

Structural phase transitions of small molecules at air/water interfaces

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Structural phase transitions have been observed using IR-VIS sum frequency generation (SFG) at the air/acetonitrile-water and the air/propionitrile-water interfaces but not at the air/butyronitrile-water interface. The phase transitions were detected by abrupt changes in the CN vibrational frequency and in the orientation of the CN chromophore as the interface nitrile density was varied. A model based on the orientational effects of hydrogen bonding and solvation of the CN group by water molecules competing with the density and orientationally dependent dipole-dipole repulsions among the CN chromophores is used to explain the results.

The geometrical arrangement and packing of the molecules that comprise a liquid interface are an expression of the intermolecular interactions of the interfacial molecules with each other and with the molecules of the two bulk phases that define the interface. The unique chemical and physical properties associated with liquid interfaces, whether they are composed of one chemical species (neat liquid interface) or a multicomponent solution interface, are directly related to the orientational structure, molecular density, and the chemical composition of the interface. The second-order non-linear spectroscopies of second harmonic and sum frequency generation are well suited to the study of orientational structure and interactions at interfaces because they are sensitive to molecules in the interface and not to the overwhelmingly larger population of molecules in the centrosymmetric bulk phases.¹

In a previous study² of interfacial orientational structure and hydrogen-bonding interactions we reported evidence of an unexpected phase transition at the air/acetonitrile(ACN)-water solution interface. Using IR-VIS SFG we observed an abrupt rearrangement of acetonitrile molecules, indicating a phase transition at the interface, as the solution composition was varied. This change was manifested by abrupt shifts in the CN vibrational frequency and orientation of acetonitrile molecules at the interface when the bulk acetonitrile concentration reached the 0.07 mole fraction. To develop a broader picture of the intermolecular interactions that resulted in the phase transition at the air/ACN-water interface, we have extended these studies to include air/propionitrile(PCN)-water and air/butyronitrile(BCN)-water interfaces. Together with ACN, they provide a convenient series to study the effect of the alkyl chain on the surface interactions which, for the acetonitrile case, appear to be dominated by the hydrogen bonding of the CN with water and by the dipole-dipole interactions among the CN chromophores. In addition, these nitrile-water binary mixtures exhibit distinct bulk behaviour; ACN is totally miscible in water, while PCN and BCN are only partially soluble in water with the maximum mole fraction solubilities of $X_{\text{PCN}} = 0.032$ for PCN and $X_{\text{BCN}} = 0.0085$ for BCN.

Our data indicate that the addition of one or two methylene groups markedly affects the molecular packing and intermolecular interactions at the interface, leading to dramatic changes in the interfacial behaviour. In the case of BCN, no phase transition was observed at the air/BCN-water interface as the bulk concentration was varied, which is in striking contrast to what we have observed for ACN. However, with PCN a phase transition was observed and was detected by changes in the CN frequency and the CN molecular orientation as the bulk concentration was varied. The chain-length dependence

of the interfacial behaviour is attributed to a lower interfacial packing density for molecules as the chain length increases. When a sufficiently close packing of molecules at the interface is not achieved, as in the case of BCN, water molecules remain in the interfacial layer, where they are hydrogen bonded to the nitrile groups and screen the nitrile-nitrile dipole repulsive interactions. Thus the change in the balance of the density-dependent attractive and repulsive intermolecular interactions, which are necessary to effect the interfacial structural phase transition, is not accomplished. We will present a model for these changes in a later section of this paper.

Experimental

Our SFG experiments have been detailed elsewhere.³ Briefly they were performed by overlapping a visible laser beam at 532 nm and an IR beam tunable around 4.5 μm on a common spot on the surface of interest. The two beams were in a counter-propagating geometry and incident at an angle of 70° from the surface normal. Both incoming beams were polarized at 45° to the surface normal and parallel to each other. The SF signal was then collected in the range 470–480 nm at an angle of *ca.* 50° from the normal to the surface as determined by the wavevector matching conditions at the interface.⁴ The SF spectra were obtained by scanning the IR light in 2 cm^{-1} increments where each point is the average signal from 3000 laser shots. The frequency of the IR beam was calibrated to $\pm 2 \text{ cm}^{-1}$ by using appropriate nitrile absorption spectra taken simultaneously with the SFG measurements. As the intensity of the light excitation was varied, we did not see any changes in the measured tilt angles or frequencies. The work reported in this paper was done at a low enough power and repetition rate (10 Hz) that there was no evidence of heating.

The samples of ACN (Aldrich, HPLC), or other aliphatic nitriles, with water were prepared volumetrically by dissolving the nitriles in double-distilled water at $24.5 \pm 0.5^\circ\text{C}$. Evaporation of the bulk solution was prevented by placing the sample container in a sealed glass and Teflon housing during the experiment.

Results and Discussion

Orientation and hydrogen bonding of ACN at the interface

Measurements of the CN SF spectra of ACN at the air/ACN-water interface as a function of the ACN bulk concentration are shown in Fig. 1. At low ACN interface densities (bulk mole fraction $X_{\text{ACN}} < 0.07$), the orientations of both the methyl and cyano chromophores were obtained independently and found to be tilted by 40° from the surface normal. The

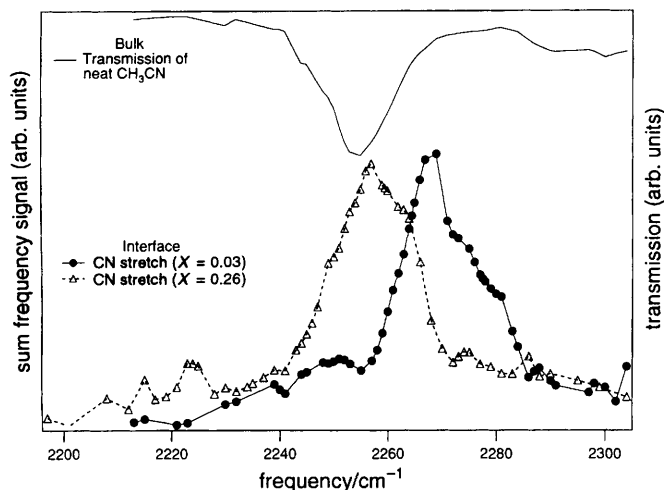


Fig. 1 Upper trace is a transmission spectrum of a neat bulk ACN sample obtained using the same IR laser pulses that were used in the SF experiments. The two bottom traces are SF spectra of the CN vibration in the air/solution interface at bulk mole fractions of $X = 0.03$ and 0.26 .

molecular orientational angles were obtained from measurements of the polarization of the SF light in combination with a phenomenological model.^{3,5,6} The CN-stretching vibrational frequency at the interface was shifted to higher frequency by *ca.* 14 cm^{-1} relative to that of the CN stretch in neat bulk ACN. This blue shift at the interface was not surprising based on earlier bulk solution work,⁷⁻⁹ which demonstrated that a cyano group hydrogen bonded and solvated in bulk protic liquids, such as water, undergoes a blue shift in its vibrational frequency. On increasing the bulk concentration of ACN to values greater than $X_{\text{ACN}} = 0.07$, a red shift was observed in the interface CN stretch frequency to a value that is within 1 cm^{-1} of the CN frequency in bulk ACN. This result indicates that the cyano chromophores in the interface are no longer hydrogen bonded and solvated by water molecules when the bulk ACN concentration exceeds 0.07 mole fraction. At all concentrations from 0.07 mole fraction extending to the largest concentration measured, $X_{\text{ACN}} = 0.6$, the CN vibrational frequency remained the same. Similarly at all mole fractions of ACN below 0.07 the CN frequency was the same, *i.e.* blue shifted by 14 cm^{-1} with respect to the CN frequency in bulk ACN. The abrupt change in the chemical environment of ACN at 0.07 mole fraction, as revealed by the CN spectral shift, was also seen in the sudden change in the orientation of ACN at the interface, Fig. 2. Below 0.07 mole fraction the ACN is tilted by 40° with respect to the interface normal, whereas at all concentrations above 0.07 mole fraction the ACN molecules assume a flatter orientation of 70° with respect to the interface normal.

Model of structural phase transition at air/ACN-water interface

These abrupt changes in molecular orientation and CN vibrational frequency with concentration indicate that a structural phase transition has taken place at the air/ACN-water interface. In contrast to these changes at the interface there were no abrupt changes observed in the vibrational frequencies of ACN in the bulk solution as the ACN concentration was varied. Combining the spectroscopic and orientational results from the SF experiments we offer the following model of the change in the interactions of the ACN molecules at the air/solution interface as the bulk ACN concentration is varied. At low bulk concentrations, and thus at low surface densities, the ACN has its methyl group projecting into the vapour phase while the CN moiety projects into the solution and is hydro-

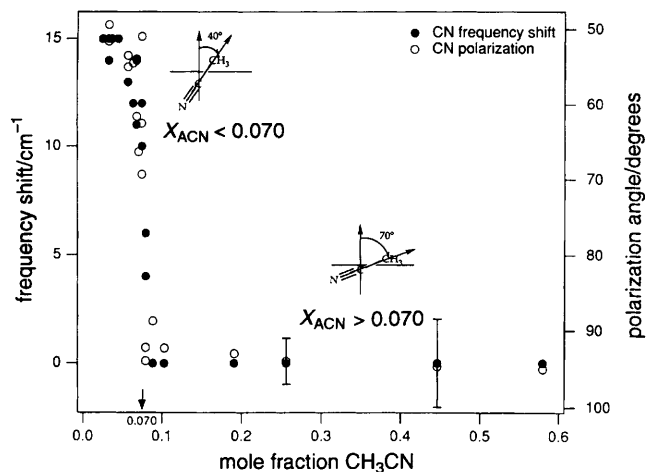


Fig. 2 Compilation of CN frequency shifts of the surface ACN with respect to the neat bulk ACN absorption, and also the measured SF polarization for the CN transition of ACN in the interface *vs.* mole fraction of ACN in the bulk water solution. Calculations using the polarization data yield a molecular orientation with respect to the surface normal of 70° at high mole fraction and 40° at low mole fraction.

gen bonded to and solvated by neighbouring water molecules. The ACN has a tilt angle of 40° from the interface normal at these low surface densities. As the ACN bulk, and thus surface density, increases the ACN molecules displace water molecules from the surface but remain separated from other ACN molecules to minimize dipole-dipole repulsions, $\mu_{\text{CN}} \approx 3.5\text{ D}$,¹⁰ and to maximize their CN hydrogen bonding and solvation interactions with water. Eventually the increased density of ACN molecules in the interface squeezes out the water molecules that were separating them. The decrease in the intermolecular distance between ACN molecules, together with the decrease in screening by water owing to their removal, greatly increases the dipole-dipole repulsions of the ACN molecules. This increase in dipole forces overwhelms the ACN-water interactions that kept the hydrogen-bonded nitriles, at lower densities, tilted at 40° to the interface normal. To reduce these dipole repulsions, which raise the energy of the interface, the ACN molecules rotate to a more horizontal orientation approaching the energetically more favourable head to tail dipole configuration. It is this reorientation, which weakens and eventually ruptures the nitrile-water hydrogen bond, that triggers the structural phase transition; thus the CN vibrational frequency abruptly shifts back to that of the non-hydrogen-bonded neat bulk ACN.

Other nitriles at the air/nitrile-water interface

In order to obtain a more complete picture of the interactions of nitrile molecules and the structural changes that occur at the air/water surface, we have also studied the air/PCN-water interface and the air/BCN-water interface. By increasing the size of the alkyl part of the molecule we can investigate the impact of the hydrophobic part of the molecule on the behaviour of the adsorbate at the air/water interface. For ACN it appears that it is the interactions of the polar nitrile groups with each other and with water, rather than the methyl groups, that determine the interfacial structural changes that we have observed. By studying other nitriles we can more fully determine how the alkyl chain affects the interface properties.

Fig. 3 shows the SF spectra of PCN at two bulk concentrations, $X_{\text{PCN}} = 0.007$ and 0.023 . As with ACN, we find that at low bulk concentration ($X_{\text{PCN}} = 0.007$), the surface CN stretching vibration is shifted by *ca.* 13 cm^{-1} to a higher frequency than that of neat bulk PCN. Again, we attribute this frequency shift to the PCN being hydrogen bonded to water molecules at the interface. On increasing the bulk PCN con-

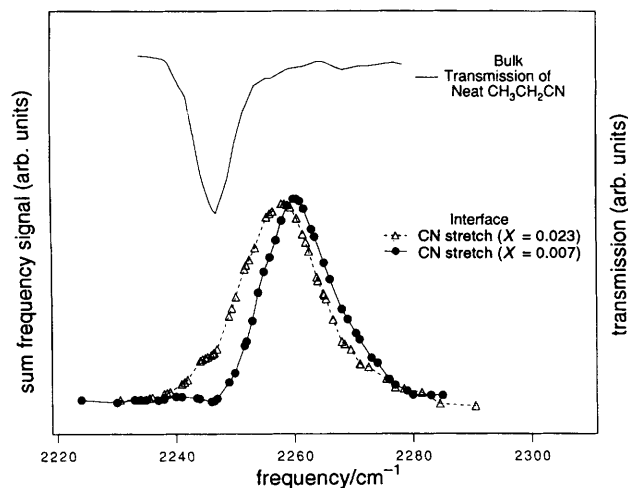


Fig. 3 Upper trace is a transmission spectrum of a neat bulk PCN sample obtained using the same IR laser pulses that were used in the SF experiments. The two bottom traces are SF spectra of the CN vibration in the air/solution interface at bulk mole fractions of $X_{\text{PCN}} = 0.007$ and 0.023 .

centration to $X_{\text{PCN}} = 0.011$, we observed that the CN vibrational frequency red shifted by $ca. 3 \text{ cm}^{-1}$, thus remaining blue shifted by 10 cm^{-1} relative to that of neat bulk PCN, Fig. 4. This result indicates that the surface PCN still exists in a chiefly hydrogen-bonded and water-solvated environment even at the higher PCN bulk concentrations, although the hydrogen bonds may be weaker and the solvation less than at lower surface densities. Notice that the blue shift of the CN frequency as compared to the neat bulk CN frequency persists from $X_{\text{PCN}} = 0.011$, where the phase transition occurs, to the saturation bulk concentration of PCN of $X_{\text{PCN}} = 0.032$, indicating that PCN remains hydrogen bonded to water at these higher bulk densities, Fig. 4. From the surface tension measurements we estimate that the maximum surface density of 26 \AA^2 as well as the maximum in the Gibbs excess, are reached close to $X_{\text{PCN}} = 0.011$. The surface density of 26 \AA^2 is found to remain constant up to the maximum bulk concentration. We have also investigated the CN orientation by measuring the polarization of the SF signal from PCN at the air/water interface. Fig. 4 shows the SF polarization *vs.* PCN bulk composition. As with ACN we calculate the orientation of PCN using a phenomenological model that relates the polarization of the

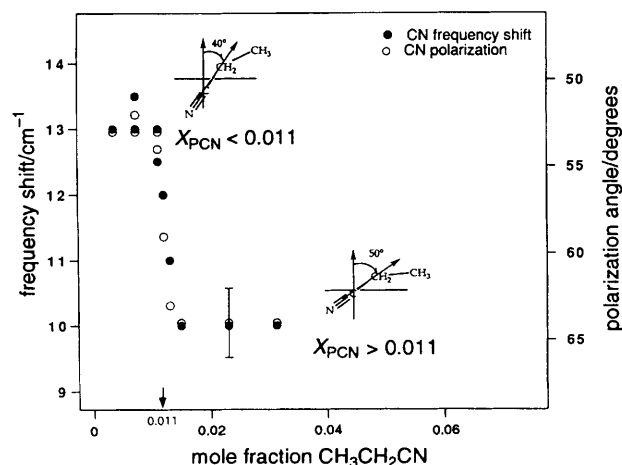


Fig. 4 Compilation of CN frequency shifts of surface PCN with respect to the neat bulk PCN and also the measured SF polarization of the CN transition of PCN at the interface *vs.* mole fraction of PCN in the bulk water solution. Calculations using the polarization data yield a molecular orientation with respect to the surface normal of 50° at high mole fraction and 40° at low mole fraction.

SF light to the molecular orientation.^{3,5,6} At low surface density the nitrile head group is tilted to an angle of 40° from the surface normal, which is the same as we found for ACN at low surface densities. At its highest surface density the PCN tilts to a more horizontal orientation of 50° , which is similar to the behaviour of ACN in also changing to a more horizontal orientation (70°) at its higher surface densities. We thus see that PCN, as we found for ACN, undergoes an abrupt structural change as its interface density is varied. The change in structural properties on either side of the phase transition, as manifested by the CN spectral shift of 3 cm^{-1} and the tilt angle shift of 10° , is not as large as that for the ACN transition. We do find, just like ACN, that the position of the shifts occurs near the maximum Gibbs excess obtained from surface tension measurements, which is close to the maximum in the nitrile surface density.

Unlike ACN and PCN we find no evidence for a phase transition at the air/BCN-water interface. The SF spectra of interfacial BCN at two bulk concentrations, $X_{\text{BCN}} = 0.0027$ and 0.0074 , are shown in Fig. 5. We see that the nitrile vibration of BCN at the water surface is shifted to higher frequency by $ca. 13 \text{ cm}^{-1}$ at both low and high concentrations. The shifts are within 1 cm^{-1} of each other at these concentrations, indicating that surface BCN is similarly hydrogen bonded to and solvated by water at both bulk concentrations. This shift persists all the way to the saturation concentration of $X_{\text{BCN}} = 0.0085$; thus the chemical environment around the nitrile group of BCN remains essentially the same even when the bulk concentration reaches saturation. We have also found that the maximum changes in molecular angle are small, going from 40° to 43° as the bulk BCN concentration is varied. This behaviour of BCN at the air/water interface is clearly very different from that of ACN and PCN. Comparing the data obtained for ACN, PCN and BCN, we see that increasing the size of the hydrocarbon group markedly affects the behaviour at the interface. We believe that the lower bulk solubility and the larger molecular area of the longer chain nitriles limits the maximum nitrile interface density. This lower interface density reduces the nitrile-nitrile interactions which are the determining interactions in effecting structural changes at the interface.

In the light of these findings for the various nitriles we must consider how the structure of the individual molecules governs the macroscopic collective properties of the monolayer. We need to describe the interfacial behaviour observed in terms of molecular packing and intermolecular interactions at the

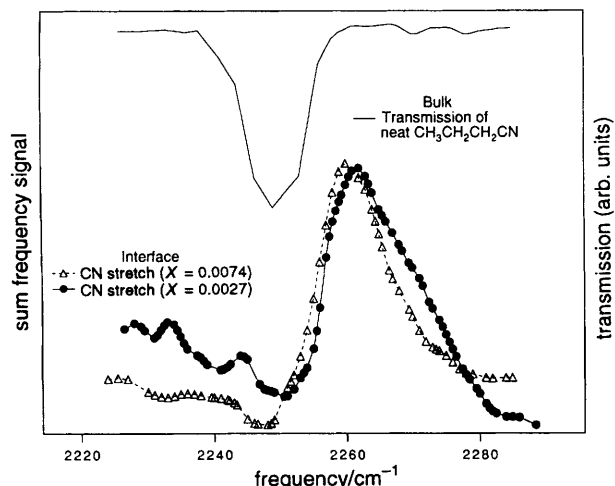


Fig. 5 Upper trace is a transmission spectrum of a neat bulk BCN sample obtained using the same IR laser pulses that were used in the SF experiments. The two bottom traces are SF spectra of the CN vibration in the air/solution interface at bulk mole fractions of $X_{\text{BCN}} = 0.0027$ and 0.0074 .

interface. From the measured surface tension as a function of the bulk solution concentration, it is possible to estimate the interfacial density of the nitriles.^{11,12} For PCN and BCN estimation of the surface density from the mentioned Gibbs excess is straightforward.^{11,12} However, for ACN the higher solubility introduces somewhat greater uncertainty in the estimation of the surface density. Fortunately the variation in the estimate of the ACN surface density is less than 10% and therefore does not alter any of the conclusions made in this paper. We found that the surface concentrations are 4.2, 3.9 and 3.1×10^{14} molecules cm^{-2} for ACN, PCN and BCN, respectively, at the air/water interface. These data are consistent with literature values.^{13–15} The surface areas for ACN and PCN are thus 24 and 26 \AA^2 per molecule at their phase transitions. For BCN the minimum surface area per molecule is 32 \AA^2 . This trend suggests that, as the size of the hydrocarbon part of the molecule increases, the molecules are further apart at their respective maximum densities. Note that the lower bulk solubilities of PCN, and especially BCN, compared with ACN, limit the maximum density of the nitrile at the air/nitrile–water interface. For ACN, which is completely miscible with water, the maximum density is determined by the maximum number of ACN molecules that can be packed into the interface, rather than being limited by the number of ACN molecules available to enter the interface. Attempts to increase the surface density of BCN by spreading with a volatile solvent did not succeed because the BCN coalesced into droplets on the water surface. In addition, for BCN, the alkyl part of the molecule can have both *trans*- and *gauche*-conformations, making it more difficult to pack the molecules closely at the interface.

In order to explain the different interfacial behaviour for ACN, PCN and BCN, we draw on the results of our study of a Langmuir monolayer of the insoluble nitrile, $\text{CD}_3(\text{CH}_2)_{19}\text{CN}$, at the air/water interface.³ Such insoluble monolayers at the air/water interface are known to exist in different states or phases, characterized by their surface densities and orientational structure. The different phases are commonly referred to as gaseous and various liquid and solid phases.¹⁶ Transitions between these different density phases can be effected either by compression of the insoluble long-chain molecules in a Langmuir trough, which decreases the area occupied by a fixed number of these molecules, or by the addition of molecules to an interface of fixed area. For the long chain nitrile $\text{CD}_3(\text{CH}_2)_{19}\text{CN}$ we were able to determine, using either surface tension methods or SF measurements, that the phase transition from the gas–liquid coexistence region into the liquid-phase region occurs at a density of 27 \AA^2 molecule⁻¹. At this density, and at densities throughout the gas–liquid coexistence region, the SF signal from the nitrile head group shows that the CN frequency is blue shifted by 11 cm^{-1} with respect to the CN frequency of the bulk solid $\text{CD}_3(\text{CH}_2)_{19}\text{CN}$ and the CN chromophore has an orientation of 53° with respect to the surface normal. The blue shift at the air/aqueous interface indicates that the CN head group is hydrogen bonded to neighbouring water molecules. On increasing the surface density to 27 \AA^2 molecule⁻¹, where the transition to the liquid phase occurs, the CN red shifts to its bulk nitrile value, indicating that the nitrile head group is no longer hydrogen bonded and the CN orientation changes to 70°. From these observations on $\text{CD}_3(\text{CH}_2)_{19}\text{CN}$ we conclude that this surface area of 27 \AA^2 molecule⁻¹ represents the minimum area required to accommodate a polar nitrile group solvated and hydrogen bonded by water molecules. Comparing the surface areas of ACN, PCN and BCN of 24, 26 and 32 \AA^2 molecule⁻¹, respectively, with the area of 27 \AA^2 molecule⁻¹, determined from the study of the long-chain nitrile $\text{CD}_3(\text{CH}_2)_{19}\text{CN}$ to be the minimum area required for the nitrile group to be hydrogen bonded, we see the origin of the different interfacial behaviour of ACN, PCN and BCN.

The area of ACN achieved at the air/ACN–water interface is 24 \AA^2 molecule⁻¹, which is less than the area of 27 \AA^2 molecule⁻¹ required by the nitrile group to remain solvated and hydrogen bonded for the long-chain nitrile and by inference roughly the minimum area required by the smaller-chain nitriles. This means that sufficiently high densities can be achieved for ACN, *i.e.* less than 27 \AA^2 molecule⁻¹, and therefore the dipole–dipole repulsions between nitrile groups on neighbouring acetonitrile molecules become large enough to drive the reorientation of the CN dipoles from 40° to the lower energy 70° orientation. The reorientation of the ACN molecules to an orientation closer to the surface plane raises the energy of the ACN–water hydrogen bonds. This leads to the breaking of the hydrogen bonds between ACN and water, squeezing out the neighbouring water molecules, and consequently producing the observed CN red shift to a value characteristic of a non-hydrogen-bonded nitrile. The density at which ACN undergoes a phase transition is in the range 23–25 \AA^2 . As for PCN, the minimum surface area of 26 \AA^2 molecule⁻¹ at the phase transition is very close to the area of 27 \AA^2 molecule⁻¹ required by the nitrile group to remain solvated and hydrogen bonded. In our SF experiments, the abrupt three wavenumber red shift in the CN vibrational frequency and the abrupt 10° change in the orientation of the CN group, at a bulk PCN concentration of $X_{\text{PCN}} = 0.011$, indicate a structural phase transition at the interface. However, unlike ACN, it is seen that the reorientation of the PCN, which reduces the dipole–dipole repulsion, was not sufficient to break the hydrogen bonds with water molecules, though it probably leads to squeezing out some water molecules separating the PCN molecules. We, therefore, observe that on the high-density side of the phase transition the CN surface vibrational frequency of the PCN is still blue shifted by *ca.* 10 cm^{-1} , which indicates that considerable hydrogen bonding and solvation persists at the lower-energy CN orientation of 50°. For ACN the closer packing and the reorientation to 70° ruptures the hydrogen bonding and restricts the solvation of CN by neighbouring water molecules. With BCN the much lower bulk solubility in water and the longer hydrocarbon chain limits the density of BCN molecules at the air/water interface to a value of 32 \AA^2 molecule⁻¹. At this maximum BCN density the repulsive dipole–dipole interactions among the nitrile groups do not reach a value sufficient to cause the reorientation of the CN dipoles. The energy-lowering contributions of solvation by and hydrogen bonding to neighbouring water molecules when BCN remains in the more upright orientation of 40°–43° dominates the interface structure of BCN. Thus we observe that the CN moieties do not undergo a sharp reorientation or hydrogen-bond rupture at the maximum BCN densities attainable at the air/BCN–water interface. There is thus no phase transition observed in the BCN structure at the air/BCN–water interface.

Conclusions

The orientational structure and hydrogen-bonding interactions at air/aqueous nitrile interfaces have been investigated using IR–VIS SFG spectroscopy. The unexpected structural phase transition, first observed for ACN at the air/ACN–water interface, was observed for PCN at the air/PCN–water interface, but not for BCN at the air/BCN–water interface. These are the first examples, to our knowledge, of phase transitions in interfaces composed of small mutually soluble molecules. For ACN and PCN the phase transition is manifested by an abrupt change in the vibrational frequency of the CN chromophore and an abrupt change in its orientation as the bulk nitrile concentration, and hence nitrile surface density, is varied.

The interfacial structural phase transition is described in terms of the competing hydrogen bonding and solvation interactions of the CN head group with neighbouring water molecules with the dipole–dipole repulsive interactions among the CN head groups. At low surface densities the CN chromophores are surrounded by water molecules, are hydrogen bonded, and are tilted by 40° to the interface normal. As the nitrile surface density increases, water molecules are squeezed out of the interface, the distances separating the aligned CN dipoles decrease, and the water screening of the nitriles is diminished. The result is to greatly increase the CN–CN dipole repulsions. At the phase transition density the large repulsive dipole–dipole interactions are relieved by the nitrile molecules reorienting towards the flatter and energetically more favourable head to tail dipole configuration. The trigger for the structural phase transition is this reorientation, which weakens or ruptures the hydrogen bonding to, and solvation by, neighbouring water molecules resulting in the observed spectral red shifts in the CN vibrational frequency.

The different interfacial behaviour for the three nitrile interfaces is attributed to the limited interfacial packing density that can be achieved for the longer-chain-length molecules. The large decrease in the bulk solubility as the chain length increases limits the maximum interface density. When the maximum density is not sufficient to yield a close packing of nitriles, as for BCN, then the repulsive dipole–dipole interactions among the CN moieties do not reach a value large enough to overcome the hydrogen bonding and solvation interactions of the CN group with neighbouring water molecules. Thus the change in the balance of intermolecular interactions as the nitrile separations decrease is not sufficient to effect a structural phase transition.

From SF studies in our laboratory of insoluble long-chain alkyl nitriles at the air/aqueous interface we estimate that the minimum area required by the nitrile head group to remain hydrogen bonded to and solvated by neighbouring water molecules is 27 Å² molecule⁻¹ or equivalently a saturation density of 3.7 × 10¹⁴ molecules cm⁻². At densities above this value we found that the CN head group of the insoluble long-chain nitrile CD₃(CH₂)₁₉CN is no longer hydrogen bonded or fully solvated and its orientation shifts from 53° to 70° with respect to the surface normal. It is at this density that the long-chain nitrile undergoes a structural phase transition from the gas–liquid coexistence region to the liquid phase region as seen by surface tension and SF studies in our laboratory.

Based on these results for the insoluble long-chain nitrile we assume that densities greater than 27 Å² molecule⁻¹ are required to raise the nitrile dipole–dipole repulsions to a value sufficient to trigger a reorientation of the CN groups and thereby a structural phase transition. We use this result to determine which nitriles (ACN, PCN, BCN) satisfy this density criterion and therefore would be expected to undergo a phase transition. From surface tension measurements it is

found that both ACN and PCN can achieve surface densities that are sufficiently high to trigger a phase transition. On the other hand, for BCN the lower bulk solubility limits the maximum BCN interface density to a value that is too small for the CN dipole–dipole repulsions to trigger a structural phase transition.

The SFG results are thus consistent with a model for structural phase transitions in alkyl nitriles at the air/nitrile–water interface, which is based on the balance of the energy lowering hydrogen bonding and solvation of the CN chromophores by water, and the energy-raising dipole–dipole repulsions of the aligned nitrile head groups. The repulsions gain in importance as the nitrile surface density increases and the nitrile–nitrile intermolecular separation decreases, finally inducing a phase transition at densities greater than 27 Å² molecule⁻¹, i.e. 3.7 × 10¹⁴ molecules cm⁻², depending on the nitrile.

The authors thank the Division of Chemical Science of the Department of Energy for their support and the National Science Foundation for their equipment support.

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Paper 5/05242D; Received 4th August, 1995