An Infrared Spectroscopic Study of the Preferential Solvation in Water–Acetonitrile Mixtures

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Abstract: Mixtures of water and acetonitrile in the full concentration range have been studied by infrared spectroscopy. OD and CN stretching vibrations of HDO and CD_3CN molecules have been used as probes of the structural environments. Acetonitrile molecules which are unaffected by water molecules are found for a broad concentration range ($0.1 \leq x_{H_2O} \leq 0.8$), showing that a preferential solvation occurs. The strong tendency for self-association of water molecules is evident from the occurrence of a broad OD stretching band. Chains of water molecules linked by hydrogen bonds are suggested to be formed rather than spherical clusters.

Introduction

The structure and other properties of mixed solvents in which water is one of the components have for a long time been a subject of considerable interest. Many observations indicate that several organic solvents such as alcohols, amines, and acetone, when dissolved in water in low concentration, enhance the water structure, i.e. modify it in the direction of greater "crystallinity".

In 1945 Frank and Evans[1] put forward a hypothesis which explained this effect as a result of accumulation of water molecules around the hydrophobic part of the nonelectrolyte molecule. Interactions in such a "microscopic iceberg" are much stronger than in pure liquid water and are more similar to interactions in ice.

Another interesting conception concerning the structure of aquoorganic mixtures was proposed by Naberukhin and Rogov.[2] They postulated that in solutions in which the mole fraction of nonelectrolyte is higher than 0.2, molecules of each of the components are preferably surrounded by molecules of the same kind. This tendency leads to formation of small clusters consisting entirely of molecules of one type. Although the solution exhibits heterogeneous character at the molecular scale, a phase separation does not occur.

The binary solution of water and acetonitrile has been investigated intensively due not only to its importance for many branches of chemistry but also to its simple structure and the fact that the CN group is a good sensor for its environment. A number of studies show that the influence of acetonitrile on the water structure is quite different from that of other organic solvents. According to Robertson and Sugamori[3] acetonitrile does not enhance the water structure; its molecules act rather like small ions which disrupt the water network in their closest vicinity.

The IR study of the OD stretching band of HDO in mixture with CH_3CN carried out by Gorbunov and Naberukhin[4] shows no structure making functionality of acetonitrile at low concentrations and no cluster formation at intermediate acetonitrile concentrations. The authors explain these results by the small size of the methyl group which cannot interact with water molecules strongly enough to dominate their interactions with the CN group. These observations are in conflict with results of other research. The investigation of the dynamic properties of MeCN–H_2O mixtures performed by Goldammer and Hertz[5] provides evidence for the existence of clusters. The increase of order in the water structure at low acetonitrile concentration was also observed.

Examination of Raman OH and CN stretching bands in the spectra of the CD_3CN-H_2O-HDO system[6] did not give any evidence for the enhancing of the water structure by acetonitrile in the range $0 < x_{MeCN} < 0.2$. On the other hand, a strong tendency for self-association of water molecules over a wide composition range was found. The applicability of the cluster formation model to the MeCN–H_2O mixture was also confirmed by MD simulation.[7] Comparison of the radial distribution functions $g_{O-O}(r)$ of pure water and 12 mol % acetonitrile solution indicates that the water structure is slightly enhanced when acetonitrile is added. A significant increase of the $g_{O-O}(r)$ function for 88 mol % acetonitrile solution and the fact that the acetonitrile structure remained practically unchanged suggest that at this concentration water exists in the form of clusters or chains inserted in the cavities between acetonitrile molecules.

A study of some thermodynamic properties of the water–acetonitrile mixture allowed Moreau and Douheret[8] to distinguish three composition regions which can be characterized by different structural patterns. In the first one, the water-rich region ($0 < x_{MeCN} < 0.2$), the acetonitrile molecules progressively occupy the cavities in the water network without enhancing the water structure. With an increase of the acetonitrile concentration ($0.2 < x_{MeCN} < 0.75$) the water structure undergoes a gradual disruption and clusters are formed. In this region the phase separation occurs at approximately 272 K and at a composition corresponding to ca. 38 mol % of acetonitrile. The third region ($x_{MeCN} > 0.75$) has characteristics similar to those of the first one and can be visualized as an acetonitrile arrangement disturbed by water molecules. From the study of the water–proton chemical shift dependence on composition, Easteal concluded that there are as many as five such regions.[9] However, the overall picture of the structural changes caused by the variation of composition is in good agreement with the characterization of Moreau and Douheret.

In the present investigation quantitative infrared spectroscopic data of isotopically diluted HDO molecules in the OD stretching region and deuterated acetonitrile CD_3CN in the CN stretching

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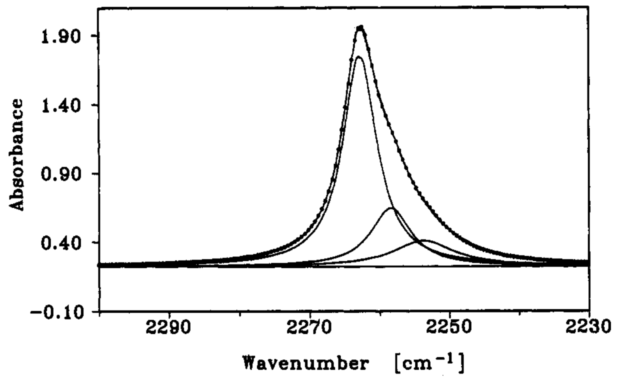

Figure 1. The CN stretching band of pure CD_3CN resolved into three Lorentzian curves and a linear baseline: (····) expermental data, (—) component bands, (—) calculated sum of the component bands.

region are presented. The spectroscopic result is compared to a theoretical model derived from randomly close-packed molecules.

Experimental Section

Acetonitrile (Merck, spectrosopic grade) was dried using thermally activated 3 Å molecular sieves. For examination of the CN stretching band deuterated acetonitrile was used due to the absence of a combination band found for CH_3CN in this region. The Merck product (NMR spectroscopic grade, 99.5% of deuterium) was used without any additional treatment. The mixtures of CD_3CN and H_2O were prepared by weight with x_{H_2O} ranging from ca. 0.1 to 0.9 with steps of 0.1. The densities of these solutions were measured with an Anton Paar density meter. Solutions of HDO in the acetonitrile–water mixture were made by adding weighed amounts of CH_3CN to the previously prepared mixture of H_2O and D_2O (99.98%) containing ca. 8% of HDO. Reference solutions were prepared by adding CH_3CN to H_2O.

The spectra were recorded on a Digilab FTS-45 FTIR spectrometer. The sample cell was equipped with CaF_2 windows separated with a Teflon spacer. The optical path length was determined interferometrically. The spectra in the CN stretching region were registered with 1 cm^{-1} resolution and a path length of 0.00178 cm. For the OD stretching region these parameters were equal to 4 cm^{-1} and 0.00493 cm, respectively. The solutions in the cell were thermostated at 20.0 °C.

Band Shape Analysis

A quantitative analysis of the spectra in the CN stretching region was carried out using a curve-fitting procedure. As a first step of these calculations the analysis of the ν_2 band of pure CD_3CN was performed. This band is significantly asymmetric due to an overlap of hot band transitions in the low-wavenumber side.[10] From a study of the gas-phase rotation–vibration spectrum they were identified as $\nu^{h1}_2 = \nu_2 + \nu_8 - \nu_8$ and $\nu^{h2}_2 = \nu_2 + 2\nu_8 - 2\nu_8$ where ν_8 denotes the degenerate C—C≡N bending mode.[11]

Accordingly, the CN stretching band of pure acetonitrile-d_3 was resolved into three Lorentzian curves and a linear base line (Figure 1). The intensity ratio $I_{\nu^{h1}_2}:I_{\nu_2}$ is very close to that calculated on the basis of the Maxwell–Boltzmann distribution while the ratio $I_{\nu^{h2}_2}:I_{\nu_2}$ is somewhat larger than the theoretical value. This increase of intensity may arise from the contribution of a CD stretching band located at approximately 2250 cm^{-1}.[6] The ν_2 band of acetonitrile-d_3 in the CD_3CN–H_2O mixtures consists of two subbands (2263 and ca. 2267 cm^{-1}) which can be assigned as coming from the free and H-bonded CD_3CN, respectively (a more detailed explanation is given in the Results and Discussion section). The 2263-cm^{-1} component has been refined with the previously obtained parameters of the CN stretching band of pure acetonitrile-d_3 as a sum of three Lorentzian curves with fixed values of their widths, centers, and relative heights. The other component of the CN band was assumed to be a single Lorentzian curve. The presence of the non-affected acetonitrile-d_3 band is not evident for $x_{H_2O} \geq 0.86$, but we decided to introduce it also in this case, because an attempt to refine the CN band with one curve only gave considerably larger error. Three examples of the curve-fitting results are shown in Figure 2.

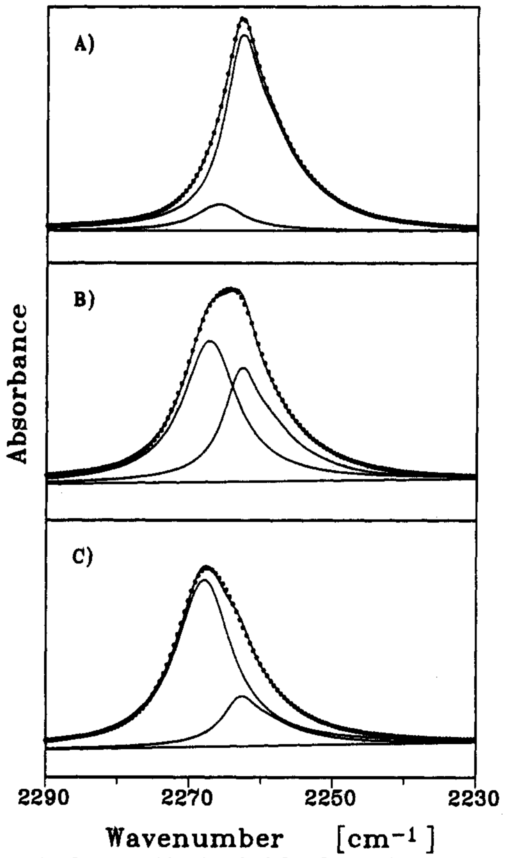

Figure 2. The CN stretching band of CD_3CN–H_2O mixtures resolved into one Lorentzian curve and a sum band describing the shape of the free acetonitrile component (see text and Figure 1) and a linear baseline: (A) $x_{H_2O} = 0.074$; (B) $x_{H_2O} = 0.523$, (C) $x_{H_2O} = 0.784$; (····) experimental data, (—) component bands, (—) calculated sum of the component bands.

Integral intensities obtained from the bandshape analysis enabled us to calculate for every solution the molar concentration of both types of acetonitrile-d_3. The concentration of non-affected CD_3CN was calculated directly on the basis of the extinction coefficient and the concentration of bonded CD_3CN was obtained as the difference $c_{\text{total}} - c_{\text{non-affected}}$. The amount of H-bonded acetonitrile-d_3 as a function of composition is presented in Figure 3.

Random Close-Packed Model

In order to determine whether the acetonitrile–water mixture can be described in terms of cluster formation it is necessary to compare the experimental $c_{\text{bonded}}(CD_3CN)$ vs $c(H_2O)$ curve (Figure 3) with the one generated for a model system in which the preferential solvation does not occur, i.e. in which all molecules are distributed in a randomly close-packed fashion.

For this purpose we created a randomly close-packed system consisting of water molecules represented by single spheres and acetonitrile molecules represented by three spheres centered on the N and C atoms (the whole methyl group was approximated by one sphere). The diameter (σ) was taken to be the same for all spheres. Two different values on σ, 2.7 and 3.0 Å, were used and the random distributions were obtained using a Monte Carlo computer program. The number of "bonded" acetonitrile molecules was calculated according to the following assumption: the acetonitrile molecule was considered as "bonded" if at least one

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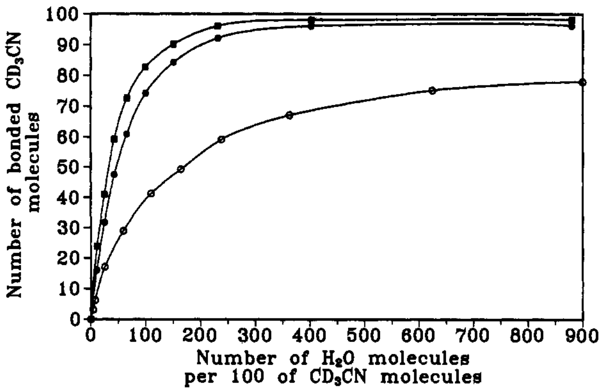

Figure 3. The amount of bonded CD_3CN as a function of composition: (○) data obtained from bandshape analysis, (●) data obtained from the randomly close-packed model (σ = 2.7 Å), (■) data obtained from the randomly close-packed model (σ = 3.0 Å).

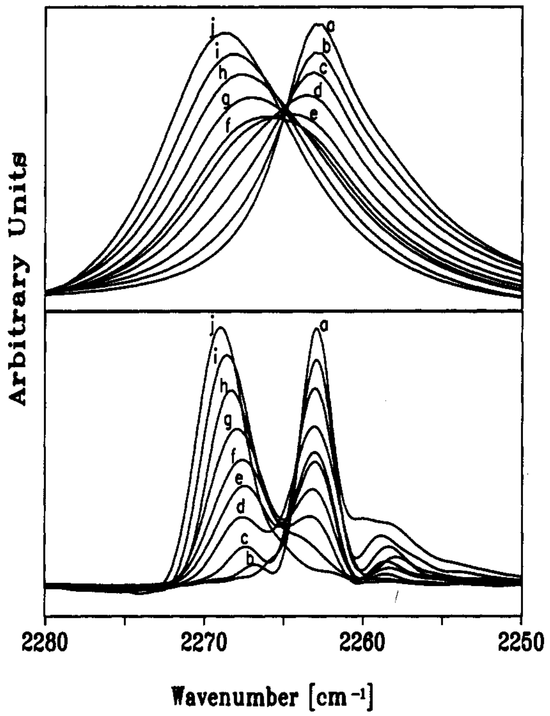

Figure 4. The original (top) and deconvoluted (bottom) spectra of CD_3-CN-H_2O mixtures in the CN stretching region. The mole fraction of H_2O equals (a) 0.000, (b) 0.074, (c) 0.204, (d) 0.373, (e) 0.523, (f) 0.622, (g) 0.705, (h) 0.784, (i) 0.862, and (j) 0.936.

water molecule could be found inside a hemisphere of a radius equal to 1.5 σ centered on an N atom. Since in the model the spheres representing an N atom and a CH_3 group are indistinguishable, the calculations were performed for both ends of the molecule and then the average value was taken. The resulting curves are given in Figure 3 together with the experimental curve.

Results and Discussion

Absorption spectra in the CN stretching region (ν_2) of CD_3-CN-H_2O mixtures at different compositions are shown in Figure 4 (top). Deconvolution of these bands indicates that in the composition range $0.07 \leq x_{H_2O} \leq 0.8$ they are a superposition of two subbands (Figure 4, bottom). One of them is located at the same wavenumber as the ν_2 band of pure acetonitrile-d_3 (2263 cm^{-1}) and therefore it can be assigned to the CD_3CN molecules which are not affected by water and exist in the same environment as in the pure solvent. The presence of this component band is not well pronounced for x_{H_2O} = 0.86 and 0.94 but nevertheless its contribution cannot be excluded. The other subband is found at higher wavenumbers with respect to the first one and it shifts to higher wavenumbers with increasing mole fraction of water. This component does not occur in the spectrum of pure acetonitrile-d_3 which allows us to assign it to CD_3CN molecules hydrogen-bonded by water molecules. In the composition range $0.07 \leq x_{H_2O} \leq 0.8$ one more subband, situated at the low-wavenumber side of the 2263-cm^{-1} component, can be observed Figure 4, bottom). It originates from hot bands which accompany the ν_2 band of pure acetonitrile-d$_3$ as discussed above.

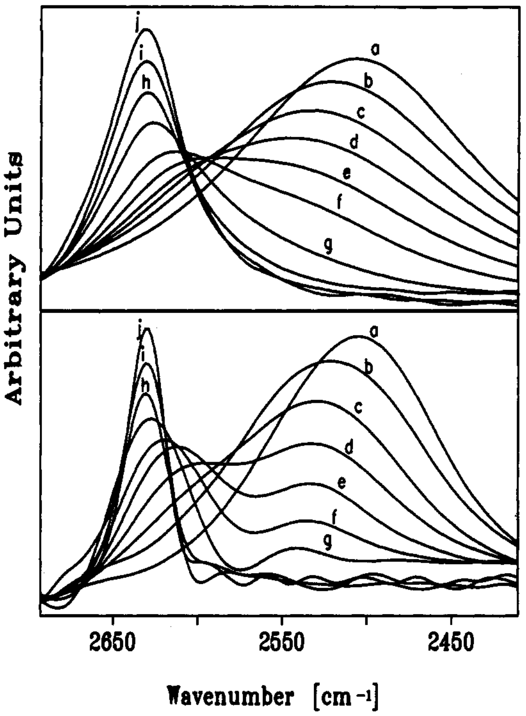

Figure 5. The original (top) and deconvoluted (bottom) difference spectra of the CH_3CN-H_2O-HDO mixture in the OD stretching region. The mole fraction of H_2O equals (a) 1.000, (b) 0.851, (c) 0.697, (d) 0.550, (e) 0.392, (f) 0.251, (g) 0.103, (h) 0.040, (i) 0.020, and (j) 0.008.

The OD stretching bands (Figure 5, top) are found in the difference spectra obtained by subtracting the spectra of reference solutions containing CH_3CN and H_2O from those of CH_3CN-H_2O-HDO mixtures. The deconvolution shows (Figure 5, bottom) that in the range $0 < x_{H_2O} \leq 0.04$ the OD bands consist of one peak only, which is located at approximately 2631 cm^{-1}. This peak shifts toward lower wavenumbers when the mole fraction of water increases. At the same time, on its low-wavenumber side a new broad band appears. Its position also varies considerably with the composition, moving toward the OD band of pure HDO with the increase of water concentration.

Taking these facts into account it seems reasonable to consider the first peak as originating from HDO molecules hydrogen-bonded to CD_3CN (and possibly to one other HDO molecule) whereas the second component band can be assigned to the self-associated HDO. The constant position and sharp shape of the first component at mole fractions lower than 0.04 and the absence of the other component indicate that in this composition range only water monomers are present.

The analysis of the deconvoluted CN and OD stretching bands allows us to state that two types of each component exist over a wide composition range. Molecules of one type are in close contact with molecules of the same kind and the interactions among them are very similar to those in the pure solvent. Molecules of the other type interact strongly through hydrogen bonds with molecules of the other component. The OD band corresponding to the self-associated HDO molecules appears only at the mole fraction of water higher than ca. 0.04. Increase of the water concentration causes low-wavenumber shifts of both OD components and a high-wavenumber shift of the CN subband corresponding to the water affected acetonitrile-d_3. These effects can be explained by formation of water dimers, trimers, and higher oligomers, which can interact with one another as well as with CD_3CN molecules. The formation of spherical clusters (globules) of water molecules would result in concentration-independent positions of the CN and OD stretching bands.

The curve-fitting procedure applied to the CN stretching band of CD_3CN-H_2O mixtures allowed us to calculate the concentrations of water bonded and free acetonitrile-d_3 in every solution. The dependence between the amount of bonded CD_3CN and the composition of the mixture differs drastically from the randomly close-packed result (Figure 3). For example, at $x_{H_2O} = 0.5$ the number of hydrogen-bonded CD_3CN molecules is predicted to be twice as large as that in the close-packed model as compared to the experimental result. This difference indicates that the arrangement in the real solution has a remarkably non-random character. In other words, a strong preferential solvation occurs in this system.

Recent MD simulations by Kovacs and Laaksonen[7] of the acetonitrile–water system also indicate a similar solvation behavior. The radial distribution functions (rdf) $g_{N-N}(r)$ and $g_{C2-C2}(r)$ remained practically constant in the range 100–50 mol % of acetonitrile, and the conclusion was that the acetonitrile arrangement is hardly affected by the addition of water.

In the three water–water rdf's ($g_{O-O}(r)$, $g_{H-H}(r)$, and $g_{O-H}(r)$) the intensity of the first peak in each case increased strongly with a decrease of the water concentration. This increase was partly interpreted as an increase in molecular association of water possibly induced by the particular choice of water potential.

No enhancement of the water structure in the sense of stronger hydrogen bonding is observed from the present spectra which on the contrary show an increase of the OD stretching frequency, i.e. weaker hydrogen bonding relative to that in pure water for all concentrations studied. The increase of the intensity in the rdf's in the MD simulation[7] is rather related to the rapidly decreasing number density for the water molecules and thus a dilution effect.

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