3\theta)] \quad (12)$$

$$\chi_{yzy} = \chi_{zxx} = \chi_{xzx} = (N/\epsilon_0)\beta_{caa}[3(\cos\alpha - \cos^3\alpha) \times (\cos\theta - \cos^3\theta)(1 + \cos 2\psi) + 2\cos^3\alpha\cos^3\theta] \quad (13)$$

$$\chi_{zzz} = (2N/\epsilon_0)\beta_{caa}[(\cos\alpha - \cos^3\alpha)\{2\cos\theta - 3(\cos\theta - \cos^3\theta)(1 + \cos 2\psi)\} + 2\cos^3\alpha(\cos\theta - \cos^3\theta)] \quad (14)$$

where N is the number density of detected molecules and ϵ_0 is the permittivity of free space. Note, α is also included in these equations, but its value is assumed to be a constant. As a consequence of this, the components of the susceptibilities in laboratory coordinates for the various polarization combinations depend only on N, β_{aac}, β_{ccc}, β_{caa}, and the molecular orientation values (θ and ψ).

These transformations should in principle enable eqs 9−14 to be substituted into eqs 4−6 to obtain the relevant values of θ and ψ. However, the values of the individual hyperpolarizabilities (β_{aac}, β_{ccc}, β_{caa}) are unknown. Therefore, the VSFS spectra of the different polarization combinations must be employed to determine the ratios of the A_q values. θ and ψ[19,36] can then be uniquely determined by assuming that the ratio of β_{aac}/β_{ccc} for 2-propanol is 3.4, which is a well accepted value.[39]

Experimental Section

Materials. 2-Propanol (spectrophotometric grade 99+%, Acros, NJ) and two types of deuterated 2-propanol, $(CD_3)_2CHOH$ and $(CH_3)_2CDOH$ (Cambridge Isotope Laboratories, MA), were used as received. All aqueous solutions were prepared with purified water (≥18.2 MΩ cm) obtained from a NANOpure Ultrapure Water System (Barnstead, Dubuque, IA). Solutions were prepared volumetrically to obtain the desired mole fractions.

VSFS Experiment. The details of our experimental setup have been described elsewhere.[40,41] Briefly, VSFS experiments were performed with a mode-locked Nd:YAG laser (PY61c, Continuum, Santa Clara, CA) operated at a 20 Hz repetition rate with a peak width of 21 ps. The laser beam, which had a wavelength of 1064 nm, was sent through an optical parametric generation/amplification (OPG/OPA) stage (Laser Vision, Bellevue, WA) to produce a tunable mid-infrared beam as well as fixed frequency radiation at 532 nm. The incident angle of the IR and visible beams were 51° and 42°, respectively.

2-Propanol/water solutions were used to fill a Teflon trough (Model 601 M, Nima Technology Ltd., Coventry, England), which was employed both for VSFS experiments and for surface tension measurements. The whole experimental setup was housed inside a Plexiglas box to reduce evaporation, and the liquid level did not change perceptibly over the course of the VSFS measurements. The spectra were collected near room temperature (ca. 18.9 °C) and normalized to spectra taken from a piece of Z-cut crystalline quartz. All data were taken at least three times and averaged before curve fitting.

Results and Discussion

Peak Assignments. In a first set of experiments, the liquid/vapor interface of various $(CH_3)_2CHOH$/water mixtures was monitored with the ssp, sps, and ppp polarization combinations (Figure 3). The values in the upper right-hand panel of each figure represent the mole fractions of 2-propanol in the mixture. Spectra taken with the same polarization combination, but different alcohol mole fractions are divided into different panels to ease crowding. The four prominent peaks in Figure 3 were fit to eqs 2 and 3 to abstract the peak positions and the oscillator strengths. The resonances were found to be centered at 2880, 2915, 2941, and 2974 cm^{-1}.

Control experiments were performed with two types of deuterated 2-propanol, $(CD_3)_2CHOH$ and $(CH_3)_2CDOH$, to aid in peak assignment (Figure 4). The spectrum for $(CD_3)_2CHOH$ contained the weak CH (methine) feature positioned around 2895 cm^{-1}. The spectrum for $(CH_3)_2CDOH$ showed three peaks at 2880, 2941, and 2974 cm^{-1}. This suggests that the 2915 cm^{-1} peak in the undeuterated sample is from the CH group and that its apparent frequency shifts slightly due to interference with the CH_3 modes. The other three peaks are from the two methyl groups.

According to previous VSFS studies of 2-propanol[39,42] and of the isopropyl group of leucine,[37] the peak at 2880 cm^{-1} is due to the CH_3 symmetric stretch (r^+). By analyzing the intensity of the 2941 cm^{-1} feature as a function of the polarization combination, Lu et al. assigned this feature to a Fermi resonance (r^+_{FR}) with the CH_3 stretch mode and the feature at 2974 cm^{-1} to the CH_3 asymmetry stretch (r^-).[39] Using their methodology in combination with our unified atom model for the isopropyl moiety, we confirmed these assignments.

VSFS Spectral Features. On the basis of the peak assignments above, this section describes the changes in peak intensities in Figure 3 as the mole fraction of 2-propanol was varied. For the ssp polarization combination, the features at 2880 and 2941 cm^{-1} changed in a nearly identical fashion with mole fraction. Their oscillator strengths grew modestly from $x_{iso} = 0.005$ to $x_{iso} = 0.073$, where they reached a maximum. Beyond

---

(38) In ref 35, the denominator for *zzz* of *bbc* should be 8 instead of 16 in the table at p. 1065

(39) Lu, R.; Gan, W.; Wu, B. H.; Zhang, Z.; Guo, Y.; Wang, H. F. *J. Phys. Chem. B* **2005**, *109*, 14118−14129.

(40) Kim, G.; Gurau, M. C.; Lim, S. M.; Cremer, P. S. *J. Phys. Chem. B* **2003**, *107*, 1403−1409.

(41) Kataoka, S.; Gurau, M. C.; Albertorio, F.; Holden, M. A.; Lim, S. M.; Yang, R. D.; Cremer, P. S. *Langmuir* **2004**, *20*, 1662−1666.

(42) Shen, Y. R. *Surf. Sci.* **1994**, *300*, 551−562.

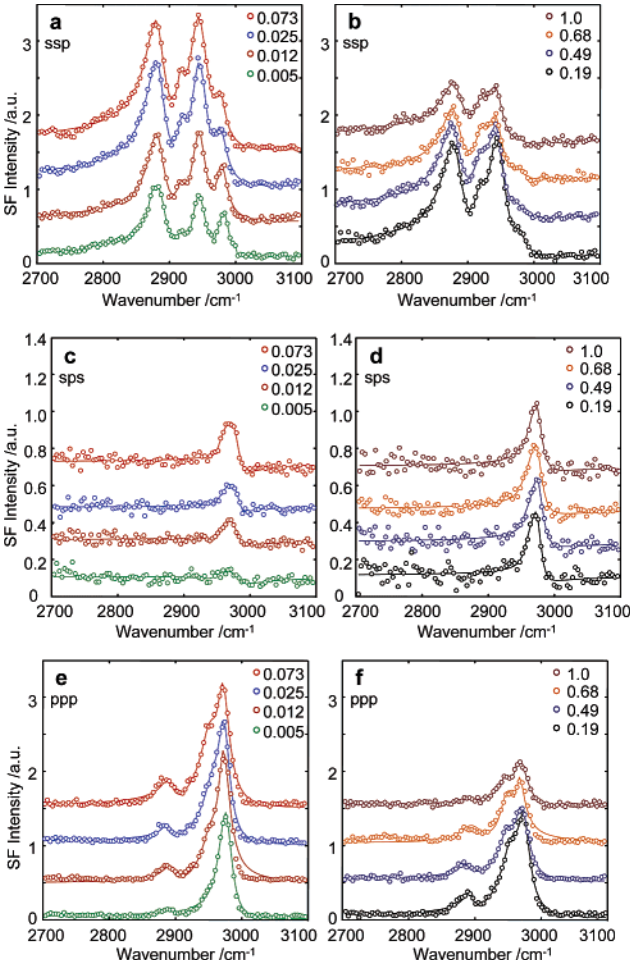

Figure 3. VSFS spectra of 2-propanol/water mixtures at the liquid/vapor interface at various alcohol mole fractions and polarization combinations: (a) and (b) are for ssp, (c) and (d) are for sps, and (e) and (f) are for ppp. The ssp and ppp spectra are offset from each other by 0.5 arbitrary units and the sps data are offset by 0.2 arbitrary units.

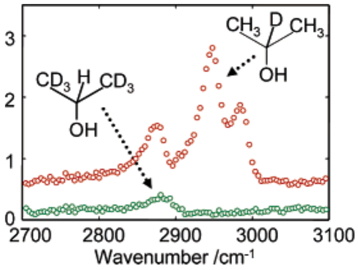

Figure 4. VSFS spectra of the 2-propanol/water system at $x_{\mathrm{iso}} = 0.012$ for two partially deuterated 2-propanol samples. Deuterated water was also used. The spectra are offset from each other by 0.5 arbitrary units.

this mole fraction, the values attenuated gradually to $x_{\mathrm{iso}} = 0.68$. At mole fractions of alcohol above the azeotrope, they remained unchanged. The fitted values for the oscillator strengths are listed in Table 1. Over the entire range from $x_{\mathrm{iso}} = 0.005$ to $x_{\mathrm{iso}} = 1.0$, the CH_3 symmetric stretch and Fermi resonance oscillator strengths changed by a factor of approximately 2 or slightly less. This contrasts with the peak at 2974 cm^{-1}, which showed substantially more pronounced changes with mole fraction in the ssp spectra (a factor of ~5.7). The r^- feature rose gradually to a maximum intensity from $x_{\mathrm{iso}} = 0.005$ to $x_{\mathrm{iso}} = 0.025$ (Table 1). Its oscillator strength then fell off rapidly at higher 2-propanol concentrations and became quite weak by $x_{\mathrm{iso}} = 0.49$.

Table 1. the Oscillator Strength of the VSFS Peaks as a Function of Isopropanol Mole Fraction[a,b]

	A_{SSP}				A_{SPS}		A_{PPP}		
x_{iso}	r^+	CH	r^+_{FR}	r^-	r^+_{FR}	r^-	r^+	r^+_{FR}	r^-
0.005	9.9	0.52	8.3	−5.4	−0.4	1.0	−1.8	−2.8	12
0.012	10	1.0	10	−5.6	−0.8	2.2	−2.5	−4.2	12
0.025	13	2.3	14	−5.7	−0.8	2.2	−3.1	−6.9	11
0.073	13	1.6	17	−4.6	−1.1	3.6	−4.1	−8.8	11
0.19	12	2.7	14	−2.2	−2.6	4.8	−3.9	−8.5	9.6
0.49	9.7	4.3	9.4	−1.4	−0.9	4.5	−3.4	−8.3	8.4
0.68	8.6	2.3	8.0	−1.3	−0.3	4.9	−2.9	−7.0	5.7
1	8.2	2.2	8.2	−1.0	−0.4	4.0	−2.7	−4.9	5.4

[a] The positive and negative signs for the oscillator strengths correspond to the signs of the calculated susceptibilities, χ^2. [b] Values for the oscillator strengths have error bars of ±15% associated with them.

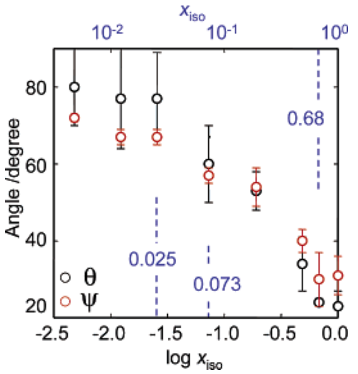

Figure 5. Change in orientation of the isopropyl group as a function of 2-propanol mole fraction: tilt angle (θ) and twist angle (ψ). The dashed blue vertical lines are a guide to the eye for three key 2-propanol mole fractions.

For the sps spectra (Figure 3c,d), the peak at 2974 cm^{-1} was dominant at all mole fractions with a very weak shoulder at 2941 cm^{-1}. The oscillator strength of the r^- feature rose steadily from $x_{\mathrm{iso}} = 0.005$ to $x_{\mathrm{iso}} = 0.19$, and all the spectra were nearly identical above $x_{\mathrm{iso}} = 0.19$ (Table 1). For the ppp combination, the peak at 2974 cm^{-1} was also dominant with a shoulder at 2941 cm^{-1}, whereas the feature at 2880 cm^{-1} had modest intensity (Figure 3e,f). The oscillator strength of the features at 2941 and 2880 cm^{-1} reached a maximum at $x_{\mathrm{iso}} = 0.073$ but attenuated at higher 2-propanol concentration, as was the case for ssp. On the other hand, the 2974 cm^{-1} feature was nearly constant up to $x_{\mathrm{iso}} = 0.073$. It then proceeded to attenuate until $x_{\mathrm{iso}} = 0.68$. After this point, it remained nearly constant to $x_{\mathrm{iso}} = 1.0$.

Angle Changes with 2-Propanol Mole Fraction. As can be seen from the data in Table 1 and the spectra in Figure 3, the peaks at 2880 and 2974 cm^{-1} displayed substantial changes in intensity as a function of mole fraction. Employing the ratios of the fitted oscillator strengths allowed the values of θ and ψ to be acquired as described in the Theory section (Figure 5).[43] Between $x_{\mathrm{iso}} = 0.005$ and $x_{\mathrm{iso}} = 0.025$, θ is approximately 77°, whereas ψ is about 67°. This indicates that the $(CH_3)_2C$ plane

---

(43) It should be noted that this analysis assumes that all signal comes from molecules in the top monolayer at the liquid/vapor interface. Oscillator strength data could potentially be affected by the presence of a well-aligned second layer of alcohol, as has been proposed for some aqueous mixtures (see refs 27−28). In these cases, however, the change in intensity of the VSFS signal was typically modest (e.g., ~30% attenuation for the CH_3 symmetric stretch intensity between $x_{\mathrm{meth}} = 0.6$ and $x_{\mathrm{meth}} = 1.0$ for methanol, as shown in ref 26). One would expect such effects to be even smaller with a branched alcohol like 2-propanol. We therefore judged the relatively large changes in oscillator strength for the isopropyl group as a function of mole fraction to be dominated by the molecule's reorientation.

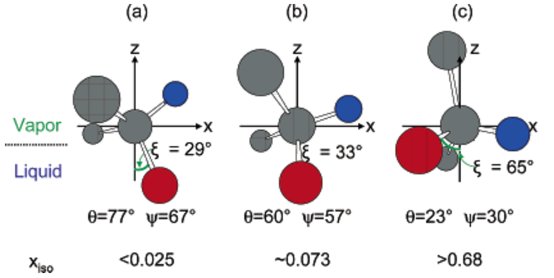

Figure 6. Molecular orientation of 2-propanol at the liquid/vapor interface; gray, red, and blue spheres denote carbon, oxygen, and hydrogen atoms, respectively. Hydrogen atoms other than methine H are not shown to avoid crowding. (a) $x_{iso} < 0.025$, (b) $x_{iso} = 0.073$, (c) $x_{iso} > 0.68$.

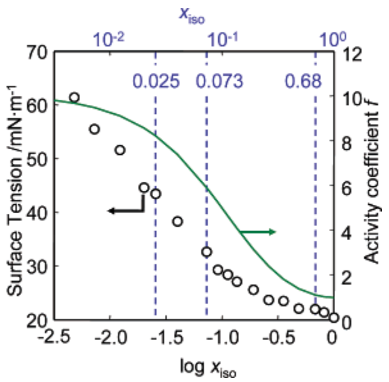

Figure 7. Surface tension (γ) and activity coefficient (f) as a function of 2-propanol mole fraction for 2-propanol/water mixtures. Open circles denote surface tension data and the solid green line is the activity coefficient. The dashed blue vertical lines are a guide to the eye for three key 2-propanol mole fractions.

is almost parallel to that of the air/water interface at low mole fractions of 2-propanol (Figure 6a). If we postulate that (i) the OH group points downward toward the bulk solution and (ii) that the H−C−O bond angle is 108°, then the angle the C−O bond of 2-propanol makes with the surface normal should be ~29° (shown as ξ in Figure 6a). Between $x_{iso} = 0.025$ and $x_{iso} = 0.68$, both θ and ψ change. At $x_{iso} = 0.073$, $\theta = 60°$ and $\psi = 57°$, whereas ξ rises to 33° with respect to the surface normal (Figure 6b). In other words, one methyl group begins to point upward toward the vapor phase, whereas the other points slightly downward into the bulk solution. At $x_{iso} = 0.68$ and above (Figure 6c), both θ and ψ become nearly constant at ~24 and ~30°, respectively. In this final case, one methyl group is almost parallel with the surface normal, whereas the second still points slightly downward. The value of ξ becomes ~65°.

Comparison with Thermodynamic Data. To aid in the interpretation of the orientational changes of 2-propanol, surface tension (γ) data measured with a Wilhelmy plate are plotted together with activity coefficient (f) data as a function of the mole fraction of 2-propanol (Figure 7). The activity coefficient was calculated using the non-random two liquid (NRTL) equation where the parameters were obtained from liquid−vapor equilibrium data at 30 °C ($A_{12} = 105.9609$, $A_{21} = 1266.7818$, $\alpha_{12} = 0.2893$).[7] The activity coefficient is a measure of how much the solution deviates from ideal behavior and provides insight into bulk liquid properties. An f value greater than 1 indicates that the interaction between 2-propanol and water is unfavorable. In this system, f is equal to or greater than 1 for all mole fractions, which is consistent with the positive excess Gibbs free energy of mixing for this system. Moreover, it is particularly large and nearly constant from $x_{iso} = 0.0$ to $x_{iso} = 0.025$. Such unfavorable interactions are usually attributed to the hydrophobic hydration of the isopropyl moiety by water molecules. These unfavorable interactions are attenuated with the increase in alcohol mole fraction, and f undergoes a corresponding decrease from $x_{iso} = 0.025$ to $x_{iso} = 0.68$. In fact, the number of hydrogen bonds with each 2-propanol molecule in bulk solution is known to decrease with increasing mole fraction of alcohol from 0.08 to 0.70.[44] Finally, above the azeotropic point, the value of f almost ceases to change, which suggests that the unfavorable interactions between 2-propanol and water are mostly alleviated.

In contrast to the activity coefficient data, the surface tension drops markedly from 72 to 32 mN/m as the alcohol mole fraction is increased from $x_{iso} = 0$ to $x_{iso} = 0.073$ (Figure 7). Above this point, the surface tension attenuates gradually to 22 mN/m at $x_{iso} = 0.68$ and appears to stay constant or perhaps drop slightly above this value. The surface tension data are consistent with the notion that 2-propanol partitions to the interface to form a Gibbs monolayer at low mole fraction.[2,45,46] It has been previously noted that the surface should be fully covered with an 2-propanol monolayer near $x_{iso}= 0.07$,[2] and this coincides with the change in the slope of the surface tension with alcohol concentration at this value.

The interfacial molecular reorientation data in Figure 5 appear to correlate well to changes in activity coefficient as a function of x_{iso} (Figure 7). By contrast, changes in surface tension do not directly correlate with the orientation of surface alcohol species. Indeed, the surface tension drops rapidly between $x_{iso} = 0.00$ and $x_{iso} = 0.025$ as the Gibbs monolayer begins to form. Under these conditions, interfacial 2-propanol molecules do not appear to show variation in orientation with increasing mole fraction (Figure 5). The value of f also remains roughly constant. Therefore, 2-propanol−2-propanol interactions should be minimal in both the bulk and at the interface under these conditions. As the alcohol concentration continues to rise, the first modest reorientation begins to occur ($0.025 \leq x_{iso} \leq 0.073$) due to the onset of alcohol−alcohol interactions. This is also the regime in which f starts to show steeper attenuation. At the interface, alcohol−alcohol interactions mean that the C−O bond migrates from a position where it is facing downward to accommodate hydrogen bonding with water to one where it extends more laterally. This should presumably allow hydrogen bonding with neighboring surface 2-propanol molecules. Furthermore, the twist in conformation of the interfacial isopropyl groups allows greater packing density of alcohol molecules at the interface. In the bulk solution, increasing the alcohol mole fraction leads to the breaking up of the organized water structure around the hydrophobic moiety of the alcohol.[47]

Although the surface tension displays a change in slope near $x_{iso} = 0.07$, both f and isopropyl orientation continue to evolve smoothly through this point. Moreover, both the surface reorientation of the 2-propanol molecules and the attenuation of the activity coefficient change ever more slowly between $x_{iso} = 0.073$ and $x_{iso} = 0.68$, after which they nearly level off.

---

(44) Takamuku, T.; Saisho, K.; Aoki, S.; Yamaguchi, T. *Z. Naturforsch., A: Phys. Sci.* **2002**, *57*, 982−994.

(45) Vazquez, G.; Alvarez, E.; Navaza, J. M. *J. Chem. Eng. Data* **1995**, *40*, 611−614.

(46) Hoke, B. C.; Chen, J. C. *J. Chem. Eng. Data* **1991**, *36*, 322−326.

(47) Hayashi, H.; Nishikawa, K.; Iijima, T. *J. Phys. Chem.* **1990**, *94*, 8334−8338.

Such correlations provide strong evidence that the molecular orientation of interfacial 2-propanol molecules is sensitive to subphase conditions. The reason that the surface tension is not directly correlated with the other two properties is that it is extremely sensitive to the number density of alcohol molecules at the interface even under conditions where 2-propanol−2-propanol interactions are minimal.

As noted in the Introduction, it has been shown that the maximum surface excess of small alcohols in aqueous binary mixtures coincides with the minimum in the partial molar volume of the alcohol.[2] This is a good example of the relationship between bulk and surface properties at the macroscopic level. To the best of our knowledge, however, the present study provides the first spectroscopic evidence of a relationship between a molecular-level surface property (i.e., interfacial orientation) and the bulk activity coefficient value. Furthermore, the variation in the number of hydrogen bonds per 2-propanol molecule with mole fraction in the bulk solution[44] also tracks the same functional form as the activity coefficient and interfacial molecular reorientation data. Because the number of hydrogen bonds per molecule is also a molecular level property, a correspondence between bulk and surface properties appears to be established at the molecular scale, as should be expected. Because thermodynamic correlations between bulk and surface properties exist for many aqueous mixtures,[2] it should be possible to find molecular scale relationships in those cases as well. We postulate that this should also involve the surface orientation of the organic component.

Conclusions

A key finding of this study is that 2-propanol reorients up to its azeotrope with water and then maintains a nearly fixed orientation at the interface. At low 2-propanol mole fractions ($x_{\mathrm{iso}} \leq 0.025$), the two methyl groups lie close to the surface. As the 2-propanol mole fraction is increased ($0.025 \leq x_{\mathrm{iso}} \leq 0.68$), the molecule twists to have one methyl group point toward the vapor phase, whereas the other is nearly parallel with the plane of the liquid/vapor interface. Interfacial molecular reorientation of 2-propanol molecules closely tracks changes in the bulk activity coefficient for this system and, thus, helps establish a molecular level nexus between the surface and bulk molecular structure.

Acknowledgment. We thank Dr. Xin Chen for insightful discussions. We also acknowledge the National Science Foundation (CHE-0094332) and the Robert A. Welch Foundation (Grant A-1421) for funding.

JA060156K