Sudden structural change at an air/binary liquid interface: Sum frequency study of the air/acetonitrile–water interface

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(Received 19 November 1992; accepted 15 January 1993)

We report the first observation of a sharp structural change in an air/acetonitrile–water interface as the solution composition varies; the abruptness of which suggests an interfacial phase transition. The structural change is manifested by shifts in the frequency and in the polarization of the signal from the acetonitrile molecules in the interface observed using infrared+visible surface sum frequency generation.

We report the first observation of a sudden structural change in an air/acetonitrile–water solution interface as the solution composition varies. This structural change is manifested by shifts in the frequency and in the polarization of the signal from the acetonitrile molecules in the interface. It is observed using the interface specific technique of infrared+visible surface sum frequency generation.[1,2] These shifts, which occur at an acetonitrile bulk mole fraction of 0.07, indicate an abrupt change in both the chemical environment and orientation of acetonitrile molecules in the interface. We attribute these abrupt changes to a phase transition in the interface. This is the first example to our knowledge of a phase transition in an interface composed of small mutually soluble molecules.

The acetonitrile–water binary mixture has been studied by many other techniques because it is a commonly used solvent.[3–5] Thermodynamic studies and diffusion measurements suggest that the bulk behavior of this mixture is far from that of a hypothetical "ideal" mixture.[3–10] Theoretical analyses of these data suggest that this binary mixture may exhibit microheterogeneity when there is a significant amount of acetonitrile in the solution at 298 K.[4,9] At temperatures below 272 K (upper critical temperature) and an acetonitrile mole fraction near 0.3 a phase separation of the binary solution into acetonitrile rich and water rich regions occurs.[8] Although there have been bulk x-ray and neutron diffraction studies of the neat liquids, there have not been any structural studies on the binary solution.[11] Studies of acetonitrile adsorbed onto the surface of zirconia were done using surface sum frequency generation.[12] There have been no structural studies of the air/acetonitrile–water solution interface. By applying surface sum frequency generation we have obtained information on the chemical environment and structure of this interface.

The mixtures of CH_3CN (Aldrich HPLC grade) and CD_3CN (Janssen Chimica 99 atom %) were made by mixing known volumes of the acetonitrile and double-distilled water at 24.5 °C±0.5 °C in a sealed container. The sum-frequency experiments were performed by focusing the visible (532 nm, ~150 μJ/pulse, ~20 ps duration) and infrared [~4.5 μm, 30–40 μJ/pulse, 15–18 ps duration, 7–10 cm^{-1} full width at half-maximum (FWHM)] radiations to a common spot on the surface in a counterpropagating geometry. A more detailed description of the experimental procedures will be published later.[13]

At bulk concentrations less than 0.07 mole fraction of acetonitrile in water we observe that the CN stretching vibrational frequency in the interface is at a higher frequency than that of neat bulk acetonitrile [Fig. 1(a)]. This shift is characteristic of nitriles hydrogen bonded to proton donors such as water in bulk solution.[14,15] At bulk concentrations greater than 0.07 mole fraction of acetonitrile in water the vibrational frequency for molecules at the surface red shifts to a value that is near to that in neat bulk acetonitrile [Fig. 1(a)]. This dependence of vibrational frequency on composition indicates that the acetonitrile molecules at the surface experience two different environments, one below 0.07 and one above 0.07 mole fraction. We suggest that at the higher bulk concentrations acetonitrile in the interface is no longer hydrogen bonded to water.

We also studied *per*-deuteroacetonitrile which allowed us to investigate the spectroscopy and polarization of both parts of the molecule, the CN and CD_3 chromophores, with a single laser dye. The behavior of the CN vibrational frequency of *per*-deuteroacetonitrile is similar to that of the acetonitrile. It also shows a shift of the CN vibrational frequency in the interface at a bulk concentration of 0.07 mole fraction of CD_3CN in water. However, at the spectral resolution of our experiment (7–10 cm^{-1} FWHM) the methyl group does not exhibit any frequency change as a function of acetonitrile concentration [Fig. 1(b)]. A possible explanation for this insensitivity of the methyl vibrational frequency to the change in the tilt angle and chemical environment at the phase transition is the methyl group's preferred orientation toward the vapor phase and away from the bulk solution.

The polarization of the sum frequency signal at a vibrational resonance reflects the orientation of the transition dipole in the interface. We find that the CN sum frequency

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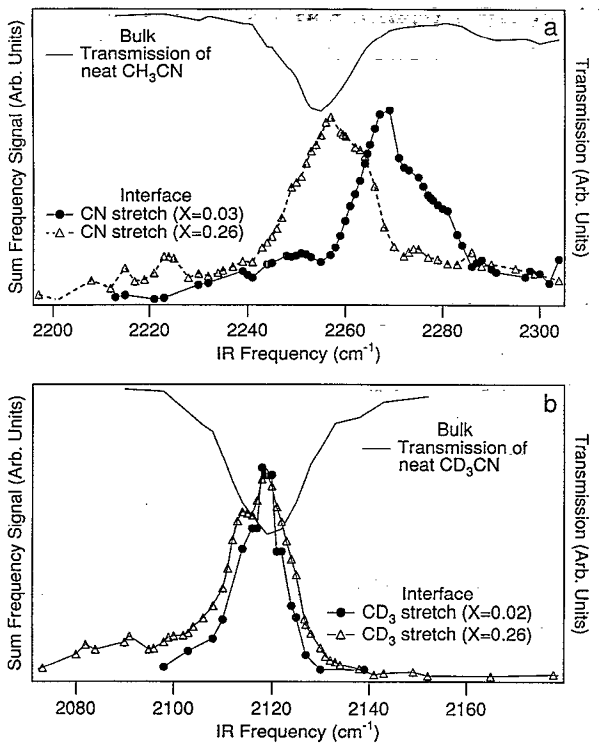

FIG. 1. (a) The upper trace is a transmission spectrum of a neat bulk CH_3CN sample. The two bottom traces are sum frequency spectra of the CN vibration in the air/solution interface at bulk mole fractions of $X=0.03$ and 0.26. (b) The upper trace is a transmission spectrum of a neat CD_3CN sample. The two bottom traces are sum frequency spectra of the CD_3 symmetric stretch in the air/solution interface at bulk mole fractions of $X=0.02$ and 0.26. The apparent difference in bandwidth is caused by variation in the laser bandwidth and the noise level.

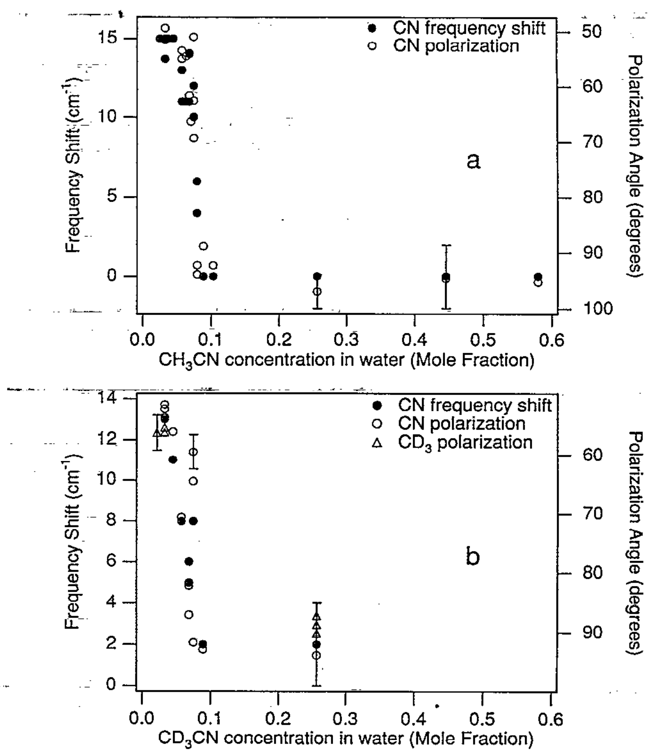

FIG. 2. (a) Compilation of frequency shifts of the resonance peak with respect to neat bulk acetonitrile absorption and polarization data for the CN transition of acetonitrile in the interface vs mole fraction of acetonitrile in the bulk water solution. (b) Same as (a) but for *per*-deuteroacetonitrile.

polarizations shift abruptly at a bulk acetonitrile concentration of 0.07 mole fraction [Fig. 2(a)]. This is the same concentration at which the CN vibrational frequency undergoes an abrupt shift. Using a phenomenological model[16,17] we can estimate that, at a concentration below 0.07 mole fraction, the molecular symmetry axis is tilted on average about 40° from the normal. Above this concentration the molecular tilt is in the range of 70°, indicating that the molecules lie flatter on the surface at the higher concentrations.

Figure 2(a) shows a compilation of frequency and polarization experiments for the CN stretching vibration of CH_3CN on water vs the bulk concentration. Figure 2(b) displays similar data for both the CD_3 and CN vibrations for CD_3CN, which show that there are no discernible effects of deuteration on the observed structural change. The abrupt shift in both the frequency of the CN vibration and the polarizations of the CN and CD_3 signals at a bulk mole fraction of 0.07 is clearly seen in Fig. 2. We interpret the sudden change in the CN frequency as a transition from a structure in which acetonitrile is hydrogen bonded to water to one where such hydrogen bonds are broken. The change in polarization indicates a sharp reorientation of the molecules in the interface at an acetonitrile concentration of 0.07 mole fraction in the bulk solution.

In addition to the sum frequency measurements, we have measured the surface tension of the acetonitrile–water mixtures, which we find to be consistent with those in the literature.[18,19] Although we observe no discontinuities in the surface tension or its slope with solution composition, we do find that the maximum in the Gibbs excess occurs in the vicinity of the bulk concentration at which we observe the sudden spectral and structural changes. The monolayer is likely to be formed near this maximum, though we cannot state this definitively since a model of the interface is necessary to obtain the interface population from the measured Gibbs excess.

The abruptness of the changes, that we observe in orientation and vibrational frequency as the concentration of acetonitrile in the interface is varied, leads us to attribute these findings to a phase transition rather than a continuous change in structure and intermolecular interactions. The CN vibrational frequency in the interface changed abruptly from one characteristic of a CN hydrogen bonded to water to a frequency close to that of neat acetonitrile. The orientation of acetonitrile in the surface also changes abruptly at the same solution composition. It changed from a more upright orientation below 0.07 mole fraction to a flatter orientation above this bulk concentration. Surface potential measurements indicate that acetonitrile lies nearly flat at the neat acetonitrile/air interface,[20] which is consistent with our sum frequency results. These observations indicate that above a bulk acetonitrile mole fraction of 0.07 the acetonitrile molecules in the interface have spectral and structural properties approaching that of the neat acetonitrile/air interface. We infer from these results that close to the acetonitrile concentration necessary to form a monolayer the change in the balance of forces triggers a sharp reorientation of the acetonitrile molecules and effects a change in their local environment. Whether this phase transition involves a phase separation into an acetonitrile rich region and a water rich region at the interface, analogous to what occurs in bulk acetonitrile–water mixtures at a lower temperature (272 K) and at a higher bulk acetonitrile mole fraction, is not known at this time. Although the sum frequency results on the high concentration side of the transition indicate that the acetonitrile vibrational spectrum and orientation approaches that of neat acetonitrile, we cannot conclude that a phase separation yielding an acetonitrile rich region has taken place at the interface. We find this possibility nonetheless to be quite interesting since there is no evidence of a phase separation in the bulk region; we are carrying out further studies to test this possibility. To our knowledge these findings provide the first evidence of a phase transition in an interface consisting of small miscible molecules.

The authors wish to thank the Division of Chemical Science of the Department of Energy for their support and the National Science Foundation and the Air Force Office of Scientific Research for their equipment support.

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