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Resolution Enhancement and Band Assignments for the First Overtone of OH Stretching Modes of Butanols by Two-Dimensional Near-Infrared Correlation Spectroscopy. 2. Thermal Dynamics of Hydrogen Bonding in *n-* and *tert*-Butyl Alcohol in the Pure Liquid States

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The temperature-dependent near-infrared (NIR) spectral variations of *n*- and *tert*-butyl alcohols in the pure liquid state have been studied by generalized two-dimensional (2D) correlation analysis. The Fourier transform (FT) NIR spectra were recorded in the 6000−11000 cm^{-1} region over the temperature ranges of 20−85 and 25−75 °C for *n*- and *tert*-butyl alcohols, respectively. In the 2D NIR correlation spectra of both alcohols appear the bands due to the OH stretching vibrations of the monomer (first and second overtones), cyclic dimer, and linear hydrogen bonds in acyclic and cyclic polymers. Moreover, the spectra of *tert*-butyl alcohol reveal the bands that can be attributed to the free terminal OH groups in open chain species (7047 cm^{-1}), bend OHO bonds (6520 cm^{-1}), and a band at 6610 cm^{-1}. The last one, not reported previously, was assigned to the small cyclic associates (trimers or tetramers). Our results evidenced that in the pure liquid state the population of rotational isomers is determined mostly by the accessibility of the OH proton. This is why the bands due to the less stable rotamers are much more intense than the energetically favorable ones in neat *n*- and *sec*-butyl alcohols. Owing to smaller population of the free OH groups, as compared to the *sec*-butyl alcohol, the rotational isomerism was not observed for *n*-butyl alcohol in the pure liquid phase. Yet, this effect was clearly seen in diluted solution of *n*-butyl alcohol. The analysis of the asynchronous 2D correlation spectra has proved that the variations in the population of the associated species and monomers do not occur at the same rate. The changes for the monomers are slower than that for any other species; however, the population of this species increases faster at higher temperatures. At elevated temperatures the rapid increase in the population of the cyclic dimers is reduced by simultaneous dissociation into the monomers. It has been demonstrated that the stability of the cyclic dimers is diminished upon branching. Our results show the relationship between the chemical structure of alcohols and dynamic properties of the hydrogen bonding.

Introduction

The first paper of the series dedicated to self-association processes in butanols in the pure liquid phase presented the results of generalized two-dimensional (2D) near-infrared (NIR) correlation analysis of temperature-dependent spectral variations of *sec*-butyl alcohol.[1] On the basis of a few assumptions, clear assignments of all observed peaks to various types of the OH bonds have been proposed. Our assignments were based on the foundation that all possible structures of associated alcohols were created by only a few types of hydrogen bonds and some of these types appeared both in the linear and cyclic aggregates. It has been shown that the monomer band of *sec*-butyl alcohol can be resolved into three components.[1] Two of them are due to the rotational isomerism (7089 and 7116 cm^{-1}), and the third one can be attributed to the free terminal OH groups in the open chain polymers (7055 cm^{-1}). The higher frequency rotamer was assigned to an energetically favorable conformer. Interestingly, the less stable rotamer was dominant in the NIR spectra of neat *sec*-butyl alcohol. The reversion of the relative intensity of these peaks was explained by reduced accessibility of the OH proton for the less stable rotamer. Also three bands were observed for the associated species. The peaks at 6275 and 6550 cm^{-1} were assigned to the linear and bend OHO bonds, respectively, in acyclic and cyclic polymers, whereas the feature at 6838 cm^{-1} was attributed to the cyclic dimers. More detailed

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insight into the complex mechanism of the thermal dissociation of the hydrogen bonds in *sec*-butyl alcohol was achieved by division of the entire temperature range into several narrower ranges. The 2D correlation analysis performed for these smaller data sets revealed that the population of the polymers and cyclic dimers changes faster than that of the monomer. At elevated temperatures an appreciable dissociation of the cyclic species took place.

This report extends our 2D NIR correlation studies of temperature-dependent spectral fluctuations of butanols in the pure liquid state to *n*- and *tert*-butyl alcohols and provides a number of new insights into the hydrogen bonding, dissociation, and rotational isomerism. The detailed exploration of the FT-NIR spectra of both alcohols was undertaken with the aim at identification of all features due to the first overtone of OH stretching vibrations of the monomers and associated species. Another challenge in the present study was the assignment of the observed peaks to various kinds of the OH bonds, in accordance with our previous work.[1] Of particular interest was the examination of how the rotational isomerism manifests itself in the NIR spectra of *n*- and *sec*-butyl alcohols. Close insight into a complex mechanism of the thermal dissociation of hydrogen-bonded species was derived from 2D correlation analysis in narrower windows of temperature changes. It has been demonstrated that the power spectra, calculated at different temperature intervals, supply useful information on the dynamics of the dissociation process. Since all the three kinds of butanols were studied under the same conditions by the same instrumentation and computational methods, they made excellent materials for comparison and discussion on the relationship between the structure of alcohols and dynamic properties of the hydrogen bonding.

Experimental and Calculations of 2D Correlation Spectra

The samples of very high purity (greater than 99.9%) were supplied by Nippon Oil and Fats Co. Ltd. (Amagasaki, Japan) and used without further purification. The FT-NIR spectra were recorded at a resolution of 4 cm^{-1} on a JEOL JRS 6500N FT-NIR/Raman spectrophotometer equipped with a TGS detector. All calculations were performed using MATLAB software (The Math Works Inc.), and during the calculations we employed the generalized 2D correlation approach.[2,3] The 2D correlation peaks are represented as pairs (ν_1, ν_2) of two independent wavenumbers (in cm^{-1}). Analyzing 2D correlation spectra we refer to the upper half of the contour map ($\nu_1 \leq \nu_2$). However, exactly the same information is included in the lower half ($\nu_1 \leq \nu_2$) of the 2D correlation plot. The negative peaks, both synchronous and asynchronous, are shaded. In a synchronous spectrum a positive peak at (ν_1, ν_2) indicates that the intensity changes at these two wavenumbers are in the same direction. A positive asynchronous cross-peak at (ν_1, ν_2) means that the spectral change at ν_1 occurs faster, as a function of increasing temperature, in comparison to ν_2. Negative synchronous and asynchronous peaks indicate the opposite. Details of the experimental conditions and data treatment were described in the preceding paper.[1]

Results

***N*-Butyl Alcohol.** FT-NIR spectra of *n*-butyl alcohol in the pure liquid phase were recorded in the 6000−11000 cm^{-1} region over the temperature range of 20−85 °C. However, during the 2D correlation analysis we concentrated mainly on the 6000−7500 cm^{-1} region (Figure 1), in which appear bands due to the first overtones of OH stretching modes of the monomer (~7100 cm^{-1}) and various hydrogen-bonded species (6200−6900 cm^{-1}). The intensities of the bands attributed to the associated species decrease while that of the monomer band increases with temperature. In the synchronous spectrum of the alcohol, shown in Figure 2A, one can see the development of two major autopeaks at (7101, 7101) and (6237, 6237). The negative sign of the synchronous cross-peak at (6237, 7101) reveals that the intensity changes at these two wavenumbers proceed in the opposite direction. The corresponding asynchronous spectrum in Figure 2B shows two cross-peaks: (6237, 7101) and (6858, 7101). The sign of these peaks indicates that the intensity changes at 6237 and 6858 cm^{-1} occur faster than that at 7101 cm^{-1}.

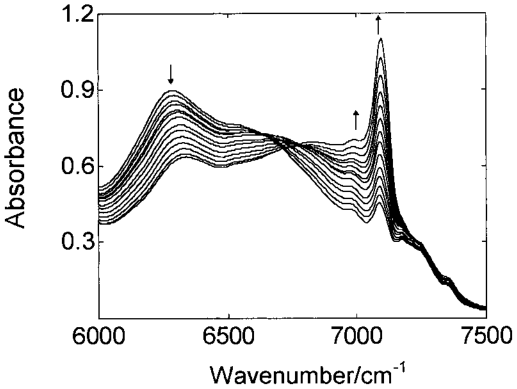

Figure 1. FT-NIR spectra of *n*-butyl alcohol in the pure liquid state over the temperature range of 20−85 °C (↑, intensity increase with temperature; ↓, intensity decrease with temperature).

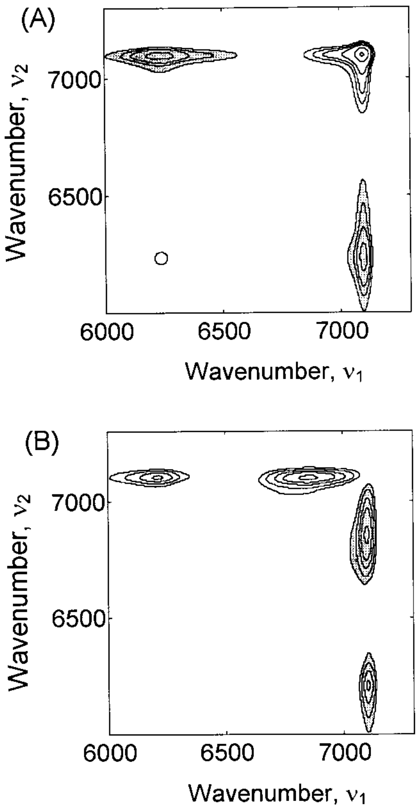

Figure 2. Synchronous (A) and asynchronous (B) 2D NIR correlation spectra of *n*-butyl alcohol in the temperature range from 20 to 85 °C.

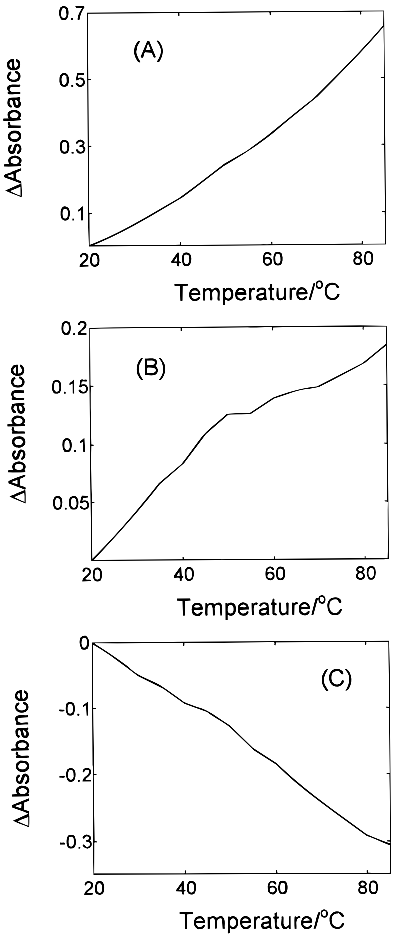

Figure 3. Absorbance variations ($A(T) - A(20\ °\mathrm{C})$) at 7101 (A), 6858 (B), and 6237 cm^{-1} (C) versus temperature for *n*-butyl alcohol.

To explore the complex mechanism of the dissociation in more detail, we have focused on a narrower window of the temperature changes. As can be seen in Figure 3, the absorbance at 6237 cm^{-1} varies nearly linearly as a function of temperature. The line for the 7101 cm^{-1} band shows a slight curvature at higher temperatures, whereas for the absorbance at 6858 cm^{-1} one can notice a distinct break point near 50 °C. Thus, we divided the entire data set into two series: 20−50 and 55−85 °C. The synchronous and asynchronous spectra were calculated for each of the series separately. Since the synchronous spectra were very similar to that shown in Figure 2B, they were not presented. It is interesting to note that the asynchronous peak at (6858, 7101) does not appear in the higher temperatures range (Figure 4B). From the sign of the asynchronous peaks we conclude that the intensity variation at 7101 cm^{-1} proceeds slower than the changes at 6237 and 6858 cm^{-1}.

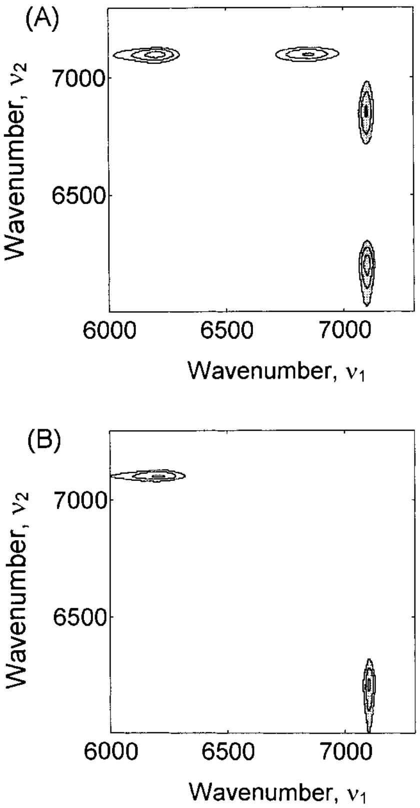

Figure 4. Asynchronous 2D NIR correlation spectra of *n*-butyl alcohol in the temperature ranges of 20−50 °C (A) and 55−85 °C (B).

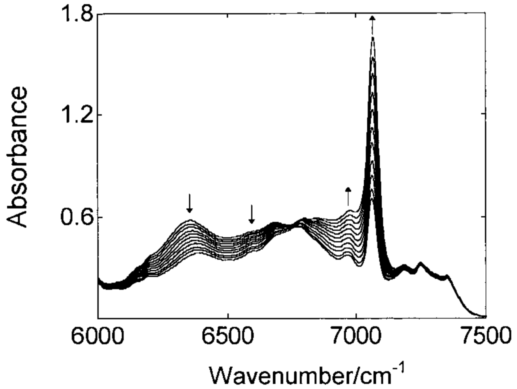

Figure 5. FT-NIR spectra of *tert*-butyl alcohol in the pure liquid state over the temperature range of 25−75 °C (↑, intensity increase with temperature; ↓, intensity decrease with temperature).

***tert*-Butyl Alcohol.** FT-NIR spectra of *tert*-butyl alcohol in the pure liquid phase were measured in the 6000−11000 cm^{-1} region over the temperature range of 25−75 °C. One can see that the intensities of bands due to the associated species (6300−6900 cm^{-1}) decrease while that of the monomer band (∼7070 cm^{-1}) increases with temperature as shown in Figure 5. The synchronous spectrum of *tert*-butyl alcohol (Figure 6A) is similar to that of *n*-butyl alcohol, developing two autopeaks at (7070, 7070) and (6322, 6322). A distinct negative cross-peak at (6322, 7070) reveals that the changes at those two wavenumbers are in the opposite direction. The asynchronous spectrum of *tert*-butyl alcohol, shown in Figure 6B, develops four cross-peaks: (6322, 7070), (6520, 7070), (6862, 7070), and (7047,7070). The sign of these peaks indicates that the intensity change at 7070 cm^{-1} is slower than that at any other wavenumbers.

The absorbance variations with temperature (not shown), for the main spectral features of *tert*-butyl alcohol, do not exhibit any distinct break points, indicating a similar mechanism of the dissociation in the entire temperature range. The asynchronous spectra presented in Figure 7 confirm above conclusion. In both spectra are present all major peaks, except the minor peak at (6520, 7070), which does not appear at lower temperatures. Fundamentally, the spectra differ only in the relative peak intensities. As can be noticed, at elevated temperatures the asynchronicity between 7047 and 7070 cm^{-1} peaks becomes stronger. The detailed inspection of the synchronous spectrum, calculated in the higher temperature range, reveals a new peak at 6610 cm^{-1} (Figure 8). Its intensity varies faster (decreases) than that of the monomer peak.

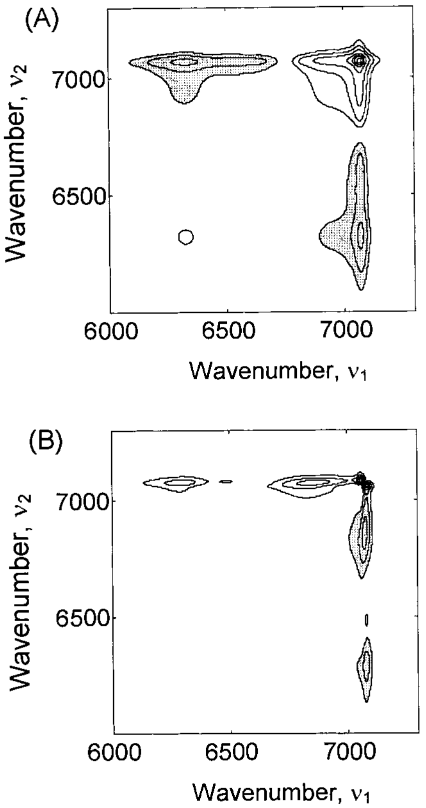

Figure 6. Synchronous (A) and asynchronous (B) 2D NIR correlation spectra of *tert*-butyl alcohol in the temperature range from 25 to 75 °C.

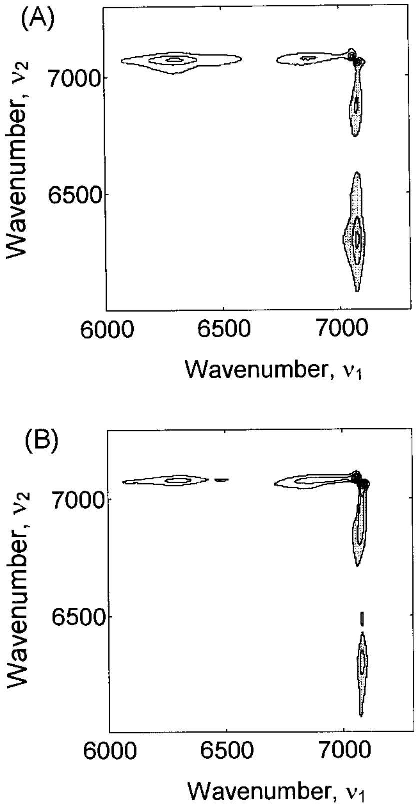

Figure 7. Asynchronous 2D NIR correlation spectra of *tert*-butyl alcohol in the temperature ranges of 25−50 °C (A) and 50−75 °C (B).

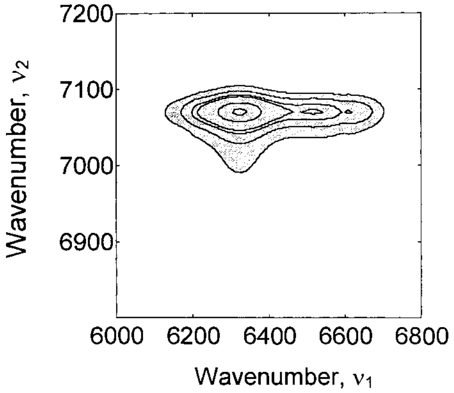

Figure 8. Localized view of the synchronous 2D NIR correlation spectrum of *tert*-butyl alcohol from 50 to 75 °C.

Discussion

Using the same assumptions as that we previously discussed,[1] we assigned all observed features due to the OH stretching modes in the first overtone region. In Table 1 are collected positions of these bands together with proposed assignments for *n*-, *sec*- and *tert*-butyl alcohols. It is readily seen that the position of the monomer band (both overtones) shows a red-shift upon branching. An opposite trend is observed for the polymer bands, whereas the location of the cyclic dimer band does not fall in line. The shift for the monomer band is due to the inductive effect, lowering the frequency. It has been shown that replacing an α-H atom by a methyl group leads to a decrease (~9 cm^{-1}) in the fundamental ν(OH).[4] On the other hand, the steric hindrance weakens the hydrogen bonding and enhances the frequency of the polymer band. Apparently, in the case of the cyclic dimers both of those effects, which act in the opposite direction, are significant and as a result the position of this band deviates from any simple trend.

The torsional potential of the OH group about the CO axis gives rise to different equilibrium positions.[4−7] As was demonstrated, two stable conformers were clearly seen in the NIR spectrum of *sec*-butyl alcohol in the pure liquid phase.[1] In principle, we may expect the existence of two different rotational isomers for *n*-butyl alcohol as well; one trans conformer (absolute energy minimum) and two equivalent gauche conformers, as illustrated in Figure 9. In the trans position the hydrogen atom of the OH group is much more accessible than in the gauche position. As will be shown, at given experimental conditions most of the OH groups are bonded. Thus, nearly all hydroxyl groups with the trans H atom are engaged in the hydrogen bonding, and hence, the corresponding band is not observed in the NIR spectrum of *n*-butyl alcohol in the pure liquid phase. In the same way we explained the intensity reversion between two rotamers of *sec*-butyl alcohol.[1] The band due to the more stable rotamer, although weak, has still appeared in the asynchronous spectrum calculated for higher temperatures. Why do not we observe the rotational isomerism for *n*-butyl alcohol in the pure liquid phase? It is well-known that the branched alcohols are less associated than the corresponding *n*-alcohols.[8−10] This means that the population of the free OH groups in *sec*-butyl alcohol is higher than that in *n*-butyl alcohol and, hence, the rotational isomers are seen more clearly in the vibrational spectra. The rotational structure of *n*-butyl alcohol should appear at higher temperatures in the pure liquid phase or in diluted solutions. Indeed, a deconvoluted NIR spectrum of *n*-butyl alcohol in CCl_4 (0.1 M) reveals the distinct doublet near 7100 cm^{-1} (Figure 10). As expected, the higher energy band attributed to the energetically favorable rotamer was more intense. It was shown that the fundamental ν(OH) band of *n*-butyl alcohol in highly diluted solutions was asymmetric. This

TABLE 1: Assignments for NIR Bands Due to the OH Stretching Modes of Various Species of *n*-, *sec*-, and *tert*-Butyl Alcohols in the Pure Liquid State

	band position (cm^{-1})		
species	*n*-butyl alcohol	*sec*-butyl alcohol	*tert*-butyl alcohol
monomer, second overtone	10386	10379	10348
monomer, first overtone	7101[c]	7089[d]	7070
free terminal OH, linear polymers		7055	7047
cyclic dimers	6858	6838	6862
cyclic polymers (small rings)			6610
(linear and) cyclic polymers[a]		6550	6520
linear and cyclic polymers[b]	6237	6275	6322

[a] Bend O−H···O. [b] Linear O−H···O. [c] In CCl$_4$ (0.1 M) this peak is split into a doublet (7084 and 7110 cm^{-1}). [d] The second rotamer is located at 7116 cm^{-1}.

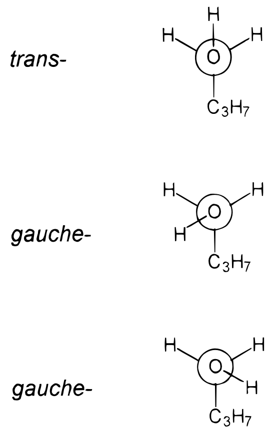

Figure 9. Rotational isomerism of *n*-butyl alcohol.

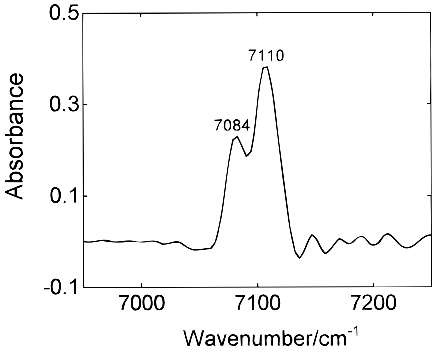

Figure 10. Deconvoluted FT-NIR spectrum of *n*-butyl alcohol in CCl$_4$ (0.1 M) at 60 °C.

effect was attributed to the presence of two rotational isomers.[11] The rotational isomerism does not occur for *tert*-butyl alcohol, as all three groups connected with the α-C atom are the same.

The fact that the hydrogen bonds in sterically hindered alcohols are considerably weaker than in straight-chain alcohols[8−10] has important consequences. First, we expect that upon branching an average chain length of the associates is shortened and, as a result, the population of the free terminal OH groups is growing. Second, the hydrogen bonds in the branched alcohols tend to break easier than in the straight chain alcohols, and during the thermal dissociation the species with shorter lengths are produced largely. Hence, a rapid increase in the population of the free terminal OH groups with temperature is expected. On this basis one can explain behavior of the band due to the free terminal OH groups in all butanols studied. The band is absent in the asynchronous 2D correlation spectrum of *n*-butyl alcohol (Figure 2B), it is hardly seen for *sec*-butyl alcohol (Figure 2B[1]), and it is the most intensive feature in the corresponding spectrum of *tert*-butyl alcohol (Figure 7B).

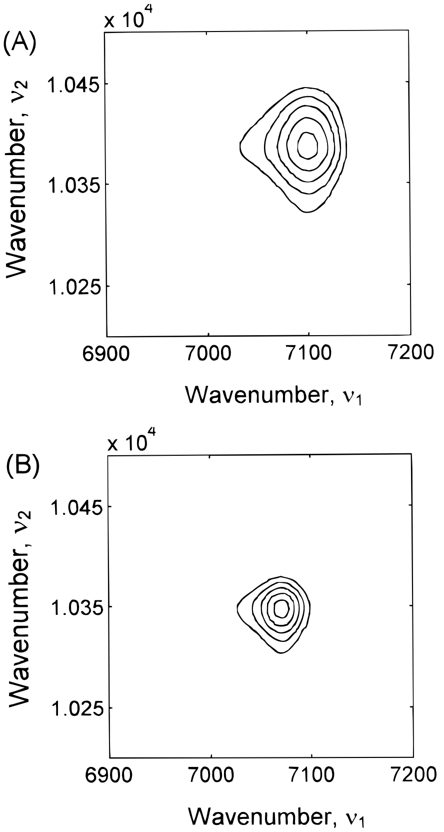

Figure 11. Expanded synchronous 2D NIR correlation spectra of *n*-butyl alcohol (A) and *tert*-butyl alcohol (B).

The "polymer" band near 6300 cm^{-1} is a composite resulting from the absorptions of OH bands at different positions in the open and cyclic chains and in the chains of various lengths. It seems reasonable that the bands due to the central OH groups of the polymers are unlikely to be distinguishable. On the other hand, the cyclic species of shorter length (dimers and trimers) are expected to be discriminated since they differ from the open chain and closed polymers in structural characteristics such as bond lengths and angles. The strains in small rings of the cyclic aggregates weaken the hydrogen bonding and give rise to a blue-shift. Hence, the band near 6850 cm^{-1} is assigned to the cyclic dimers that are intermediate species between the polymers and monomers. Initially, this band should gain in intensity, yet further temperature rise leads to a decrease in the intensity of the band. Since the observed intensity increases in the entire temperature range, we conclude that the extent of the self-association in the three kinds of butanols is high. This agrees with the results obtained for *n*-decyl alcohol, where the fraction of the free OH group was found to be less than 6% at 50 °C.[12] The more drastic changes in the hydrogen-bonding stability are expected at higher temperatures, in the vicinity of the boiling point.

It has been shown that 2D correlation spectroscopy is powerful in correlating various bands to establish unambiguous assignments.[13] As can be seen in Figures 11 and 12[1] there is a strong correlation between the first and second overtones of the OH stretching modes for all the alcohols studied. Simultaneously, no significant asynchronicity is found in this region. Therefore, the observation clearly proves that these two bands

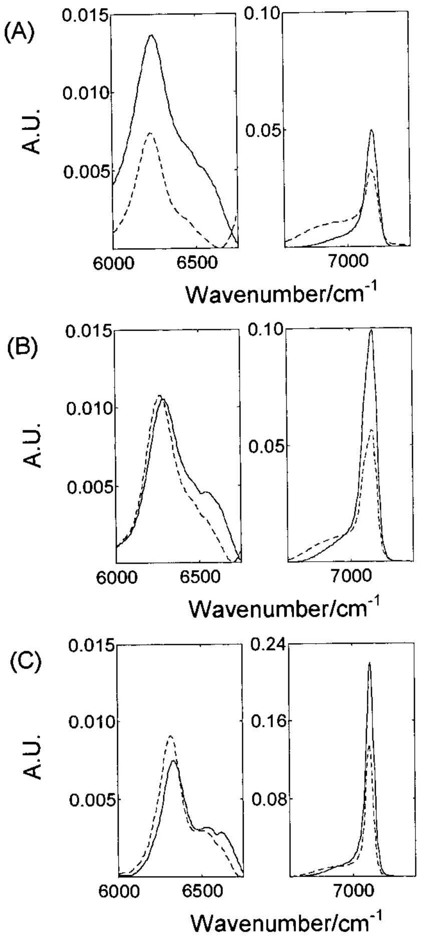

Figure 12. Power spectra of *n*-butyl alcohol (A), *sec*-butyl alcohol (B), and *tert*-butyl alcohol (C) in the temperature ranges of 25−50 °C (dashed line) and 50−75 °C (solid line).

share the identical temperature-dependent pattern of the intensity changes and that they come from the same molecular fragment.

The general mechanism of the thermal dissociation is very similar for all butanols examined. The bands due to the monomer and cyclic dimer gain in intensity as temperature increases at the expense of the polymer bands (Figures 1, 5, and 1[1]). This signifies that the dissociation of the polymers leads to the increase in the population of the cyclic dimers and monomers. From the sign of the asynchronous cross-peaks (Figures 2B, 6B, and 2B[1]), it results that the changes for the monomers occur slower than that of the polymeric species. The careful examination of the asynchronous 2D correlation spectra in the different temperature ranges (Figures 4, 8, 4,[1] and 6[1]) shows that the rate of the initial increase in the population of the dimers is diminished by the dissociation into monomers at elevated temperatures. Therefore, the intensity changes due to the cyclic dimers and monomers happen more accordingly. This effect is particularly noticeable for *n*-butyl alcohol, where the dimer band does not appear in the asynchronous spectrum calculated for higher temperatures.

Additional information about the mechanism of dissociation provided an analysis of the power spectra calculated in the low and high temperature ranges (Figure 12). To compare the absolute values of the autocorrelation intensities (diagonal of the synchronous spectrum), all the power spectra were determined in the same temperature intervals by using the same number of the spectra. One can easily notice that the monomer band is always more intense in higher temperature range, indicating that the population of this species is growing faster at elevated temperatures. A marked increase in the intensity of the monomer band on going from *n*- to *tert*-butyl alcohol is consistent with the direction of decreasing stability of the hydrogen bonding. On the other hand, the rate of population decay of the polymeric species varies from one butanol to another. For *n*-butyl alcohol the polymers dissociate faster at higher temperatures range. In the case of *sec*-butyl alcohol this rate seems to be temperature-independent, whereas for *tert*-butyl alcohol the population of the polymers decreases more slowly at elevated temperatures. The intensity and half-width of the polymer band in the 50−75 °C range systematically decrease upon branching, revealing the additional peaks on the high-frequency side of this band. It has been shown that at elevated temperatures an appreciable dissociation of the cyclic species into open chain ones takes place.[1] Opening of the closed polymer rings increases the population of the free terminal OH groups and linear hydrogen bonds contributing to the polymer band. Thus, this process partially compensates the rapid intensity drop of the polymer band at higher temperatures. As stated earlier, the band due to the free terminal OH group appears more clearly upon going from *n*- to *tert*-butyl alcohol. In the same direction the rate of the intensity variations in the polymer band decreases. On the other hand, the intensity of the monomer band is growing faster at higher temperatures for all the samples studied. It is obvious that this growth comes from the dissociation of the transition species, mainly short cyclic associates. The appearance of the 6610 cm^{-1} peak for *tert*-butyl alcohol supports the above conclusion.

The temperature dependence of ΔA at 6858 cm^{-1} for *n*-butyl alcohol exhibits a distinct break point near 50 °C (Figure 3B). Above this temperature the population of the cyclic dimers increases slower because of the dissociation into monomers. Such a break point indicates that the dissociation of the dimers is not a continuous process but requires activation energy comparable with kT, where k is the Boltzmann constant and T is the absolute temperature. The break point is less clear for more branched butanols. Hence, one may conclude that the stability of the cyclic dimers is reduced upon branching.

Conclusions

Three bands have been found in the 2D NIR correlation spectra of *n*-butyl alcohol in the pure liquid phase. They were assigned to the first overtone of the OH stretching modes of the monomer (7101 cm^{-1}), cyclic dimers (6858 cm^{-1}), and linear hydrogen bonds in polymers (6237 cm^{-1}). The corresponding bands in the 2D correlation spectra of *tert*-butyl alcohol in the pure liquid phase were localized at 7070, 6862, and 6322 cm^{-1}, respectively. The spectra of *tert*-butyl alcohol developed additional bands attributed to the free terminal OH groups (7047 cm^{-1}), hydrogen-bonded OH groups in small cyclic rings (6610 cm^{-1}), and bend hydrogen bonds in polymers (6520 cm^{-1}). The band at 6610 cm^{-1} was reported for the first time. These assignments are consistent with our previous work on *sec*-butyl alcohol. In contrast to *sec*-butyl alcohol, rotational isomerism was not detected for *n*-butyl alcohol in the pure liquid state. This fact was explained by smaller population of the free OH groups in *n*-butyl alcohol as compared to *sec*-butyl alcohol. The splitting of the monomer band due to the rotational isomerism was clearly observed in the diluted solutions of *n*-butyl alcohol. It has been shown that the dissociation of the polymers leads to an increase in the population of the cyclic dimers and monomers. The changes for the monomers are slower than that of the polymeric species. At elevated temperatures the dimers tend to dissociate into monomers. This tendency is seen more clearly for *n*-butyl alcohol. An analysis of the power spectra revealed that the population of the monomers is growing faster at higher temperatures and the extent of these changes increases upon branching. As the rate of the intensity changes for the polymer band decreases in the same direction, this means that the population of the monomers is growing at the expense of the small cyclic species. The effect is more distinct on going from *n*-butyl alcohol to *tert*-butyl alcohol.

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