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Effect of Temperature and Concentration on the Structure of *sec*-Butyl Alcohol and Isobutyl Alcohol/Water Mixtures: Near-Infrared Spectroscopic Study

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The effect of temperature and concentration on the structure of *sec*-butyl alcohol and isobutyl alcohol/water binary mixtures in the alcohol-rich region (mole fraction of water $X_{H2O} < 0.3$) has been studied using Fourier transform (FT) near-infrared (NIR) spectroscopy. The experimental data were analyzed by a two-dimensional (2D) correlation approach and chemometric methods. It was found that molecules of both alcohols in the mixture with water are in the same environment as those in the pure alcohols. Even at very low water content ($X_{H2O} = 0.001$) we did not observe water free from any specific interactions. The molecules of water are attached to the end free OH groups in the open chain associates of alcohol. In this way the structure of neat alcohol remains intact by addition of water. The water−alcohol interactions in *sec*-butyl alcohol and isobutyl alcohol/water mixtures are stronger than those in bulk water. The results obtained at higher water content or elevated temperatures indicate the possibility of water−water interaction. In the alcohol-rich region the hydrophobic effects are of minor importance and the structure and properties of these systems are determined by hydrogen bonding through the hydroxyl groups. Both alcohols behave similarly on the temperature or water content variation; the minor difference results from a different degree of self-association for *sec*-butyl alcohol and isobutyl alcohol.

Introduction

Mixtures of alcohols with water are widely used in many chemical and biochemical processes. The structure and properties of these systems result from the balance between the hydrophilic and hydrophobic part of the alcohol molecule. A detailed examination of the structure and properties of alcohol/water mixtures at a molecular level is essential to understand the nature of the hydrophobic effects.[1−16] In general, at low alcohol content the hydrophobic hydration and hydrophobic interaction are believed to dominate the physicochemical properties.[4−7,9,10,12] At the opposite end of the concentration scale, the alcohol molecules in the mixture are in almost the same environment as in the pure alcohol.[1,4,8,11] In other words, the structure of the alcohols remains essentially unchanged by addition of a small amount of water. In contrast, there is little agreement concerning the role of water in the alcohol-rich region. For example, Koga claims that molecules of water lose the hydrogen-bond network completely and are dispersed as single molecules,[1] whereas Bowron and Moreno suggest that water forms small hydrogen-bonded clusters consisting of two or three molecules.[2] The other authors claim that molecules of water are incorporated into the alcohol hydrogen-bonded zigzag structure.[9]

Four isomers of butyl alcohol (*n*-butanol, *sec*-butyl alcohol, isobutyl alcohol, and *tert*-butyl alcohol) are interesting systems since even a small variation in the alkyl chain structure or the OH group position effects the physical properties of pure alcohols and their mixtures with water. The properties of *tert*-butyl alcohol differ from those of the other isomers of butanol, and thus examination of this alcohol has received considerable attention.[1−13] In contrast, relatively few experimental studies on the other isomers of butanol have been undertaken, and they mainly refer to the pure liquid state or dilute CCl_4 solutions.[14−20] To date, a systematic study of the effect of temperature and concentration on the structure of *sec*-butyl alcohol/water and isobutyl alcohol/water mixtures has not been reported.

The present work provides new experimental information on the effect of temperature and water content on FT-NIR spectra of *sec*-butyl alcohol and isobutyl alcohol/water mixtures. Previous experimental work on alcohol/water systems was performed mostly in the water-rich region, whereas the exploration of the opposite end of the concentration scale is limited. This study is thus focused on the alcohol-rich region, allowing evaluation of the influence of a small water content on the structure of both alcohols as well as the state of water in the mixture. Experimental data were analyzed by a 2D correlation approach and chemometric methods. The current results are discussed with those recently published for *n*-butanol[16] and *tert*-butyl alcohol[13] as well as with the other available literature data.

Experimental Section

Materials and Spectroscopic Measurements. *sec*-Butyl alcohol and isobutyl alcohol were purchased from Aldrich Chemical Co. (Germany). The chemicals were obtained at the highest purity (>99%) and dried under freshly prepared molecular sieves (4A). High-purity water (resistivity 18.2 MΩ cm) was obtained by the Simplicity 185 Ultrapure Water System (Milliphore Corp.). FT-NIR spectra were recorded at a resolution of 4 cm^{-1} on a Nicolet Magna 860 spectrometer with a DTGS detector, and 512 scans were accumulated. The sample chamber was purged with dry nitrogen. Spectra were measured in a variable-temperature quartz cell (Hellma) of 5 mm thickness. The spectroscopic measurements provided few series of the spectra recorded as a function of temperature (10:5:75 °C for

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sec-butyl alcohol and 10:5:80 °C for isobutyl alcohol) at constant X_{H2O} (0, 0.001, 0.01, 0.1, 0.25) and varying water content (X_{H2O} = 0.001:0.001:0.01, 0.01:0.01:0.1, 0.1:0.01:0.25, 0.05:0.05:0.45) at 30 °C. Here we used Matlab's notation: initial_value:step: final_value.

2D Correlation Analysis. Prior to 2D correlation analysis the spectra were corrected for the density change with temperature and then baseline fluctuations were minimized by an offset at 9000 cm^{-1}. The dynamic spectrum was obtained by subtraction of a reference spectrum from an ordered series of experimental spectra. The spectrum of pure alcohol at 30 °C and average spectrum were used as a reference for the concentration- and temperature-dependent data, respectively. The synchronous intensity was calculated as a cross-product of the dynamic intensity at two different wavenumbers, whereas the asynchronous intensity was computed using Hilbert transform.[21,22] The 2D correlation spectra were computed using MATLAB 6.5 (The Math Works Inc.) based software written in our laboratory.

Chemometric Analysis. The spectral data matrix (D) is product of the concentration profiles matrix (C) and the matrix of pure component spectra (S^T)

$$D = CS^{T} + E = \sum_{i=1}^{A} c_i {s_i}^{T} + E$$

where matrix E includes the residual error and A is the number of significant species present in the mixture. The value of A was estimated by principal component analysis (PCA)[23] and then confirmed by the cross-validation procedure[24] and evolving factor analysis (EFA).[25] The results of EFA provide an initial estimation for C. The concentration profiles and the pure component spectra were obtained by a multivariate curve resolution (MCR) approach with constraints (nonnegativity on concentration and spectra).[26,27] The chemometric analysis was performed by PLS-Toolbox 3.0 (Eigenvector Research Inc.) for use with MATLAB.

Results and Discussion

Effect of Temperature on Spectra of Pure *sec*-Butyl Alcohol and Isobutyl Alcohol and Mixtures with Water. Figure 1 displays the effect of temperature on FT-NIR spectra of *sec*-butyl alcohol and isobutyl alcohol/water mixtures with X_{H2O} = 0.1. In Table 1 are collected assignments of major NIR bands of pure *sec*-butyl alcohol and *sec*-butyl alcohol/water mixture. The analogous data for isobutyl alcohol are shown in Table 2. Careful examination of all collected spectra reveals that like for *tert*- and *n*-butanol,[13,16] the position of the bands attributed to C−H vibrations do not depend on the temperature and concentration, showing a minor role of the hydrophobic effect in the studied systems. The higher multimer band of both butanols significantly shifts to higher wavenumbers ($\Delta\nu > 50$ cm^{-1}) with increasing temperature. The band due to the free OH group of *sec*-butyl alcohol does not vary in position, whereas the corresponding band of isobutyl alcohol is blue shifted ($\Delta\nu = 15$ cm^{-1}). The origin of this shift is not clear and requires further studies. The water bands have a similar location in both *sec*-butyl alcohol and isobutyl alcohol/water mixtures. The temperature increase does not alter the position of the band assigned to the free OH group of water, whereas the other band of water is blue shifted ($\Delta\nu \approx 30$ cm^{-1}). Interestingly, the position of the hydrogen-bonded band of water in the mixture at elevated temperatures (Tables 1 and 2) is the same as that in bulk water at 30 °C (5183 cm^{-1}). It is probable that increasing the mobility of water at higher temperatures facilitates formation of the water clusters.

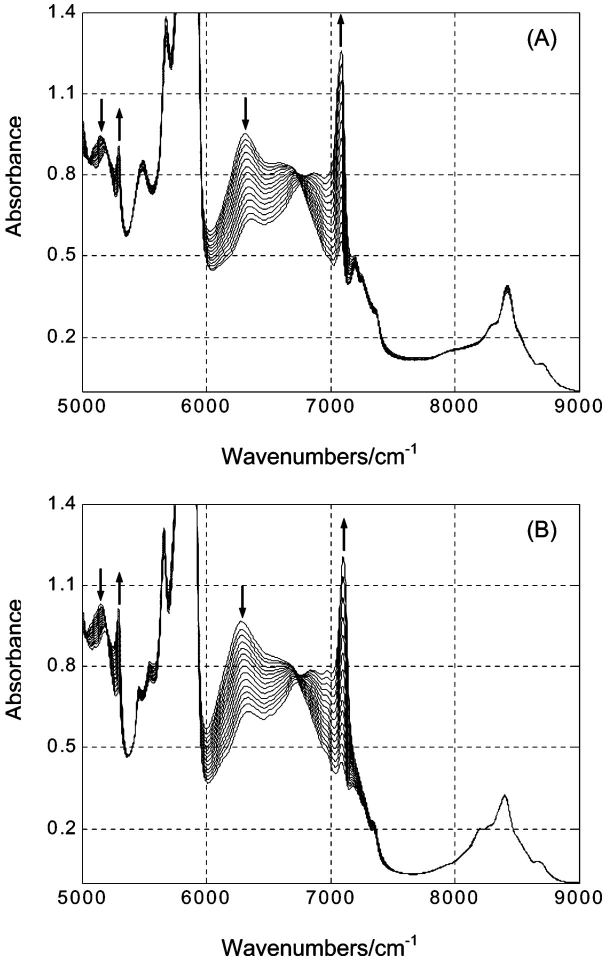

Figure 1. FT-IR spectra of a pure *sec*-butyl alcohol/water mixture from 10 to 75 °C (A) and isobutyl alcohol/water mixture from 10 to 80 °C (B); X_{H2O} = 0.1. Arrows indicate the direction of intensity change as the temperature is increases.

TABLE 1: Frequencies and Assignments of Selected NIR Bands of a *sec*-Butyl Alcohol/Water Mixture[a]

position [cm^{-1}]	vibration	species	molecule
5153[b]/5186[c]	$\nu_2 + \nu_3$	associated	water
≈5210	$\nu_2 + \nu_3$	*associated*	*water*
5298	$\nu_2 + \nu_3$	free	water
5888, 5928	2ν(CH)	*sec*-butyl alcohol	
6310[b]/6360[c]	2ν(OH)	higher multimers	*sec*-butyl alcohol
6871	$\nu_1 + \nu_3$	associated	water
6833[d]*/6865*[e]	*2ν(OH)*	*dimer*	*sec-butyl alcohol*
7054	*2ν(OH)*	*free (end chain)*	*sec-butyl alcohol*
7089	*2ν(OH)*	*free*	*sec-butyl alcohol*
{*7081/7116*}[f]	*2ν(OH)*	*free*	*sec-butyl alcohol*
7195, 7255	2ν(CH) + δ(CH)	*sec*-butyl alcohol	
7205	$\nu_1 + \nu_3$	free	water
8422	3ν(CH)	*sec*-butyl alcohol	
10373	3ν(OH)	free	*sec*-butyl alcohol

[a] Peaks resolved only in 2D correlation spectra are given in italics. [b] Position at 10 °C. [c] Position at 75 °C. [d] In pure *sec*-butyl alcohol.[e] In the mixture with X_{H2O} = 0.25. [f] Position of the rotational isomers.

Figure 2 shows the power spectra of pure *sec*-butyl alcohol and isobutyl alcohol from 10 to 70 °C. The power spectrum is a diagonal of the synchronous spectrum and represents the overall extent of intensity changes at particular wavenumbers. As can be seen, the band assigned to the free OH groups of isobutyl alcohol is weaker and shifted to higher frequencies relative to that of *sec*-butyl alcohol. One has to remember that

TABLE 2: Frequencies and Assignments of Selected NIR Bands of an Isobutyl Alcohol/Water Mixture

position [cm^{-1}]	vibration	species	molecule
5153[b]/5184[c]	$\nu_2 + \nu_3$	associated	water
≈5225	$\nu_2 + \nu_3$	*associated*	*water*
5297	$\nu_2 + \nu_3$	free	water
5874, 5911	$2\nu(CH)$	isobutyl alcohol	
6273[b]/6345[c]	$2\nu(OH)$	higher multimers	isobutyl alcohol
6867	$\nu_1 + \nu_3$	associated	water
6840[d]/6858[e]	$2\nu(OH)$	*dimer*	*isobutyl alcohol*
n.o.	$2\nu(OH)$	free (end chain)	isobutyl alcohol
7091[b]/7106[c]	$2\nu(OH)$	free	isobutyl alcohol
{7085/7132}[f]	$2\nu(OH)$	*free*	*isobutyl alcohol*
7178	$2\nu(CH) + \delta(CH)$	isobutyl alcohol	
7205	$\nu_1 + \nu_3$	free	water
8402	$3\nu(CH)$	isobutyl alcohol	
10404	$3\nu(OH)$	free	isobutyl alcohol

[a] Peaks resolved only in 2D correlation spectra are given in italics. n.o. = not observed. [b] Position at 10 °C. [c] Position at 80 °C. [d] In pure isobutyl alcohol. [e] In the mixture with $X_{H2O} = 0.1$. [f] Position of the rotational isomers.

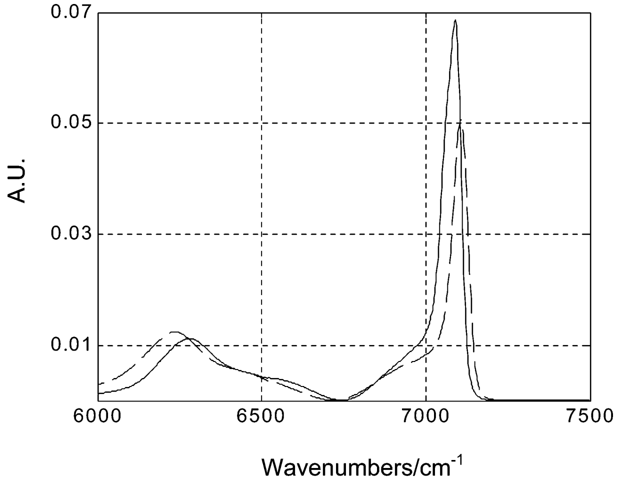

Figure 2. Power spectra obtained from the synchronous spectra of pure *sec*-butyl alcohol (solid line) and isobutyl alcohol (dashed line) from 10 to 70 °C.

this band includes contributions from both the OH groups in the monomers and the end free OH groups in the open chain associates.[28,29] The hydrogen bonding in the secondary alcohols is weaker relative to the primary ones. Therefore, the thermal breaking of hydrogen bonds in *sec*-butyl alcohol occurs easier, and as a result, population of the monomers and the end free OH groups increases faster (Figure 2). It is well evidenced that the band due to the free OH groups in the primary alcohols is located at higher wavenumbers than that in the secondary and tertiary alcohols.[28,30,31] This tendency is well seen in Figure 2 and explained by Krueger and Wieser by trans intramolecular delocalization of the oxygen lone pairs.[32] The position of the bands due to the higher multimers (Tables 1 and 2) indicates that the hydrogen bonding in isobutyl alcohol is stronger.

In Figure 3 are compared the power spectra of pure alcohols with the spectra of the mixtures with $X_{H2O} = 0.1$. Evidently, addition of water leads to an increase in the intensity of the peak due to the free OH groups of alcohol, whereas for the higher multimer peak an opposite effect is observed. At higher water content the difference is more pronounced (not shown). This means that the temperature-induced breaking of the associates of alcohols occurs more easily in the presence of water. On the other hand, a drop in the extent of intensity changes for the higher multimer band suggests that molecules of water stabilize larger associates. The above two observations imply that water promotes breaking mainly the shorter associates.

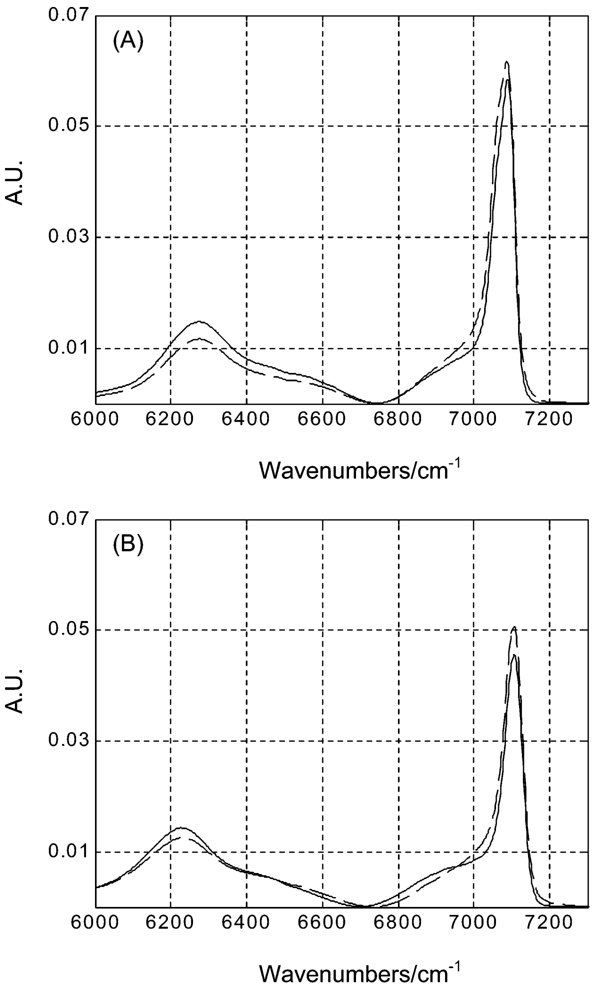

Figure 3. Power spectra of pure *sec*-butyl alcohol (solid line) and a *sec*-butyl alcohol/water mixture with $X_{H2O} = 0.1$ (dashed line) from 10 to 75 °C (A), and the corresponding spectra for isobutyl alcohol (B).

The most important differences in the asynchronous spectra of pure *sec*-butyl alcohol and isobutyl alcohol occur near the diagonal (Figure 4). Despite the smaller extent of temperature changes, the peak due to rotational isomerism is more distinct for *sec*-butyl alcohol. A detailed examination of Figure 4A reveals an additional peak at 7054 cm^{-1} that has been assigned to the end-free OH groups of the open chain associates of *sec*-butyl alcohol. On the other hand, this peak does not occur in the asynchronous spectra of isobutyl alcohol (Figure 4B). It is of interest that this peak was found also in the asynchronous spectrum of 2-octanol.[30,31] The appearance of the peak due to the free terminal OH groups is associated with a smaller extent of self-association for secondary alcohols. At elevated temperatures the equilibrium shifts toward the smaller species including monomers, dimers, and trimers.[29] In the 6000−6500 cm^{-1} region occurs a broad peak due to the higher multimers of alcohol. The structure of this peak is not resolved in the asynchronous spectrum, giving evidence for a distribution of cluster size rather than a limited number of a very few species. The above conclusion is consistent with the finding of DeBolt and Kollman derived from molecular dynamic calculations.[29]

In Figure 5 are shown the asynchronous spectra of mixtures with $X_{H2O} = 0.1$. The peak due to the rotational isomerism of isobutyl alcohol disappears after addition of water (Figure 5B),

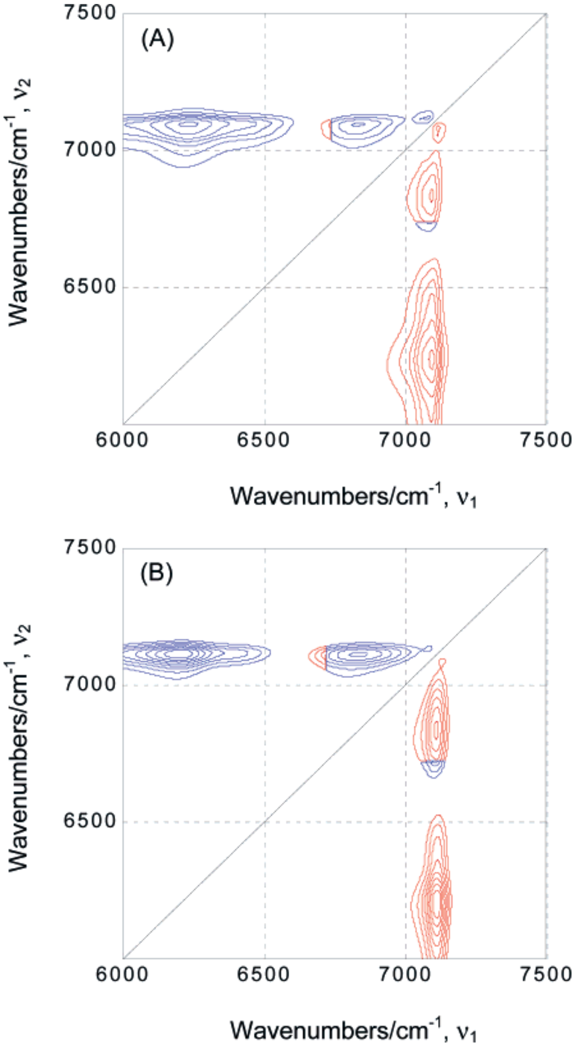

Figure 4. Asynchronous spectra of pure *sec*-butyl alcohol from 10 to 75 °C (A) and pure isobutyl alcohol from 10 to 80 °C (B). Red lines represent positive correlation peaks, whereas blue lines represent negative peaks.

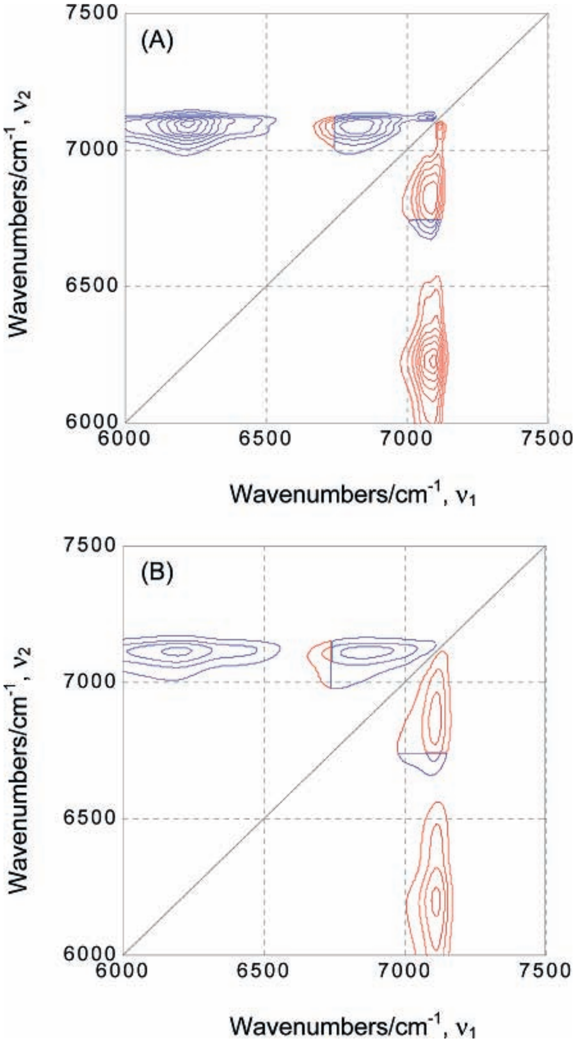

Figure 5. Asynchronous spectra of a *sec*-butyl alcohol/water mixture from 10 to 75 °C (A) and an isobutyl alcohol/water mixture from 10 to 80 °C (B); $X_{H2O} = 0.1$. Red lines represent positive correlation peaks, whereas blue lines represent negative peaks.

whereas it is still noticeable in the asynchronous spectrum of *sec*-butyl alcohol (Figure 5A). This difference results from higher population of the free OH groups in the secondary alcohols. At higher water content ($X_{H2O} = 0.25$) this peak vanishes also for *sec*-butyl alcohol (not shown). Clearly, in the presence of water the population of both rotational isomers changes more accordingly. Our previous studies demonstrate that unlike molecules of alcohols, water molecules do not reveal the conformational selectivity on hydrogen-bonding formation.[13,16]

Effect of X_{H2O} on Spectra of *sec*-Butyl Alcohol and Isobutayl Alcohol/Water Mixtures. The spectral changes resulting from addition of water are better seen in the difference spectra obtained by subtraction of the spectrum of pure alcohol at 30 °C from each of the concentration-dependent spectra (Figure 6). In this way contributions from the bands that do not vary in intensity are removed from the spectra. Subtraction of very strong bands ($A > 2$) provides unreliable results, and therefore, the spectral region of 5500−6000 cm^{-1} was set to zero. As can be seen, the changes appear mainly in the regions of water absorption. Of particular note is that the position of the bands due to water does not depend on X_{H2O} and that they have the same location in both *sec*-butyl alcohol and isobutyl alcohol (Tables 1 and 2). The relative intensities of the peaks at 5300 and 5150 cm^{-1} are similar for both alcohols. The above observations support the model of one-bonded water to end-free OH group of the alcohol. It is very likely that molecules of water interact with the monomers of alcohol as well.[28] Yet, the population of the monomeric species at 30 °C is too small to associate all molecules of water. On the basis of microwave dielectric analysis Sato et al. concluded that in the methanol-rich region the water molecule is attached to the hydrophilic site of the methanol molecule at the end of the chain.[33] This is similar to what Dixit et al. obtained from high-resolution Raman spectroscopy of a methanol/water mixture.[34] When $X_{H2O} < 0.3$, addition of water leaves the chain structure of pure methanol substantially intact. Hydration takes place at the chain ends, and the molecules of methanol act as hydrogen-bond acceptors.[34] The presence of one-bonded water was also found in solutions of water with organic molecules with an ether or a carbonyl group in heptane.[35] Careful examination of Figure 6 reveals a sudden intensity drop at the position of the free OH band of alcohol (∼7100 cm^{-1}). This indicates that addition of water at constant temperature reduces the population of the free OH groups of the alcohol.

In Figure 7 are shown the asynchronous spectra of *sec*-butyl alcohol and isobutyl alcohol constructed from the difference spectra. The peaks in the difference spectra do not vary in position, and hence, the asynchronous intensity calculated from these data has a physical meaning. A significant asynchronicity

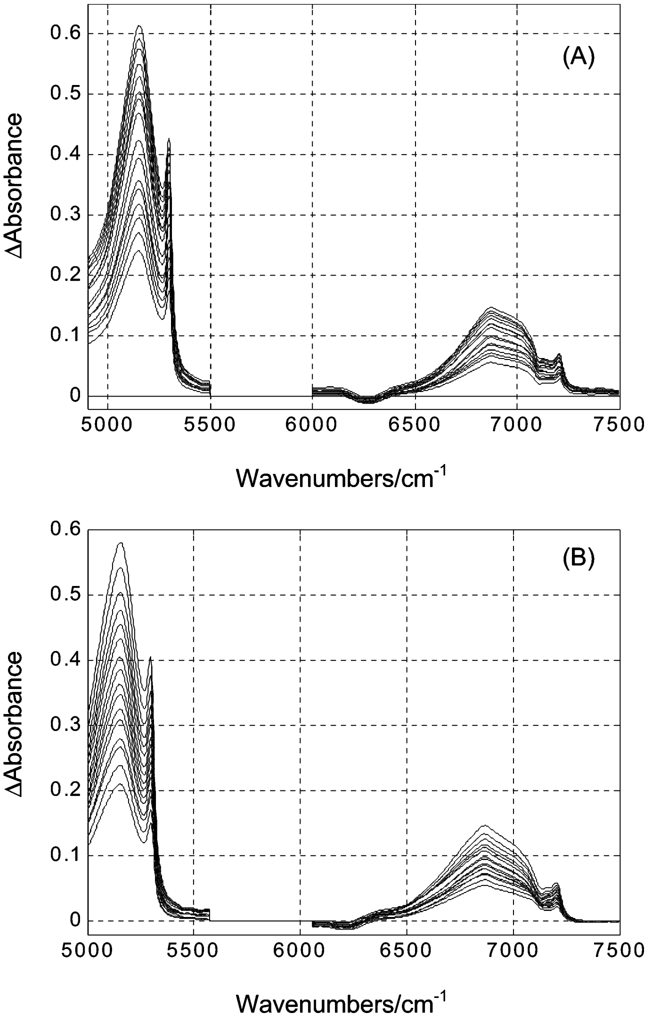

Figure 6. Difference spectra of *sec*-butyl alcohol/water (A) and isobutyl alcohol/water (B) mixtures with X_{H2O} from 0.1 to 0.25 at 30 °C.

in the 5000−5500 cm^{-1} region implies that the population of the free and bonded OH groups of water does not vary in the same way when X_{H2O} increases. The appearance of a third peak in this region confirms the above conclusion. At higher water content this new peak is more evident (not shown), and it was assigned to water−water interaction. This peak is blue shifted in the mixture relative to bulk water (5183 cm^{-1}), suggesting the rather small size of the clusters. The existence of small pockets with two to three molecules of water in *tert*-butyl alcohol was suggested by Bowron and Moreno.[2] Notable is the distinct asynchronous intensity between the peaks assigned to water and alcohol. A fraction of water molecules interact with molecules of alcohol, whereas the others participate in water−water interaction, which explains the origin of this asynchronicity.

Figure 8 displays details of MCR of *sec*-butyl alcohol and isobutyl alcohol/water mixtures with X_{H2O} from 0.1 to 0.25. For the sake of comparison, we added to the figure the spectrum of pure water at 30 °C. From PCA and EFA analysis the presence of two species in the mixture is observed. Thus, spectra of the mixtures were resolved into two components; attempting to obtain more components was not successful. One of the resolved spectral profiles was assigned to alcohol and the other to water. As expected, the position of the bands assigned to water does not vary on going from *sec*-butyl alcohol to isobutyl alcohol. The spectral profiles of both alcohols are similar to the spectra of pure alcohols. This is one more evidence that the structure of the alcohols remains intact by addition of water. On the other hand, the hydroxyl band from hydrogen-bonded water in the mixture is red shifted relative to bulk water. The same value of the shift ($\Delta\nu \approx 30$ cm^{-1}) was found both for $\nu_2 + \nu_3$ and $\nu_1 + \nu_3$ bands of water. A similar shift was reported also for a methanol/water mixture.[36] Hence, one can conclude that molecules of water in alcohol are involved in stronger hydrogen bonding than in bulk water.

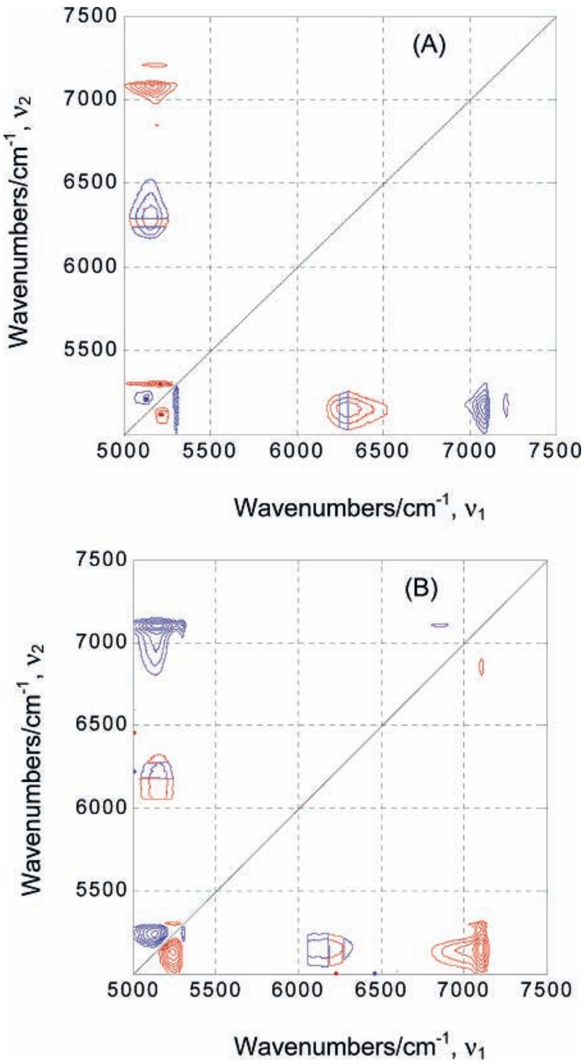

Figure 7. Asynchronous spectrum of *sec*-butyl alcohol/water (A) and isobutyl alcohol/water (B) mixtures with X_{H2O} from 0.1 to 0.25 constructed from the difference spectra shown in Figure 6.

Conclusions

This work provides no evidence for the importance of the hydrophobic effects in the alcohol rich-region ($X_{H2O} < 0.3$). Hydrogen bonding through the OH groups determines the structure of the mixtures. A small and moderate amount of water stabilizes the higher associates of alcohols but facilitates breaking of shorter associates with increasing temperature. As a result, the temperature-induced increase in the population of the free OH groups of alcohol occurs faster in the presence of water. It was found that molecules of water are one-bonded to the end free OH groups of the alcohol open chain associates, while the other OH group of water remains nonbonded. The strength of alcohol−water bonding is similar in both alcohols yet stronger than in bulk water. The end chain association of water in *sec*-butyl alcohol and isobutyl alcohol does not have a

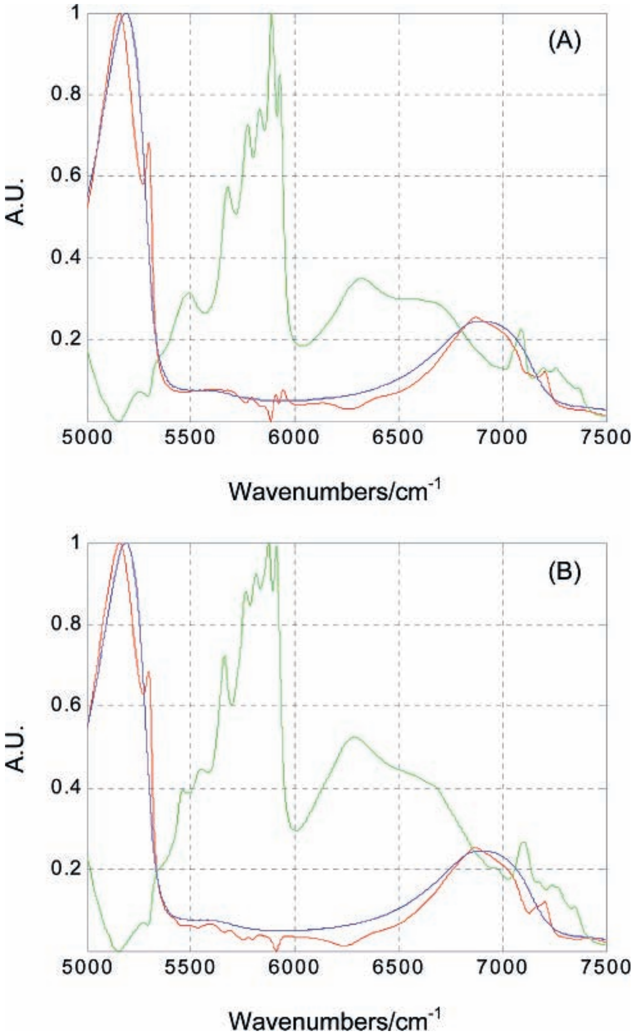

Figure 8. Spectral profiles obtained from MCR of *sec*-butyl alcohol/water (A) and isobutyl alcohol/water (B) mixtures with X_{H2O} from 0.1 to 0.25. Green line represents the spectral profile of the alcohol, red shows the profile of water, while the spectrum of pure water at 30 °C is displayed in blue. All spectra were normalized to unity absorbance.

significant effect on the structure of alcohols. Even at low water content ($X_{H2O} = 0.001$) the $\nu_2 + \nu_3$ band has two components. Thus, the current experimental data give no evidence for significant amounts of free molecules of water in the studied mixtures. This is in accord with what we found for *tert*-butyl alcohol.[13] Our results suggest that at higher water content ($X_{H2O} > 0.1$) the direct water−water interaction becomes more important. Increasing temperature also facilitates formation of water clusters. Variation of the temperature and water content has a similar effect on the structure of both alcohols. The subtle difference observed in the asynchronous spectra is due to the different extent of self-association for the primary and secondary alcohols.

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