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Two-Dimensional FT-NIR Correlation Study of Hydrogen Bonding in the Butan-1-ol/Water System

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The effects of temperature and concentration on hydrogen bonding in butan-1-ol/water binary mixtures have been studied by using generalized 2D Fourier transform (FT) near-infrared (NIR) correlation spectroscopy. Particular attention has been paid to the analysis of changes in the self-association of butan-1-ol resulting from the presence of water. The obtained results indicate that the self-association of butan-1-ol is not influenced by small additions of water. When the molar fraction of water (X_{H_2O}) increases, bands due to water appear in the spectra. The number of correlation peaks suggests the presence of two different species of hydrogen-bonded water. In addition, molecules of non-hydrogen-bonded water dispersed among molecules of butan-1-ol were detected. An increase in X_{H_2O} at constant temperature reduces the population of the polymeric species of butan-1-ol and leads to growth in the number of free OH groups. When X_{H_2O} increases further, the free OH groups of butan-1-ol interact with molecules of water. The asynchronous peak originating from the rotational isomerism of butan-1-ol disappears from the spectra of the mixtures with higher values of X_{H_2O}. This observation indicates that the molecules of water do not reveal conformational selectivity upon the formation of hydrogen bonds with molecules of butan-1-ol. In contrast, due to larger molecular size, this selectivity appears for butan-1-ol. Both the temperature- and concentration-dependent correlation spectra provide evidence that in the studied system water−water and alcohol−alcohol interactions dominate, whereas the water−alcohol interactions are weaker.

Introduction

Aqueous solutions of alcohols are an important group of solvents applied in various chemical and biological processes. These systems have been extensively studied by both experimental[1−16] and theoretical[17−19] methods. Most of these studies have been devoted to hydrophobic interactions in aqueous solutions of alcohols miscible with water in all proportions (methanol, ethanol, propanols, and *tert*-butyl alcohol). The hydration of alcohols strongly depends on the size and shape of the solute molecules.[9,10] *tert*-butyl alcohol (TBA) is the largest alcohol that is soluble in water in all proportions. For this reason, TBA is considered to exhibit the largest hydrophobic effect and was the subject of numerous studies.[1−8,17,18] At low concentrations, molecules of TBA are dispersed as monomers, and the solute−solute interaction does not occur.[1,2,7,14,19] The association of the alcohol molecules is through their methyl groups rather than via hydrogen-bonding interactions of the OH groups.[1,7,14,18] The self-association of TBA molecules was observed beyond a threshold value ($X_{TBA} > 0.025$).[7,14] In the TBA-rich region ($X_{TBA} > 0.6$), TBA molecules in the solution are in almost the same environment as in the pure liquid.[4] However, H_2O molecules lose their hydrogen-bond network and are dispersed among TBA molecules as a single molecule with a repulsion from TBA and a resulting attraction from H_2O molecules.[4]

In contrast, the solute−solute association for n-alcohols is highly preferable even at very low concentrations.[11−13] This means that the branched alcohols have a weaker tendency to gather in the aqua solution than n-alcohols.[12] On increasing alcohol concentration, the hydrophobic effects become negligible, and interactions of water with OH groups of alcohols and self-association of the alcohol molecules are predominant.[14,15] At high concentrations, the IR spectra are similar to those of pure alcohols.[14] The almost constant position of the ν(C−H) band indicates that weak or no hydrocarbon chain−water contact in the associates is present.[14]

NIR spectroscopy is particularly useful for explorations of the hydrogen-bonded systems. In the overtone region, the bands due to the monomer and various associated species are better separated than in the IR region. Besides, the less-associated species are better seen in the NIR spectrum. For example, the absorption of free OH groups in the fundamental region is very weak, whereas it clearly appears in the NIR region.[20,21] Finally, because of small molar absorptivities in the overtone region, one can employ more convenient cell path lengths. Yet, the bands in NIR region are broad and often heavily overlap with each other. Hence, it is difficult to extract useful information from NIR spectra. Two-dimensional correlation analysis is a powerful tool for spectral data analysis. Because the temperature and concentration affect the monomers and various associated species to different extents, the corresponding peaks appear as separate features in the asynchronous spectra, regardless of the separation in the normal spectrum.[22] The selective correlation of the peaks in the synchronous and asynchronous spectra makes the band assignment more reliable, whereas the sign of the correlation peaks provides information about the dynamics of the changes induced by applied perturbations.

As yet, the aggregation process has been examined by looking at the behavior of water molecules rather than that of alcohol molecules. In this paper, we focus our attention on the changes in self-association of butan-1-ol molecules resulting from the

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presence of small and moderate amounts of water. Butan-1-ol is the smallest n-alcohol that is only partially soluble in water (8/100 g). Therefore, one can expect the structure of aqueous solutions of butan-1-ol to differ from those found for alcohols miscible with water in all proportions. Explorations of butan-1-ol/water mixtures are rare.[9,17] This work provides new experimental details of the effect of temperature and X_{H_2O} on the structure and molecular interactions in butan-1-ol/water mixtures by using 2D FT-NIR correlation spectroscopy.

Experimental Section

Spectroscopic Measurements. Butan-1-ol (99.8%) was purchased from Aldrich Chemical Co. (Germany) and was used as received. High-purity water (resistivity 18.2 MΩ-cm) was obtained by the Simplicity 185 Ultrapure Water System (Milliphore Corporation). Solutions were prepared gravimetrically from these materials. FT-NIR spectra were recorded at a resolution of 4 cm^{-1} on a Nicolet Magna 860 spectrometer equipped with a DTGS detector, and 512 scans were accumulated. The temperature-dependent spectra of the mixture were measured in a thermostated quartz cell (Hellma) of 5-mm thickness from 20 to 80 °C with a step of 5 °C. The spectra of pure water were recorded in a 0.1-mm cell. The actual temperature of the sample was controlled by means of a digital thermometer dipped into the cell, which guaranteed a stability of ±0.1 °C. Two series of concentration-dependent spectra (X_{H_2O} was changing from 0.001 to 0.01 and from 0.01 to 0.1) were recorded in the same cell at 25 °C. A temperature-dependent data set consisted of 13 spectra, and a concentration-dependent series included 10 spectra.

Data Treatment and 2D Correlation Analysis. Prior to 2D correlation analysis, the spectra were corrected for the density change with temperature, and the integrated intensity of the second overtone of the CH stretching band (8000−8600 cm^{-1}) was used as a reference.[23] The baseline fluctuations were minimized by an offset at 9000 cm^{-1}. The dynamic spectrum $A^d(\nu, T)$ was created by subtracting a reference spectrum from an ordered series of the experimental spectra. The spectrum of pure butan-1-ol and an average spectrum were used as references for concentration- and temperature-dependent spectra, respectively. The synchronous intensity $\Phi(\nu_1, \nu_2)$ was calculated as a cross product of the dynamic intensity at two different wavenumbers (ν_1, ν_2), whereas the asynchronous intensity $\Psi(\nu_1, \nu_2)$ was computed as a cross product of the dynamic intensity at ν_1 and the Hilbert transform (H) of the dynamic intensity at ν_2.[24]

$$\Phi(\nu_1, \nu_2) = \frac{1}{m-1}\sum_{T_{\min}}^{T_{\max}} A^d(\nu_1, T)\cdot A^d(\nu_2, T) \qquad (1)$$

$$\Psi(\nu_1, \nu_2) = \frac{1}{m-1}\sum_{T_{\min}}^{T_{\max}} A^d(\nu_1, T)\cdot H\cdot A^d(\nu_2, T) \qquad (2)$$

The synchronous spectrum $\Phi(\nu_1, \nu_2)$ yields information on how much the features at ν_1 and ν_2 are similar to each other from $T_{\min}$ to $T_{\max}$. The spectrum is symmetric with respect to a diagonal, and the peaks along the diagonal are called the autopeaks. The autopeaks are always positive and represent the overall extent of spectral changes at particular wavenumbers. The diagonal of the synchronous spectrum is called the power spectrum. The peaks located off the diagonal (cross peaks) can be either positive or negative and represent simultaneous variation of the spectral intensities at two different wavenumbers ν_1 and ν_2. A positive synchronous peak at (ν_1, ν_2) means that the intensity changes at these two wavenumbers are in the same direction, whereas a negative synchronous peak indicates the opposite. The existence of the cross peaks at (ν_1, ν_2) suggests the possibility that the peaks at ν_1 and ν_2 originate from the same fragment of the molecule or two different strongly interacting fragments.

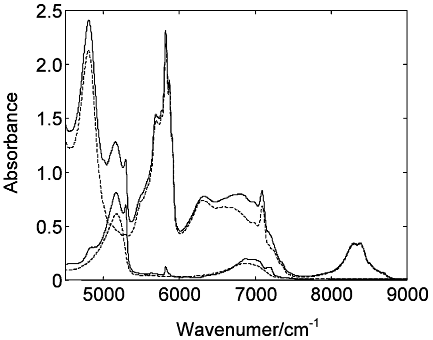

Figure 1. FT-IR spectra of pure butan-1-ol (- - -, top), a butan-1-ol/water mixture (X_{H_2O} = 0.122) (−, top), and pure water (- - -, bottom) and the difference spectrum (−, bottom).

The asynchronous spectrum $\Psi(\nu_1, \nu_2)$ provides information about how much the features at ν_1 and ν_2 are different from each other between $T_{\min}$ and $T_{\max}$. The spectrum is antisymmetric with respect to the diagonal and consists exclusively of the cross peaks. The sign of the asynchronous cross peaks can be either positive or negative. To simplify the interpretation of the asynchronous spectra, we multiplied them (array multiplication) by the sign of the corresponding synchronous spectra. In this way, one can directly interpret the sign of the asynchronous peaks without taking into account the sign of the corresponding synchronous peaks, and Noda's rules[22] are simplified. Accordingly, a positive asynchronous cross peak at (ν_1, ν_2) means that the spectral change at ν_1 occurs faster (earlier) than that at ν_2. Negative asynchronous peaks indicate the opposite. The asynchronous spectrum develops a peak at (ν_1, ν_2) if the spectral changes at ν_1 and ν_2 vary out of phase at least for some values of the perturbation over the range of $\langle T_{\min}, T_{\max}\rangle$. This feature is very helpful in resolving highly overlapped peaks. As long as the responses at ν_1 and ν_2 to the applied perturbation are different, two separate peaks appear in the asynchronous spectrum, regardless of the separation between the original peaks. Because of the symmetry properties, it is enough to take into account only one-half of the synchronous (asynchronous) spectrum. Throughout this work, the upper half of each 2D correlation spectrum ($\nu_2 > \nu_1$) is analyzed. The 2D correlation analysis was performed using MATLAB 6.5 software (The Math Works Inc.).

Results and Discussion

Band Assignments. Figure 1 shows the FT-NIR spectra of pure butan-1-ol, pure water, a butan-1-ol/water mixture (X_{H_2O} = 0.122), and the difference between the spectrum of the mixture and that of pure butan-1-ol. The positions and assignments of the main spectral features in this region are collected in Table 1. The assignments of butan-1-ol bands were based on a previous 2D correlation study,[25] and the bands originating from water were assigned on the basis of Perchard's work.[26] The absorbance of the combination band (~4800 cm^{-1}) and the first overtone of the CH stretching vibration (~5820 cm^{-1}) is outside the range of accurate measurements ($A > 2$). In addition, the combination band shifts with temperature from 4787 to 4819 cm^{-1}, giving rise to a complex pattern in the 2D correlation spectra.[27−29] Therefore, the correlation peaks at these

TABLE 1: Frequencies and Assignments of Selected NIR Bands of a Butan-1-ol/Water Mixture

vibration	species	position [cm^{-1}]	molecule
$\nu(OH) + \delta(OH)$	associated	~4800	butan-1-ol
$\nu_2 + \nu_3$	associated	5134	water
$\nu_2 + \nu_3$	associated	~5200	water
$\nu_2 + \nu_3$	monomeric	5294	water
$2\nu(CH)$		5820	butan-1-ol
$2\nu(OH)$	higher multimers	6240	butan-1-ol
$\nu_1 + 2\nu_2$		6770	water
$2\nu(OH)$	dimer	6852	butan-1-ol
$2\nu_2 + \nu_3$	associated	6872 → 6939[a]	water
$2\nu(OH)$	free	7099 (7130, 7080)[b]	butan-1-ol
$\nu_1 + \nu_3$	monomeric	~7200	water
$3\nu(CH)$		8300, 8385	butan-1-ol

[a] Position (6872 cm^{-1}) in pure water; position (6939 cm^{-1}) in the mixture ($X_{H_2O} = 0.122$) at 20 °C. [b] Positions of the rotational isomers are given in parentheses.

coordinates were not interpreted. The bands due to the second overtone of the CH stretching vibrations (~8300, 8385 cm^{-1}) are well separated from the other spectral features and do not vary in position when the temperature or X_{H_2O} are altered. Thus, the integral intensity of this band was applied as the reference for the density correction.[23]

The difference spectrum (Figure 1) is similar to that of pure water, but the main bands in this spectral region ($\nu_2 + \nu_3$, $2\nu_2 + \nu_3$) have high-frequency components. These additional bands probably originate from the monomeric molecules of water dispersed among molecules of butan-1-ol. The existence of molecules of water that lose their hydrogen-bond network was also suggested for a TBA/H_2O mixture in the TBA-rich region.[4]

Two-Dimensional Correlation Analysis of the Temperature-Dependent FT-NIR Spectra of Pure Butan-1-ol. Though the results of 2D correlation analysis of the temperature-induced changes in the FT-NIR spectra of pure butan-1-ol have already been reported,[25] the spectra were recorded once more. First, the previous analysis was restricted to the 6000−7500-cm^{-1} region, and the current studies extended this range down to 4500 cm^{-1}. Second, the spectra of pure butan-1-ol recorded at different temperatures were used as references for the spectra of the mixtures. Thus, the spectra of the mixture and the reference should be collected under the same experimental conditions. Figure 2, parts A and B display the synchronous and asynchronous spectra of pure butan-1-ol, respectively, from 20 to 80 °C. The sign of the asynchronous peaks indicates that the spectral changes for the monomer band occur faster than the changes for the other bands. This results from the fact that the terminal hydrogen bonds break more easily than the interior ones with rising temperature.[30] The expanded view of the asynchronous spectrum from 6800 to 7200 cm^{-1} (Figure 2C) reveals the peak due to the rotational isomerism of the free OH group at (7080, 7130 cm^{-1}). The presence of this peak proves that the temperature-induced intensity changes for both rotamers appear at different rates. This observation was explained by the different hydrogen-bond-forming ability of the OH groups of both rotational isomers.[25,31]

Two-Dimensional Correlation Analysis of Temperature-Dependent FT-NIR Spectra of Butan-1-ol/Water Mixtures. The correlation spectra (not shown) constructed from mixtures with low water content ($X_{H_2O} \leq 0.005$) are the same as those of pure butan-1-ol, revealing that in the alcohol-rich region molecules of butan-1-ol are in almost the same environment as in the pure liquid. In other words, a small addition of water does not have noticeable effect on the structure and population of the associates of butan-1-ol. The same conclusion was obtained for TBA/water mixtures.[4]

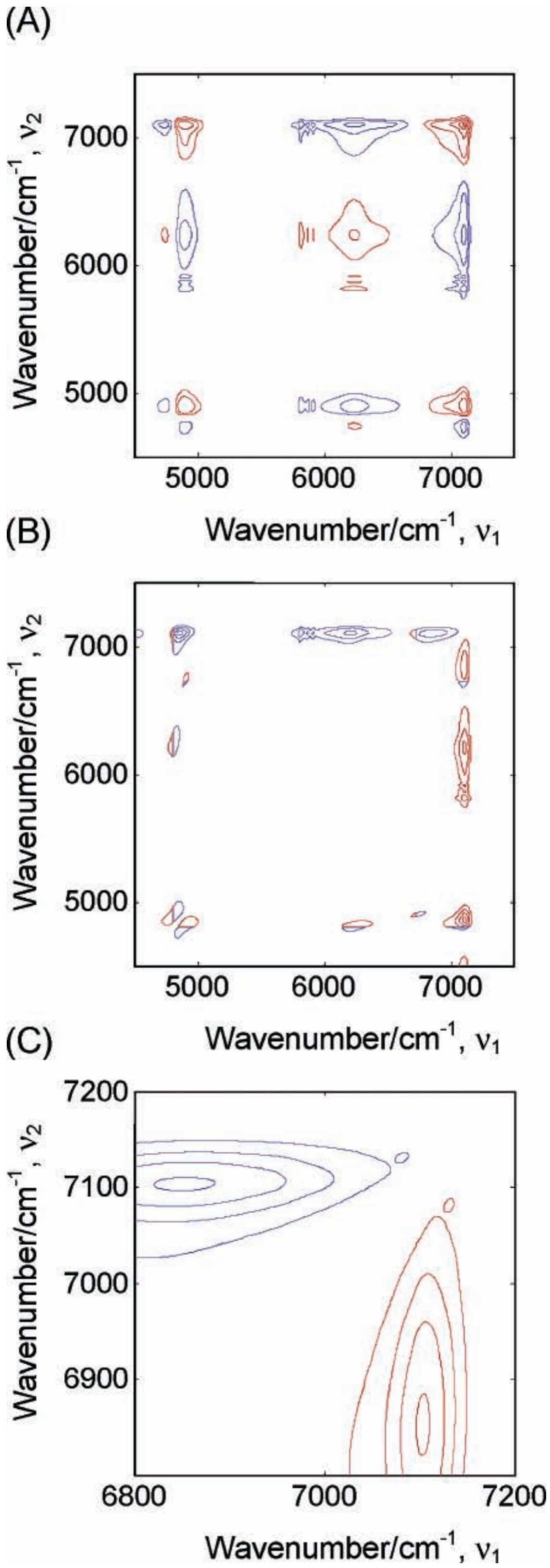

Figure 2. (A) Synchronous and (B) asynchronous spectra of pure butan-1-ol from 20 to 80 °C. (C) Expanded view of the asynchronous spectrum from 6800 to 7200 cm^{-1}. Red lines represent positive correlation peaks, whereas blue lines represent negative peaks.

Figure 3 shows the 2D correlation spectra of the mixture ($X_{H_2O} = 0.122$) from 20 to 80 °C. The most distinct difference, as compared with the spectra of pure butan-1-ol, is the presence

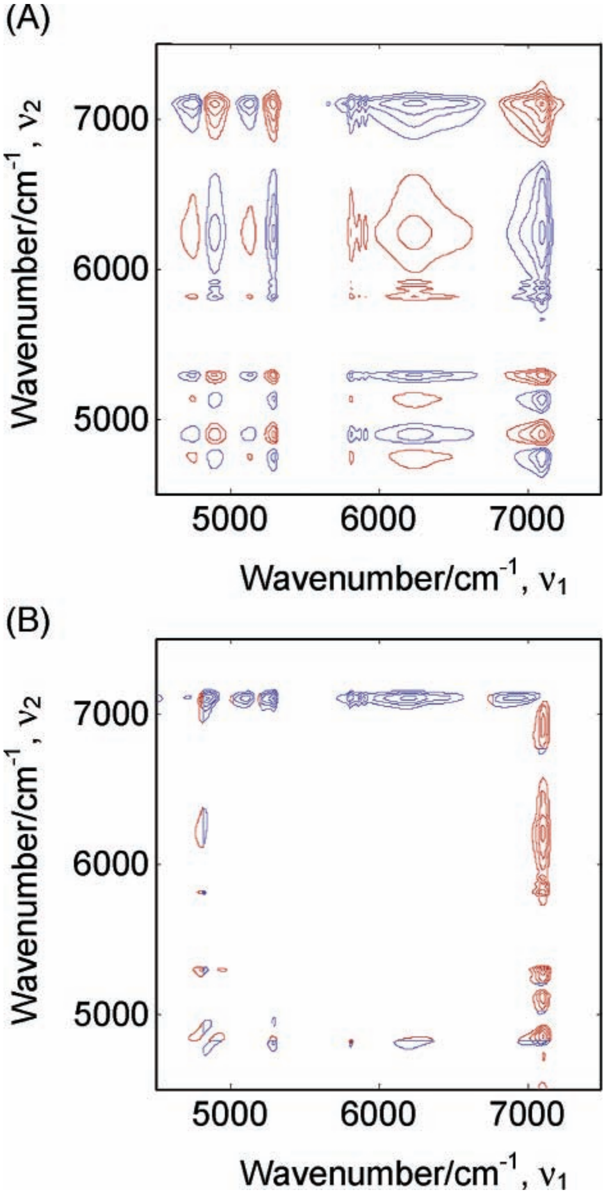

Figure 3. (A) Synchronous and (B) asynchronous spectra of a butan-1-ol/water mixture ($X_{H_2O} = 0.122$) from 20 to 80 °C. Red lines represent positive correlation peaks, whereas blue lines represent negative peaks.

of two peaks at 5134 and 5294 cm^{-1} that are assigned to $\nu_2 + \nu_3$ vibrations of water (Table 1). The sign of the corresponding synchronous peaks imply that the intensity variations at both wavenumbers occur in opposite directions when the temperature is rising. Therefore, it is very likely that both bands originate from different species of water. It seems that the broad band at 5134 cm^{-1} is due to hydrogen-bonded water whereas the narrow band at 5294 cm^{-1} can be assigned to the overtone of the non-hydrogen-bonded OH stretching vibration. The molecules of monomeric water are dispersed among hydrocarbon chains of butan-1-ol and do not interact with the other molecules of water or with the OH groups of butan-1-ol. The almost constant value of 2ν(CH) indicates that the specific interaction between the hydrocarbon chain and water in the aggregates is very weak or absent. A similar observation was reported for TBA/water mixtures.[4] It has been suggested that in the TBA-rich region the molecules of water are dispersed as monomers in micellelike microaggregates. The higher-frequency band (at 5294 cm^{-1}) may also originate from a singly bonded complex, where water is hydrogen bonded to alcohol by one OH group only whereas the other OH group is free. This free OH group could absorb at 5294 cm^{-1} as well. Recently, this kind of interaction has been reported for complexes of water with molecules having an ether or carbonyl group.[31] However, on the basis of the present data, it is not possible to establish the exact origin of the 5294-cm^{-1} band.

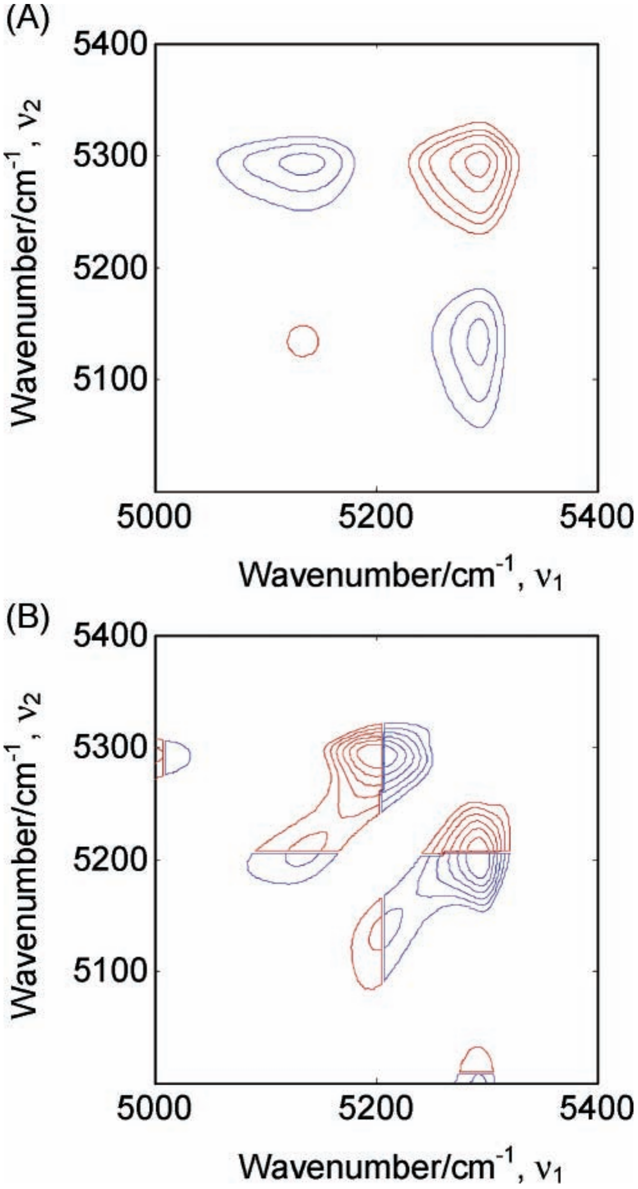

Figure 4. Expanded view of (A) synchronous and (B) asynchronous spectra shown in Figure 3. Red lines represent positive correlation peaks, whereas blue lines represent negative peaks.

An increase in temperature breaks the hydrogen bonds and leads to an increase in the intensity of the 5294-cm^{-1} band at the expense of the 5134-cm^{-1} band. From the asynchronous spectrum (Figure 3B), one can deduce that this process is slower than the increase in intensity of the monomer band of butan-1-ol. A detailed analysis of 2D correlation spectra in the 5000−5400-cm^{-1} region (Figure 4) reveals asynchronous peaks between the $\nu_2 + \nu_3$ bands and a new peak located near 5200 cm^{-1}. The reversal of the sign of the asynchronous peaks in Figure 4B results from the multiplication of the asynchronous spectra by the sign of the corresponding synchronous spectra and indicates the regions where the synchronous intensity-changes its sign. According to Noda's rules,[22] the sign of the asynchronous peak cannot be interpreted if the sign of the corresponding synchronous peak is not determined. Conse-

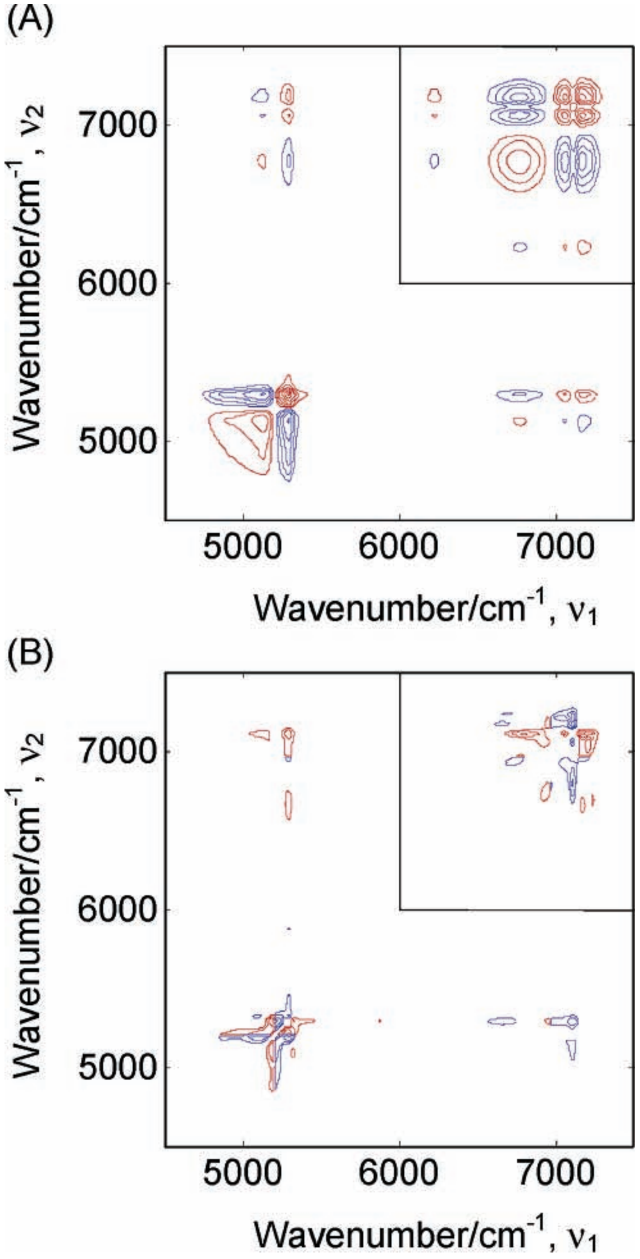

Figure 5. (A) Synchronous and (B) asynchronous spectra constructed from the difference spectra. The difference spectra were calculated by subtracting the spectra of pure butan-1-ol from the spectra of the mixture ($X_{\mathrm{H_2O}} = 0.122$) at each temperature. The intensities in the 6000−7500-cm^{-1} range were enlarged to appear on this scale. Red lines represent positive correlation peaks, whereas blue lines represent negative peaks.

quently, the sign of the asynchronous peaks was not interpreted in the regions where the synchronous spectrum changes sign. The position of this new peak suggests that it represent the molecules of water with weaker hydrogen bonding as compared with the species contributing to the 5134-cm^{-1} band. This observation indicates the presence of two different hydrogen-bonded states of water that differ in the number of hydrogen bonds per molecule. Analogous results were obtained by the other authors.[32−34] For example, Iwamoto et al. suggested the presence of molecules of water with one and two hydrogen bonds.[32] In contrast, Holden et al. reported that pure water, pure methanol, and methanol/water 1:1 and 1:4 complexes are present in a methanol/water mixture.[34]

The asynchronous spectra of pure butan-1-ol (Figure 2C) and the mixtures with small water contents display the peak due to the rotational isomerism. This peak disappears from the spectra when $X_{\mathrm{H_2O}}$ increases. Because of differences in the shielding of the OH group by the alkyl group, both rotational isomers of butan-1-ol have different hydrogen-bond-formation ability. As a result, the hydrogen bonding between two molecules of butan-1-ol is conformational-selective and gives rise to the asynchronous peak. In contrast, the molecules of water that are much smaller than the molecules of butan-1-ol interact with both rotational isomers of butan-1-ol with comparable probability. Consequently, the populations of both conformational isomers of butan-1-ol change more similarly, and the corresponding asynchronous peak is not observed.

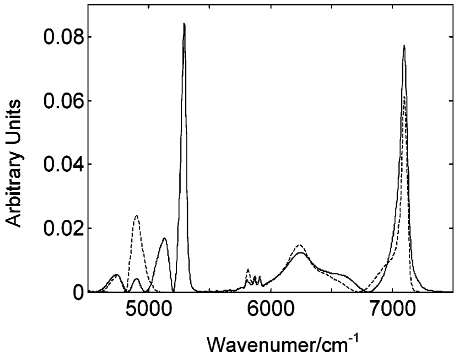

Figure 6. Power spectra constructed from the spectra of pure butan-1-ol (- - -) and the butan-1-ol/water mixture with $X_{\mathrm{H_2O}} = 0.246$ (−).

As yet, the analysis emphasized the behavior of the bands assigned to butan-1-ol. Except for the $\nu_2 + \nu_3$ bands, the other correlation peaks due to water were obscured by intense bands of alcohol. To obtain more detailed information about the water bands, 2D correlation analysis of the difference spectra was performed. The difference spectra were calculated by subtracting the spectra of pure butan-1-ol from those of the mixture (at each temperature). In this way, the spectral changes of butan-1-ol are strongly suppressed, and the variations due to water become more distinct. The 2D correlation spectra constructed from the difference spectra are shown in Figure 5. Interestingly, the synchronous spectrum in 6000−7500-cm^{-1} region (Figure 5A) develops four correlation peaks, whereas in Figure 3A only two peaks attributed to butan-1-ol are observed. These two additional peaks at 7172 and near 6770 cm^{-1} can be assigned to $\nu_1 + \nu_3$ and $\nu_1 + 2\nu_2$ vibrations of water, respectively. The asynchronous peak near 5200 cm^{-1} (Figure 5B) has two components, supporting the conclusion of the presence of two associated species of water. The asynchronous spectrum (Figure 5B) develops a series of peaks between the bands assigned to water and butan-1-ol, indicating that the temperature-induced spectral changes for alcohol and water appear at different rates.

Figure 6 display the power spectra of pure butan-1-ol (dashed line) and the butan-1-ol/water mixture with $X_{\mathrm{H_2O}} = 0.246$ (solid line). As can be easily seen, the spectra of the mixture include new bands near 5200 and 5300 cm^{-1} that are due to water. We note in particular that the spectral changes for the polymer band of butan-1-ol decrease, whereas those of the intermediate species and the monomer band reveal an opposite trend on the addition of water to alcohol. This observation suggests that the thermal dissociation of the aggregates of butan-1-ol into monomers occurs more easily in the presence of water.

The temperature-induced asynchronous spectra of pure butan-1-ol (Figure 2, parts B and C) develop a band at 6852 cm^{-1} that is assigned to the open dimer. This band noticeably shifts to higher frequencies (6939 cm^{-1}) on increasing $X_{\mathrm{H_2O}}$ (Figure 3B). The $2\nu_2 + \nu_3$ band of water is located in the same region (Figure 1). In pure water, this band shifts from 6872 to 7035 cm^{-1} (not shown) on increasing temperature from 20 to 80 °C.

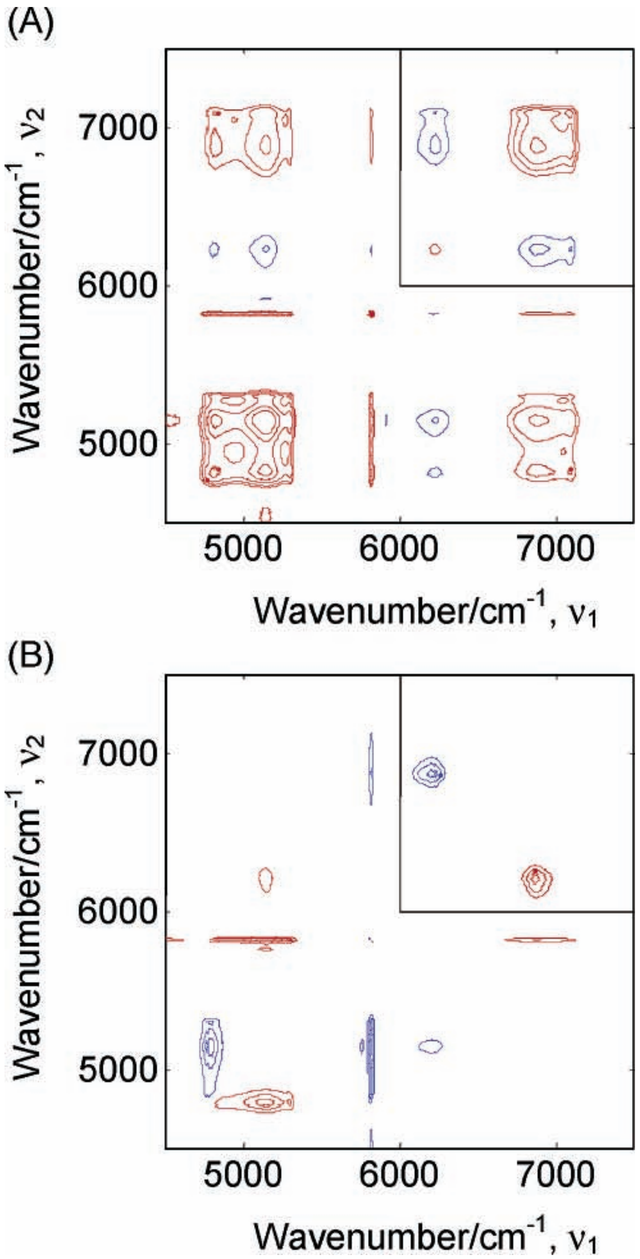

Figure 7. (A) Synchronous and (B) asynchronous spectra constructed from the concentration-dependent spectra ($X_{\mathrm{H_2O}} = \langle 0.001, 0.01\rangle$). The intensities in the 6000−7500-cm^{-1} range were enlarged to appear on this scale. Red lines represent positive correlation peaks, whereas blue lines represent negative peaks.

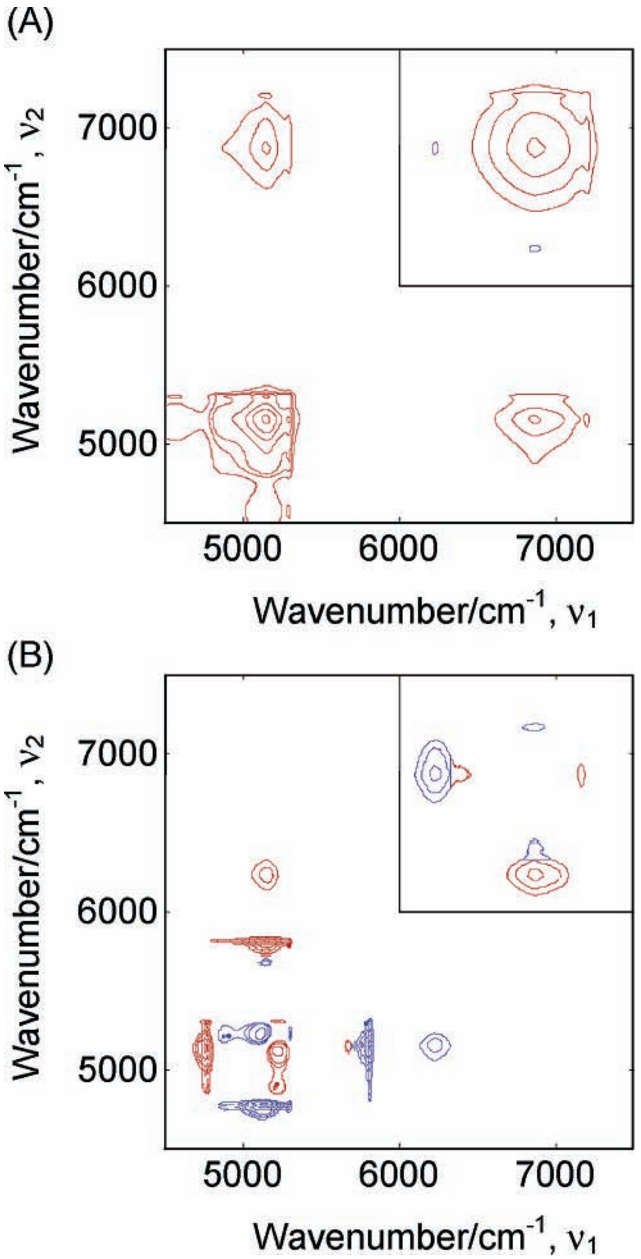

Figure 8. (A) Synchronous and (B) asynchronous spectra constructed from the concentration-dependent spectra ($X_{\mathrm{H_2O}} = \langle 0.01, 0.1\rangle$). The intensities in the 6000−7500-cm^{-1} range were enlarged to appear on this scale. Red lines represent positive correlation peaks, whereas blue lines represent negative peaks.

Thus, one can conclude that the shift from 6852 to 6939 cm^{-1} on going from pure butan-1-ol to the mixture ($X_{\mathrm{H_2O}} = 0.122$) can be attributed to the $2\nu_2 + \nu_3$ band of water.

Two-Dimensional Correlation Analysis of Concentration-Dependent FT-NIR Spectra of Butan-1-ol/Water Mixtures. Figures 7 and 8 show 2D correlation spectra constructed from the concentration-dependent spectra of the mixtures with $X_{\mathrm{H_2O}}$ ranging from 0.001 to 0.01 and from 0.01 to 0.1, respectively. As expected, the peaks due to water dominate the synchronous and asynchronous spectra. The intensities of these peaks increase on increasing water concentration. Interestingly, the spectra also include the peaks assigned to butan-1-ol. Near 6200 cm^{-1} appears a series of negative synchronous peaks (Figure 7A), indicating that increasing $X_{\mathrm{H_2O}}$ is correlated with the decreasing population of the polymeric species of butan-1-ol. This observation supports the conclusion obtained from Figure 6 that the dissociation of the associates of butan-1-ol proceeds faster in the presence of water. However, the asynchronous peak at this coordinate (Figures 7B and 8B) reveals that both processes occur at different rates.

The power spectrum constructed from the concentration-dependent spectra of butan-1-ol with a small amount of water (Figure 9A) develops a peak at 7078 cm^{-1}. This peak is assigned to the free OH groups of butan-1-ol (Table 1). The reduction in the population of the polymers of butan-1-ol decreases the average size of the associates and leads to an increase in the population of the free OH groups. As $X_{\mathrm{H_2O}}$ increases, the free OH groups interact with the molecules of water. As a result, the 7078-cm^{-1} band does not appear in the power spectrum of the mixture with higher values of $X_{\mathrm{H_2O}}$ (Figure 9B). The $\nu_2 + \nu_3$ band of water shows two components. The broader band located near 5150 cm^{-1} can be assigned to hydrogen-bonded

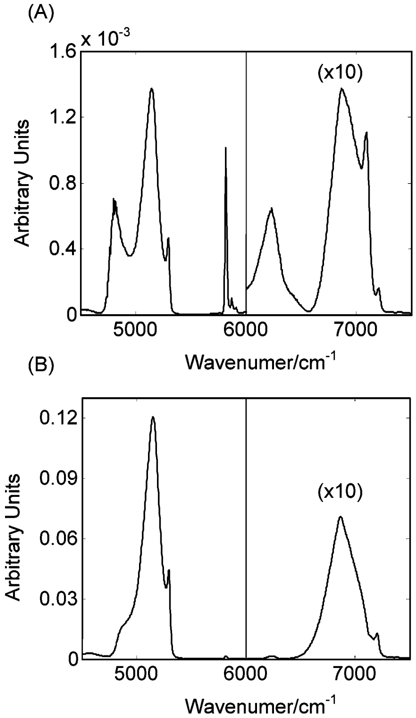

Figure 9. Power spectra constructed from the concentration-dependent spectra (A) $X_{H_2O} = \langle 0.001, 0.01\rangle$ and (B) $X_{H_2O} = \langle 0.01, 0.1\rangle$.

water, and the narrow band at 5300 cm^{-1} is due to non-hydrogen-bonded water or free OH groups in singly bonded water.

Conclusions

The present results show that a small amount of water (X_{H_2O} < 0.005) does not have a noticeable effect on the number or structure of hydrogen-bonded species of butan-1-ol. At higher values of X_{H_2O}, the spectra of mixtures reveal the peaks due to water. Of particular importance is that these peaks have high-frequency components that can be assigned to the monomeric molecules of water being dispersed among molecules of butan-1-ol or free OH groups in a singly bonded complex. The splitting of the $\nu_2 + \nu_3$ band into two components, as observed in the asynchronous spectra, indicates the presence of two different forms of hydrogen-bonded water. The position and intensity of the second overtone of the CH stretching band do not depend on X_{H_2O}. Therefore, one can conclude that the interaction between water and the hydrophobic part of butan-1-ol is weak and does not have a specific character. The concentration-dependent 2D correlation spectra show that an increase in X_{H_2O} is accompanied by a decrease in the population of the polymers of butan-1-ol. However, the later process occurs at a slower rate. The decrease in the population of the polymeric species of butan-1-ol leads to a reduction of the average size of the aggregates and increases the population of the free OH groups of butan-1-ol. At higher values of X_{H_2O}, the free OH groups of butan-1-ol form complexes with water, and their population is reduced. Two-dimensional correlation spectra of pure butan-1-ol and mixtures with small amounts of water develop a peak assigned to the rotational isomerism that results from the conformational selectivity of molecules of butan-1-ol when hydrogen bonding is created. In contrast, the molecules of water are much smaller than those of butan-1-ol and interact with nearly equal probability with both rotational isomers of butan-1-ol. As a result, the band intensities of both rotamers are changing more accordingly, and the asynchronous intensity between these peaks vanishes. The presence of significant asynchronous intensity between the bands of water and butan-1-ol suggests that in the studied system the solute−solute and solvent−solvent interactions are stronger than the solute−solvent interactions.

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