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IR Study of Hydrogen Bonds in Halogenoalcohol−Water Mixtures

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The IR bending vibrational (ν_2) band of the water molecules in aqueous haloethanol (XCH_2CH_2OH; X = Cl, Br, I) mixtures has been studied, and the haloethanols are found to give rise to red shifts of the ν_2 band. Since the frequency of the ν_2 band is reciprocally proportional to the hydrogen-bonding strength of water molecules, the results lead us to a conclusion that a breakdown of water structure occurs in the mixtures. The red shifts occur gradually in the whole range of the haloethanol concentrations, showing gradual breakdown of the water structure with an increase in the alcohol concentration. The effect of the alcohols on the red shift is found to be in the order $ClCH_2CH_2OH < BrCH_2CH_2OH < ICH_2CH_2OH$. The red shifts are discussed in comparison with the blue shifts of the ν_2 band previously observed for the aqueous ethanol mixtures. The conclusion is consistent with that of the ^{1}H-NMR studies of the same mixtures in which the water structure is discussed in terms of the chemical shift of the water proton.

Introduction

We have been interested in the water structure in binary aqueous mixtures of halogenated alcohols such as 2-chloroethanol (ClC_2H_4OH), 2-bromoethanol (BrC_2H_4OH), 2-iodoethanol (IC_2H_4OH), and 3-chloro-1-propanol.[1] ^{1}H- and ^{17}O-NMR studies of these mixtures indicate that the hydrogen bonds of the water molecules become weak and the water structure breaks down with an increase in the alcohol concentration, the number of halogen atoms, or the size of halogen atom in the alcohols.[2,3] The measurements of the relaxation time of water ^{17}O in the same mixtures revealed that the breakdown of the water structure occurs around the halogen atoms of the alcohols.[3] On the basis of these results, we presented a mechanism of the breakdown;[2] the halogen atoms behave as weak proton acceptors in hydrogen-bonding interaction with the surrounding water molecules, which results in the reduction of the polarity and hydrogen-bonding strength of other water molecules in the vicinity of the halogen atoms. A dipole−dipole interaction between the halogen atoms and the surrounding water molecules is also responsible for the breakdown.

In the ^{1}H-NMR spectra of all the aqueous halogenoalcohol mixtures[2] and of aqueous ethanol (EtOH) mixtures at low EtOH concentrations,[4] the resonance peaks of water and alcohol OH protons coalesce into a single peak because of a rapid proton exchange. The coalescing peak shifts to high field and to low field with the increase in concentrations of the halogenoalcohols and EtOH, respectively. Consequently, we evaluated the chemical shift of the water ^{1}H from that of the coalescing peak on the basis of an approximation that the high-field and the low-field shifts of the coalescing peak should be entirely due to the water ^{1}H resonance peak. The approximation is reasonable at low alcohol concentrations, but some uncertainty is left in the chemcial shift of the water ^{1}H thus evaluated at high alcohol concentrations. Even if the resonance peaks of water and alcohol are separated as in ^{17}O-NMR, the chemical shift of the observed water ^{1}H peak still gives only the weighted mean value for all the water molecule species present in different hydrogen-bonding states in a mixture because of the long time scale of NMR measurements. In other words, information about the distribution of the hydrogen-bonding strengths among the water molecules is hardly obtained from NMR measurements. Physicochemical properties of the water in aqueous alcohol mixtures have been studied widely with X-ray or light scattering, dielectric relaxation, thermodynamic, and many other methods as well as NMR.[5,6] Among these methods, IR spectroscopy is one of the most promising ones for the study of the distribution of hydrogen-bonding strengths of the water molecules in the mixtures because of the short time scale of measurements.

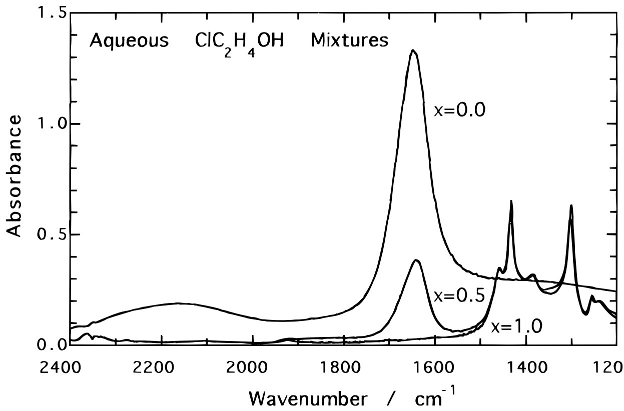

Figure 1. IR spectra of pure water, pure ClC_2H_4OH, and the aqueous ClC_2H_4OH mixture at $x = 0.5$ in the region of 2400−1200 cm^{-1}.

Since the O−H stretching vibrational (ν_1 and ν_3) bands of water overlap the alcoholic O−H band, the IR spectra in the stretching region are of no use for studying hydrogen bonds of the water molecules in aqueous alcohol mixtures. In the region of the bending vibrational (ν_2) band of water, on the other hand, alcohols have no absorption bands so that the IR spectra in the bending region are available for the present study. Falk found that there is an inverse proportionality of the bending frequency to the stretching frequency.[7] We actually observed blue shifts of the ν_2 band, i.e., strengthening of hydrogen bonds, for the water molecules in aqueous EtOH mixtures for which ^{1}H-NMR studies also revealed the formation of stronger hydrogen bonds

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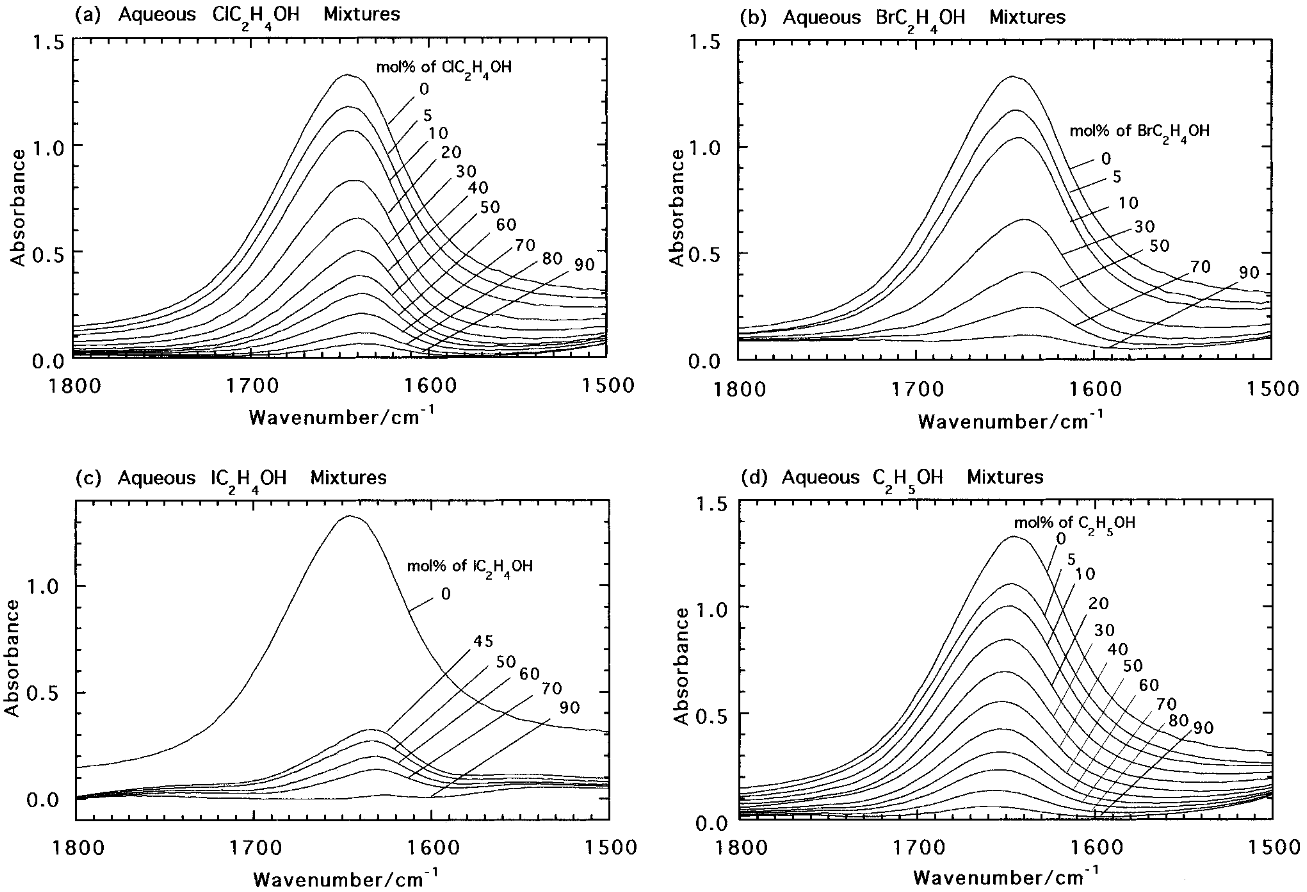

Figure 2. IR spectra in the region of 1800−1500 cm^{-1} of aqueous mixtures at various alcohol mol. %: (a) ClC_2H_4OH, (b) BrC_2H_4OH, (c) IC_2H_4OH, and (d) EtOH.

among water molecules with increasing EtOH concentration.[4] We obtained a good correspondence between the concentration dependences of the hydrogen-bonding strengths determined in terms of the chemical shift of water ^1H and the frequency of the ν_2 band.[4] The frequency shifts of the ν_2 band are much smaller than those of the stretching bands. However, one ν_2 band is assigned strictly to one distinct species of water molecules present in solution, in contrast with the presence of two stretching bands.[8] Thus, the number of observed ν_2 bands should provide the number of water species with different hydrogen-bonding strengths. Consequently, the spectra of the ν_2 band for the water molecules in organic solvents have been the subject of a number of investigations.[8] In the present work, we measured FT-IR spectra of aqueous haloethanol mixtures to verify the conclusions of the previous ^1H- and ^{17}O-NMR studies of the same mixtures.

Experimental Section

Materials. Water was deionized and distilled twice. ClC_2H_4OH and EtOH were purchased from Wako Pure Chemical, BrC_2H_4OH from Tokyo Kasei Organic Chemicals, and IC_2H_4OH from Aldrich. Alcohols were preserved with 3 Å molecular sieves and distilled in vacuo. The compositions of the mixtures are denoted by the mole fraction, x, or mol % of the alcohols. IC_2H_4OH is not miscible with water in the range $0.02 < x < 0.4$.

Measurements. IR spectra were measured at 22 ± 1 °C in a N_2 gas atmosphere with a JASCO FT-IR/8000 spectrometer equipped with a DTGS (deuterium triglycine sulfate) detector. The wavenumber resolution was 2 cm^{-1}, and a boxcar function was used as a window function. A liquid cell with CaF_2 window plates separated by a Teflon sheet was used. The path length was 0.011 mm.

Results and Discussion

Figure 1 shows an IR spectrum in the wavenumber region of 2400−1200 cm^{-1} of the aqueous ClC_2H_4OH mixture at 50 mol % of ClC_2H_4OH, as one of the spectra of the mixtures, together with those of pure water and ClC_2H_4OH. Liquid water has three absorption bands in the wavenumber region: an intermolecular combination band at 2125 cm^{-1},[9] the ν_2 band at 1647 cm^{-1}, and the first overtone of the far-infrared band at about 1350 cm^{-1}.[10] Figure 2 shows IR spectra in the region of 1800−1500 cm^{-1} of the aqueous mixtures of ClC_2H_4OH, BrC_2H_4OH, IC_2H_4OH, or EtOH at various alcohol mol %. Alcohols have no absorption bands in the region of the ν_2 band as illustrated in Figure 1. However, the base line at the low-wavenumber side of the ν_2 band is slightly affected by the absorption of the alcohols at high concentrations as noticed in Figure 2. In order to obtain an unaffected spectrum of the ν_2 band, we first subtracted the absorption by the alcohol component from that of a mixture and then resolved the resulting spectrum of the water molecules into the above three bands according to the least-squares method proposed by Motojima et al.[11] Figure 3 shows the molar absorptivity spectra of the ν_2 band of the water molecules in the aqueous ClC_2H_4OH, BrC_2H_4OH, IC_2H_4OH, or EtOH mixtures. The spectra at high alcohol concentrations are excluded from Figure 3 because of uncertainties in their molar absorptivity values.

We notice three spectral changes from Figure 3 with an increase in the alcohol concentrations; frequency shifts, asymmetric band shapes, and increases in the molar absorptivity. We first focus our attention on the frequency shifts of the ν_2 band.

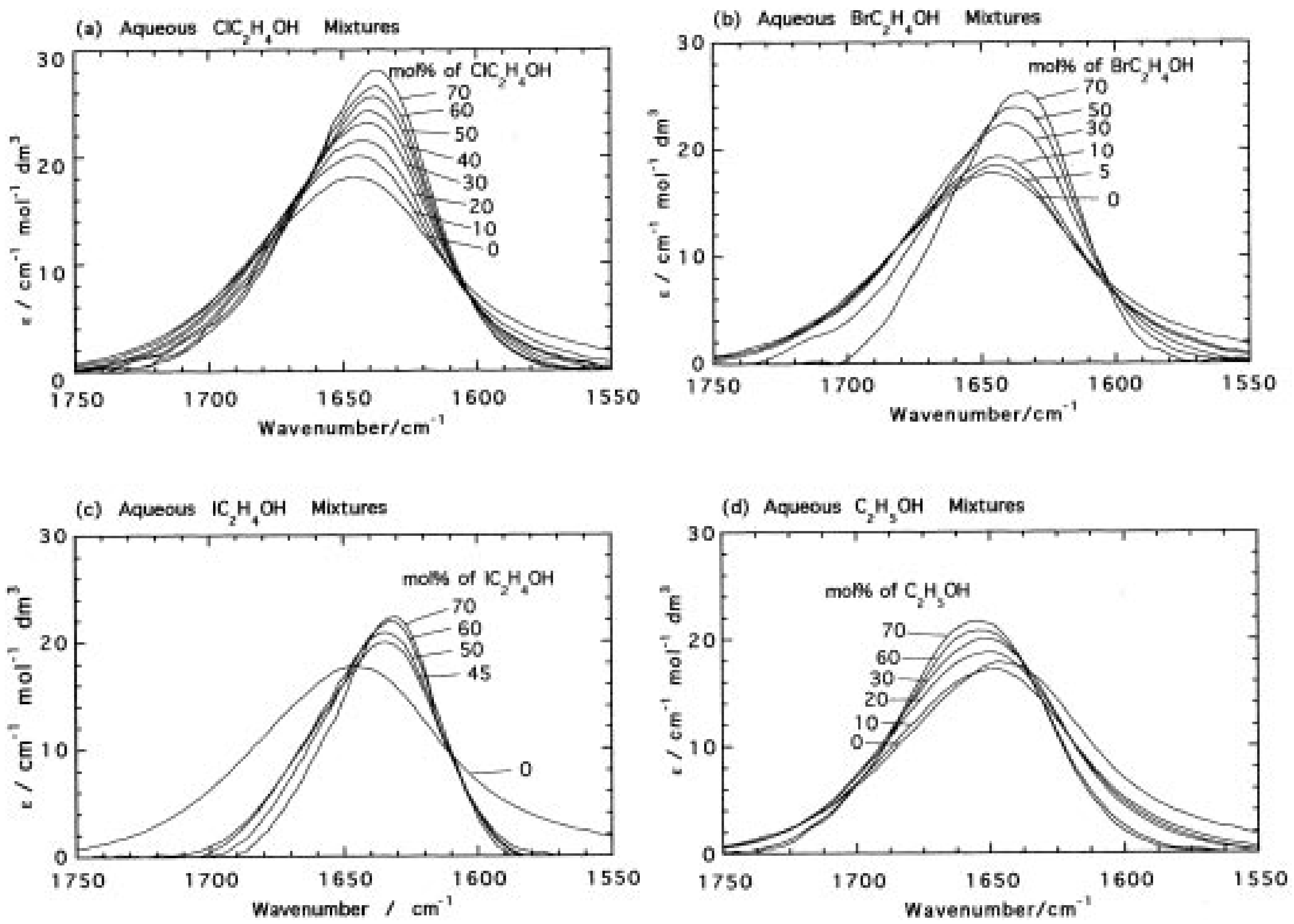

Figure 3. Molar absorptivity of ν_2 band of the water in aqueous mixtures at various alcohol mol. %: (a) ClC_2H_4OH, (b) BrC_2H_4OH, (c) IC_2H_4OH, and (d) EtOH.

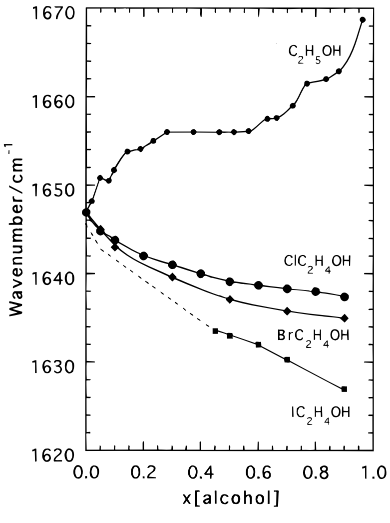

Figure 4. Plots of the wavenumber at the peak of the ν_2 band vs mole fraction of alcohol in the aqueous mixtures of ClC_2H_4OH, BrC_2H_4OH, IC_2H_4OH, or EtOH.

Figure 4 shows the peak wavenumber plotted against the alcohol concentration. The peak shifts to lower wavenumber with an increase in the haloethanol concentrations. Since a red shift of the ν_2 band is attributed to a decrease in the hydrogen-bonding strength of water molecules,[7] we can conclude that the breakdown of water structure is caused by the haloethanols. In our previous paper, we drew the conclusion from the high-field shifts of the water ^{1}H resonance peak that the breakdown of water structure occurs in the aqueous halogenoalcohol mixtures.[2]

The conclusion of the present IR studies is consistent with that of the ^{1}H-NMR studies. From the fact that the red shifts progress gradually in the whole concentration range of ClC_2H_4OH and BrC_2H_4OH, a gradual breakdown of water structure is found to occur with an increase in the concentrations.

In the aqueous EtOH mixtures, on the other hand, blue shifts occur in the whole range of the concentration. From Figure 4, we notice sharp blue shifts, or increases in the hydrogen-bonding strength of the water molecules, in the water-rich region up to about $x = 0.07$ followed by gradual blue shifts up to about $x = 0.2$. These changes are likely to be associated with drastic changes in solution structure that have been deduced from the measurements of ^{1}H-NMR,[4] dielectric constant,[12] the partial molar volume of EtOH,[13] excess partial molar enthalpy of EtOH,[14] radial distribution functions from X-ray,[15] and other physicochemical properties.[5,6]

The ν_2 band of pure water has an unusually broad width of 82 cm^{-1} at half-maximum. As shown in Figure 5, the ν_2 band is found to become narrower with an increase in the alcohol concentrations. Falk found a rather small narrowing of 5 cm^{-1} of the ν_2 band on heating pure water from 25 to 70 °C and a remarkable narrowing of 20 cm^{-1} on diluting pure water with heavy water.[16] He concluded from these facts that the broadening of the ν_2 band is not attributable to the dynamic effect associated with the motional correlation time of water molecules[16] but predominantly to the distribution of hydrogen-bonding strengths and vibrational coupling.[17,18] Consequently, the narrowing of the ν_2 band as shown in Figure 5 is considered to be due to the weakening of the vibrational coupling as a result of dilution by the alcohols.

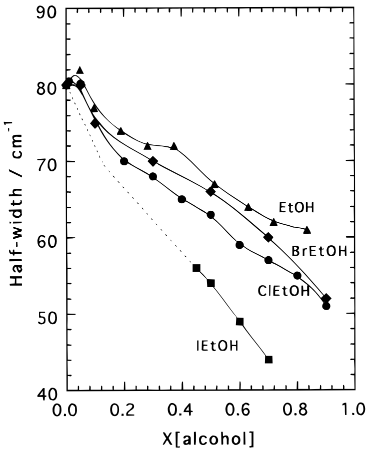

Figure 5. Plots of the full-width at half-maximum vs mole fraction of alcohol in aqueous ClC_2H_4OH, BrC_2H_4OH, IC_2H_4OH, and EtOH.

What should be noted here is that the band shape becomes less symmetric with an increase in alcohol concentrations. The asymmetry is more prominent in the aqueous haloethanol mixtures than in the aqueous EtOH mixtures. This result implies that the hydrogen-bonding strengths of the water molecules in the aqueous haloethanol mixtures are more widely distributed than those in the aqueous EtOH mixtures. The NMR relaxation study of water ^{17}O revealed that the water structure is broken down in the vicinity of the halogen atoms while the water structure around the rest of the halogenoalcohol molecules is almost similar to that around the corresponding alkanol molecules.[3] The asymmetric shapes of the spectra in Figure 3 (a and b) verify qualitatively the conclusion of our relaxation study because the spectra are considered to be composed of at least two bands. The absorption at the lower wavenumber region may be assigned to the water molecules in the vicinity of the halogen atoms, whereas the absorption at the higher wavenumber region is assigned to those around the rest of the halogenoalcohol molecules.

From Figure 3, the molar absorptivity at the peak frequency is found to increase with an increase in the concentrations of the alcohols irrespective of the directions of the frequency shifts. Since the shape of the ν_2 band depends in a complicated way on both the degree of the vibrational coupling and the distribution of hydrogen-bonding strengths, a quantitative analysis of the molar absorptivity at the absorption maximum, as well as the analysis of the band width, is beyond the scope of the present study. Nevertheless, it should be remarked from Figure 3 that the increases in the molar absorptivity are not correlated to the changes in the hydrogen-bonding strength of the water molecules but to the change in the solvent of the water molecules from water itself to the alcohols.

Conclusion

The haloethanols are found to give rise to red shifts of the ν_2 band. Since the red shift of the ν_2 band is attributed to the decrease in the hydrogen-bonding strength of the water molecules in the mixtures, the result indicates definitely that a breakdown of water structure occurs in the mixtures. The effect of the alcohols on the breakdown is found to increase in the order $ClC_2H_4OH < BrC_2H_4OH < IC_2H_4OH$, in agreement with the results of the previous ^{1}H-NMR studies.[2]

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