Pressure-Enhanced C−H···O Interactions in Aqueous *tert*-Butyl Alcohol

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We have investigated pressure-enhanced C−H···O interactions in *tert*-butyl alcohol (TBA)/D_2O mixtures. On the basis of its responses to changes in pressure and concentration, TBA appears to be the ideal candidate to study the variations in structural and dynamical properties of C−H···O interactions. For dilute aqueous TBA, the pressure dependence of the C−H bands yielded blue frequency shifts at pressures below 0.3 GPa, but an increase in pressure leads to a red frequency shift at pressures above this value. This discontinuity in frequency shift is related to enhanced C−H···O interactions. The frequency of the C−H stretching modes that characterize C−H···O hydrogen bonding undergoes a blue shift with pressure. This behavior is in contrast with the general trend of red shifts observed in strongly hydrogen-bonded systems that occur through O−H···O and C═O···H interactions. We discuss the results of density functional theory calculations that predict the frequency shift of the C−H stretching vibrations.

Introduction

The importance of understanding the nature of intermolecular interactions, such as hydrogen bonding, has been recognized for some time.[1,2] A characteristic feature of hydrogen-bond formation in an X−H···Y system is X−H bond lengthening with a concomitant red shift of the X−H stretching frequency.[1,2] A number of experimental and theoretical studies have reported, however, the existence of an unusual class of blue-shifted hydrogen bonds in which H-bond formation leads to C−H bond shortening and to a blue shift of the C−H unit's IR stretching frequency.[3,4] Because C−H···O hydrogen bonds are typically weaker than those of the more conventional O−H···O and N−H···O hydrogen bonds, direct measurements of their strength are very difficult to achieve. Nevertheless, the widespread occurrence of C−H···O interactions has made them an active topic of research from both theoretical and experimental perspectives.[5−13] It has been suggested that C−H···O interactions play important functional and structural stabilization roles in biological systems.[4,5] Conclusive experimental evidence for the existence of C−H···O hydrogen bonding in biological macromolecules is notoriously difficult to obtain because C−H···O hydrogen bonds, which are typically weak in biological systems, usually coexist with many other types of strong interactions.[14−21] Because alcohol molecules are amphiphilic, that is, they possess both alkyl and hydroxyl groups, their hydrophobic and hydrophilic interactions are subtly balanced in aqueous alcohol solutions. Therefore, a detailed investigation of aqueous alcohol solutions may provide information necessary for understanding hydrophobic hydration mechanisms in biological systems.

Within the class of water-soluble monohydric alcohols, *tert*-butyl alcohol (TBA) is the molecule that has the largest alkyl group, and, hence, it exhibits the largest hydrophobic effect.[22−31] The other isomers of butyl alcohol (*n*-butyl, iso-butyl, and *sec*-butyl) are only sparsely soluble in water. At the same time, solutions of TBA in water show an anomalously large volume contraction, which indicates that the bulky trimethyl group must be more readily accommodated in the hydrated structure.[22] For these reasons, TBA appears to be the ideal candidate for investigating the variations in the structural and dynamical properties of C−H···O interactions. Indeed, a great deal of attention has been devoted to the hydration properties of TBA.[22−31] In computer simulation studies of aqueous TBA solutions, the hydration structure of TBA is observed to be markedly different from that of methanol, which indicates that the steric bulk of the *tert*-butyl group has a large effect on hydrogen bonding.[22,23] Extreme values of the physical properties exhibited by aqueous TBA solutions at the water-rich end of the composition scale have been observed by various techniques and are attributed to the effects of C−H···O interactions.[25−27] In our current investigation, we used pressure as a variable to explore the hydrophobic structure of aqueous TBA solutions and to alter the noncovalent interactions from van der Waals-types to hydrogen-bond-like interactions.

Although blue shifts of C−H frequencies were first detected experimentally several decades ago, it has been only recently that they have received much attention in the literature.[2−13] Despite the rather large number of papers devoted to the phenomenon of blue-shifting hydrogen bonds, the mechanism by which C−H bonds are strengthened by C−H···O interactions

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is still the subject of debate; two schools of thought have emerged to try to explain its physical basis.[3-7] Hobza et al. suggested[3] that the strengthened C−H bond originates from a new mechanism, called anti-hydrogen bonding. Scheiner[4] and Dannenberg,[5] however, view conventional and C−H···O hydrogen bonds to be very similar in nature, and that both types of hydrogen bonds result from a combination of electrostatic, polarization, charge-transfer, dispersion, and exchange/steric repulsion forces between the proton donor and acceptor. Additional factors, such as the anharmonicity and details of structurally mediated bond changes, may also be required for the correct explanation to be made. One of the underlying reasons for this controversy is the weakness of C−H···O interactions. Therefore, methods that enhance C−H···O interactions are crucial to provide scientists with a clear and unified view of this important phenomenon. Studies have shown the potential significance that pressure has on controlling the strength of C−H···O interactions.[18-21] In this study, we present a novel means of looking at this controversy, by using variable pressure as a window into the nature of C−H···O interactions.

The use of pressure as a variable allows one to change, in a controlled way, the intermolecular interactions without encountering the major perturbations produced by changes in temperature and chemical composition.[32,33] The pressures used to investigate biochemical systems typically range from ambient to several GPa; such pressures mainly change intermolecular distances and affect conformations.[33] In fact, pressures in excess of 30 GPa are required to change the electronic structure of a molecule.[33] For the pure solvent in general, it is well known that the hydrogen-bond network is distorted by pressure. For solutions, on the other hand, how the hydration shell responds to pressure variation remains to be investigated. In this paper, we report how in situ high-pressure FTIR spectroscopy using a diamond anvil cell (DAC) was applied to study the changes in C−H···O interactions of aqueous TBA solutions.

Experimental Section

Samples of binary mixtures were prepared using 99.5% *tert*-butyl alcohol (TBA) and 99.97% D_2O, supplied by Merck. A diamond anvil cell (DAC) of Merril-Bassett design, having a diamond culet size of 0.6 mm, was used for generating pressures up to ca. 3 GPa. Two type-IIa diamonds were used for mid-infrared measurements. The samples were contained in 0.3-mm-diameter holes in 0.25-mm-thick stainless steel gaskets mounted on the diamond anvil cell. To reduce the absorbance of the samples, CaF_2 crystals (prepared from a CaF_2 optical window) were placed into the holes and compressed firmly prior to inserting the samples. A droplet of a sample filled the empty space of the entire hole of the gasket in the DAC, which was subsequently sealed when the opposed anvils were pushed toward one another. Infrared spectra of the samples were measured on a Perkin-Elmer Fourier transform spectrophotometer (model Spectrum RXI) equipped with a LITA (lithium tantalate) mid-infrared detector. The infrared beam was condensed by a 5X beam condenser (Perkin-Elmer) onto the sample in the diamond anvil cell. Typically, we chose a resolution of 4 cm^{-1} (data point resolution of 2 cm^{-1}). For each spectrum, typically 1000 scans were compiled. To remove the absorption of the diamond anvils, the absorption spectra of DAC were measured first and subtracted from those of the samples.

Spectra of samples measured at ambient pressure were taken by filling the samples in a cell having two CaF_2 windows but lacking the spacers (thickness of samples $< 100\ \mu m$).

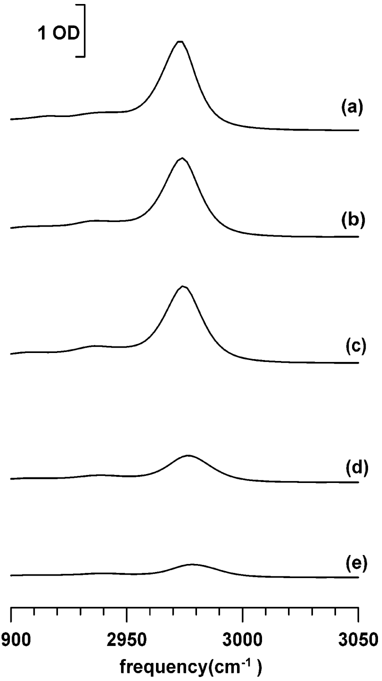

Figure 1. IR spectra displaying the region of the C−H stretching band of (a) pure TBA and of mixtures of TBA/D_2O having mole fractions of TBA equal to (b) 0.5, (c) 0.3, (d) 0.1, and (e) 0.04, respectively.

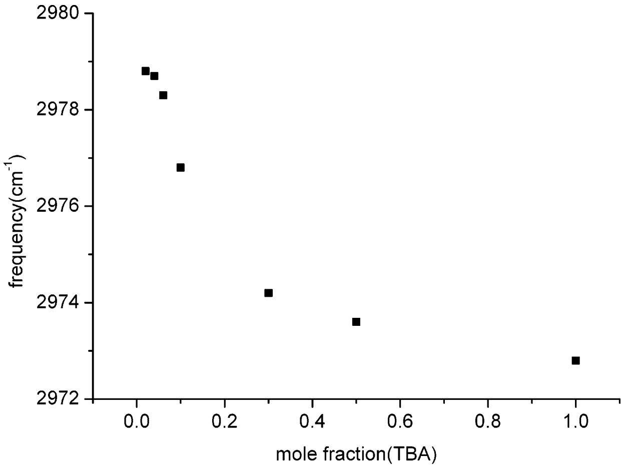

Figure 2. Concentration dependence of the C−H stretching frequency of TBA/D_2O versus the mole fraction of TBA.

Results and Discussion

Figure 1 presents infrared spectra of pure TBA (curve a) and TBA/D_2O mixtures having mole fractions of TBA equal to (b) 0.5, (c) 0.3, (d) 0.1, and (e) 0.04 within the frequency range 2900−3050 cm^{-1}. The C−H stretching of TBA overlaps with the O−H stretching bands of H_2O, so we studied C−H stretching vibrations at ambient pressure for TBA in a solution of D_2O,[26,27] rather than H_2O, by varying its concentration. Thus, the solutions contain mixtures of TBA−OH, TBA−OD, H_2O, HDO, and D_2O. We see that dilution of TBA leads to a shift of the C−H signal to higher frequencies. Previous studies have shown that the blue shifts of the C−H bands for TBA are closely related to changes in the liquid structure and hydration states of TBA.[26,27] Looking into more detail in Figure 2, we observe no drastic change in the concentration dependence of the C−H band frequency at high concentrations of TBA, that is, $0.5 \leq X_{TBA} \leq 1$. This behavior may indicate a clustering of the TBA molecules and a slight perturbation by the presence of D_2O. We stress that the C−H stretching absorption exhibits an

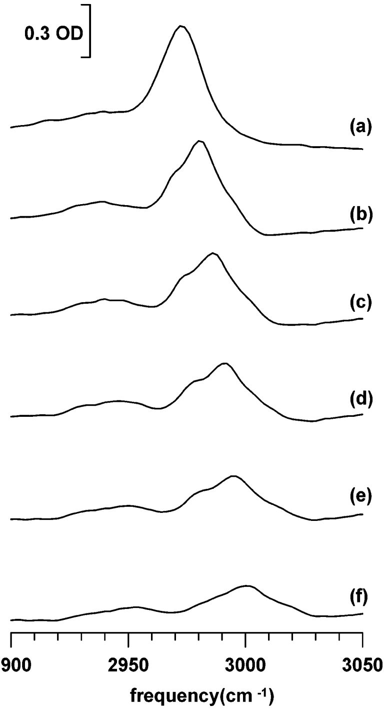

Figure 3. IR spectra displaying the C−H stretching region of pure TBA under (a) ambient pressure and at (b) 0.3, (c) 0.9, (d) 1.5, (e) 1.9, and (f) 2.3 GPa.

increase in frequency upon dilution at low concentration of TBA ($X_{TBA} < 0.5$), but its frequency appears to be constant in the range of very low concentrations ($X_{TBA} < 0.05$). The investigations reported so far have suggested the formation of a certain water structure around TBA molecules in water-rich regions ($X_{TBA} < 0.05$), but the details remain controversial.[22−31] Therefore, much more effort needs to be exerted to illustrate the nature of C−H bonds in aqueous TBA.

Figure 3 presents infrared spectra of pure TBA obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), and 2.3 GPa (curve f). Analyzing the pressure dependence of the dominant C−H stretch at ca. 2973 cm^{-1} yielded a blue frequency shift of ca. 11 cm^{-1}/GPa, which corresponds to contraction of the C−H bond. Because direct methyl group contacts are dominant in pure TBA, the blue shift observed in Figure 3 may originate from the overlap repulsion effect enhanced by hydrostatic pressure.[18] Pressure might also change the anharmonic nature of the potential well for C−H stretching in such a way as to increase the observed frequency. It is known that hydrogen-bonded networks can be modified by varying pressure.[1,20,21] Thus, the sharper structure revealed in Figure 3b−f is in part due to the higher order and anisotropic environment in a solid structure.

Figure 4 displays IR spectra of a TBA/D$_2$O mixture having its mole fraction of TBA equal to 0.09 obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), and 2.3 GPa (curve f). Analysis of the pressure dependence of the C−H absorption peaks yields blue frequency shifts at pressures below 0.3 GPa (Figs. 4a,b), but a further increase in pressure leads to a red frequency shift of the dominant C−H band (Figure 4c). This discontinuity in frequency shift should be related to the mechanism of C−H hydration, that is, enhanced C−H···O interactions.[35] By comparing Figures 3 and 4, the red shift in the frequency of the C−H bands is obvious in the dilute solution of TBA in D$_2$O (i.e., in Figure 4). Recently, consistent models have been proposed for the theoretical understanding of the C−H---O interactions. For example, when a molecule that is capable of forming blue-shifting hydrogen bonds binds to a site with a sufficiently strong electrostatic field to dominate over the overlap effect, that molecule is predicted to display a red-shifting hydrogen bond;[34] experimental evidence is still lacking, however. In this Article, we present a means of looking at this issue by employing the high-pressure method.[18−21] The spectral features in Figure 4, that is, their sensitivity to changes in concentration and pressure, may also arise from changes in the geometrical properties of the hydrogen-bond network. In the case of aqueous acetone, the enhancement of C−H···O interactions in the cyclic isomeric structure is attributed to both the cooperative and the geometric effects of hydrogen bonds.[35]

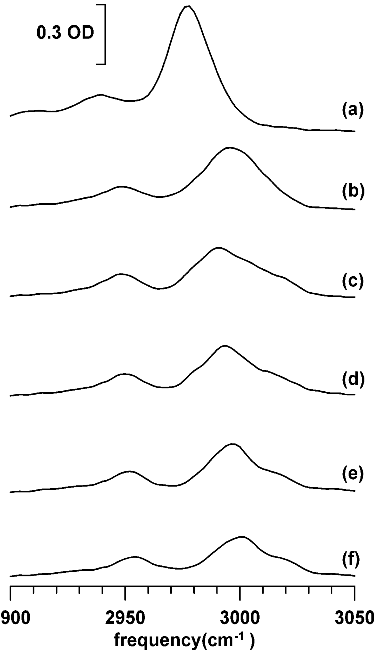

Figure 4. Pressure dependence of the C−H stretching in a TBA/D$_2$O mixture with a TBA mol fraction of 0.09 under the following pressures: (a) ambient, (b) 0.3 GPa, (c) 0.9 GPa, (d) 1.5 GPa, (e) 1.9 GPa, and (f) 2.3 GPa.

To obtain a direct comparison of the effects of varying the composition, we performed density functional theory calculations using the Gaussian 98 program package, which revealed the predicted structures displayed in Figure 5.[36] Density functional theory (DFT) calculations were performed at the B3LYP/6-31+G* level. The scaling factor for the calculated frequencies is 0.955. As illustrated in Figure 5a, the energetically most favored approach for the water molecule to interact with the TBA molecule is through the formation of O−H···O hydrogen bonds. The prominent C−H absorption band peaks at ~2979 cm^{-1} in Figure 5a and Table 1. Figure 5b depicts the optimized geometry of the low-energy isomer of TBA−(water)$_4$ with the participation of C−H···O interactions. By comparing Figure 5a and b, we find that the C−H band frequencies are blue shifted by ca. 4 cm^{-1}, as is indicated in Table 1. For instance, the prominent C−H absorption band is blue shifted in frequency to ~2982 cm^{-1} in Figure 5b. To develop further insight into the hydrophobic hydration mechanism of TBA, we calculated the stable hydrophobic isomeric forms of TBA−(water)$_n$ (n = 5, 6), which are displayed in Figure 5c and d. The frequencies of strong C−H stretching vibrations of TBA−(water)$_5$ are predicted to appear at ~2982 cm^{-1} for Figure 5c. Nevertheless, Figure 5d indicates the strongest absorption bands are switched to the lower energy bands at 2968 and 2973 cm^{-1} for TBA−(water)$_6$. As the clusters increase in size, the number

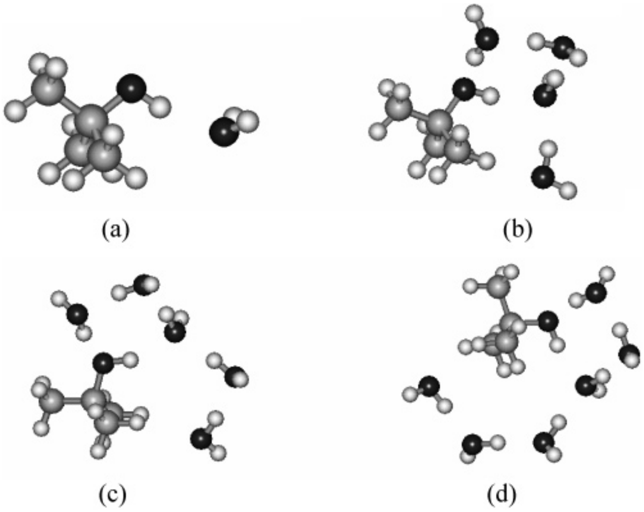

Figure 5. Optimized structures of (a) TBA−(water), (b) TBA−(water)$_4$, (c) TBA−(water)$_5$, and (d) TBA−(water)$_6$.

TABLE 1: DFT-Calculated C−H Stretching Frequencies (cm^{-1}) and Absorption Intensities (km/mol) of TBA/(water)$_n$[a]

species[a]	calcd. frequencies (intensities)[b−d]
a	2896 (31), 2901 (35), 2913 (15), 2955 (0.6), 2962 (65), 2971 (9), 2971 (12), **2979 (67)**, **2980 (46)**
b	2903 (32), 2906 (16), 2914 (22), 2965 (7), 2970 (18), 2974 (24), 2977 (34)-asym, **2982 (56)**, **2983 (10)**-sym
c	2904 (32), 2906 (19), 2914 (18), 2966 (2), 2969 (21), 2973 (35), 2980 (23)-asym, **2982 (54)**, **2986 (15)**-sym
d	2904 (31), 2907 (30), 2914 (4), 2964 (8), **2968 (48)**, **2973 (36)**, 2983 (15), 2989 (10)-asym, 2996 (21)-sym

[a] Structures illustrated in Figure 5. [b] Frequencies scaled by 0.955. [c] sym, symmetric C−H···O mode; asym, asymmetric C−H···O mode; the other unassigned modes are free C−H modes. [d] Essentially identical DFT results were obtained when replacing H_2O by D_2O.

of low-lying isomers increases exponentially. Thus, the structural identification of the hydrophobic isomers is complicated by the presence of more than one stable isomeric form. The questions of which clusters are responsible and how the weak hydrogen bond looks in detail may be settled by molecular dynamics, which is not the scope of this Article. It is instructive to note that DFT calculations may only provide qualitative support for the suggested C−H···O interactions, because the calculations are based on gas-phase structures.

It is known that in a hydrogen-bonding system XH/Y (where X−H is the hydrogen-bond donor and Y is the hydrogen-bond acceptor), the X−H stretching absorption band of the hydrogen-bonded species shifts toward lower frequency. In a comparison of Figure 4b and c, the red frequency shift revealed in the latter should arise from an enhancement of the strength of C−H···O interactions, that is, from C−H···O hydrogen bonding. We note that the frequency of the C−H stretching modes that characterize the C−H···OD_2 hydrogen bonding increases with increasing pressure, as is revealed in Figure 4c−f. The increase in the frequency of the vibration of the C−H bonds is a result of their decreased bond length. This behavior is in contrast with the general trend observed of a red shift with pressure for O−H and C═O stretching modes in strongly hydrogen-bonded O−H···O and C═O···H systems, respectively.[37−39] For instance, an increase in pressure shortens and strengthens the intermolecular hydrogen bond in ice VII, while intramolecular OH bonds lengthen as pressure is increased.[37−39] In C−H···O hydrogen bonding, the C−H unit acts as the proton donor. This type of hydrogen-bonding interaction is, in general, weak when compared to more-conventional hydrogen bonds.[2] It is instructive to note that the effect of Fermi resonance should not be excluded in this study. The Fermi resonance is typically observed between nearly resonance C−H stretch fundamentals and C−H bending overtones in many organic compounds. The pressure-dependent vibrational Fermi resonance of methanol has been investigated by measuring changes of Raman bands.[40] The methanol results revealed a pressure-induced transition through exact resonance at 1.25 GPa, where the two coupled states decompose into a pair of fully mixed hybrid bands.[40] We do not know how significant this effect is for *tert*-butyl alcohol. Recently, the "Fermi resonance" versus "C−H···O hydrogen-bonding" assignment is the subject of debate.[41,42] C−H···O hydrogen bonding plays a more significant role than Fermi resonance as revealed in refs 41 and 42. The C−H modes of ethane, ethane/CH_2Cl_2, and CH_3I were found to soften anomalously at high density, suggesting the formation of C−H hydrogen bonds.[43] The anomalous softening of C−H vibrations does not appear to be the result of pressure-dependent changes in Fermi resonance between the C−H stretch and overtone of the C−H bending vibration.[43]

Conclusions

In this paper, we show that high pressure has a pronounced effect on C−H···O interactions in aqueous *tert*-butyl alcohol. A pressure-dependent study of the C−H absorption bands indicated that the peak frequency of the strongest C−H stretch band of *tert*-butyl alcohol in a dilute D_2O solution has a unusual nonmonotonic pressure dependence; it initially blue shifts, then red shifts, then blue shifts again with increasing pressure. The unusual pressure shifts may be relevant to C−H···O hydrogen bonding. This study demonstrates that high pressure can be applied to aqueous *tert*-butyl alcohol mixtures to induce the transition from the van der Waals-type interactions to C−H···O hydrogen-bond formation.

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