Quantitative Information about the Hydrogen Bond Strength in Dilute Aqueous Solutions of Methanol from the Temperature Dependence of the Raman Spectra of the Decoupled OD Stretch

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We have obtained quantitative information about the hydrogen bond strength in pure water and in dilute aqueous solutions of methanol by analyzing the temperature dependence of Raman spectra of the decoupled OD stretch from 21 to 160 °C with the hydrogen bond energy dispersion method. A minimum at 2440 cm^{-1} assigned to strong icelike hydrogen bonds and a maximum at 2650 cm^{-1} due to maximally (but not completely) broken hydrogen bonds result in all cases. The energy of the minimum decreases upon addition of methanol due to formation of stronger water−methanol hydrogen bonds, whereas the energy of the maximum increases because water hydrogen atoms in the vicinity of the methyl group might participate in “more broken” hydrogen bonds than in bulk water.

Introduction

Amphiphilic molecules are central to biology, most notably in making up cell membranes, but they also have numerous applications in the chemical industry, e.g., as detergents. Amphiphiles are bipolar molecules with solvent-loving and solvent-hating moieties which self-assemble to form superstructures (micelles, bilayers, etc.) in highly polar or highly nonpolar solvents.[1] In aqueous solutions the degree of self-assembly depends, of course, on the size of the hydrophobic groups which bundle together in the interior, leaving the hydrophilic groups exposed to water. Amphiphiles can also be excellent model systems for studying hydrophobic effects especially when one considers that the “real” hydrophobes such as alkanes are practically insoluble in water. Hydrophobic hydration theories based on the “iceberg model” of Frank and Evans,[2] which assumes additional structuring of water molecules in the vicinity of an apolar solute, have formed for many years the basis for explaining hydrophobicity and hydrophobic effects. The tendency of water molecules to avoid entropically unfavorable interactions with apolar solutes was then considered as the driving force for protein folding and other aggregation phenomena in aqueous solutions.[3] However, recent neutron diffraction studies,[4−6] MD simulations,[7] and ab initio calculations[8,9] have shown no enhancement of the water structure around the nonpolar groups. NMR studies[10,11] have suggested that any enhancement of the water structure around hydrophobic groups of an alcohol, an example of an amphiphile, as evidenced by the downfield shift of the proton signal is only observed at low temperatures near the freezing point and whatever excess structure exists in the chilled solutions soon melts out when the temperature is raised.

Monohydric alcohols are arguably the simplest and the most well-known amphiphilic molecules. The C_1−C_3 members of the series and *tert*-butyl alcohol (tBA) of the C_4 isomers are totally miscible with water, while the other members are only partially soluble. Despite their apparent simplicity, it is well-known that the thermodynamic and transport properties of alcohol−water mixtures, such as the mean molar volume, the diffusion coefficient, the compressibility, and the excess entropy, are significantly smaller whereas other properties, such viscosity and light scattering intensity, are significantly larger than the values that might be expected from an ideal mixture of the pure liquids.[12−18] In the dilute alcohol regime some of the anomalous properties of the alcohol−water mixtures can be explained with the aggregation of alcohol molecules, which in case of tBA molecules is shown to take place at concentrations as low as 2−3 mol %.[6,18,19] Our interest in studying the water structure around nonpolar groups as a possible underlying cause for the hydrophobic effects and for understanding the anomalous properties of alcohol−water solutions was the main motivation for the work presented here. As part of an ongoing study of hydrogen bonding and hydrophobic hydration in aqueous solutions of monohydric alcohols, we report here results for dilute aqueous solutions of methanol. We used visible Raman spectroscopy of the decoupled OD stretch to probe the hydrogen bond strength in pure water and in solutions of methanol. The decoupled OD stretch has been shown to be very sensitive to the hydrogen bond environment of OD oscillators,[20−25] and as such we can use it as a tool to study changes induced by methanol molecules in the hydrogen bond network of water.

Experimental Method

The Raman spectra were recorded with a Spex triplemate monochromator equipped with a CCD detector. The 488 nm line of an Ar^+ laser with about 150 mW of power at the sample was used as the excitation source. All the samples were prepared with distilled and subsequently deionized water. Deuterated methanol-d_3 (CD_3OH) and D_2O with D atom contents of 99% and 90%, respectively, were purchased from Sigma-Aldrich Inc. Raman spectra in the region of the decoupled OD stretch of samples of 5 mol % D_2O in pure H_2O and in solutions of 0.5, 1, 4, and 8 mol % CD_3OH were recorded at 10 different temperatures in the range 21−160 °C. The main background contribution due to the overlap of the decoupled OD stretch

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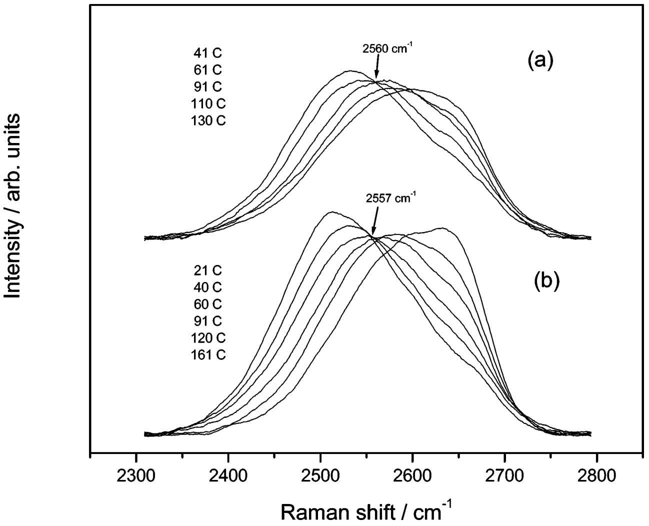

Figure 1. Raman spectra of the decoupled OD stretch for 10% HOD in pure H_2O (a) and in an aqueous solution of 1 mol % CD_3OH (b). Notice the existence of an isosbestic point around 2560 cm^{-1}.

with the OH stretch band of H_2O was removed by subtracting the spectra of pure H_2O recorded at the same temperatures. Deuterated methanol was used because of the adverse effect of the significant overlap of the CH stretch of CH_3OH at 2837 cm^{-1} with the decoupled OD stretch. This overlap is very difficult to correct because in this region the OH stretch band of water also has significant intensity. The high-frequency CD stretch at 2240 cm^{-1}, on the other hand, occurs in a region where the water band has no intensity, and hence, its partial overlap with the OD stretch is much easier to correct by subtracting the spectra of CD_3OH in H_2O with no D_2O added. The CD stretch at 2082 cm^{-1} was used as an internal intensity standard.

Results and Discussion

The Raman spectra of the decoupled OD stretch of 10% HOD in pure H_2O and in a 1 mol % CD_3OH solution are shown in Figure 1. First, we notice that there is an isosbestic point at about 2560 cm^{-1} in the 21−91 °C temperature range. However, isosbestic behavior no longer persists at temperatures higher than 91 °C. The same picture, more or less, also holds true for the other concentrations of CD_3OH studied here. The position of the isosbestic point in this work is in good agreement with the results of Walrafen,[20] who reports an isosbestic point in the Raman spectra of 10% HOD in H_2O at 2570 ± 5 cm^{-1} in the temperature interval 16−97 °C. The agreement is even better if we consider that the resolution used in Walrafen's measurements was on the order of 10−15 cm^{-1}.

We seek to extract quantitative information about the strength of hydrogen bonds from the temperature dependence of the Raman spectra of the decoupled OD stretch. The method used was the so-called hydrogen bond energy dispersion (HBED) analysis originally developed by Hare and Sorensen.[21] Just to briefly describe the HBED principles, we assume that since the hydrogen bond energy and vibrational frequency are both functions of the O−D···O angle, OD oscillators with a hydrogen bond energy $E(\omega)$ will give rise to the Raman intensity at frequency ω, i.e., there is a one-to-one correspondence between the hydrogen bond energy $E(\omega)$ and the vibrational frequency ω. The number $N(\omega)$ of OD oscillators with respect to some reference state N_0 is given by the Boltzmann distribution

$$N = N_0 e^{-E(\omega)/kT} \tag{1}$$

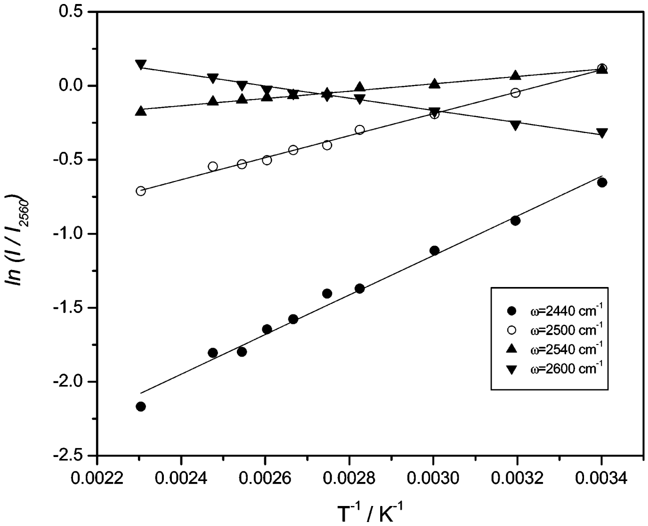

Figure 2. Boltzmann plots for the decoupled OD stretch in 1 mol % CD_3OH.

Since $I(\omega) \approx \sigma(\omega)\, N(\omega)$, where $I(\omega)$ and $\sigma(\omega)$ are the Raman intensity at frequency ω and the cross-section, respectively, we could write

$$\ln \frac{I(\omega)}{I_0} = -\frac{E(\omega)}{kT} + \ln \frac{\sigma(\omega)}{\sigma_0} \tag{2}$$

As seen from the last equation, plots of $\ln(I(\omega)/I_0)$ vs $1/T$ should be linear with the slope equal to $-E(\omega)/k$. It is shown in ref 21 for the case of 10% HOD in H_2O and it can also be clearly seen in Figure 2 for the new data presented here that this is indeed the case.

In this work we first tried to reproduce the results of Hare and Sorensen for the decoupled OD stretch of 10% HOD in H_2O. Using the HBED analysis with their set of spectra, they found the energy difference between the weak, maximally (but not completely) broken hydrogen bonds and the strong, icelike bonds to be $\Delta E = 3.2 \pm 0.2$ kcal/mol.[21] We find for the same system an energy difference of 3.4 ± 0.13 kcal/mol, in excellent agreement with the earlier result. Walrafen has recently reported a ΔE value of 3.3 kcal/mol,[26] which independently confirms our results and thus gives us confidence that the HBED analysis is a sound and mature method.

We then applied the same analysis for the decoupled OD stretch in aqueous solutions of CD_3OH with different concentrations. H ↔ D exchange will not affect our results to any significant extent because for the small concentrations of methanol used in this study the portion of D atoms which will exchange with the methanol OH group is negligible. Indeed, if we dissolve x mol % CD_3OH in an aqueous solution of 5 mol % D_2O in H_2O, the concentration of exchanged CD_3OD molecules will be $5(x/95)$ mol % because 5 mol % D atoms will be distributed between x mol % CD_3OH and $(95 - x)$ mol % H_2O. For our series of CD_3OH solutions, $x = 8$, 4, 1, and 0.5 mol %, respectively, which yields corresponding concentrations of CD_3OD of 0.42, 0.21, 0.053, and 0.0026 mol %. These will then constitute, respectively, 4.2%, 2.1%, 0.53%, and 0.026% of the total number of OD oscillators, and as such either they will not contribute at all in the OD spectrum if the concentration is below the detection limit of our spectrometer or, in the worst case, when they can be detected, the contribution will be quite insignificant.

To apply the HBED analysis for the methanol solutions, the isosbestic point was chosen as the reference state and hence

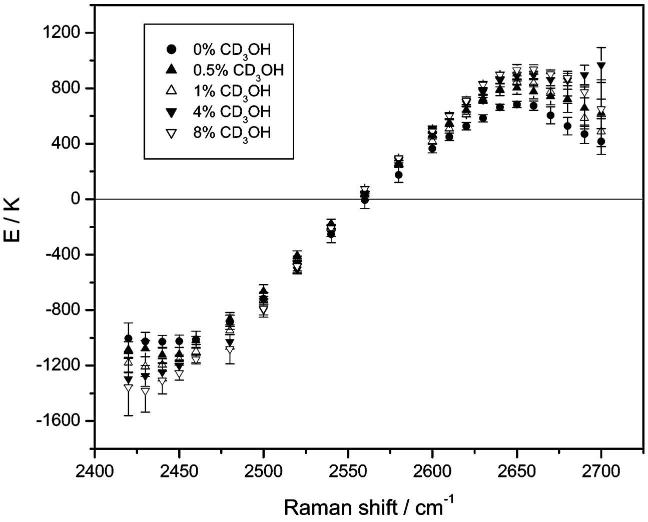

Figure 3. Hydrogen bond energy dispersions for the decoupled OD stretch in pure H_2O and in aqueous solutions of CD_3OH with different concentrations.

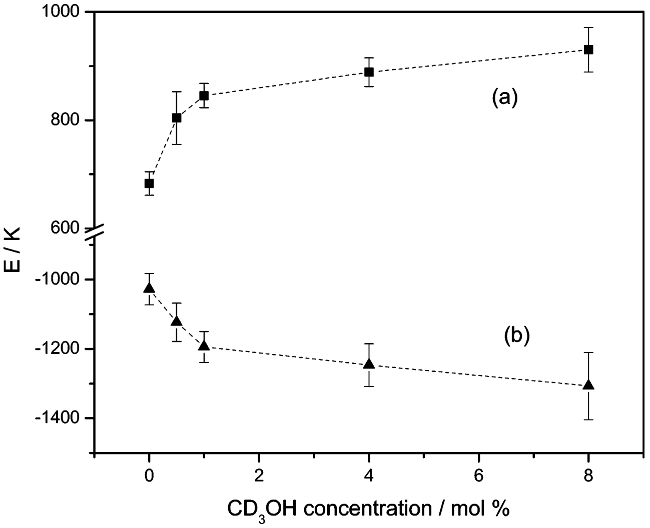

Figure 4. Energy at the maximum (2650 cm^{-1}) (a) and the minimum (2440 cm^{-1}) (b) as a function of CD_3OH concentration.

the hydrogen-bonding energy of OD oscillators at 2560 cm^{-1} was arbitrarily set to zero. We would like, however, to point out that our results do not depend on the choice of the reference state. In fact, any point in the spectrum can be chosen as the reference state, and the corresponding energy dispersion curve would only shift up or down by a certain amount without affecting the relative changes discussed in this paper. The fact that the intensity at 2560 cm^{-1} is temperature independent, at least in a certain temperature interval, makes this point a natural choice as the reference state. Also, data points at high temperatures (see Figure 2), where the isosbestic behavior does not hold, do not show any deviation from the linear relationship predicted by eq 2. The energy dispersion curves are shown in Figure 3. The hydrogen bond energy (determined by the slope of the Boltzmann plots such as those in Figure 2) depends very strongly on the frequency position in the middle-spectrum region. This functionality, however, weakens very significantly in the low- and high-frequency sides of the spectrum, resulting in a shallow minimum at 2440 cm^{-1} and a rough maximum at 2650 cm^{-1}. As seen in Figure 1 there is little intensity beyond 2400 and 2700 cm^{-1} in the spectra of the decoupled OD stretch, and hence, continuing our analysis beyond these limits would be associated with large errors. The minimum at 2440 cm^{-1} becomes a rather flat region for the methanol concentrations of 4 and 8 mol % due to corrections that had to be made for the overlap with the CD stretch which occurs in the low-frequency side of the OD stretch. Also, in the case of the 4% methanol solution the last 2−3 data points in the maximum region in Figure 3 deviate from the general behavior due to small imperfections in the spectra in this region. The error bars are reported as 2σ, i.e., 90% confidence intervals for the slopes of the Boltzmann plots, and result mostly from scattering of the data points due to spectral noise and other experimental errors. A relatively sharp band at 2440 cm^{-1} is observed in the spectra of frozen dilute solutions of HOD in H_2O,[27] which clearly suggests that the minima found in our energy dispersion curves correspond to strong, icelike hydrogen bonds. The maximum at 2650 cm^{-1} would then correspond to weak, maximally (but not completely) broken hydrogen bonds of OD oscillators. The latter are not completely broken bonds because in that case we would observe a sharp feature on the high-frequency side of the OD stretch band. This picture also agrees with the spectroscopist's intuition that strongly hydrogen bonded OD oscillators would vibrate further away from the gas-phase frequency, which is 2724 cm^{-1} for gaseous HDO,[28] than the weakly bonded OD groups. As clearly seen from the hydrogen bond energy dispersion curves and from Figure 4, the energy at the minimum becomes more negative upon addition of methanol, hence indicating that the strong hydrogen bonds get stronger while at the same time the energy at the maximum becomes more positive, which corresponds to the weak hydrogen bonds getting weaker.

Stronger hydrogen bonds in methanol solutions compared to bulk water could be explained by stronger water−methanol as compared to water−water hydrogen bonds or by enhanced structuring of water around the hydrophobic methyl group as suggested by hydrophobic hydration theories. According to Muller,[11] strengthening of hydrogen bonds due to structuring of water around hydrophobic moieties is only observed at low temperatures, and when the solutions are heated to room temperature and above, any such structures melt away. Since our measurements were from 21 to 160 °C, we believe that the observed strengthening of hydrogen bonds is very likely to be due to stronger water−methanol hydrogen bonds. Huyskens[29] estimated the methanol−methanol hydrogen bond energy to be about 6.7 kcal/mol compared to 4.6 kcal/mol estimated by Pauling[30] for water−water hydrogen bonds. More recently, in a computational study[31] the hydrogen-bonding energies of water−water and water−methanol complexes were calculated. Among the different methods employed by the authors, CCSD(T), which can be regarded as one of the most accurate computational methods available, yielded hydrogen bond energies of 4.41 and 5.02 kcal/mol for the water−water and water−methanol complexes, respectively. These values suggest that the oxygen atom in alcohols is more capable of strong hydrogen bonding and hence water−alcohol hydrogen bonds would be stronger than water−water bonds.

Additional weakening of the weak hydrogen bonds in aqueous solutions of methanol could be explained by assuming that OD oscillators in the vicinity of methanol's CD_3 group participate in even weaker hydrogen bonds than in bulk water because the space where the nearest oxygen atom should be is now occupied by the methyl group. This contention is supported by the results of Brown et al.,[32] who observed free OH groups in the interface of water with different hydrophobic molecules such as CCl_4, hexane, heptane, and octane. In our case the macroscopic interface is substituted by "nanopools" of hydrophobic methyl groups which cause additional hydrogen bond breaking.

In a neutron diffraction study of a 5 mol % aqueous solution of methanol, Dixit et al.[4] determined that there are, on average, 17.6 ± 0.8 water molecules in the hydration shell of a methanol molecule. This number was derived from the analysis of the carbon−water oxygen radial distribution function, and it is not far from the result of De Jong et al.,[33] who determined that the hydration shell of methane contains 19 ± 2 water molecules. These results would then imply that at a methanol concentration of about 5 mol % all the water molecules would be in hydration shells. A further increase of the methanol concentration would then lead to association of methanol molecules. Aggregation of methanol molecules in a 5 mol % aqueous solution was indeed observed in the neutron diffraction study of Dixit et al. These authors found that more than 80% of the methanol molecules are associated in clusters of 3−8 molecules. Methanol molecules can stick together through their methyl groups coming together or through the formation of methanol−methanol hydrogen bonds. If the first scenario takes place, aggregation of methanol molecules would decrease the solvent-accessible area of the hydrophobic groups, whereas in the second case the number of OH groups available to form hydrogen bonds with water molecules would be reduced. Stronger methanol−methanol hydrogen bonds formed in the latter case would not contribute in our spectra because of our choice of the $H_2O/D_2O/CD_3OH$ system in which stretching of the methanol OH group occurs outside the decoupled OD stretching range. Hence, whichever way the methanol molecules aggregate, the combination of both effects mentioned above would account for the saturation of hydrogen bond strengthening and hydrogen bond breaking observed in Figure 4.

Conclusions

In this study, we observed both structure-making (hydrogen bonds getting stronger) and structure-breaking (weak hydrogen bonds getting weaker) properties of methanol, the simplest example of an amphiphile. We believe, however, that the results do also depend on the temperature interval in which the measurements are taken. Studies in the cooled and supercooled regions could well produce different results, especially because at these temperatures enhanced structuring of water molecules around hydrophobic parts takes place. It could also be that in the low-temperature regime water molecules are so strongly involved in regular structures around hydrophobic groups that an insignificant number of water hydrogen atoms point to the hydrophobe and thus participate in “more broken” hydrogen bonds. In this situation we would then observe no structure-breaking properties of hydrophobic molecules. Finally, studies of methane dissolved in water (which unfortunately require high pressure and sophisticated equipment since concentrations of 0.5 mol % methane in water can only be obtained at pressures in excess of 400 bar) compared to methanol−water solutions would significantly contribute to removing the effects of the polar group and would elucidate the behavior of real hydrophobes in water.

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