Hydrogen Bonding in Concentrated Aqueous Solutions of 1,2-Dimethoxyethane: Formation of Water Clusters

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The hydrogen bonding in concentrated aqueous solutions of 1,2-dimethoxyethane was studied by Raman spectroscopy of the O−H stretching band of water at various concentrations in the temperature range 218−315 K. The isotropic Raman spectra were analyzed by band decomposition, and two major components were identified in the spectra. They were assigned to the O−H stretching vibrations of water monomers and water molecules participating in clusters, respectively. The following picture of the hydration structure in the solutions emerged. Water molecules in concentrated aqueous solutions of 1,2-dimethoxyethane can exist in two stable configurations—either participating in water clusters enclosed in cavities of 1,2-dimethoxyethane molecules, or as monomers bridging ether oxygen atoms. The clustering of water is driven by the cooperative strengthening of the hydrogen bonds in the clusters. The clusters and the cavities are mutually stabilized by the extensive hydrogen bonding, and the size of the clusters is almost independent of temperature.

1. Introduction

Poly(oxyethylene) (POE) ($-OCH_2CH_2-)_n$ has various technological applications,[1,2] most of them relying on its easy hydration and unlimited solubility in water. POE is the simplest structure of the water-soluble polymers,[2] and therefore its interaction with water can be considered as an elementary model of the hydration of more complex biopolymers. For this reason, the hydration of POE has been a subject of ongoing research for many years. However, a general model of POE hydration has not yet been fully attained, as the contribution of various molecular level mechanisms has to be accounted for.

With the aim of clarifying POE hydration, we have started a series of studies on hydrogen bonding in aqueous solutions of model POE compounds by Raman and IR spectroscopy of the water O−H stretching band.[3−5] In the papers on the hydration of diethylene glycol dimethyl ether [$CH_3(OCH_2CH_2)_2OCH_3$][3] and 1,2-dimethoxyethane [$CH_3OCH_2CH_2OCH_3$],[4] we focused our attention on dilute and moderately concentrated solutions, which are most relevant to the practical applications of POE. In a recent paper,[5] we have explored the hydration of crown ethers in the whole miscibility range by IR spectroscopy. During these studies we found that, with respect to hydrogen bonding with water molecules, the hydration of POE is practically insensitive to the length of the POE chain and actually depends only on the mole ratio of water to oxyethylene monomer units.[6] Other studies have lead to the same conclusion.[7−10] Thus, the general features of POE hydration in aqueous solutions are already revealed for the shortest POE model compounds. Therefore, in this work, we extend our spectroscopic studies to concentrated aqueous solutions of 1,2-dimethoxyethane. Our primary objective is to clarify some aspects of the immediate hydration of 1,2-dimethoxyethane as influenced by the hydrogen bonding with water molecules.

2. Hydration of Poly(oxyethylene)

The water affinity is not a constant characteristic of POE. It has been recognized that there is a correlation between the conformation of the POE chain and its hydration.[11−13] On the other hand, both conformation and hydration depend on temperature and concentration of the aqueous solutions. Furthermore, various additives may alter the conformation and the hydration of the polymer leading to structural transformations of the aqueous solutions. Thus, in some cases POE behaves as a typical hydrophilic polymer, while in others it exhibits some features of the hydrophobic polymers.[14] Probably the best-known manifestation of this dual nature of POE is the phase separation of its aqueous solutions into water-rich and water-depleted phases encountered at high temperatures.[11]

2.1. Hydration of Poly(oxyethylene) in Dilute Solutions. On a molecular level the POE chain can be regarded as being composed of hydrophilic units (the oxygen atoms) and hydrophobic units (the ethylene groups). Accordingly, the hydration of POE in dilute solutions should involve both direct hydrogen bonding and hydrophobic hydration. Interestingly, at ambient temperatures, these are balanced in such a way that the POE chain is effectively hydrophilic. The hydrophilicity is one among many peculiar features of POE. The structurally related poly(oxymethylene), with one hydrophobic CH_2 group less in the monomer unit, and poly(oxytrimethylene), with one hydrophobic CH_2 group more, are both hydrophobic and practically insoluble in water. It has been recognized that the water affinity of POE is intimately related to a structural similarity between the POE chain and liquid water,[15,16] which is not encountered for the other polyethers. The basis of the structural similarity concept is the experimental observation that, when substantially hydrated, the POE chain assumes local conformations with most of the $O-CH_2-CH_2-O$ groups in the trans−gauche−trans (TGT) conformation. For this conformation, the distances between the nearest neighbor oxygen atoms and the distances between the next nearest neighbor oxygen atoms in the polymer chain almost perfectly match the corresponding distances

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between the oxygen atoms in the structure of liquid water. Hence, it is anticipated that the POE chain would be easily incorporated into the structure of liquid water with the ether oxygen atoms replacing some of the water molecules and with the hydrophobic ethylene groups being encaged in voids between the water molecules.[16]

The idea that the POE chain can be easily incorporated into a slightly perturbed water lattice is essential for explaining several important experimental results, all of them suggesting partially hydrophobic-like type of hydration of POE in dilute solutions. For example, the partial molar volumes of water in dilute aqueous solutions of short-chain POEs are slightly larger than the molar volumes of pure water,[17−19] the rotational mobility of hydration water is reduced,[20−22] and the tetrahedral coordination of hydration water is improved up to some critical concentration of oxyethylene monomer units.[3,4] The increased structuring of water is in line with the thermodynamical properties of the solutions.[16] Although it is apparent that the hydration of POE in dilute solutions and hydrophobic hydration bear several common features, they cannot be considered as fully analogous. The perfection of the tetrahedral coordination between liquid water molecules hydrating the POE chain is accompanied by a gradual decrease of the strength of hydrogen bonding between them, while for the typical hydrophobic hydration the strength of hydrogen bonding is preserved or even slightly increased, the latter effect being yet a subject of controversy.[23,24] The weakening of the hydrogen bonds between hydration water molecules has been clearly evidenced by our Raman and IR spectroscopic studies on the O−H stretching band of the aqueous solutions of methyl-terminated model POE compounds.[3−5] The same phenomenon has also been confirmed by an independent study on the hydration of 1,4-dioxane by IR spectroscopy of the vibrationally decoupled O−H stretching band of water.[7] For low concentrations of POE, the weakening of the hydrogen bonds can be explained by the expansion of the inherent cavities in the water structure, required to accommodate the hydrophobic ethylene and methyl groups of the polymer.

2.2. Hydration of Poly(oxyethylene) at Intermediate Concentrations. While the hydrophobic-like hydration seems to be a good description of the hydration of POE in dilute solutions, this model is not applicable to more concentrated solutions. Our Raman and IR spectroscopic studies have shown that, for higher concentrations, another model of the hydration of POE should be adopted.[3,4] The most developed network of hydrogen-bonded and tetrahedrally coordinated water molecules in aqueous solutions of POE is formed for a mole ratio of water molecules to oxyethylene monomer units around 2:1. Brillouin scattering and ultrasonic velocity studies[9,10] have shown that aqueous solutions of POEs with concentrations corresponding to a mole ratio of water molecules to oxyethylene monomer units of 2:1 have the most compact structure. Then, the low number of water molecules hydrating one oxyethylene monomer unit suggests that the hydrophobic hydration is most probably not relevant to this range of concentrations. Nevertheless, Raman and IR O−H stretching spectra of the solutions indicate that a significant part of the water molecules still participate in tetrahedral structural units and have hydrogen bonding similar to the one in liquid water.[3−5] Therefore, an assumption that water molecules have a definite affinity to form clusters in moderately concentrated solutions of POE can be inferred. Taking into account the compact structure of the solutions at these concentrations, the water clusters should be relatively small and homogeneously distributed with no large domains of bulk water being present in the solutions.[9,10] When the concentration of water is reduced beyond the concentration of optimal hydration (2:1 mole ratio of water molecules to oxyethylene monomer units), the tetrahedral structural pattern of hydrogen bonding is rapidly diminished, evidencing a break down of the network of hydrogen-bonded molecules.

The question how the hydration structure of the solutions evolves at higher concentrations of POE has remained unaddressed in our previous studies on short-chain POEs.[3,4] Our IR spectroscopic study on the hydration of crown ethers has provided, however, a useful insight into this region of concentrations.[5] The IR O−H stretching spectra contain a contribution from the tetrahedrally coordinated water molecules down to the lowest mole ratio of water molecules to oxyethylene monomer units studied, supporting the idea of clustering of the water molecules in the solutions. By analyzing the vibrationally decoupled O−H stretching IR spectra of aqueous solutions of 1,4-dioxane,[7] which is another simple model of POE, a similar conclusion has been reached. Smith and co-workers have approached the same problem by molecular dynamics simulations.[25,26] The tendency of the water molecules to form clusters up to rather high concentrations of POE was clearly seen in the simulations. As the formation of clusters of water molecules may contribute to the peculiar phase behavior of aqueous POE solutions, it needs to be further verified experimentally. In particular, identification of the driving force of the water cluster formation in the solutions is important.

3. Experimental Section

3.1. Materials. 1,2-Dimethoxyethane of analytical grade (Katayama Chemical Industries, Osaka) and doubly distilled deionized water were used to prepare aqueous solutions with different mole fractions. Solutions of 1,2-dimethoxyethane with mole fractions of the solute 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.88, 0.95, 0.98, and 0.99 were prepared. The samples were sealed in glass ampules for the Raman spectroscopic experiments.

3.2. Raman Spectroscopy. The Raman spectra were recorded on a JASCO NR-1800 Raman spectrometer equipped with a Princeton Instruments CCD detector. An NEC argon ion laser GLG 2162 operating at 514.5 nm was used for excitation. The unpolarized Raman spectra of all samples were taken at room temperature. Polarized Raman spectra were measured at various temperatures in the range 218−315 K in the conventional 90° geometry for highly concentrated samples of 1,2-dimethoxyethane with 0.88, 0.98, and 0.99 mole fractions. The resolution of the Raman spectra is 1 cm^{-1}. The temperature was varied by an Oxford Instruments Optistat cryostat. The isotropic Raman spectra were calculated from the parallel and perpendicular O−H stretching spectra of the solutions employing the standard relation.[27] All spectral processing was performed by using the GRAMS/32 software package (Galactic Industries, Salem, NH).

4. Results and Discussion

4.1. Concentration Evolution of the O−H Stretching Raman Spectra. Examples of unpolarized O−H stretching Raman spectra of aqueous solutions of 1,2-dimethoxyethane with different solute mole fractions from 0.10 to 0.95 recorded at room temperature under the same experimental conditions are shown in Figure 1. A substantial contribution to the background of the O−H stretching spectra from the higher-wavenumber wing of the C−H stretching band of 1,2-dimethoxyethane was observed at high concentrations. Hence, all our attempts to analyze correctly the spectra in this

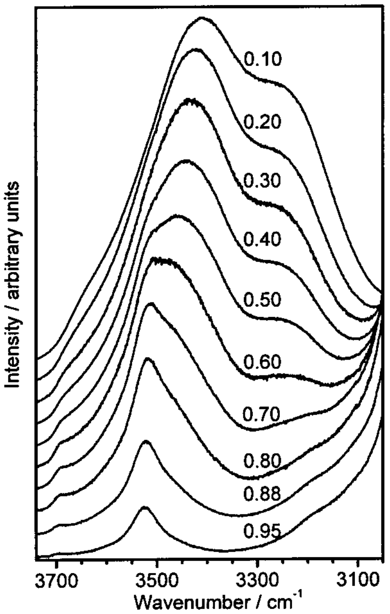

Figure 1. Examples of unpolarized O−H stretching Raman spectra of aqueous solutions of 1,2-dimethoxyethane. The mole fractions of 1,2-dimethoxyethane are marked above each spectrum.

concentration range by Fourier deconvolution and/or quantitative band decomposition have failed, because this background could not be reasonably accounted for in the attempted schemes for band decomposition. Thus, the unpolarized O−H stretching Raman spectra are discussed here only in a qualitative manner.

At low concentrations of 1,2-dimethoxyethane, the shape of the O−H stretching band is similar to that of liquid water. Three components can be easily identified. They are centered at about 3250, 3400, and 3650 cm^{-1}. Water molecules, participating in tetrahedrally coordinated structures with hydrogen bonding similar to, but on a scale smaller than, the hydrogen bonding in ice, perform collective O−H stretching vibrations, which are characterized by the component observed at about 3250 cm^{-1}.[28−30] Water molecules, which are not completely tetrahedrally coordinated and form less than four hydrogen bonds, are characterized by the higher-wavenumber component centered at about 3400 cm^{-1}.[28−30] The weak shoulder observed at about 3650 cm^{-1} is usually assigned to the O−H stretching vibrations of the weakly bonded or "free" O−H oscillators of water molecules, in which only one proton is engaged in hydrogen bonding.[31,32] This appearance of the spectra is preserved up to about 0.3 mole fraction, but the intensity of the component at 3250 cm^{-1} decreases relative to the one at 3400 cm^{-1}, showing that the tetrahedral arrangement characteristic of liquid water is gradually destroyed.

In the intermediate concentration range from 0.4 to 0.7 mole fractions, the component at 3250 cm^{-1} progressively disappears. Meanwhile, the component at about 3400 cm^{-1} shifts to higher wavenumber and evolves into a slightly asymmetric band centered at about 3530 cm^{-1}. This asymmetric band dominates the spectra of the highly concentrated solutions. According to our analysis to be described below, the band at about 3530 cm^{-1} is actually composed of two components, which we assign to water molecules that form bridges between oxygen atoms of 1,2-dimethoxyethane molecules and to water molecules that form small clusters. The component at about 3650 cm^{-1} becomes better defined with increasing concentration and shifts to about 3690 cm^{-1} for the highly concentrated solutions.

4.2. Highly Concentrated Aqueous Solutions of 1,2-Dimethoxyethane. For high concentrations of 1,2-dimethoxyethane, one may expect that the population of water molecules hydrogen-bonded to other water molecules will be reduced in comparison with the population of water molecules hydrogen-bonded directly to 1,2-dimethoxyethane molecules. Thus, the O−H stretching spectra of water at high concentrations should reflect more closely the immediate hydration of 1,2-dimethoxyethane.

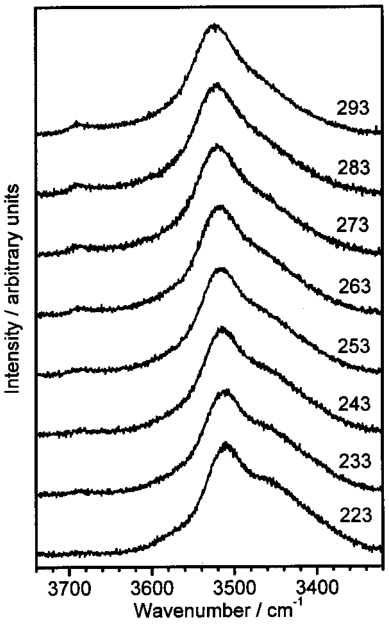

Figure 2. Examples of isotropic O−H stretching Raman spectra of aqueous solutions of 1,2-dimethoxyethane with mole fraction of 1,2-dimethoxyethane 0.88. The temperatures in K are marked above each spectrum.

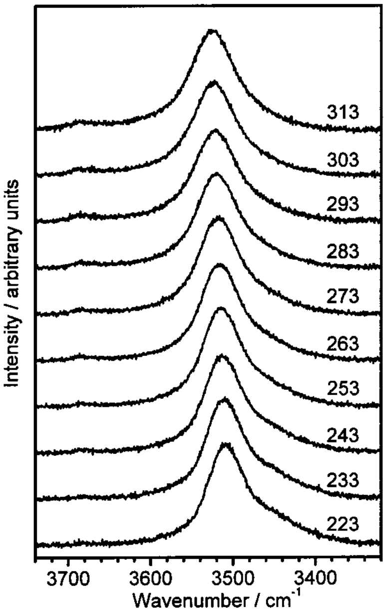

Figure 3. Examples of isotropic O−H stretching Raman spectra of aqueous solutions of 1,2-dimethoxyethane with mole fraction of 1,2-dimethoxyethane 0.98. The temperatures in K are marked above each spectrum.

The isotropic O−H stretching Raman spectra of solutions with mole fractions of 1,2-dimethoxyethane 0.88, 0.98, and 0.99 were studied in the temperature range 218−315 K as shown in Figures 2−4, respectively. Fortunately, the contribution of the background due to the C−H stretching band is highly diminished and is practically absent in the isotropic Raman spectra. Thus,

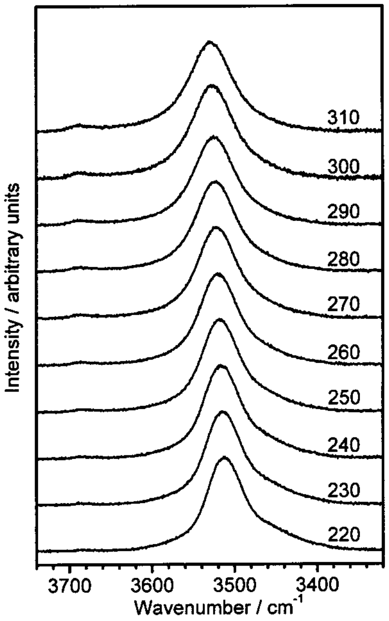

Figure 4. Examples of isotropic O−H stretching Raman spectra of aqueous solutions of 1,2-dimethoxyethane with mole fraction of 1,2-dimethoxyethane 0.99. The temperatures in K are marked above each spectrum.

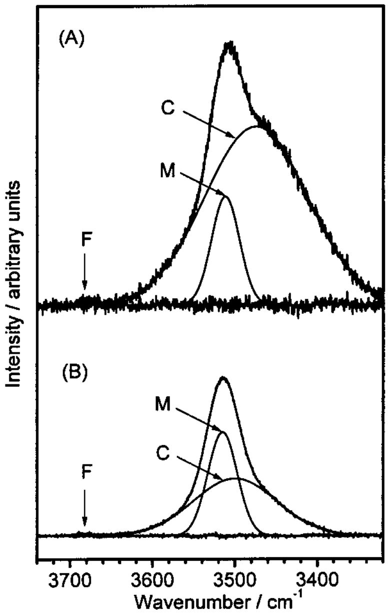

Figure 5. Examples of band decomposition of the isotropic O−H stretching Raman spectra of aqueous solutions of 1,2-dimethoxyethane: (A) mole fraction of 1,2-dimethoxyethane 0.88 and temperature 228 K, and (B) mole fraction of 1,2-dimethoxyethane 0.99 and temperature 230 K. Component C corresponds to clustered water, while component M corresponds to water monomers that bridge oxygen atoms of 1,2-dimethoxyethane. Component F is associated with weakly hydrogen-bonded or "free" O−H groups.

it was possible to analyze the spectra by band decomposition. Attempting different schemes for decomposition, we have found that all spectra can be adequately decomposed into three components—two Gaussian components denoted here by M and C, and one asymmetric log-normal component denoted by F. Examples of the band decomposition are shown in Figure 5. We want to point out that this scheme for band decomposition is not apparent in the case of the high-temperature spectra due to the similar peak wavenumbers of components M and C. On reducing temperature, however, a small difference appears between the peak wavenumbers, which is sufficient for distinguishing the overlapped components. Hence, the measurement of the O−H stretching Raman spectra at low temperatures was crucial in revealing the presence of water clusters (component C) in the highly concentrated solutions (see below).

Component F, which is located at about 3690 cm^{-1} at room temperature, is assigned to the stretching vibrations of weakly hydrogen-bonded or "free" O−H groups. The very low intensity of component F proves that almost all water molecules form two hydrogen bonds with their protons. To clarify the origin of components M and C, we have analyzed how their parameters change with water concentration and temperature.

The dependencies of the peak wavenumbers of components M and C on temperature are shown in Figures 6. Interestingly, the behavior of the peak wavenumber of component M is the same for the three solutions of 0.88, 0.98, and 0.99 mole fractions. After a careful examination, component M can also be found in the unpolarized O−H stretching Raman spectra in Figure 1 for concentrations from 0.4 to 0.8 mole fractions. Apparently component M does not change its position in these spectra too. Therefore, the water molecules giving rise to component M do not change their hydrogen bonding on changing water concentration. This fact gives us a reason to assume that component M is due to the O−H stretching vibrations of water molecules that do not interact with other water molecules, namely water monomers. As there are only a small number of "free" O−H groups, we can conclude that the water monomer species bridge both oxygen atoms of one 1,2-dimethoxyethane molecule, or oxygen atoms of different 1,2-dimethoxyethane molecules. Unfortunately, it is practically not possible to decide, on the basis of the present experimental results, which of these bridging configurations is actually observed.

The peak wavenumber of component C, on the other hand, depends significantly on water concentration—a trend that is clear even in the unpolarized Raman spectra in Figure 1. The lower the concentration of water is, the higher the wavenumber of component C becomes. Accordingly, we assign component C to the O−H stretching vibrations of water molecules that interact with each other and can therefore be considered to participate in clusters of water molecules. These water clusters should be smaller than a tetrahedral water pentamer, as the collective in-phase O−H stretching mode at 3250 cm^{-1} is not observed in the spectra.

The formation of water clusters in the aqueous solutions of 1,2-dimethoxyethane can be easily understood. The hydrogen bond between an ether oxygen atom and a water molecule is slightly stronger than the hydrogen bond between two water molecules. This has been evidenced by IR spectroscopic studies on complexes of dimethyl ether with water[33] and by ab initio molecular orbital calculations.[34,35] The hydrogen bonds between water molecules are, however, highly cooperative. As a result, the hydrogen bonds in clusters of water molecules are gradually strengthened on increasing the size of the clusters.[36−38] The wavenumbers of the O−H stretching vibrations of the clustered water molecules in the concentrated solutions studied are lower than the wavenumbers of the O−H stretching vibrations of the monomer (bridging) water molecules (Figure 6). Therefore, the hydrogen bonding in the observed water clusters is, indeed, stronger than the direct hydrogen bonding between water and 1,2-dimethoxyethane. The energy difference between the single and cooperative hydrogen bonds should be the driving force of the water cluster formation in the concentrated solutions of 1,2-dimethoxyethane. As we have already mentioned, the bigger

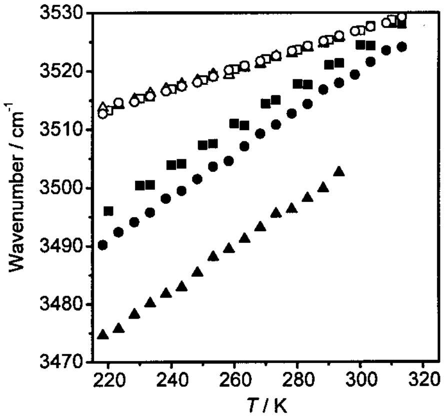

Figure 6. Dependencies of the peak wavenumbers of components M and C on temperature: △ component M for mole fraction of 1,2-dimethoxyethane 0.88, ○ component M for mole fraction 0.98, □ component M for mole fraction 0.99, ▲ component C for mole fraction 0.88, ● component C for mole fraction 0.98, and ■ component C for mole fraction 0.99.

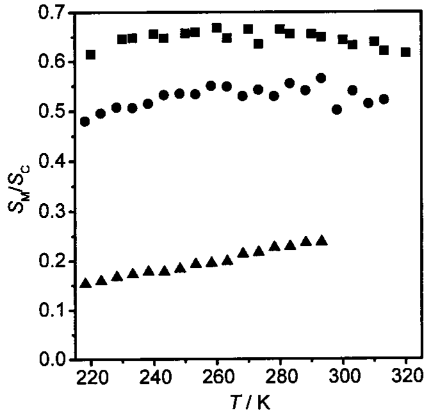

Figure 7. Dependencies of the ratio of the areas, S_M and S_C, of components M and C on temperature: ▲ mole fraction of 1,2-dimethoxyethane 0.88, ● mole fraction 0.98, and ■ mole fraction 0.99.

the water cluster is, the stronger the hydrogen bonding between the molecules in the cluster becomes, the relevant O−H stretching wavenumber being lowered accordingly. Thus, the progressive red wavenumber shift of component C, observed in the isotropic and unpolarized O−H stretching Raman spectra, indicates that the water clusters rapidly grow up on addition of water to the solution. The same trend has been observed in the molecular dynamics simulations performed by Smith and co-workers.[25,26]

Although the cluster formation is energetically favorable, there is always an entropy penalty for it. Thus, at high temperatures, one may expect that the water clusters would break down into smaller clusters and monomers, increasing the entropy of the system. To analyze this possibility, we have examined the ratio of the areas of components M and C as shown in Figure 7, which reflects the ratio of the populations of monomer and clustered water molecules. If there is a breakdown of the water clusters on increasing temperature, it should result in a substantial increase of the relative population of monomer water and a concomitant increase of the ratio of the areas of components M and C. Figure 7 shows, however, that the ratio of the areas of components M and C is almost constant with increasing temperature for the solutions of 0.88, 0.98, and 0.99 mole fractions. We can therefore conclude that the size of the water clusters is not very sensitive to temperature changes at these concentrations. This is rather unusual behavior of water clusters, but we have a rational explanation for it as described below.

The water molecules always tend to form the maximum possible number of hydrogen bonds. In aqueous solutions of 1,2-dimethoxyethane, this may include water−water hydrogen bonds as well as hydrogen bonds between water molecules and oxygen atoms of 1,2-dimethoxyethane. Due to its cooperative nature, the water−water hydrogen bonding dominates and leads to water cluster formation. The water clusters cannot, however, be formed via hydrogen bonding between water molecules only. Any water cluster in the solution should always end up with hydrogen bonds with ether oxygens, as otherwise there will be some dangling O−H groups at the surface of the cluster, violating the principle of maximum number of hydrogen bonds. Therefore, each water cluster should be enclosed in a cavity formed by ether oxygens. The advantages of this configuration are 2-fold; from one side the cavity and the water cluster are mutually stabilized by the hydrogen bonds, and from the other side the water molecules from the cluster realize the highest possible number of hydrogen bonds. As a result of the mutual stabilization of clusters and cavities, the clusters do not break down on increasing temperature.

The wavenumbers of the components of clustered water (C) and of monomer water (M) gradually increase with temperature (Figure 6), in accord with the inherent decrease of hydrogen bond strength on increasing temperature. The wavenumber of the O−H stretching vibration of clustered water increases much faster than that of monomer water. This shows that the hydrogen bonds in the clusters weaken faster than the direct hydrogen bonds between water and 1,2-dimethoxyethane on increasing temperature. Thus, the bridging hydrogen bonding seems to be more stable with a temperature increase than the hydrogen bonding between the water molecules in the clusters. It is rather interesting to note that, by extrapolation of the wavenumbers of components M and C at 0.98 and 0.99 mole fraction in Figure 6 to temperatures above 320 K, a crossover of the wavenumbers of the O−H stretching vibrations of the monomer and clustered water will occur somewhere at higher temperatures. Such a crossover would imply that the strength of hydrogen bonding in the clusters and the strength of direct hydrogen bonding between water and 1,2-dimethoxyethane would become equal. Then the energy gain on forming clusters of water molecules would vanish and the clusters may break down. Unfortunately, this interesting temperature region was not accessible in our experiments.

Finally, it is worth mentioning that, when the number of hydrogen bonding sites on 1,2-dimethoxyethane molecules is substantially reduced, for example by increasing the population of the less hydrophilic TGG′ conformer[13] on increasing temperature, it may happen that the water molecules are forced to form rather large clusters to realize all the possible hydrogen bonds predominantly between themselves. The formation of large clusters was not observed in the present study, but it may eventually be observed in dilute aqueous solutions of long POEs at high temperatures. The natural limit of such cluster growth due to increasing hydrophobic nature of the solute molecules at high temperatures would be indeed the phase separation of the solution into water-rich and water-depleted phases.

5. Conclusions

By employing Raman spectroscopy of the O−H stretching band of water, new experimental data on the hydration of 1,2-dimethoxyethane have been obtained. We have shown that water molecules in concentrated aqueous solutions of 1,2-dimethoxyethane can exist in two stable configurations—either participating in water clusters enclosed in cavities of 1,2-dimethoxyethane molecules, or as monomers bridging ether oxygen atoms. The clustering of water is driven by the cooperative strengthening of the hydrogen bonds in the clusters. The clusters and the cavities are mutually stabilized by the extensive hydrogen bonding, and the size of the clusters is almost independent of temperature.

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