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Effect of Temperature and Concentration on Self-Association of Octan-1-ol Studied by Two-Dimensional Fourier Transform Near-Infrared Correlation Spectroscopy

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Temperature- and concentration-dependent variations in self-association of octan-1-ol were studied by two-dimensional (2D) Fourier transform near-infrared (NIR) correlation spectroscopy. The obtained results suggest a similar mechanism of the thermal dissociation of hydrogen-bonded species for octan-1-ol and other straight chain alcohols (butan-1-ol, decan-1-ol). However, the extent of self-association in neat butan-1-ol seems higher than that for longer chain alcohols (octan-1-ol, decan-1-ol) under the same experimental conditions. At low and moderate concentrations of octan-1-ol in CCl_4 the dimers are open, while in the pure liquid alcohol one can find some cyclic dimers. In both phases the cyclic aggregates dominate and the amount of the linear species is negligible. The population of the free OH groups increases with temperature, reaching 13% at 80 °C, and this increase occurs faster at elevated temperatures. The synchronous peak near 6600 cm^{-1} is shown to be a part of the broad polymer band, whereas the feature near 6500 cm^{-1} was assigned to the $\nu_{CH} + \nu_{OH}$ combination mode involving the free OH group. The molar absorptivities of the first and second overtones of the monomer band are similar for various alcohols and do not depend on the solvent. As shown, the second overtone of the monomer band is 20 times less intense than the corresponding first overtone.

Introduction

The self-association of alcohols is a complex phenomenon, since a large number of open and cyclic associates of many sizes can be formed. The mid- and near-infrared spectra of alcohols were discussed in the literature for more than half a century,[1−13] and there are numerous more recent studies.[14−23] Nevertheless, there are still controversies on the nature and amount of various hydrogen-bonded forms. A particular controversy concerns the structure and population of dimeric species. Although the cyclic dimers have frequently been postulated in the past,[1,3,13] nowadays a dimer is expected to have an open structure.[14,20−23] Some authors report that the amount of the dimers in nonpolar solvents is negligible.[4,5,19] In contrast, others prove that these species exist over all alcohol concentrations, from diluted solutions to neat alcohol, with the maximum at about 0.1 M.[10,14] Many reports show that the monomer−cyclic tetramer[4,5,15,19] or monomer−linear dimer−cyclic tetramer[10,12,14,24] equilibrium fits the best experimental data. On the other hand, one can find works showing that linear multimers are dominant and the number of n-mers increases as the concentration of alcohol increases.[20,25,26]

Most studies on the self-association behavior of alcohols have been performed at low or moderate concentrations of the sample. Despite a great progress in the instrumental techniques and computational methods, explorations of pure liquid alcohols are still rare.[15−17] The IR spectra of neat alcohols, in the ν(OH) region, are dominated by a broad polymer band, and the shorter associates (if existed) are obscured. The monomer band also is very weak under these conditions. In contrast, the NIR region offers some advantages. The less associated species have the stronger overtones.[27,28] Moreover, the bands due to different hydrogen-bonded forms are better separated at the level of the overtones.[28] Unfortunately, most of the NIR spectra consist of a series of heavily overlapped bands and the analysis in this region demand extensive use of computational methods.

An application of the generalized two-dimensional correlation approach provided more detailed information and more insight into the self-association behavior of the alcohols.[29−32] The resolution enhancement in 2D correlation spectra permits identification of many peaks due to free and associated OH groups. The selective correlation of these peaks makes the band assignment easier and more reliable. The sign of the asynchronous peaks provides information about the relative rate of the intensity changes at particular wavenumbers. This feature is especially useful for exploration of the mechanism of the self-association process. Furthermore, the 2D correlation spectra are simpler than the normal NIR spectra, as the bands that do not vary in their intensities do not appear in the correlation spectra. All former 2D correlation studies on self-association of alcohols applied temperature as a perturbation.[29−32] However, the generalized 2D correlation method is applicable to various kinds of perturbations, including concentration.[33,34] In principle, decreasing concentration at constant temperature and increasing temperature at constant concentration (in neat alcohol) should lead to enhancement in the population of the monomers at the expense of the polymers. Since the concentration of octan-1-ol in CCl_4 (0.003−1.0 M) and in the pure liquid alcohol (6.28 M) differs appreciably, one may expect some differences in the mechanism of this process.

The present paper provides new experimental information on the effect of temperature and concentration on the self-association of octan-1-ol by using 2D FT-NIR correlation spectroscopy and classical methods such as second-derivative or Fourier self-deconvolution (FSD). On the basis of these results, a general model of the self-association of octan-1-ol in CCl_4 and in the pure liquid phase is proposed. From the measurements at low concentrations the molar absorption

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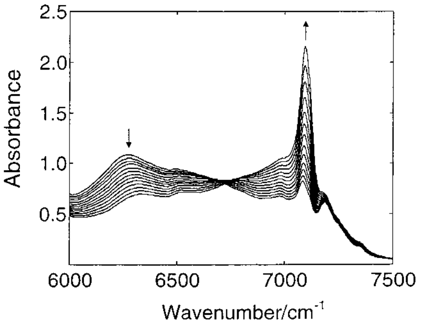


Figure 1. FT-NIR spectra of liquid octan-1-ol over the temperature range of 20−80 °C (↑, intensity increases; ↓, intensity decreases).

coefficients for the first and second overtones of the monomer band are determined. Next, these values were used for the estimation of the population of the monomers in the pure liquid octan-1-ol as a function of temperature. The present results are discussed with relevant previous studies.

Experimental Details and Data Processing

Octan-1-ol and CCl_4 (spectroscopic grade) were purchased from Aldrich Chemical Co. and used without further purification. 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 spectral measurements of octan-1-ol in CCl_4 were performed in a thermostated quartz cell of 1 cm thickness (Hellma) at 25 °C in the range of concentrations 0.003−1.0 M, while the spectra of pure octan-1-ol were measured in the same cell from 20 to 80 °C in increments of 5 °C. The spectra recorded as a function of temperature were corrected for the density change with temperature, whereas the concentration-dependent spectra were concentration-normalized.[34]

The calculations of the generalized 2D correlation approach were based on the Hilbert transformation of the dynamic spectra,[35] and temperature- or concentration-averaged spectra were employed as references. The negative peaks, both synchronous and asynchronous, were striped. To simplify interpretation of the correlation spectra, the asynchronous spectra were multiplied by a sign of the companion synchronous spectra. In a synchronous spectrum, a positive peak at (ν_1, ν_2) reveals that the intensity changes at these two wavenumbers are in the same direction. A positive asynchronous peak at (ν_1, ν_2) means that the spectral change at ν_1 occurs faster than that at ν_2. Negative synchronous and asynchronous peaks indicate the opposite. The 2D correlation analysis was carried out using MATLAB 4.2 (The Math Works Inc.), while the second derivative and FSD were achieved using GRAMS/386 (Galactic Inc.)

Results and Discussion

2D Correlation Analysis of Temperature-Dependent Spectra of Pure Liquid Octan-1-ol. Figure 1 displays density-normalized FT-NIR spectra of neat octan-1-ol in the temperature range 20−80 °C. The arrows show directions of the intensity changes with an increase in temperature. The first overtone of the monomer (7100 cm^{-1}) and the polymer (6250 cm^{-1}) bands are overlapped by the C−H combination bands (7180 and 6980 cm^{-1}).[36] Since the C−H combination bands are not involved in hydrogen bonding, they do not vary in their intensities with temperature (after normalization). As a result, these bands do not appear in the 2D correlation spectra. The band assignments of various 2ν(OH) modes due to the free and associated species (Table 1) are based on the foundations presented in a previous paper.[30] In Figure 2 are shown 2D correlation spectra of liquid octan-1-ol over the temperature range 20−80 °C. The synchronous spectrum develops autopeaks at 7095 and 6250 cm^{-1}. A negative cross-peak at (7095, 6250 cm^{-1}) reveals that the intensity changes for both bands occur in the opposite direction. In other words, the increase in population of the monomers is correlated with the decrease in population of the polymers. However, the asynchronicity between these peaks (Figure 2b) suggests that the polymers do not dissociate directly into the monomers but the process proceeds through intermediate species. Moreover, the asynchronous spectrum develops a peak at (7095, 6850 cm^{-1}) and the other one near the diagonal (7105, 7075 cm^{-1}). The feature at 6850 cm^{-1} may tentatively be assigned to the cyclic dimers,[30−32] but its exact origin will be discussed afterward. The doublet near 7100 cm^{-1} is due to the rotational isomerism of the free OH group.[29−32] The sign of the asynchronous peaks reveals that the population of the monomers changes slower than that of the associated species. As the low-frequency rotamer (gauche) is less accessible for hydrogen bonding than the other rotamer (trans), its intensity increases faster upon increase of temperature. The asynchronous spectra of neat octan-1-ol (Figure 2b) and decan-1-ol (Figure 2b, ref 32) are similar. In contrast, the spectrum of butan-1-ol

TABLE 1: Frequencies (cm^{-1}) and Assignments of the NIR Bands Due to the OH Stretching Modes of Various Species of Octan-1-ol

species	2D correlation spectra				2nd deriv/FSD	
	a		b		*a*	*b*
	syn	asyn	syn	asyn		
monomer, 1st overtone	7095		7105			
trans rotamer		7105		7110	7110	7115
gauche rotamer		7075		7080	7080	7085
cyclic dimer, 1st overtone		6850				
$\nu_{CH} + \nu_{OH(free)}$			≈6500			
polymer, 1st overtone	6250	6200	6290	6190		

[a] In the pure liquid octan-1-ol. [b] Octan-1-ol in CCl_4 at 25 °C.

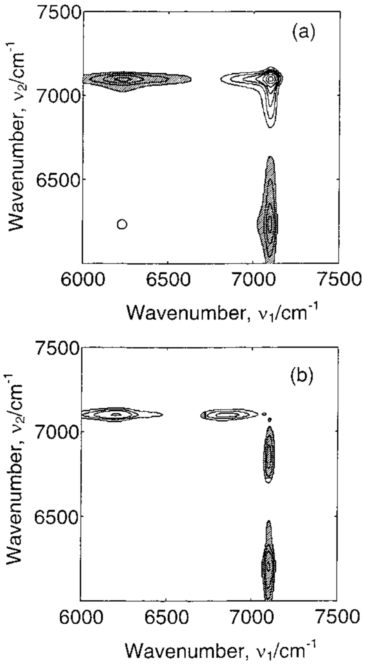
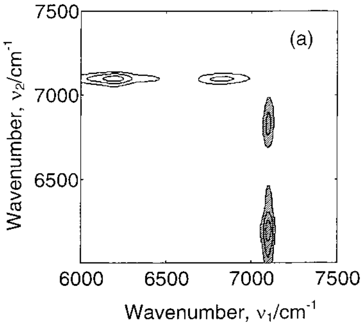


Figure 2. Synchronous (a) and asynchronous (b) 2D NIR correlation spectra of liquid octan-1-ol in the temperature range from 20 to 80 °C. The negative synchronous and asynchronous peaks are striped.



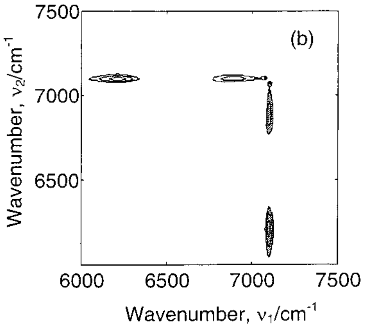


Figure 3. Asynchronous 2D NIR correlation spectra of liquid octan-1-ol in the temperature ranges of 20−50 °C (a) and 50−80 °C (b). The negative synchronous and asynchronous peaks are striped.

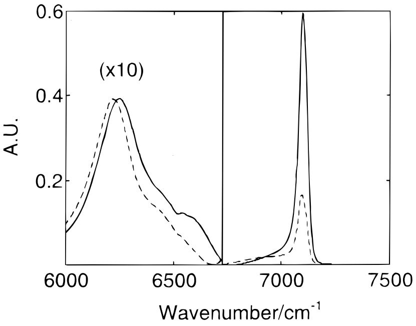
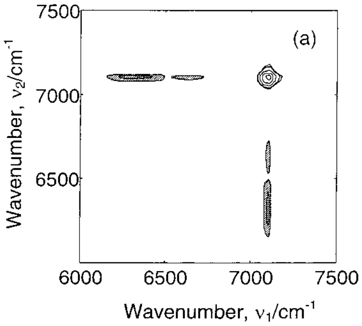


Figure 4. Power spectra of liquid octan-1-ol in the temperature ranges of 20−50 °C (dashed line) and 50−80 °C (solid line).

(Figure 2b, ref 31) does not develop a peak due to the rotational isomerism of the free OH group. This band occurs at relatively high population of the monomers, so one can conclude that butan-1-ol is more associated than octan-1-ol and decan-1-ol. Figure 3A,B show 2D asynchronous spectra of liquid octan-1-ol in the low (20−50 °C) and high (50−80 °C) temperature ranges, respectively. Note that the peak originating from the rotational isomerism appears only at higher temperatures. This observation evidences that the increase in the population of the monomers is faster at higher temperatures.

Further details one can obtain by comparison of the power spectra calculated in the low- and high-temperature ranges (Figure 4). The power spectrum is a diagonal of the synchronous spectrum and yields information about the overall extent of the intensity variations at particular wavenumbers. As can be seen, the intensity of the monomer band of octan-1-ol increases more rapidly at higher temperatures. This result agrees with the earlier conclusion. On the other hand, the polymer band has comparable intensity for both temperature ranges, but its position shifts toward higher wavenumbers at elevated temperatures. Such a shift, connected with a simultaneous fast increase in the population of the monomers, suggests the reduction of an average size of the hydrogen-bonded associates.



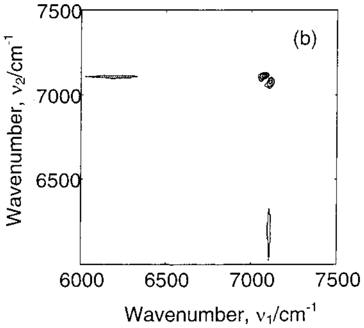


Figure 5. Synchronous (a) and asynchronous (b) 2D NIR correlation spectra of octan-1-ol in the concentration range from 0.1 to 1.0 M. The negative synchronous and asynchronous peaks are striped.

2D Correlation Analysis of Concentration-Dependent Spectra of Octan-1-ol in CCl_4. The concentration-dependent dynamic spectrum was arranged in increasing order of concentrations. Thus, the concentration-normalized intensity of the monomer band decreases, while that of the polymer peak increases. Figure 5 shows 2D correlation spectra of octan-1-ol in CCl_4 over the range of concentrations 0.1−1.0 M. The synchronous spectrum is dominated by the autopeak due to the monomer (7105 cm^{-1}) that is negatively correlated with the polymer band (6290 cm^{-1}) and a peak near 6600 cm^{-1}. The companion asynchronous plot develops a peak between the monomer and polymer at (7110, 6190 cm^{-1}). The sign of this peak suggests that the normalized intensity of the monomer peak decreases faster than increases the intensity of the polymer peak. Close to the diagonal appears an intense peak at (7110, 7080 cm^{-1}), which originates from the rotational isomerism of the free OH group. The observation that the monomer peak also has a fine structure at low concentrations (<0.02 M) supports this assignment. The low-frequency component is assigned to the less stable gauche rotamer, while the other peak is attributed to the more stable *trans* rotamer.[30−32] As expected, the population of the *trans* rotamers decreases faster with an increase in concentration.

The 2D correlation spectra of some alcohols reveal a feature in the 6500−6600 cm^{-1} range.[30,31] Increasing temperature leads to a reduction in the intensity of this feature, and hence it was assigned to the associated species (O−H···O bending).[30,31] However, this peak does not occur in the asynchronous spectra though its pattern of the intensity changes is expected to be different from that of the monomer band. Interestingly, this feature appears more distinctly in the synchronous spectra of branched alcohols at higher temperatures, where the population of the monomers is relatively high.[30,31] All these facts suggest that the feature near 6600 cm^{-1} is only a part of the polymer band and cannot be assigned to any particular species. Thus, the previous assignment of this band reported for some butanols was not correct.[30,31] The actual spectral feature is found near 6500 cm^{-1} and it originates from the $\nu_{CH} + \nu_{OH}$ combination

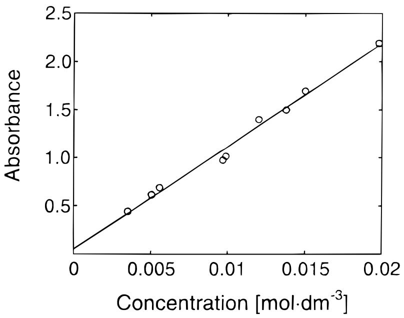


Figure 6. Concentration dependence of the integrated intensity of the first overtone of the monomer band for octan-1-ol in CCl_4.

TABLE 2: Molar Absorptivities of the First (2ν(OH)) and Second (3ν(OH)) Overtones of the Monomer Band for Selected Alcohols[a]

alcohol	2ν(OH)		3ν(OH) Int	solvent	ref
	Int	PH			
octan-1-ol	107.0 ± 2.0	1.78 ± 0.05	5.4 ± 0.2	CCl_4	this work
		1.6		decane	4
		1.65 ± 0.03		CCl_4	5
		1.68 ± 0.05		octane	10
		1.65		decane	15
pentan-1-ol		1.76		heptane	14
pentan-3-ol		1.68		heptane	14
decan-1-ol	111.1		5.5	CCl_4	17
dodecan-1-ol		1.61 ± 0.05		octane	10
oleyl alcohol	103.2	1.63	5.0	CCl_4	18
		1.64		decane	16

[a] Int, integrated, in $dm^3 \cdot mol^{-1} \cdot cm^{-2}$. PH, at peak height, in $dm^3 \cdot mol^{-1} \cdot cm^{-1}$.

mode involving the free OH group. The present assignment is consistent with earlier reports showing that the alcohols and phenols reveal a few weak bands near 6500 cm^{-1}, which are due to $\nu_{CH} + \nu_{OH(free)}$ combination modes.[8,28] As the intensity changes for the combination and the polymer bands are in opposite direction, the former band appears as a hole on the broad polymer band envelope. Obviously, the relative population of the free OH groups is higher for octan-1-ol in CCl_4 than for the liquid alcohol, and therefore, the combination band is more evident in the former case.

Determination of the Molar Absorptivities for 2ν(OH)$_{free}$ and 3ν(OH)$_{free}$. At low concentrations of octan-1-ol in CCl_4 (0.003−0.02 M) the intensity of the monomer is a linear function of the total concentration (Figure 6). This relationship permits determination of the molar absorptivities for the first and second overtones of the monomer band. In Table 2 are collected the values obtained for octan-1-ol together with available literature data for other alcohols.[4,5,10,14−18] Interestingly, the molar absorptivities for all alcohols are similar and do not depend on the solvent. Many studies also reveal that these values are temperature independent.[4,5,15,17] Note, that the integrated molar absorptivity of the first overtone of octan-1-ol is 20 times higher than the corresponding value for the second overtone, just as for decan-1-ol[17] and oleyl alcohol.[18]

Temperature Dependence of the Degree of Dissociation in the Pure Liquid Octan-1-ol. The determination of the integrated intensity of the first overtone of the monomer band and the corresponding molar absorptivity permits the estimation of the degree of dissociation in liquid octan-1-ol as a function of temperature.[17] As can be seen (Figure 7), most of the molecules of octan-1-ol are involved in hydrogen bonding in the studied temperature range, and the population of the monomers at 80 °C is smaller than 14%. Extrapolation of this dependence to the boiling point (196 °C) provides a value of about 85%, indicating that even at this temperature the population of the hydrogen-bonded species still is appreciable. One has to admit that this relationship is closely similar to an analogous plot for decan-1-ol,[17] showing comparable strength of the hydrogen bonding for both alcohols.

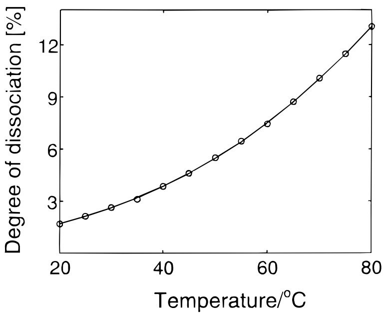


Figure 7. Temperature dependence of the degree of dissociation for liquid octan-1-ol.

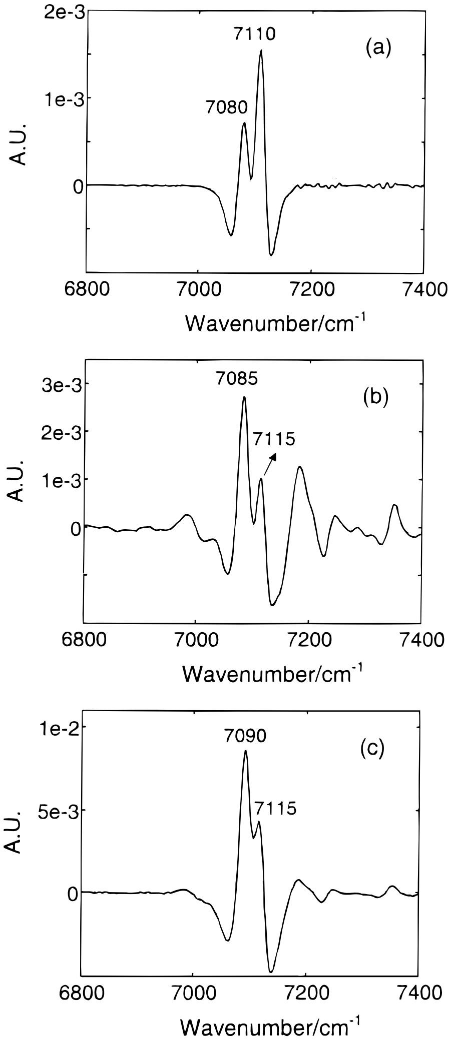


Figure 8. Second derivative FT-NIR spectra of octan-1-ol in CCl_4 (0.1 M) at 25 °C (a) and in the pure liquid phase at 25 °C (b) and 80 °C (c). The spectra were multiplied by (−1).

Second Derivative Spectra. In Figure 8 are displayed the second derivative spectra of octan-1-ol in CCl_4 at 25 °C and in the liquid alcohol at 25 and 80 °C. FSD spectra (not shown) yield the same information as the second derivative data. As can be seen, in each case the monomer band splits into a doublet. This splitting was also found for others alcohols and was attributed to the rotational isomerism of the free OH group.[17,29−32] As expected, in solution in CCl_4 the more stable *trans* rotamer (higher frequency) dominates, while in the liquid octan-1-ol the opposite is the case. Due to the higher accessibility of H in the *trans* position the population of this species is reduced faster upon going from a diluted solution to the neat alcohol.[31] The above example reveals the significant effect of concentration on the relative intensities of both rotational isomers, whereas the influence of temperature is less prominent. As a result, a strong asynchronicity occurs between both rotamers in the concentration-dependent spectra (Figure 5). The analogous peak in the temperature-perturbed spectra is less evident (Figures 2 and 3).

Assignment of the Dimer Band. The linear relationship between the intensity of the monomer band and the concentration shows that primary alcohols exist as monomers up to a concentration of at least 0.02 M.[10,17] The encounter of two molecules is more likely than that of three or more molecules. Thus, it seems reasonable that a dimer is the first associated species formed as the concentration increases. As stated earlier, the temperature-dependent 2D correlation spectrum of neat octan-1-ol reveals a peak near 6850 cm^{-1}. On the basis of the foundations previously described,[30] this peak was assigned to the cyclic dimer. The lack of this peak in the concentration-dependent spectra proves that, at low and moderate concentrations of alcohol, the dimers are open. Since the strength of hydrogen bonding in the open dimers seems to be not very different from that in the open chain polymers, the corresponding band should absorb in the region of the polymer band.[3,30] On the other hand, the band due to the free OH group in the dimers is heavily overlapped by the monomer band. As a result, the open dimer does not have its own band in the normal NIR spectrum. Yet, the resolution enhancement in the asynchronous spectra does not depend on the separation of the peaks but is based on the difference in the response function at particular wavenumbers.[33−35] The patterns of the intensity changes for the bands originating from the monomers and the free terminal groups in the open-chain associates are expected to be different. This means that, at small and moderate concentrations of octan-1-ol in CCl_4, the cyclic associates dominate, while the amount of the linear associates is negligible. This result appears to be consistent with numerous reports for other alcohols.[4,5,12,15,19,22,23]

In the literature one can find reports showing the validity of the same model of self-association of alcohols for a wide range of concentrations,[4,13,15,19] from diluted solution to the pure liquid. However, the present study does not support this picture. Different numbers of peaks observed in octan-1-ol in CCl_4 and in neat alcohol make clear that the same model of self-association cannot be applied in both cases. Interestingly, the peak near 6850 cm^{-1} was observed for all alcohols studied by the 2D correlation method.[29−32] The position of this feature suggests that it originates from a weakly hydrogen-bonded species. The only reasonable candidates in this case seem to be the short cyclic species.[3,30] Ehbrecht and Huisken argued that the absorption spectra of the larger clusters are similar to those of the trimer spectrum.[21] This means that all those species should absorb in the same region, e.g. contribute to the polymer band, and none of those species could be responsible for the absorption at 6850 cm^{-1}. Therefore, this band can be assigned to the cyclic dimers. Ab initio calculations for methanol and ethanol show that the cyclic dimer is a transition state rather than a stable form.[22,23] However, one has to stress that these calculations were performed for the isolated small size hydrogen-bonded aggregates. Thus, these results may help in a band assignment for gas phase, matrix isolation, or diluted solution experiments. Ab initio calculations of hydrogen-bonded systems are not yet well developed[22,23] and cannot be used as a reliable basis for interpretation of the results for liquid alcohols.

Conclusions

The temperature- and concentration-dependent studies reveal that octan-1-ol in CCl_4 (at low and moderate concentrations) forms mainly cyclic aggregates, while the population of the open species seems to be relatively small. The dimers are open under these conditions and have two nonequivalent O−H bonds. The bonded OH group absorbs in the region of the polymer band, whereas the band originating from the free OH group is overlapped by the monomer band. The band due to the free terminal OH group in linear polymers does not occur in the temperature-dependent 2D correlation spectra of liquid octan-1-ol. This reveals that in neat alcohol the cyclic associates also dominate. The population of the monomers in neat octan-1-ol increases as the temperature increases, but even at 80 °C this value does not exceed 14%. The presence of the peak near 6850 cm^{-1} suggests that some cyclic dimers exist in liquid octan-1-ol. The feature near 6600 cm^{-1} has appeared to be part of the polymer band, while the hole near 6500 cm^{-1} was assigned to the $\nu_{CH}+\nu_{OH}$ combination mode involving the free OH group. The molar absorptivities of the first and second overtones of the monomer band for octan-1-ol are compared to those found in the literature for other alcohols. It appears that these values are similar and do not change significantly with the solvent. Furthermore, the second overtone of the monomer band is 20 times weaker than the corresponding first overtone.

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