

LETTERS

Evidence for a Diffuse Interfacial Region at the Dichloroethane/Water Interface

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The 1,2-dichloroethane (DCE)/water interface is important because of its suitability as an electrochemical interface between two immiscible electrolyte solutions (ITIES). An issue of particular interest is whether the interfacial region is molecularly sharp or whether the interface is comprised of a diffuse mixed interfacial region. These studies using vibrational sum-frequency spectroscopy as a probe of the structure, orientation, and bonding of interfacial water show that the interface is molecularly disordered with properties similar to a mixed phase interfacial region. It does not have the characteristics of a sharp interface that have been shown to occur at other liquid/liquid interfaces such as $\text{CCl}_4/\text{H}_2\text{O}$ and alkane/ H_2O .

Introduction

The structure and dynamics of molecules at the liquid/liquid interface have been widely studied topics over recent years because of the importance of this type of interface in organic synthesis, chemical separations, and electrochemistry.^{1–15} Over the past few decades, many theoretical studies have examined the molecular properties of the liquid/liquid interface, yet only recently have experimental techniques been developed enough to provide molecular-scale information regarding these buried systems.^{16,17} As an interface between two immiscible electrolyte solutions (ITIES), 1,2-dichloroethane/water is one liquid/liquid system that has drawn considerable attention.^{18,19} A long-standing issue surrounding this system is whether the interface consists of two distinct phases or whether the interfacial region is a mixture of the two phases.²⁰ Molecular dynamics simulations suggest that thermal fluctuations roughen the interface, yet it is sharp on a molecular scale.²¹

The second motivation for understanding this interface is its relevance to understanding water at hydrophobic surfaces. Recent studies from this laboratory have probed the molecular properties of various liquid/liquid interfaces by vibrational sum-frequency spectroscopy.^{22–24} Thus far these studies have

involved hydrophobic organic liquids that are nonpolar (alkanes $\text{C}_6\text{--}\text{C}_8$ and CCl_4). By examining the vibrational spectroscopy of water at these interfaces we have found them to be relatively sharp on a molecular level. Interfacial water molecules in these systems show strong orientation relative to the surface normal, the orientation being induced by interactions at the interface between water and the organic liquid. Our interest in the DCE/ H_2O interface is to understand how the polarity of DCE impacts the interfacial structuring in addition to addressing the issue of the sharp/diffuse nature of the DCE/ H_2O interface. Unlike nonpolar molecules such as CCl_4 or the alkanes, DCE has a dipole moment in its gauche form (2.1D).

Experimental Section

Vibrational sum-frequency spectroscopy (VSFS) is a second-order nonlinear optical technique that can be used to study buried interfaces under ambient conditions.^{17,24,25} In our VSFS experiments, tunable infrared light (ω_{IR}) is overlapped with visible light at a fixed frequency (ω_{VIS}) at the interface under study. Sum-frequency light is emitted at the sum of these frequencies ($\omega_{\text{SF}} = \omega_{\text{IR}} + \omega_{\text{VIS}}$). A total internal reflection geometry for coupling the beams in and out of the cell has been used to maximize the emitted sum-frequency intensity.^{26–28} When the infrared light is tuned over a vibrational mode, the quantity of

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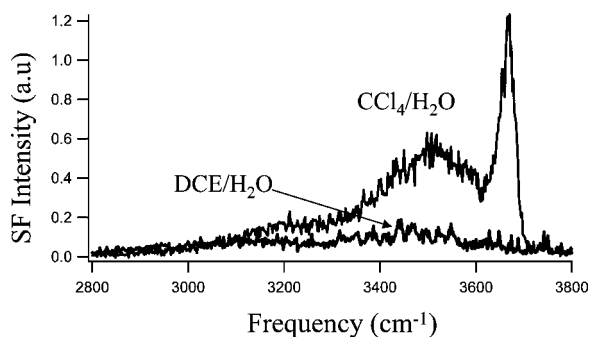


Figure 1. Vibrational sum-frequency spectra for the DCE/H₂O and CCl₄/H₂O interfaces. The large reduction in signal for the DCE/H₂O spectrum is indicative of a more isotropically mixed interface.

sum-frequency light generated is resonantly enhanced, resulting in the formation of a spectrum by molecules that are exclusive to the surface region. The polarization scheme used to generate the spectra described in this report is S,S,P, which probes vibrational modes with dipole components perpendicular to the interface. The laser system used in these experiments and the spectral routines used to analyze the VSF spectra have been described elsewhere.^{23,24}

The routine used to fit the experimental spectra in this work was first developed by Bain for use in sum-frequency spectroscopy,²⁹ and is described in more detail elsewhere.³⁰ For the spectra of CCl₄ and DCE mixtures, attempts to extract peaks that correspond to distinct H₂O–DCE interfacial interactions as have been done in our previous CCl₄/H₂O²³ and alkane/water²⁴ studies did not produce meaningful results, indicative of the complex bonding, spectral overlap, phase, and orientational changes occurring at the interface induced by the introduction of DCE. As an alternative we have fit the spectra of the mixtures to the primary peaks in the CCl₄/H₂O spectra (free OH, donor OH, and tetrahedral water) to obtain a general picture of water interacting with the combined organic mixture (DCE+CCl₄) as the interface is made increasingly polar.

Interfacial pressure measurements have been conducted with the Wilhelmy plate method in which a plate is immersed normal to the surface plane of a given interfacial system and the line tension across the plate is measured.^{31,32} The interfacial pressure was determined by subtracting the tension of the (DCE+CCl₄)/H₂O system from that of pure CCl₄/H₂O. The surface excess has been calculated from the measured interfacial pressure using the Gibbs equation.³³ The mean molecular surface area has been obtained from the surface excess using eq 1:

$$A_i = \frac{1}{\Gamma_i + X_i(\rho_i)^{2/3}} \quad (1)$$

where Γ_i is the surface excess, X_i is the mole fraction, and ρ_i is the bulk density of the species in excess.³⁴ The H₂O used in these experiments was obtained from a Millipore Nanopure system (17.8 M Ω ·cm), whereas the HPLC grade DCE and CCl₄ were purchased from Aldrich and twice distilled before use in our VSFS experiments.

Results and Discussion

Figure 1 shows VSF spectra of the CCl₄/H₂O and DCE/H₂O interfaces. Clear differences are apparent in the spectroscopy of interfacial water for these two systems. The CCl₄/H₂O spectrum shows broad intensity from 3000 cm⁻¹ through 3600 cm⁻¹, along with a sharp peak located at approximately 3670 cm⁻¹. Previous work has shown that the CCl₄/H₂O spectrum is

dominated by the response from water molecules that straddle the interface with one OH stretch mode protruding into the organic liquid phase (free OH, 3669 \pm 3 cm⁻¹) and the adjoining OH mode pointing into the water phase (donor OH, 3439 \pm 10 cm⁻¹). Smaller contributions arise from tetrahedrally coordinated water molecules (centered at 3247 \pm 15 cm⁻¹) and water monomers (3617 \pm 3 cm⁻¹, 3716 \pm 3 cm⁻¹) near the free OH mode.²³ Alkane/H₂O interfaces (C₆–C₈) also show the major features observed in the CCl₄/H₂O spectrum including the free OH mode which indicates weaker alkane–H₂O interactions relative to CCl₄–H₂O. Both previous VSF studies and MD simulations indicate that the CCl₄/H₂O and alkane/H₂O interfaces are relatively sharp on a molecular scale, with significant orienting of interfacial water molecules due to weak organic–water interactions.²⁴

In contrast, the DCE/H₂O intensity is dramatically lower than that of CCl₄/H₂O. The DCE/H₂O spectrum is broad and featureless with weak intensity spanning the range from 3000 cm⁻¹ to 3700 cm⁻¹. There is a slight increase in intensity in the region of 3400–3600 cm⁻¹. The straddling water molecules that give rise to the free and donor OH frequencies in other liquid/liquid systems are absent at this interface. No evidence of the strong orientation effects observed for the CCl₄/H₂O or alkane/H₂O systems are present at this interface.

FTIR studies performed on DCE/H₂O mixtures indicate that water obtains a number of different inhomogeneous environments when dilute quantities are mixed with DCE. Water monomers in DCE display vibrational frequencies at 3595 cm⁻¹ and 3678 cm⁻¹.³⁵ The uncoupled OH mode measured from HOD studies occurs at 3635 cm⁻¹. Water trimers are expected in the 3500–3600 cm⁻¹ region of the spectrum. The broad sum-frequency spectrum of the DCE/H₂O interface shown in Figure 1 is spectroscopically consistent with a combination of these different H₂O–DCE interactions, analogous to a randomly mixed interfacial region with minimal water orientation perpendicular to the interface. Also present is a small contribution from relatively strong hydrogen bonded water molecules at lower energies (3000–3300 cm⁻¹). Even though H₂O is far more soluble in DCE than it is in CCl₄,³⁶ irrefutable evidence of oriented water monomers within the interfacial region as found previously in the CCl₄/H₂O spectrum could not be identified.

These results clearly indicate that DCE/H₂O does not have the characteristics of the highly oriented and relatively sharp interfacial regions that have been observed for CCl₄/H₂O and alkane/H₂O systems.²⁴ The featureless spectrum of the DCE/H₂O interface indicates that interfacial water does not have a preferred orientation relative to the surface normal. This picture coincides with a rougher and broader interfacial region as suggested by MD simulations,²¹ yet on a molecular scale. To understand more fully these molecular interactions that cause a liquid/liquid system to go from a relatively sharp to a rough interface as the polarity of the organic liquid increases, we analyzed a series of CCl₄/H₂O interfaces where DCE was progressively added to the CCl₄ phase, as described below.

Measurements of interfacial pressure for the (DCE+CCl₄)/H₂O systems are shown in Figure 2a. The interfacial pressure progressively increases as X_{DCE} increases. The relatively large rate of increase at lower X_{DCE} values shows that DCE is surface-active and partitions favorably to the interface. Figure 2b shows the surface coverage of DCE (as a function of X_{DCE}), calculated from the surface excess as obtained from eq 1. The surface partitioning of DCE is far greater at lower concentrations and the surface excess does not become negligible until DCE is approximately 40% composition by volume ($X_{\text{DCE}} > 0.34$).

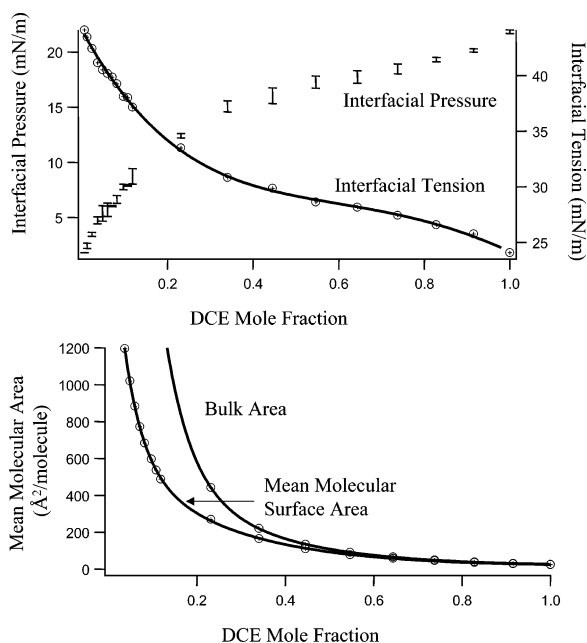


Figure 2. (a) Interfacial tension and pressure isotherms for (DCE+CCl₄)/H₂O interfaces as a function of DCE mole fraction, X_{DCE} . Error bars are indicated on the pressure isotherm. (b) Mean molecular surface area, calculated from surface excess, of (DCE+CCl₄)/H₂O as a function of X_{DCE} . Bulk area contribution is also shown for comparison.

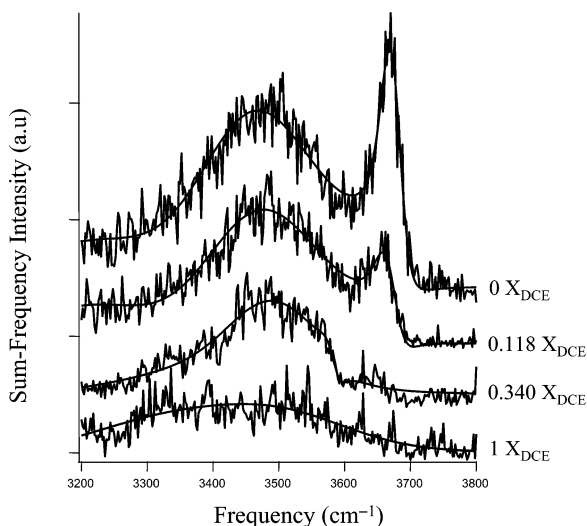


Figure 3. Sum-frequency spectra of water at (DCE+CCl₄)/H₂O interfaces. The top graph ($X_{\text{DCE}} = 0$) corresponds to the pure CCl₄/H₂O interface, and the bottom graph ($X_{\text{DCE}} = 1$) corresponds to the pure DCE/H₂O interface; the remaining graphs correspond to indicated compositions of DCE at the (DCE+CCl₄)/H₂O interface. Spectra are offset vertically for visual clarity.

Interfacial tension values for pure CCl₄/H₂O and DCE/H₂O are 45.9 mN/m and 23.1 mN/m, respectively, in good agreement with previous results.^{36,37} The mean molecular surface area of pure DCE is determined to be $24.7 \pm 0.2 \text{ \AA}^2$, in good agreement with the value of 26 \AA^2 calculated from the bulk density of pure DCE.

Figure 3 shows the sum-frequency spectra from pure CCl₄/H₂O to pure DCE/H₂O as the concentration of DCE in the organic liquid phase is increased. Consistent with Figure 1, the overall sum-frequency intensity of the spectra shown in Figure 3 decreases along the entire water region as X_{DCE} is increased. The spectral fitting routine used to extract trends in the data shows that the free OH region undergoes a red shift simultaneous with a blue shift observed in the donor OH region as the

organic phase becomes more polar. The free OH is largely uncoupled from the adjoining donor OH bond at low X_{DCE} , and consequently its spectral shift represents increased bonding interaction with neighboring solvent molecules in the organic phase as X_{DCE} is increased, along with progressive coupling to the donor OH mode. The free OH intensity decreases as the oriented water molecules that straddle the interface take a more random orientation while hydrogen bonding to other water molecules. At $X_{\text{DCE}} = 0.34$, the spectral shifts and reduced intensity of the free and donor OH modes result in a clearly visible destructive interference around 3600 cm^{-1} . All these changes are indicative of increased water interactions with DCE relative to CCl₄. The interface retains some degree of structure for lower values of X_{DCE} but loses all evidence of the free and donor OH modes near $X_{\text{DCE}} = 0.4$. This value coincides with the region where the surface excess of DCE becomes negligible and the DCE and CCl₄ interfacial concentrations become comparable (Figure 2b).

The sum-frequency spectra of the (DCE+CCl₄)/H₂O interfaces clearly show the progression from a sharp, well-structured interface (CCl₄/H₂O) with a significant fraction of oriented water molecules to a mixed interface with more randomly oriented water molecules relative to the surface normal (DCE/H₂O). H₂O–DCE interactions dominate the interface as evidenced by the lack of spectral features corresponding to H₂O–CCl₄ interactions when DCE and CCl₄ have comparable concentrations. The red shift in the free OH with increasing DCE concentration shows that H₂O–DCE interactions are stronger than H₂O–CCl₄ interactions. This stronger interaction, however, does not lead to more interfacial structuring; instead, spectral features more indicative of a range of DCE–H₂O interactions are observed.

The solubility of water in DCE due to the dipole moment of the gauche form plays a role in this interphase region. Since the trans DCE conformer contains no dipole moment, we expect that gauche DCE is the dominant species present at the water interface. This higher solubility clearly plays a role in the mixing of the interfacial region where water monomers and clusters are likely to exist in high quantities yet experience no significant orienting effects. MD simulations of the DCE/H₂O interface observe a widening of the interface compared to more structured systems and preliminary results of simulations performed in our laboratory suggest an interface that roughly doubles in thickness when CCl₄ is replaced with DCE.³⁸

Conclusions

Results from vibrational sum-frequency spectroscopy measurements show that compared to the CCl₄/H₂O and alkane/H₂O interfaces, the DCE/H₂O interface is relatively disordered on a molecular scale beyond the normal fluctuations that occur with thermal perturbations such as capillary waves. Although there is a measurable interfacial region as shown from interfacial tension measurements and these vibrational spectroscopic studies, the interface has spectral characteristics of a mixed phase interfacial region consisting of randomly oriented water molecules with a broad distribution of interactions with DCE and other water molecules.

The progression of VSF spectra for the (DCE+CCl₄)/H₂O systems clearly show that as X_{DCE} is increased, the interface loses its orientational characteristics, and in particular, the straddling water molecules that produce donor OH and free OH vibrations. For low X_{DCE} values the structure of the interface maintains enough stability for the observation of a red shift in free OH intensity and a blue shift in donor OH intensity.

Interfacial pressure results show that DCE is surface active when mixed with CCl_4 and used to generate an interface with water; this observation is indicative of stronger interactions that occur between DCE and H_2O than those between CCl_4 and H_2O . Instead of leading to increased water orientation at the interface, the high solubility of DCE in H_2O causes the interface to become more random and mixed, an effect observed progressively as the polarity of the organic phase is increased.

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