

Hydration of the CH Groups in 1,4-Dioxane Probed by NMR and IR: Contribution of Blue-Shifting $\text{CH}\cdots\text{OH}_2$ Hydrogen Bonds

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^1H NMR and IR studies were carried out for 1,4-dioxane/ H_2O mixtures over the whole concentration range at temperatures of 1, 25, and 50 $^\circ\text{C}$. ^1H NMR spectra were also acquired for 1,3-dioxane/ H_2O and 4-methyl-1,3-dioxane/ H_2O mixtures. All the chemical shift data were measured by referring to an external reference and corrected using in situ bulk susceptibilities as determined on a unified scale. The results are compared with those previously obtained for dimethyl sulfoxide/ H_2O and acetone/ H_2O mixtures in order to determine the influence of the polar group on the hydrogen bond formation of water at the polar and hydrophobic groups. It was found that an anomalous polarization of the water molecules, which had been observed in the dimethyl sulfoxide/ H_2O and acetone/ H_2O mixtures, did not occur in the three different aqueous dioxane mixtures. Thus, we have concluded that the hydrophobic moiety in an organic solute having a polar group does not play a role in anomalously high polarization of the water molecules. We have also concluded that the hydrogen-bonding basicity of the polar group is an important factor for the anomalous polarization of the water in the water-rich region and that the basicities of the ether oxygens in the three dioxanes are not strong enough to cause the anomalous polarization of water. It was found that the frequencies of IR C–H stretching vibration modes of 1,4-dioxane increase and the absorption intensities of the modes decrease with increasing water concentration. Since these spectroscopic features correspond well to the formation of the blue-shifting $\text{C–H}\cdots\text{OH}_2$ hydrogen bonds obtained from ab initio calculations for complexations in gas phases, we can categorize the solvation of the C–H groups in the dioxanes in aqueous solutions as blue-shifting $\text{C–H}\cdots\text{O}$ hydrogen bonding. Thus, we propose for the first time that the hydration of CH groups in organic solutes having a polar group is due to the formation of blue-shifting $\text{C–H}\cdots\text{OH}_2$ hydrogen bonds. As a picture of the hydration of the C–H groups in 1,4-dioxane, we propose the formation of a bifunctional hydrogen-bonded hydration complex in which each water molecule plays a role as both a proton donor in the conventional $\text{O–H}\cdots\text{O}$ hydrogen bonding with the ether oxygen and a proton acceptor in the blue-shifting $\text{C–H}\cdots\text{O}$ hydrogen bonding simultaneously.

Introduction

It is of great importance to study the hydration of the hydrophobic parts of organic solutes having a polar group because we can obtain information about the contribution of the hydrophobic moieties in biopolymers to the structure in living cells.¹ When organic solutes with a polar group, e.g., alkyl alcohols, are mixed with water, they exhibit the same characteristic changes in thermodynamic properties as those observed for nonpolar solutes on hydrophobic hydration,² i.e., negative ΔH and ΔS and positive ΔC_p .³ An issue arises here; what role does the polar group play on hydration of the hydrophobic moieties?

In the paper presenting the iceberg structure model,⁴ Frank and Evans discussed the hydration of nonpolar moieties in alkyl alcohols as well as apolar solutes. They considered that the effect of hydrogen bonding between OH of the alcohols and water on the thermodynamic properties may be decreased by increasing the size of the alkyl moiety and concluded that the changes in the thermodynamic quantities for the aqueous alkyl alcohol systems could be interpreted in terms of the formation of the iceberg structure around the alkyl moieties, the same as those for aqueous nonpolar systems. More recently, it has been

reported that the highly negative enthalpy changes on solvation of apolar compounds in water can be conveniently explained on the basis of interactions between water and the apolar solutes without taking into account the increase and/or strengthening in the hydrogen bonding within hydration shells.^{3,5} In addition to several theoretical^{6–10} and simulation studies,¹¹ some experimental evidence supporting the current model has been provided by neutron scattering and EXAFS techniques.¹²

Thus, the interpretation of the effect of polar groups on hydration of hydrophobic moieties by Frank and Evans should be also reconsidered. The iceberg interpretation stands on the idea that the hydration shell around an alkyl moiety is independent and distinctive from that of the hydroxyl group. As such, the two hydration shells model has been extended to an additive model. For example, attempts to consider the hydration of polar organic solutes as an intramolecular overlap of the hydration shells around the hydrophobic moiety and the polar group have been reported.^{13,14} However, the results obtained show that the analysis on the basis of such an additive theory is inappropriate.¹⁵

While many thermodynamic quantities reflect bulk properties, molecular dynamics approaches can give useful information in generating atomic-level descriptions in agreement with experimental results. Meng and Kollmann reported that the hydration

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of the methyl groups in methane, ethane, methanol, acetate, and methylammonium changes continuously according to the nature of the neighboring functional groups, suggesting that the polar groups play dominant roles not only in the formation of hydrogen bonds with water but also in the hydration of the hydrophobic group.¹³

We are interested in the hydration of organic solutes having a polar group. Previously, we studied the changes in the polarization of water molecules and hydration state of C—H groups as a function of the concentration for acetone/H₂O and dimethyl sulfoxide/H₂O mixtures by probing the chemical shift of water protons and the frequency of IR C—H stretching vibration mode, $\delta_{\text{H}_2\text{O}}$ and $\nu(\text{C—H})$, respectively.^{16,17} We found that both the $\delta_{\text{H}_2\text{O}}$ and the $\nu(\text{C—H})$'s increase with increasing water concentration and are related to the hydrogen-bonding basicities of the polar groups in the solutes, in agreement with the suggestion by Meng and Kollman.¹³ A natural extension of this work is to study solutes having a lower hydrogen-bonding basicity than acetone. Thus, in the present work we chose three cyclic ethers: 1,4-dioxane, 1,3-dioxane, and 4-methyl-1,3-dioxane. The hydrogen-bonding basicity of the oxygens in 1,4-dioxane was reported to be smaller than that of the acetone carbonyl as probed by the frequency shift in the H—O—H bending vibration band of water.¹⁸ According to the IR studies by Berthelot et al., the hydrogen-bonding basicity of 1,4-dioxane is slightly greater than that of 1,3-dioxane.¹⁹

A variety of experimental techniques have been applied to 1,4-dioxane/H₂O mixtures to elucidate the liquid structure including calorimetry,²⁰ densitometry,^{21,22} X-ray diffraction,²³ neutron diffraction,²⁴ NMR relaxation,²³ IR,^{25,26} Raman,²⁷ and NMR chemical shift.^{28,29} Although Lee and Jonas concluded the formation of the iceberg structure at low concentrations of 1,4-dioxane/D₂O mixtures on the basis of spin—lattice relaxation time,³⁰ Hey and Jackson did not find any strengthening of the water—water hydrogen bonds in the water-rich region but only a net weakening of the hydrogen bonds over the whole concentration range.²⁶

Raman, IR, and NMR are useful techniques to experimentally obtain atomic-level descriptions to assess the roles of polar groups in the solvation of hydrophobic moieties of organic solutes in water. Carius et al. observed that the Raman $\nu(\text{C—H})$'s for acetone, dimethyl sulfoxide, and hexamethylphosphoric acid triamide exhibit blue shifts with increasing water concentrations, in contrast to the red shifts of the stretching bands for polar groups.³¹ Thomzik et al. obtained similar results for *n*-propylamine, piperidine, morpholine, and 1,4-dioxane to those obtained by Carius et al.³² The blue shift in the $\nu(\text{C—H})$ is contrary to what can be expected for the solvation of a C—H group by water acting as a polar solvent. The blue shift cannot be considered to be a result of conventional hydrogen-bonding interaction between the polar group and water either, because such an interaction would result in a red shift in the $\nu(\text{C—H})$ according to the conventional hydrogen bond concept. Kamogawa and Kitagawa found that the concentration dependence of the blue shifts in the $\nu(\text{C—H})$'s in Raman spectra of ethanol on mixing with water is very similar to that of the partial molar volume of ethanol; i.e., the blue shifts are closely related to the change in the liquid structure.³³ They also observed the blue shifts in the Raman $\nu(\text{C—H})$'s of aqueous 1,4-dioxane mixtures, while zero and red shifts were observed for the C—C and C—O stretching modes, respectively.²⁷ They concluded that the blue shift is a consequence of direct intermolecular interaction between C—H group and water, though the molecular force of the interaction was not discussed.

We previously proposed a mechanism for the blue shifts in the $\nu(\text{C—H})$'s in a hydration model for acetone, dimethyl sulfoxide, and *tert*-butyl alcohol.^{16,17,34} We inferred that a partial electron of the C—H hydrogen is pushed into the C—H bond by water oxygen due to a dispersion interaction, which results in a contraction of the C—H bond and thus gives rise to the blue shifts observed. However, we could not describe the observed concentration dependence of the chemical shift of the C—H protons using the model alone.

Recently, the roles of CH \cdots O hydrogen bonds in liquid methanol,³⁵ formic acid,³⁶ and other organic compounds have been studied,^{37,38} and the existence of a H₂C—H \cdots O hydrogen bond has been shown.^{35–39} Fundamental properties of C—H \cdots O interactions were discussed on the basis of the results of ab initio calculations for interactions in the gas phase by Scheiner et al.⁴⁰ They predicted not only the blue shifts in the $\nu(\text{C—H})$'s but also the decreases in the absorption intensity of the C—H stretching bands resulting from the formation of bimolecular complexes F_nH_{3–n}CH \cdots X, where X = H₂O, CH₃OH, or H₂CO. They concluded that there are no fundamental distinctions between conventional red-shifting hydrogen bonds and the blue-shifting hydrogen bonds.⁴⁰ Hobza and Havlas also carried out ab initio calculations for Y—C—H \cdots X interactions and proposed a new type of intermolecular binding mechanism called the “improper blue-shifting hydrogen bond”.⁴¹ Masunov et al. suggested that the C—H bond shortening should be explained in terms of the effect of the electric field exerted by the proton acceptor molecules.⁴² Hermansson proposed (i) the presence of a negative dipole moment derivative, $d\mu^0/d\gamma_{\text{CH}}$, for the isolated hydrogen bond donor molecule, as a dominant factor for blue-shifting hydrogen bonding to occur, and (ii) an additional blue shift due to electronic exchange overlap.⁴³

Now it must be elucidated if the blue shifts in the $\nu(\text{C—H})$'s observed for the aqueous solutions should be categorized as the same blue-shifting hydrogen bonds as those formed between a proton donor and a water molecule in the gas-phase calculations, because molecular interactions in aqueous solutions are much more complex than those in gas phases. Thus, in the present work, we studied both the changes in the $\nu(\text{C—H})$'s and the absorption intensities of the C—H stretching vibration bands as a function of water concentration. All the chemical shifts were measured with the external double reference method and are expressed on the same unified scale as in the previous studies.^{16,17,34} The results are discussed by referring to those obtained for acetone/H₂O and dimethyl sulfoxide/H₂O systems.

Experiments and Methods

Materials. Water was distilled twice after deionization. 1,4-Dioxane (Wako Pure Chemicals Co.), 1,3-dioxane (Tokyo Chemical Co.), and 4-methyl-1,3-dioxane (Nakarai Chemical Co.) were used without further purification. Deuterium oxide (99.7%) was from Eurisotop.

NMR Measurements. ¹H NMR spectra were measured with a JEOL EX-400 NMR spectrometer operating at 400 MHz at temperatures of 1.0, 25.0, and 50.0 °C with an accuracy of ± 0.1 °C. The temperature was calibrated with a thermocouple inserted into the sample tube set into the SCM probe prior to the measurements of sample solutions.

All the chemical shifts were measured by the external reference method^{16,44,45} and corrected in terms of the difference in bulk volume magnetic susceptibilities between the sample and a reference solution (liquid tetramethylsilane) obtained in situ at every temperature. In previous works, the chemical shift data at 1.0 and 50.0 °C were corrected with respect to the

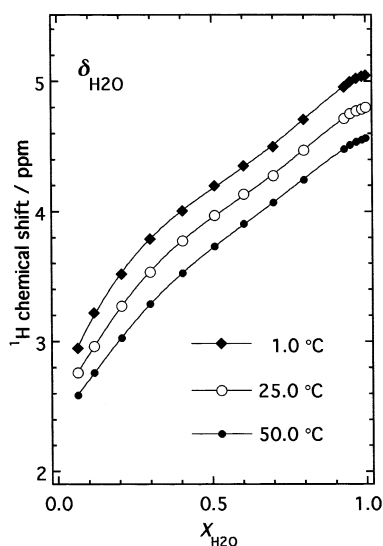


Figure 1. $\delta_{\text{H}_2\text{O}}$ for 1,4-dioxane/ H_2O mixtures vs $X_{\text{H}_2\text{O}}$ at 1.0, 25.0, and 50.0 °C.

temperature dependence of the chemical shift of the reference solution.^{17,34} In the present work for the first time, we took also the temperature dependence of the bulk volume magnetic susceptibility of the reference solution. Thus, the data at 1.0 and 50.0 °C were corrected with respect to the temperature dependence of both the chemical shift and the susceptibility of the reference solution to refer all the data to the peak of liquid TMS at 25.0 °C and to compare them on the unified scale. We call the method an external double-reference method. The digital resolutions of the chemical shifts were 0.0012 ppm, and the total experimental errors are within ± 0.005 ppm.

IR Measurements. IR spectra were obtained with a JASCO FT-IR/620 spectrometer at 23 °C using several liquid cells of calcium fluoride windows with path lengths ranging from 0.015 to 2.0 mm. The resolution was 2 cm^{-1} , and the data were encoded every 0.5 cm^{-1} .

Results

1,4-Dioxane/ H_2O Mixtures. Figure 1 shows the concentration dependence of ^1H chemical shifts of water, $\delta_{\text{H}_2\text{O}}$, for 1,4-dioxane/ H_2O mixtures at 1.0, 25.0, and 50.0 °C. $\delta_{\text{H}_2\text{O}}$ values at the mole fraction of water $X_{\text{H}_2\text{O}} = 0.05$ are in the range 2.6–2.9 ppm, 2 ppm less than the value for pure water, indicating that the polarization of the water molecules in the 1,4-dioxane-rich region is much less than that of pure water. With increasing $X_{\text{H}_2\text{O}}$, $\delta_{\text{H}_2\text{O}}$ increases until reaching the value for pure water, suggesting that the anomalous polarization of the water molecules observed for acetone/ H_2O and dimethyl sulfoxide/ H_2O mixtures^{16,17} does not occur in 1,4-dioxane/ H_2O mixtures. However, $\delta_{\text{H}_2\text{O}}$ is not the value for the water molecules in the hydration shell, but simply an average value over all the water molecules in the sample solution. Thus, a value of $\delta_{\text{H}_2\text{O}}$ smaller than that for pure water does not completely deny the contribution of highly polarized water molecules.

We obtained IR spectra of 1,4-dioxane/($\text{D}_2\text{O} + \text{H}_2\text{O}$) mixtures, where $\text{D}_2\text{O}:\text{H}_2\text{O}$ was 95:5 by volume ratio, and all the H_2O molecules were found to be converted to HOD. Figure 2 shows the spectra of O–H stretching vibration band of HOD at small mole fractions of 1,4-dioxane, $X_{\text{dio}} \leq 0.20$. The absorbances are multiplied to be the same as that of the spectrum for pure water ($X_{\text{dio}} = 0.0$) in order to study the change in the half-width of the bands with concentration. Figure 3 shows the

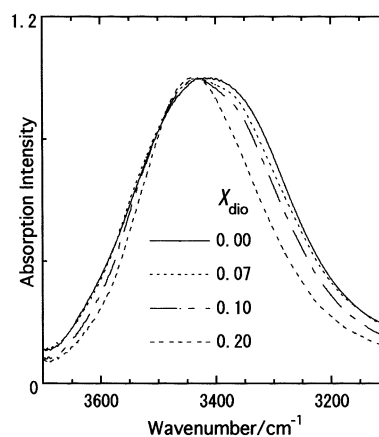


Figure 2. IR spectra for the O–H vibration mode of HOD in 1,4-dioxane/($\text{D}_2\text{O} + \text{H}_2\text{O}$; 95:5 by volume) mixtures at the mole fractions of 1,4-dioxane from 0.00 to 0.20.

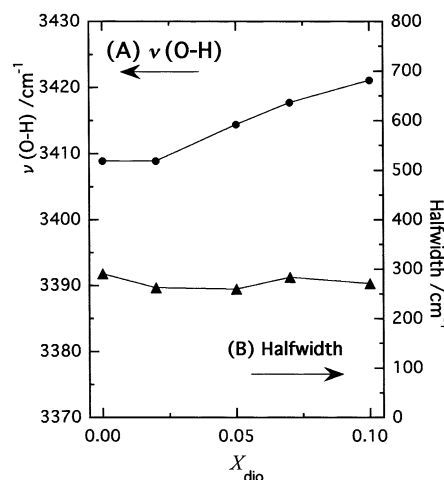


Figure 3. Wavenumber, (A) $\nu(\text{O–H})$, and the (B) half-width of the O–H vibration mode for HOD in 1,4-dioxane/($\text{D}_2\text{O} + \text{H}_2\text{O}$; 95:5 by volume) mixtures vs the mole fraction of 1,4-dioxane.

wavenumber, $\nu(\text{O–H})$, and the half-width of the O–H stretching band for HOD plotted as functions of X_{dio} . Only blue shifts and narrowings of the band occur with increasing X_{dio} , confirming the reduction in hydrogen-bonding strength of ($\text{HOD} + \text{D}_2\text{O}$) in mixtures with 1,4-dioxane. The results show the absence of anomalously high polarization of water in 1,4-dioxane/ H_2O mixtures, in agreement with the result of the $\delta_{\text{H}_2\text{O}}$ measurement above.

Water structure in 1,4-dioxane/ H_2O mixtures in the water-rich region has been the subject of many studies.^{20–30} In the present work, we present experimental evidence based on NMR and IR studies confirming the “reduction” in the polarization and hydrogen-bonding strength of the water molecules from those of bulk water, in addition to the studies so far reported.^{23,24,26}

Figure 4 shows the changes in the IR spectra of C–H stretching modes for 1,4-dioxane in water with X_{dio} . The molar absorption coefficient per 1 mm path length is taken as the longitudinal axis. The IR spectrum of liquid 1,4-dioxane exhibits absorption bands at 2960 and 2850 cm^{-1} assigned as C–H stretching modes of equatorial CH and axial CH groups,⁴⁶ and the wavenumbers of the bands are denoted below as $\nu(\text{C–H})_e$ and $\nu(\text{C–H})_a$, respectively. The bands shift to the higher wavenumber side, and the absorption intensities decrease with decreasing X_{dio} . The decreases in the absorption intensity of the band for the axial CH are especially great. While we have

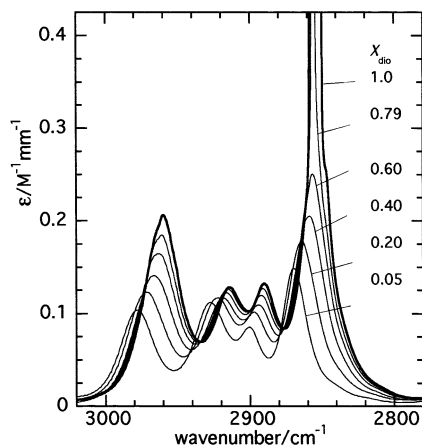


Figure 4. Changes in the IR spectra of C–H stretching modes for 1,4-dioxane/H₂O with the mole fraction of 1,4-dioxane.

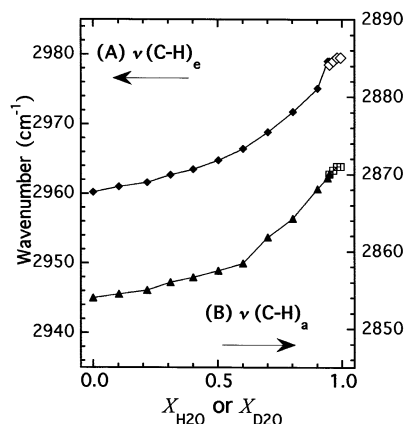


Figure 5. Concentration dependence of (A) $\nu(\text{C-H})_e$ and (B) $\nu(\text{C-H})_a$ for 1,4-dioxane/H₂O ($X_{\text{H}_2\text{O}} \leq 0.93$) and 1,4-dioxane/D₂O ($X_{\text{D}_2\text{O}} \geq 0.93$).

reported the blue shifts in $\nu(\text{C-H})$'s for acetone,¹⁶ dimethyl sulfoxide,¹⁷ and *tert*-butyl alcohol³⁴ in aqueous solutions with decreasing solute concentrations, we have paid no attention to the changes in the absorption intensities of the bands with concentration. In the present work, we calculated the molar absorption intensities of the C–H stretching modes for the solutes in the previous works as well as those for 1,4-dioxane and found that they also decrease with decreasing solute concentrations.

The concentration dependence of $\nu(\text{C-H})_e$ and $\nu(\text{C-H})_a$ was studied for 1,4-dioxane/H₂O mixtures up to $X_{\text{H}_2\text{O}} = 0.93$ and for 1,4-dioxane/D₂O mixtures at $X_{\text{D}_2\text{O}} \geq 0.93$ and is plotted against $X_{\text{H}_2\text{O}}$ or $X_{\text{D}_2\text{O}}$ in Figure 5. The blue shifts correspond well to the corresponding Raman bands reported by Kamogawa and Kitagawa,²⁷ who concluded that the blue shifts are the consequences of direct hydration of the C–H groups. We also obtained the IR spectra of the mixtures at 40 and 60 °C and found $\nu(\text{C-H})_a$ and $\nu(\text{C-H})_e$ to be independent of temperature over the range 23–60 °C.

The ¹H chemical shift for the four magnetically equivalent CH₂ groups in 1,4-dioxane, δ_{CH} , is plotted vs $X_{\text{H}_2\text{O}}$ in Figure 6. Whereas δ_{CH} increases with increasing $X_{\text{H}_2\text{O}}$ up to ca. $X_{\text{H}_2\text{O}} = 0.95$ as well as $\delta_{\text{H}_2\text{O}}$, it does not almost change with temperature unlike $\delta_{\text{H}_2\text{O}}$. On the other hand, the concentration dependence of δ_{CH} is similar to that of $\nu(\text{C-H})_e$ and $\nu(\text{C-H})_a$ as seen from the comparison between Figures 5 and 6, and both the δ_{CH} and $\nu(\text{C-H})$'s are independent of temperature.

Figure 7 shows the changes in the IR spectra of H–C–H

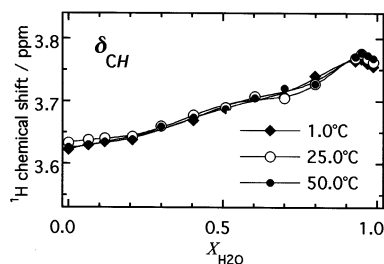


Figure 6. δ_{CH} for 1,4-dioxane/H₂O mixtures vs $X_{\text{H}_2\text{O}}$ at 1.0, 25.0, and 50.0 °C.

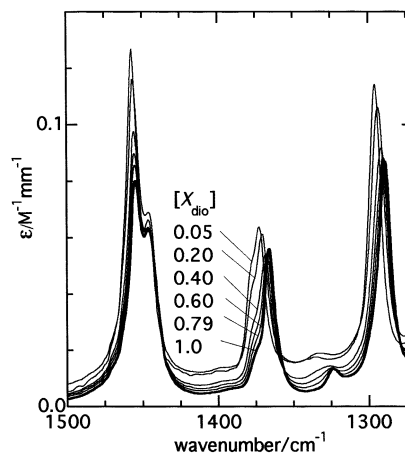


Figure 7. Changes in the IR spectra of H–C–H and O–C–H bending modes for 1,4-dioxane/H₂O with the mole fraction of 1,4-dioxane.

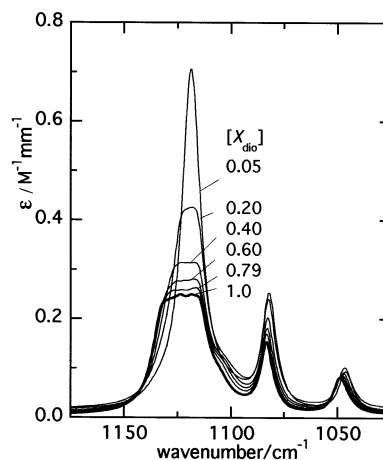


Figure 8. Changes in the IR spectra of C–O stretching mode for 1,4-dioxane/H₂O with the mole fraction of 1,4-dioxane.

and O–C–H bending modes for 1,4-dioxane in water with X_{dio} . The three absorption bands of liquid 1,4-dioxane at 1455, 1366, and 1290 cm^{−1} are assigned as H–C–H, O–C–H, and O–C–H bending modes, respectively.⁴⁶ The bending vibration bands also shift to higher wavenumber side with decreasing X_{dio} , though the shifts are much smaller than those observed for $\nu(\text{C-H})_e$ and $\nu(\text{C-H})_a$. The blue shifts in the bending vibration modes imply that the CH groups are subjected to attractive interaction with water molecules.

Figure 8 shows the changes in the IR spectra of the C–O stretching vibration mode for 1,4-dioxane in water with X_{dio} . The C–O band for liquid 1,4-dioxane is broad and shifts to the lower wavenumber side, and the absorption intensity increases with decreasing X_{dio} . These can be attributed to the formation of a conventional O–H···O hydrogen bond between water and the ether oxygen.

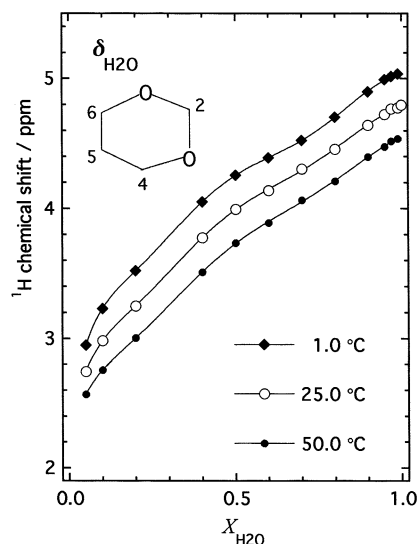


Figure 9. $\delta_{\text{H}_2\text{O}}$ for 1,3-dioxane/ H_2O mixtures vs $X_{\text{H}_2\text{O}}$ at 1.0, 25.0, and 50.0 °C.

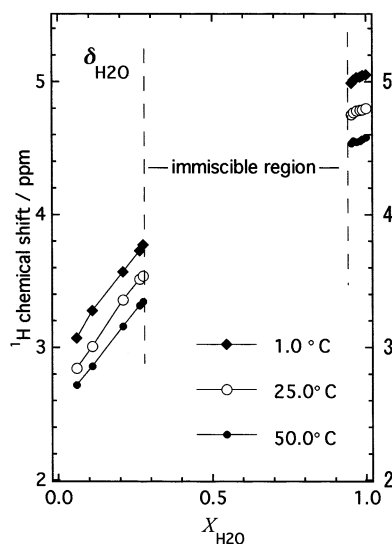


Figure 10. $\delta_{\text{H}_2\text{O}}$ for 4-methyl-1,3-dioxane/ H_2O mixtures vs $X_{\text{H}_2\text{O}}$ at 1.0, 25.0, and 50.0 °C.

1,3-Dioxane/ H_2O and 4-Methyl-1,3-dioxane/ H_2O Mixtures.

Figures 9 and 10 show the concentration dependence of $\delta_{\text{H}_2\text{O}}$ for 1,3-dioxane/ H_2O and 4-methyl-1,3-dioxane/ H_2O mixtures at 1.0, 25.0, and 50.0 °C, respectively. 4-Methyl-1,3-dioxane is soluble in water in the limited regions of $X_{\text{H}_2\text{O}} < 0.37$ and $X_{\text{H}_2\text{O}} > 0.95$. In Figure 9, $\delta_{\text{H}_2\text{O}}$ does not exceed the value for pure water but decreases with increasing 1,3-dioxane. $\delta_{\text{H}_2\text{O}}$ values in the water-rich region of 4-methyl-1,3-dioxane/ H_2O mixtures also do not exceed the value for pure water.

Discussion

Effects of Polar Groups on the Polarization of Water. $\delta_{\text{H}_2\text{O}}$ vs $X_{\text{H}_2\text{O}}$ curves for the three different dioxane/ H_2O systems at 25.0 °C are shown in Figure 11 together with those for acetone/ H_2O and dimethyl sulfoxide/ H_2O systems obtained in previous works.^{16,17} The curves for 1,4-dioxane/ H_2O and 1,3-dioxane/ H_2O are similar to each other despite the different atomic arrangements. The curve of $\delta_{\text{H}_2\text{O}}$ for 4-methyl-1,3-dioxane/ H_2O systems in the water-rich region does not exceed the value for pure water, suggesting that the hydrophobic moiety in 4-methyl-1,3-dioxane, $-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-$, does not contribute to

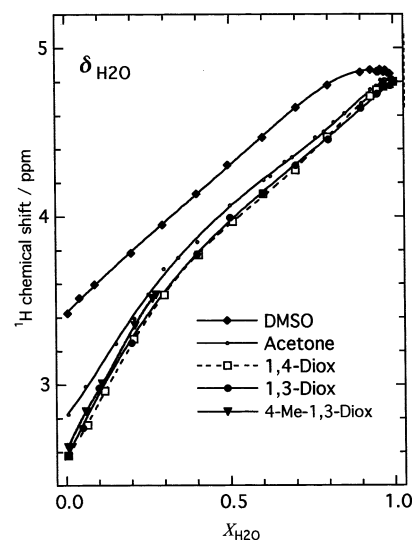


Figure 11. $\delta_{\text{H}_2\text{O}}$ for aqueous binary mixtures of dimethyl sulfoxide, acetone, 1,4-dioxane, 1,3-dioxane, and 4-methyl-1,3-dioxane vs $X_{\text{H}_2\text{O}}$ at 25 °C.

anomalous polarization of water molecules. In previous works, on the other hand, we found that dimethyl sulfoxide has a much larger effect on the polarization of water molecules than acetone as shown in Figure 11, though both solutes have hydrophobic moieties of the same size. Then it follows that, in aqueous mixtures of the organic solutes we have so far investigated, the hydrophobic moieties themselves play no dominant role in inducing anomalous polarization of the water in the water-rich region, in agreement with the results of several simulation and experimental studies carried out for 1,4-dioxane/ H_2O mixtures.^{23,24,26}

The polarity of $\text{S}=\text{O}$ in dimethyl sulfoxide is greater than that of $\text{C}=\text{O}$ in acetone, and we can attribute the difference in the effect of dimethyl sulfoxide and acetone on polarization of water qualitatively to that of the polarity and hydrogen-bonding basicity between them. The hydrogen-bonding basicities of the ether oxygens in 1,4-dioxane are smaller than that of the acetone carbonyl.¹⁸ Thus, we can consider that the hydrogen-bonding basicities of the dioxanes are not large enough to induce anomalous polarization of surrounding water molecules. According to the studies by Berthelot et al., on the other hand, hydrogen-bonding basicity of 1,4-dioxane is a little greater than that of 1,3-dioxane, but the difference in the basicity between them is not reflected in the $\delta_{\text{H}_2\text{O}}$ curves. This implies that there is another factor affecting the polarization of water besides the polarity of the functional group.

A Category of the Blue Shifts in $\nu(\text{C}-\text{H})$'s for Aqueous Organic Solutions. The results of IR analysis show that the blue shifts in the frequencies and the decreases in the absorption intensities of the $\text{C}-\text{H}$ stretching vibration modes occur with increasing water concentrations not only in the three dioxane/ H_2O mixtures but also in acetone/ H_2O and dimethyl sulfoxide/ H_2O mixtures. This was predicted by Scheiner et al. in ab initio calculations for bimolecular blue-shifting $\text{CH}\cdots\text{O}$ hydrogen-bonding complexation in gas phases.⁴⁰ Therefore, it is reasonable for us to categorize the interaction between CH groups and water in the dioxane/ H_2O mixtures as blue-shifting hydrogen bonding.

Whereas the $\delta_{\text{H}_2\text{O}}$ for the three dioxane/ H_2O mixtures changes $\approx +2.2$ ppm over the whole concentration range, δ_{CH} changes only $\approx +0.15$ ppm. Such a small change in the chemical shift can be measured accurately only with the combination of an external reference method and a correction in terms of in situ

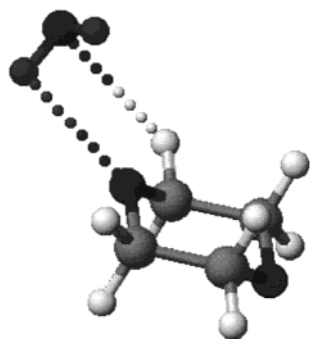


Figure 12. Bifunctionally hydrogen-bonded hydration complex of 1,4-dioxane.

bulk magnetic susceptibilities. Our NMR measurements indicate that the δ_{CH} of 1,4-dioxane increases slightly with increasing water concentration but does not change with temperature between 1 and 50.0 °C.

Hydration of CH Groups through Bifunctional Hydrogen Bonds. The blue shifts in the $\nu(\text{C-H})$'s for 1,4-dioxane begin at the lowest water concentrations analyzed as shown in Figure 5, indicating that $\text{CH}\cdots\text{OH}_2$ blue-shifting hydrogen bonding begins together with hydrogen-bonding interaction between the ether oxygen and water. This leads to a conception of a bifunctionally hydrogen-bonding hydration complex in which a water molecule plays the roles of both a proton donor in a conventional $\text{OH}\cdots\text{O}$ hydrogen bonding with an ether oxygen and an acceptor in $\text{CH}\cdots\text{OH}_2$ blue-shifting hydrogen bonding, as shown in Figure 12. For this model, the atomic arrangement of a solute necessary in order to form a bifunctionally hydrogen-bonding hydration complex is also an important factor for stable complexation between water and CH groups, in addition to the hydrogen-bonding basicity of the polar group. The interpretation of hydration of CH groups in terms of a bifunctionally hydrogen-bonding hydration complex may throw light on the hydration of hydrophobic moieties in organic solutes having a polar group, especially in optically active biopolymers such as proteins.

Formation of Hydration Clusters. Maxima in the $\nu(\text{C-H})$ vs $X_{\text{H}_2\text{O}}$ curves were observed for dimethyl sulfoxide/ H_2O , acetone/ H_2O , and *tert*-butyl alcohol/ H_2O mixtures at high mole fractions of water. The decreases in the $\nu(\text{C-H})$ are related to the changes in the property of the C-H bond due to the formation of hydration clusters.^{16,17,34} We believe that the ether oxygens may play a role in anchoring the first water molecule to the dioxane at a low concentration of water and that $\text{OH}\cdots\text{O}$, $\text{CH}\cdots\text{OH}_2$, and $\text{OH}\cdots\text{OH}_2$ hydrogen bonds are formed cooperatively by the following water molecules as they surround the whole dioxane. Then at high concentrations of water, the $\text{CH}\cdots\text{OH}_2$ hydrogen bonds should become as strong as the conventional red-shifting hydrogen bonds because of the strong polarization of the water molecules.^{16,17,34} Hermansson showed that the blue-shifting CH_4 and its relatives can also give rise to red-shifting hydrogen bonds when the electric field from the acceptor is sufficiently strong at the intermolecular equilibrium distance.⁴³ This supports the above concept that the decreases in $\nu(\text{C-H})$'s at high mole fractions of water are related to the strong polarization of the water molecules verified by large values of $\delta_{\text{H}_2\text{O}}$ and to the formation of hydration clusters.

Matsuo et al. confirmed a very shallow minimum in the partial molar volume of 1,4-dioxane at $X_{\text{H}_2\text{O}}$ ca. 0.97 at 25 °C, which they interpreted in terms of structural changes of water.²¹ Sakurai, who also observed the minimum, disagreed with the interpretation.²² We also observed a low maximum in δ_{CH} vs $X_{\text{H}_2\text{O}}$ curve near $X_{\text{H}_2\text{O}} = 1$ for 1,4-dioxane and the ending of

the blue shift in $\nu(\text{C-H})$ at high mole fractions of water, which implies that the dioxane molecules form hydration clusters within which $\text{OH}\cdots\text{O}$, $\text{CH}\cdots\text{OH}_2$, and $\text{OH}\cdots\text{OH}_2$ hydrogen bonds are formed cooperatively.

A Mechanism for Hydrophobic Hydration. Inglesse et al. reported the molar excess enthalpy, H_E , of the 1,4-dioxane/ H_2O system over the whole concentration range.²⁰ The mixing is exothermic in the water-rich region, and a H_E vs $X_{\text{H}_2\text{O}}$ curve has a minimum at $X_{\text{H}_2\text{O}} = 0.85$, exhibiting a so-called hydrophobic hydration. They concluded that the exothermic contribution was derived from an increase or rearrangement of the water structure by the formation of hydrogen bonds. However, hydrogen-bonding strength of the water becomes weaker with an increasing 1,4-dioxane concentration as probed by the decrease in $\delta_{\text{H}_2\text{O}}$ shown in Figure 1. This means that as far as the $\text{OH}\cdots\text{O}$ and $\text{OH}\cdots\text{OH}_2$ hydrogen-bonding interaction of water is concerned, the mixing is endothermic over the whole concentration. Thus, the exothermic contribution should be considered as being derived from some interaction of water other than the $\text{OH}\cdots\text{O}$ and $\text{OH}\cdots\text{OH}_2$ hydrogen-bonding interaction.

The stabilization energy, ΔE , of the $\text{C-H}\cdots\text{OH}_2$ interaction has been calculated by some groups,^{40,47} and ΔE ranges from 0.2 kcal/mol for the methane-water complex to 3.2 or 3.7 kcal/mol for the $\text{F}_3\text{CH}\cdots\text{OH}_2$ complex. The ΔE for water dimer $\text{HO-H}\cdots\text{OH}_2$ is 4.8–5.1 kcal/mol. So, it is reasonable to consider that the $\text{C-H}\cdots\text{OH}_2$ interaction in the 1,4-dioxane/ H_2O system should be exothermic and that the contribution to the negative ΔH becomes larger with increases in the blue shifts of $\nu(\text{C-H})$'s as exemplified in the calculations by Gu et al.⁴⁰ The blue shifts in $\nu(\text{C-H})$'s are largest in the water-rich region. Then it follows that we may attribute the $\text{C-H}\cdots\text{OH}_2$ interaction as the dominant cause of not only the large negative ΔH but also the negative change in entropy resulting from molecular arrangement occurring during the formation of the bifunctionally hydrogen-bonding hydration complex presented above.

Conclusion

The hydrogen-bonding strength of the water molecules in the three different dioxane/ H_2O systems decreases with increasing dioxane concentrations. From these results, together with those previously obtained, it can be concluded that the hydrophobic moiety in an organic solute with a polar group does not play a role in inducing anomalous polarization of the water molecules. The hydrogen-bonding basicity of the polar group is an important factor for the occurrence of the anomalous polarization of the water molecules in acetone/ H_2O and dimethyl sulfoxide/ H_2O mixtures. Thus, it follows that the hydrogen-bonding basicities of the three dioxanes are not strong enough to induce anomalous polarization of the water molecules.

Hydration of the C-H groups in 1,4-dioxane is characterized by the blue shifts in $\nu(\text{C-H})$'s and decreases in the absorption intensities of the IR C-H stretching bands as well as the small increase in δ_{CH} with increasing $X_{\text{H}_2\text{O}}$. Since these spectroscopic features correspond well to the formation of the blue-shifting $\text{C-H}\cdots\text{O}$ hydrogen bond, we can categorize the solvation of the C-H groups in the dioxanes in water as blue-shifting $\text{C-H}\cdots\text{O}$ hydrogen bonding. We propose the formation of a bifunctionally hydrogen-bonding hydration complex, in which water molecules play the roles of both a proton donor in conventional $\text{HO-H}\cdots\text{O}$ hydrogen bond and an acceptor in blue-shifting $\text{C-H}\cdots\text{OH}_2$ hydrogen bond simultaneously. Thus, we may attribute the formation of the bifunctionally hydrogen-bonding hydration complexes to the hydrophobic hydration of the dioxanes.

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