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When the Solute Becomes the Solvent: Orientation, Ordering, and Structure of Binary Mixtures of 1-Hexanol and Cyclohexane over the (0001) α-Al_2O_3 Surface

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Abstract: Mixtures of 1-hexanol in cyclohexane over the (0001) α-Al_2O_3 surface were probed in the CH stretching region using vibrational broadband sum frequency generation (SFG). Below 10 mol % 1-hexanol, the alcohol adsorbs to the surface through interactions that result in observed free adsorption energies of around 14−15 kJ/mol obtained from the Langmuir adsorption model. Polarization-resolved SFG spectra indicate ordering of the alkyl tails with increasing surface coverage. Highly correlated with the ordering of 1-hexanol is an orientational change of the cyclohexane solvent from flat to most likely tilted, suggesting that cyclohexane mediates the adsorption of 1-hexanol via intercalation. Above 10 mol %, the SFG signals for 1-hexanol and cyclohexane decrease with increasing concentration of 1-hexanol, consistent with the notion that cyclohexane is excluded from the interfacial region while 1-hexanol becomes increasingly disordered. At the interface, the alcohol solute becomes the solvent at a mole fraction of only 10%, i.e., five times below what is considered the solute-to-solvent mole fraction transition in the bulk. These results provide an important benchmark for theory, inform reaction design, and demonstrate that bulk thermodynamic properties of binary mixtures are not directly transferable to interfacial environments.

1. Introduction

Solute/solvent interactions are universally relevant to chemistry, biology, physics, and materials science,[1−6] especially when they occur in interfacial environments.[6−12] In general, these interactions depend on the molecular properties of the solute and the solvent, their respective mole fractions, and the strength of their attractions to the surface. It is therefore of interest to ask at which mole fraction the solute becomes the solvent. The answer is straightforward for bulk solutions of real and ideal binary mixtures, where transition occurs when the mole fraction of one component exceeds that of the other, i.e., at mole fractions of >50%.[13] Here, we show that this definition does not hold in interfacial environments, for which polarization-resolved vibrational sum frequency generation (SFG) studies of 1-hexanol/cyclohexane mixtures over the (0001) surface of α-Al_2O_3 demonstrate a solute-to-solvent changeover in the interfacial region at bulk mole fraction of 10%. This changeover coincides with major changes in the molecular orientation and structure of 1-hexanol and cyclohexane.

The results from this study are important for many areas of science and engineering: for example, knowing which compound acts as the solvent at an interface will help rationalize the observation that the choice of solvent can often lead to orders of magnitude of differences in the rates of heterogeneously catalyzed reactions at liquid/solid interfaces.[14−20] Similar circumstances exist in materials applications where thin films are often prepared by choosing solvents on a semiempirical basis or by referring to macroscopic solvent properties.[21,22] Key parameters to consider for understanding, controlling, and predicting chemistry in these fascinating environments include selective solvation, the accessibility of the active surface sites to the solvent and the solute, and the mediation or curtailing of favorable interactions with the surface by the solvent, the solute,

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or both.[15,17,19,20,23−25] The importance of these considerations may be understated in the literature, as most classes of heterogeneous reactions are already optimized such that only a small number of solvents are ever used. However, since changes in the polarity and the chemical nature of the reactive surface can favor one solvent over another to promote a particular interfacial process of interest,[14,15,17,26,27] there is a need for predictive ability in the decision processes that lead to a particular solvent choice and amount, i.e., mole fraction. Given the fact that the molecular orientation, geometry, and ordering of solutes and solvents at interfaces can directly control the rate and product distributions in heterogeneous reactions,[28−32] and given that these properties may, in turn, be influenced by the chemical environment of the surface-localized species,[27,33−37] it is of general interest to develop predictive models for these complex systems. Ideally, such models are guided by molecular insight, which this work aims to provide as outlined below.

Much can be learned from interfacial tension, surface energy, and calorimetry measurements,[38−41] especially when the results are interpreted using theoretical models aimed at elucidating the thermodynamic properties of pure liquids and binary mixtures over solid surfaces.[39,40,42−45] However, selectively probing the interfacial region between a liquid and a solid directly, with chemical specificity and sensitivity to molecular structure and the distribution of orientations, remains an experimental challenge. In addition to neutron scattering techniques, which are applied mostly to thin films and require neutron sources,[46,47] the nonlinear-optical technique, sum-frequency generation (SFG), has emerged as a powerful tool for elucidating molecular orientation and structure at liquid/solid interfaces.[33,36,37,48−77] The selectivity of SFG to the anisotropic interfacial region and its applicability for probing buried interfaces with chemical specificity at ambient temperature and pressure make it particularly well-suited to the study of liquid/oxide interfaces.[36,37,48,49,52,59,66−69,78−82] In contrast to the vast amount of literature on the role of water as a universal solvent at interfaces,[63−66,70−77,83] which can be complicated by interfacial acid−base chemistry,[84,85] fewer studies exist that probe molecular orientation of organic liquids at solid interfaces using SFG.[36,37,48,49,52,59,66−69] An important result from these activities, and related work utilizing solvatochromic probes,[26,27,86] is that polarity of the interfacial region, as determined by the

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choice of surface and solvent, plays a key role in controlling the orientation and structure of adsorbates and the accessibility of active sites in the interfacial region.[15,17,19,20,26,35,87,88] Even sparser than studies of neat liquids over solids is work on how organic solutes mixed into solvents interact with solids.[48,49] Here, we help fill this knowledge gap by focusing on a model system representative of a polar adsorbate on a polar surface but in a nonpolar solvent. We investigate the molecular structure, order, and orientation of 1-hexanol/cyclohexane binary mixtures adsorbing to the (0001) basal surface of α-Al_2O_3, covering 5 orders of magnitude in mole fraction, using broadband SFG. To our knowledge this is the first study to demonstrate, by directly probing both the solvent and the solute with exquisite sensitivity to molecular structure, that solvent and solute in the interfacial region at an oxide surface induce in each other extensive concentration-dependent changes in molecular ordering and orientation. The choice of this system is directly motivated by its relevance to selective alcohol oxidation, one of the most extensively studied heterogeneously catalyzed reactions at the organic liquid/solid interface, which is accomplished in a nonpolar solvent (usually cyclohexane) using metal particles on a polar catalyst support such as alumina.[89−95] Furthermore, pure alcohols at various interfaces ranging from polymers to graphite have been studied by several groups,[36,37,47,54,81] and the results from this present work can be compared to those of these earlier studies to gain insight into the role of solvent in controlling interfacial adsorption, molecular orientation, ordering, geometry, and site accessibility.

2. Experimental Section

2.1. Laser System, Sample Cell, and Materials. The laser system and sample cell used in SFG experiments are described in previous work,[28,33,96−98] and the theoretical background for SFG is outlined in several other sources.[78−82] To summarize, a pulsed laser beam from a regenerative amplifier (800 nm, 120 fsec, 1 kHz, from a SpectraPhysics Spitfire laser system) is split with a 50:50 beam splitter. Half of the beam is used as the 800 nm up-converter, while the other half pumps an optical parametric amplifier (SpectraPhysics) to generate mid-IR light, tunable from 3.0−3.6 μm. The two beams are focused and overlapped at the interface between an α-Al_2O_3 single crystal window ((0001) face, ISP optics or MTI crystals) and the liquid solution, contained in a custom, home-built, small volume (0.5 or 0.1 mL) Teflon cell. Signal at the sum of the incident laser frequencies is generated via a second-order, symmetry-forbidden, nonlinear process at the liquid/oxide interface,[78−82] and resonantly enhanced for input IR frequencies corresponding to vibrational resonances of molecules at the interface. Following Ding et al.,[99] all frequencies were calibrated to the absorbances of a 70 μm thick polystyrene film placed in the IR beam (ICL crystal laboratories). The normalization procedure for the SFG signal follows Esenturk and Walker[100] and is explained in the Supporting Information, as well as in previous work.[28,33,96]

Cyclohexane (>99.7%) and 1-hexanol (>99%) were purchased from Sigma-Aldrich, cyclohexane-d_{12} (99.6 atom % D) was purchased from Aldrich, and *n*-hexyl-d_{13} alcohol (99.2 atom % D, referred to below as 1-hexanol-d_{13}) was purchased from CDN Isotopes. Liquid solutions are introduced and removed from the cell via a syringe, and the experiments proceeded from low to high concentration. We allowed the SFG signal intensity to reach steady state, which took less than 20 min, before acquisition and tested for possible accumulation of 1-hexanol at the surface after repeated injections of solution by reintroducing the same concentration of 1-hexanol six times. These control experiments showed no changes in the SFG intensity of the CH_3 symmetric stretching mode, and no changes in the SFG intensity of the CH_2 symmetric stretching mode (vide infra) after the first 20 min of the first repetition.

2.2. Vibrational SFG Spectroscopy of Hydrogenated and Perdeuterated 1-Hexanol in Cyclohexane. Vibrational SFG spectra were collected at the α-Al_2O_3/liquid interface for solutions containing 1-hexanol in cyclohexane. In order to isolate the C−H vibrational signatures of 1-hexanol and cyclohexane, which would normally overlap, separate experiments were conducted in which either 1-hexanol was dissolved in cyclohexane-d_{12}, or 1-hexanol-d_{13} was dissolved in cyclohexane, because all C−D stretches occur at frequencies lower than those probed in this work. The experiments were repeated for 1-hexanol in two other perdeuterated solvents, tetrahydrofuran-d_8 and acetonitrile-d_3, but no SFG signal was observed from 1-hexanol at any concentration. By selecting the polarization of the light probing the surface and of the detected signal, adsorbate vibrational modes of specific orientations are accessed. The spectra displayed in this work were collected in the SSP polarization combination, meaning the s-polarized SFG signal is detected when probing with s-polarized visible and p-polarized IR light. The selection rules for SSP polarization require that the vibrational modes have IR transition dipole components oriented along the surface normal and that the α_{yy} element of the Raman transition tensor be nonvanishing.[34,35,79,81,82,100] Spectra were also collected using the SPS polarization combination, which requires that vibrational modes have a component of their IR dipoles in the surface plane. In addition to peaks corresponding to vibrational resonances, SPS-polarized spectra also exhibited broad nonresonant signals that introduced coherent interferences with spectral features, albeit with unknown phase between resonant and nonresonant components, which made their spectral analysis less straightforward than in the SSP-polarized spectra. SPS-polarized spectra were therefore not used to infer chemical behavior because peak positions were difficult to ascertain but are included in Supporting Information for completeness.

2.3. Probing Molecular Order at Interfaces in Vibrational SFG. Because of its nature as a second-order nonlinear spectroscopy, SFG is insensitive to vibrational motions that possess inversion symmetry.[101] Yet, while many vibrational modes in isolated molecules possess centers of inversion, symmetry is broken at an interface and centrosymmetric molecules such as cyclohexane and benzene can generate nonzero vibrational SFG signal at interfaces.[33,102] The concept of broken local symmetry can be exploited for evaluating the molecular structure of surface-localized organic species. Specifically, SFG spectra are well-known to exhibit zero or small signal intensity for the $(CH_2)_n$ portions of well ordered alkyl chains because the vibrations of pairs of trans-configured CH_2

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groups possess inversion symmetry.[50,54,100,103−105] Thus, the ratio of the SFG signal from the CH_3 symmetric stretch (r^+) of a terminal methyl group to the CH_2 symmetric stretches (d^+) of the carbon chain, denoted r^+/d^+, is a well-established descriptor assessing the ordering of alkyl groups along carbon chains.[50,54,100,104,105] As the number of gauche defects within the aliphatic chain diminish, the r^+/d^+ ratio is expected to become larger due to decreased contributions from the now symmetrically arranged CH_2 moieties.

Because fitting each spectrum to extract the amplitudes of all of the peaks requires 10 parameters to describe the amplitude, line width, and the frequency of all peaks, low signal-to-noise spectra were difficult to fit with a high degree of certainty in the resulting amplitudes. Therefore, the square root of signal intensity was used as an approximation for the SFG E-field (E_{SFG}) in order to quantitatively analyze the results. Because the same trends in amplitudes are obtained from fits and the square root of the raw intensities (please see Supporting Information), this approximation is justified.

3. Results and Discussion

3.1. SFG Spectra of Liquid 1-Hexanol in Cyclohexane at the α-Al_2O_3 Surface. Representative SFG spectra of 1-hexanol in cyclohexane-d_{12} at various mole fractions of 1-hexanol are shown in Figure 1A. Three vibrational resonances were observed and assigned based on well-established literature frequencies for alkyl chains.[35−37,81,100,104−111] The mode at 2939 cm^{-1} is assigned as a CH_3 Fermi resonance, the mode at 2872 cm^{-1} as the CH_3 symmetric stretch, and the mode at 2850 cm^{-1} as the CH_2 symmetric stretch. The methyl and methylene asymmetric stretches were not observed in SSP polarization at any concentration, though they may contribute to the CH_3 Fermi resonance peak but are not separately resolved. In general, the SFG signal intensities increase up to about 10 mol % of 1-hexanol and then decrease (see sections 3.2 and 3.3). Two resolved peaks are observed for cyclohexane when the deuteration scheme was reversed, (Figure 1B), and they occur at 2924 cm^{-1}, assigned as asymmetric methylene stretches, and at 2845 cm^{-1}, assigned as symmetric methylene stretches.[33,96,111−114] In general, the SFG signal intensities decrease with increasing 1-hexanol mole fraction for mole fractions greater than 10%, which will be discussed below.

3.2. Solvent and Solute Behavior at 1-Hexanol Concentrations <10 Mol %. For low concentrations of 1-hexanol, i.e., less than approximately 10 mol %, the 1-hexanol SFG signals increase with concentration (Figure 2). Specifically, the SFG E-field of the CH_3 symmetric stretching mode begins to increase at 0.2 mol % 1-hexanol and continues to increase until it reaches a plateau at 5 mol %. In contrast, the SFG E-field of the CH_2 symmetric stretch is constant below 0.1 mol % and then abruptly increases to a constant value, at a concentration 50 times lower than the concentration at which the CH_3 symmetric stretching signal saturates.

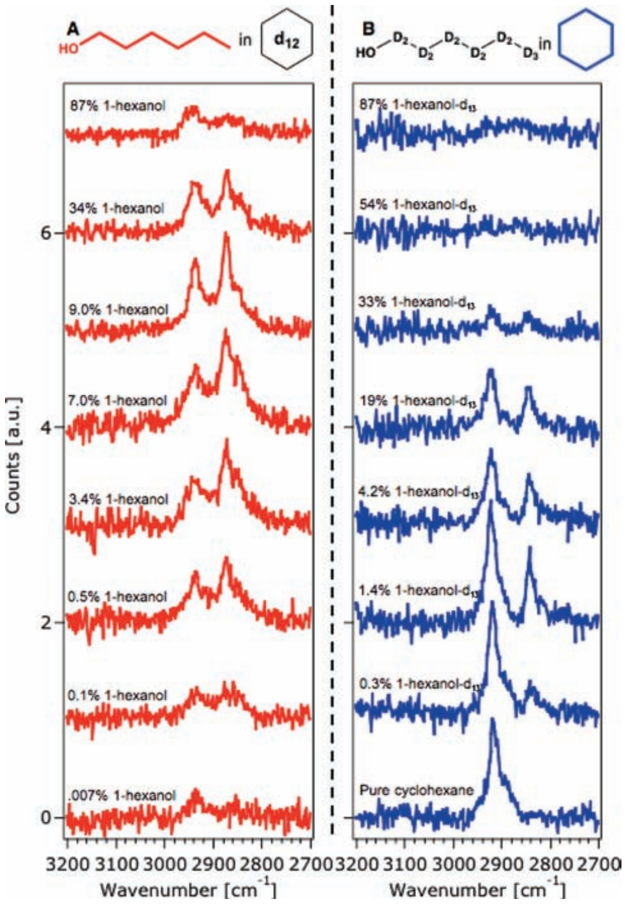

Figure 1. Representative SFG spectra of solutions of 1-hexanol in cyclohexane-d_{12} of the indicated 1-hexanol mole percents ranging from 0.007% to 87% at the organic liquid/α-Al_2O_3 interface. The data are corrected for the input IR frequency distribution and normalized to the intensity of the CH_3 symmetric stretch at 6 mol % 1-hexanol. The ratio of the E_{SFG} of CH_3 symmetric stretch at 2872 cm^{-1} to the E_{SFG} of CH_2 symmetric stretch at 2850 cm^{-1} indicates the extent of ordering of 1-hexanol alkyl groups (A). Representative SFG spectra of solutions of 1-hexanol-d_{13} in cyclohexane of the indicated 1-hexanol-d_{13} mole percents ranging from 0% to 87% at the organic liquid/α-Al_2O_3 interface. The data are corrected for the input IR frequency distribution and normalized to the intensity of the CH_2 asymmetric stretch of pure cyclohexane. The ratio of the E_{SFG} of CH_2 symmetric stretch at 2845 cm^{-1} to the E_{SFG} of CH_2 asymmetric stretch at 2924 cm^{-1} indicates molecular orientation of cyclohexane at the interface (B).

3.2.1. 1-Hexanol Orientation, Surface Coverage, and Ordering. Three contributing factors may influence the concentration-dependent features observed in the SFG spectra of 1-hexanol: molecular orientation, surface coverage, and molecular ordering in adsorbed 1-hexanol. They are each discussed as follows.

3.2.1.1. 1-Hexanol Orientation is Invariant with Concentration. Given that CH_3 asymmetric stretches are weak or even absent in the SSP-polarized SFG spectra, as evidenced by the lack of signal intensity near 2955 cm^{-1} in Figure 1, the average molecular orientation of the hexanol methyl group likely remains centered along the surface normal at all concentrations. This

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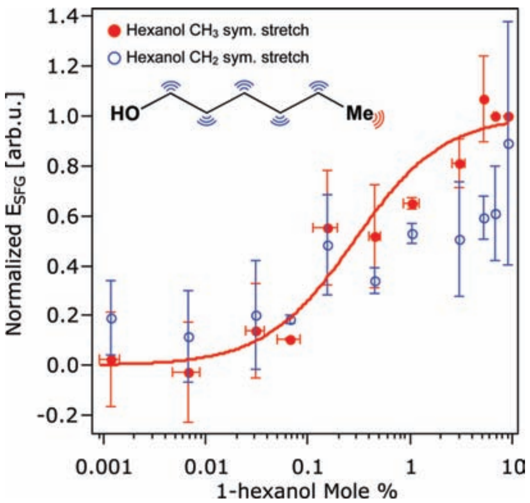

Figure 2. E_{SFG} for the CH_3 symmetric stretching mode (filled red circles) and CH_2 symmetric stretching mode (empty blue circles) of 1-hexanol in cyclohexane-d_{12} as a function of 1-hexanol mol %, plotted on a logarithmic scale. Data are normalized to the value for the CH_3 symmetric stretch at 6 mol % 1-hexanol. The CH_3 symmetric stretch data are fitted to a Langmuir adsorption isotherm which is plotted as a solid line. Error bars represent standard deviation of the several measurements.

interpretation is supported by the presence of signal at 2950 cm^{-1} in the SPS spectra found in Supporting Information as would be expected for a methyl group oriented normal to the interface. Our conclusion is also consistent with SFG work by Li et al., who used similar reasoning to conclude that pure hexadecanol adopts an orientation perpendicular to the sapphire interface, which is one important reference point for our present work.[37] Similar behavior has been reported for other interfaces as well: Sefler et al. reported that alcohols of all chain lengths at the air/liquid interface orient along the surface normal,[36] and Jacquemain et al. used grazing incidence X-ray diffraction and reported that amphiphilic alcohols at the air/water interface adopt an orientation close to normal to the surface.[115] We therefore conclude that the orientation of hexanol is invariant with the mole fraction of hexanol in cyclohexane, and that the concentration-dependent changes in the SFG spectra are due to either changes in surface coverage or ordering, as discussed next.

3.2.1.2. Langmuir Model Describes 1-Hexanol Surface Coverage. Ruling out orientation changes as a cause of concentration-dependent changes in the SFG intensity of the CH_3 symmetric stretching mode, we next tested whether the SFG *E*-field changes observed between 0 and 10 mol % are due to increasing surface coverage. We modeled the concentration-dependent SFG *E*-field of the CH_3 symmetric stretch using the standard Langmuir model for surface coverage.[116] We note that although lateral interactions between 1-hexanol molecules are expected,[45,48] adsorption models that include lateral interactions, such as the Frumkin−Fowler−Guggenheim (FFG) model,[44,117] do not result in significant lateral interaction parameters within the experimental uncertainty. However, the Langmuir fit results in a binding constant of $K_{ads} = 3.5(7) \times 10^2$ referenced to the molarity of 1 L of cyclohexane-d_{12}. This binding constant corresponds to an observed adsorption free energy of $\Delta G_{ads,obs} = -14.5(5)$ kJ/mol. This quantity includes the establishment of hydrogen bonds with the surface, loss of hydrogen bonds between molecules in the bulk, and any lateral interactions between molecules at the surface. The free energy involved is comparable to one net hydrogen bond formation in each molecular adsorption event.[45,116] Considering that at 2.5 mol % 1-hexanol dissolved in *n*-hexane von Solms et al. determined that 83% of 1-hexanol molecules are in fact hydrogen bonded in the bulk,[118] there are likely significant lateral interactions between 1-hexanol molecules on the surface, in addition to hydrogen bonding to α-Al_2O_3. Thus, our first-order approximation treatment of the CH_3 symmetric stretch signal as a measure of surface coverage in this system is consistent with chemical intuition and straightforward adsorption models.

3.2.1.3. Molecular Order along the Carbon Chain Increases with 1-Hexanol Coverage. Although the SFG response from the CH_3 symmetric stretch mode is readily explained by changes in the hexanol surface coverage, the concentration-dependent behavior of the CH_2 symmetric stretching mode exhibits a somewhat sudden increase in SFG signal that occurs at about 0.2 mol %. Above 0.2 mol %, the SFG signal from the CH_2 symmetric stretching mode remains fairly constant while the signal from the CH_3 symmetric stretch continues to increase (Figure 2). The observed behavior of the CH_2 symmetric stretch SFG signal is unlikely to be due to surface coverage buildup alone. Rather, the SFG response of the CH_2 symmetric stretch mode can be described by concerted increases in surface coverage, which will increase the SFG response, and alkyl chain ordering, which will lower the SFG response due to a lowering of gauche defects along the carbon chain. In order to assess the degree of molecular ordering in the system, we determined the r^+/d^+ ratio, which also references to the SFG intensity from the CH_3 symmetric stretch and, indirectly, to surface coverage (see section 2.3).[50,100,104,105] This analysis (Figure 3) clearly shows that the number of gauche defects decreases with increasing 1-hexanol surface coverage, at least up to 1 hexanol mole fraction of roughly 10%. A cartoon of this behavior is sketched in Scheme 1.

3.2.2. Orientation Changes of Cyclohexane during 1-Hexanol Adsorption. During the interfacial build up of 1-hexanol, which reduces its number of gauche defects while maintaining a net molecular orientation along the surface normal in the low concentration range, the orientation of cyclohexane at the interface changes as well. We begin with neat cyclohexane, whose SFG spectrum shows a clear asymmetric CH_2 stretching mode at 2924 cm^{-1} and a remarkable absence of any symmetric CH_2 stretching mode, which occurs at 2845 cm^{-1}. As described in our previous work,[33] these results are consistent with a molecular orientation of cyclohexane that is mainly parallel to the interface.

Interestingly, addition of even less than 0.3 mol % 1-hexanol-d_{13} results in the appearance of the symmetric CH_2 stretching mode, whose SFG signal intensity continues to grow with increasing 1-hexanol-d_{13} mole percent and reaches a maximum at about 5 mol % 1-hexanol-d_{13}, after which it decreases again together with a proportional decrease in the asymmetric CH_2 stretching peak at 2924 cm^{-1}. The appearance of a symmetric CH_2 stretch is likely the result of a different (i.e., tilted) orientation of cyclohexane when 1-hexanol molecules are

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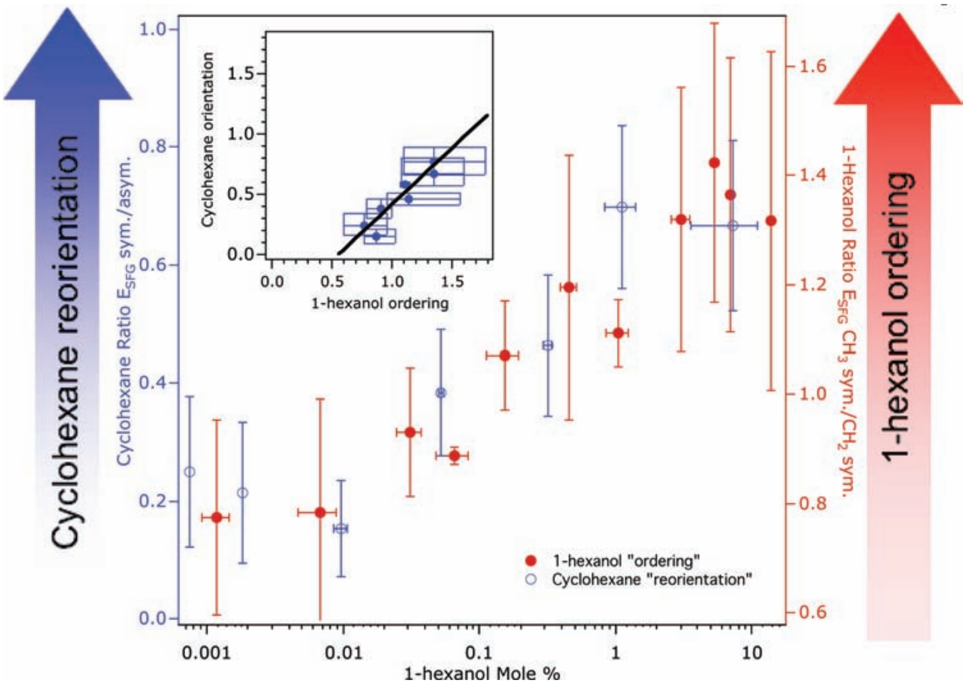
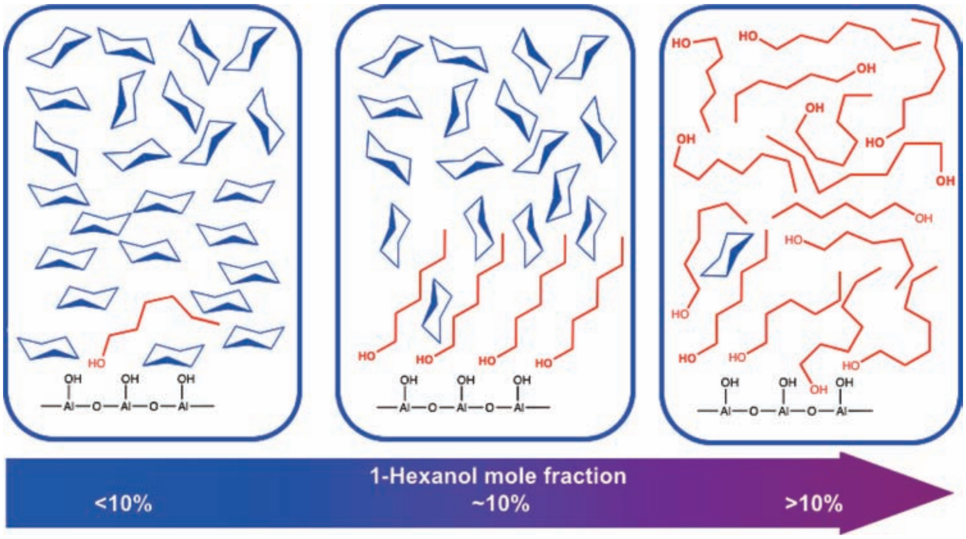


Figure 3. The E_{SFG} CH_2 symmetric stretch/CH_2 asymmetric stretch ratio for cyclohexane, representing tilting of the solvent molecules (left axis; blue, empty circles) and the E_{SFG} r^+/d^+ ratio for 1-hexanol, representing ordering of the adsorbates (right axis; red, filled circles), are plotted as functions of added 1-hexanol-d_{13} mole percent and 1-hexanol mole percent, respectively (main plot). Inset: Correlation plot of cyclohexane orientation and 1-hexanol ordering.

Scheme 1. Descriptive Scheme of the Proposed Molecular Structures of the 1-Hexanol Adlayer and Surrounding Cyclohexane Solvent as a Function of Bulk 1-Hexanol Concentration



present at the interface compared to the clean α-Al_2O_3 surface. Tilting of cyclohexane out of the plane of the surface would place a significant component of the symmetric stretch transition dipoles of individual CH_2 groups along the surface normal, which would give rise to a symmetric CH_2 stretching mode at 2845 cm^{-1}.

3.2.3. Correlation of 1-Hexanol Ordering and Cyclohexane Orientation. A key question that arises from the results presented above is how the orientational changes involving cyclohexane are correlated with the ordering occurring in 1-hexanol. To answer this question, we quantify the reorientation of cyclohexane by the ratio of the CH_2 symmetric stretch to the CH_2 asymmetric stretch SFG *E*-fields, which is found to increase with bulk concentration of 1-hexanol-d_{13}, and the ordering of 1-hexanol by the corresponding r^+/d^+ ratio, as discussed above (Figure 3). We note that our approximation for the orientation of cyclohexane assumes a quasi-local mode approximation, which is justified given that signal is observed only because of a decrease in symmetry as compared to isolated or bulk phase molecules.

The correlation between the two processes is remarkably strong (inset of Figure 3), which may be explained by the notion that cyclohexane interactions with an oxide surface are different from cyclohexane interactions with an oxide surface covered with the alkyl chains of physisorbed 1-hexanol. First, the cyclohexane molecules may tilt into the freshly forming 1-hexanol adlayer to maximize hydrophobic interactions within the system. This explanation is consistent with the ordering of

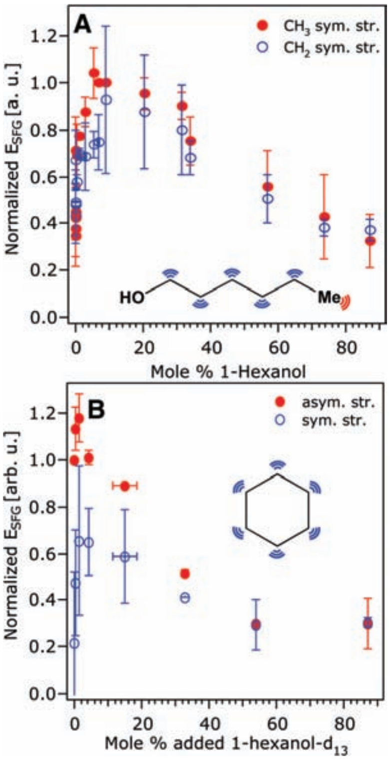


Figure 4. E_{SFG} for the CH_3 symmetric stretching mode (filled red circles) and the CH_2 symmetric stretching mode (empty blue circles) of 1-hexanol in cyclohexane-d_{12}, normalized to the value for the CH_3 symmetric stretch at 6 mol % 1-hexanol, as a function of 1-hexanol mole %. Error bars represent standard deviation of the several measurements (A). E_{SFG} for the CH_2 asymmetric stretch (filled red circles) and CH_2 symmetric stretch (empty blue circles) of cyclohexane with added 1-hexanol-d_{13}, normalized to the value for the CH_2 asymmetric stretch of pure cyclohexane, plotted as a function of 1-hexanol-d_{13} mole %. Error bars represent standard deviation of the several measurements (B).

surfactant alkyl tails mediated by long-chain alkanes at fused silica surfaces observed by Miranda et al.[48] Second, changes in molecular orientation can critically depend on the polarity of the interfacial region, which clearly changes when going from an α-Al_2O_3 surface to one covered with physisorbed 1-hexanol. This scenario has been demonstrated for the case of fused silica by Brindza et al. who used second harmonic generation to compare the orientation of *p*-nitroanisole in a polar vs a nonpolar solvent.[26] This correlation between orientation and ordering for two layers of material on insulating surfaces is also reminiscent of surface-induced alignment of a 4-*n*-octyl-4′-cyanobiphenyl liquid crystal layer on a polyvinyl-alcohol surface demonstrated by Wei et al.[119]

3.3. Solvent and Solute Behavior at 1-Hexanol Concentrations >10 Mol %. 3.3.1. 1-Hexanol. At concentrations above 10 mol % 1-hexanol, the SFG signals for both components of the mixture decrease with increasing 1-hexanol mole percent. As shown in Figure 4A, the SFG signal intensities of the CH_3 symmetric and CH_2 symmetric stretches of 1-hexanol decrease linearly and with very similar slopes with increasing mole fraction. A small amount of signal is still present at 87 mol %, but no SFG signal was observed for pure 1-hexanol if the sample cell and surface had not been exposed to cyclohexane. The decrease of overall 1-hexanol signal with increasing concentration can be explained in one of two ways.

In the first possibility, multilayers of 1-hexanol are formed at the surface at concentrations higher than the concentration required for monolayer formation, and the net SFG signal from 1-hexanol decreases due to cancelation of the lower layer(s) by the higher one(s). This scenario would be similar to the cancelation of SFG signal in a lipid bilayer reported by Liu and Conboy,[53] where the presence of two symmetric leaflets leads to a decrease in signal due to the formation of inversion symmetry in the interfacial region. We also note that pure 1-hexanol, as well as alcohols in nonpolar solvents, are expected to form partial hydrogen bonding networks in bulk liquid.[45,118] Although this network would not result in frozen bilayers as is the case for lipids, the attraction between 1-hexanol molecules in the interfacial region may be sufficient to form a second layer with a modest amount of ordering. Evidence for similar multilayers has been observed using differential scanning calorimetry and neutron diffraction by Messé et al. for pure liquid alcohol thin films on graphite.[47]

The second possibility is that the data presented in Figure 4 then suggest that the interfacial region becomes disordered at higher concentrations of 1-hexanol, resulting in a loss of anisotropy and hence a loss of signal. This scenario is illustrated in Scheme 1. Complete disorder of pure 1-hexanol due to comparatively weak intermolecular interactions would explain the absence of signal as compared to the longer-chain hexadecanol used by Li et al.[37] The disorder that is observed at relatively low alcohol concentrations could be a sign of low selective solvation of nonpolar molecules by aliphatic alcohols, a concept suggested for solution phase alcohols by Hunter and co-workers to explain why alcohols deviate from the otherwise linear relationship between number of hydrogen bonding groups and solvation.[24,25]

3.3.2. Cyclohexane. As shown in Figure 4B, the SFG signal from the C−H symmetric and C−H asymmetric stretches of cyclohexane with added 1-hexanol-d_{13} also diminishes above 10 mol % and 4 mol %, respectively, and falls below the detection limit at mole fractions above 50%. This decrease in the cyclohexane SFG signal is consistent with the presence of disordered 1-hexanol adlayers as opposed to ordered layers: the presence of ordered layers would induce order in any remaining cyclohexane in the interfacial region and increase the SFG signal from cyclohexane, which is not observed. If 1-hexanol at the interface were to become disordered, which appears most likely from our discussed presented in the previous section, cyclohexane would either not be present near the interface or it would be disordered as well and decrease the SFG signal from cyclohexane, which is indeed observed.

4. Conclusions

By probing vibrational transitions at the buried liquid/oxide interface using SFG, we have characterized the molecular structure and orientation of 1-hexanol and cyclohexane liquid mixtures over α-Al_2O_3 (0001) surfaces at room temperature. Below 10 mol % of 1-hexanol, the alcohol adsorbs to the oxide surface while reducing the number of gauche defects. Simultaneously, cyclohexane undergoes a dramatic orientational change from flat to most likely tilted, and this change is driven by the 1-hexanol solute. This behavior highlights a strong interplay between the solvent and the solute, which directly control each other's ordering and orientation in the interfacial region. Above 10 mol %, the SFG signals for 1-hexanol and cyclohexane indicate that cyclohexane is excluded from the interfacial region while 1-hexanol becomes increasingly disordered. We thus conclude that the alcohol solute has become

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[119] Wei, X.; Hong, S.-C.; Zhuang, X.; Goto, T.; Shen, Y. R. *Phys. Rev. E.* **2000**, *62*, 5160.

the solvent at a mole fraction of only 10%, i.e., five times below what is considered the solute-to-solvent mole fraction transition in the bulk.

The results from this study provide an important benchmark for theory and demonstrate that bulk thermodynamic properties of binary mixtures are not directly transferable to interfacial environments. The detailed insight into molecular structure at the interface between an organic binary mixture and an oxide surface can be applied toward informing solvent choice and to understanding, predicting, and controlling solute−solvent effects in heterogeneous systems. The ability of one species to orient another is likely to significantly affect reactivity at interfaces that are of importance in chemistry, biology, materials science, and nature.

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Supporting Information Available: SFG signal normalization procedure, sps spectra, repetitive exposure of samples to the same concentration of 1-hexanol, fit to the FFG model, raw SFG responses for the methyl and methylene symmetric stretch modes, and SFG amplitudes from spectral fitting. This information is available free of charge via the Internet at http://pubs.acs.org/.

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