INTERMOLECULAR HYDROGEN BOND IN TERTIARY BUTYL ALCOHOL AND ITS SOLUTIONS. RAMAN SCATTERING SPECTRA

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It is found that the 750 cm^{-1} band in pure tertiary butyl alcohol shows attributes of a complex structure that can be interpreted as a result of the superposition of several closely located lines belonging to different aggregates of alcohol molecules. As the alcohol is diluted with neutral solvents, the width of this band passes through a maximum that corresponds to the concentration of the mixture with comparable contents of various most stable aggregates in the solution. The performed quantum-chemical calculations confirm the complexity of the 750-cm^{-1} band of pure alcohol caused by the aggregation of molecules by means of hydrogen bonds. The calculated energy gain due to the formation of a hydrogen bond (dimer) amounts to 19.7 kJ/mole, and the length of the hydrogen bridge equals 2.068 Å.

1. Introduction

Tertiary butyl alcohol (TBA) is notable for its poor solubility in water, which results in weaker proton-donor and proton-acceptor properties of TBA as compared to other low-molecular alcohols. A definite role is evidently played here by large dimensions of the TBA molecule. According to [1], the Rayleigh light scattering in water solutions of tertiary butyl alcohol is characterized by a high intensity of scattering by concentration fluctuations, which is an evidence of the poor solubility of this alcohol on the molecular level. In addition to the peak of light scattering by concentration fluctuations appearing at an alcohol content of 0.15 MF, the concentration dependence of the intensity of Rayleigh isotropic light scattering contains a narrow peak at the 0.03 MF alcohol concentration. The height of this intensity peak is twice larger than that of light scattering by concentration fluctuations. This additional maximum is associated with the rearrangement of the structure of liquid water [1].

There arises a natural question about how this rearrangement manifests itself in the vibrational spectrum of Raman scattering (RS)?

It was supposed in [2, 3] that, in water solutions of ethyl and isopropyl alcohols, there exists a parallelism between the concentration dependence of the Rayleigh light scattering intensity (additional maximum) and the concentration dependence of the form of the C–O and C–C vibrational bands in the RS spectra. According to the interpretation proposed in [2, 3], the C–C or C–O vibrations in ethyl and isopropyl alcohols belong to such a kind, where vibrating atoms do not directly participate in the hydrogen bond, but its formation has an effect on these vibrations as well. As was shown in [4–7], the bands of such vibrations have a complex structure related to the superposition of bands of various aggregated formations weakly differing in frequency, but (possibly) differing in the depolarization coefficients. In some cases, this complexity of the resulting band can lead to the noncoincidence of the maxima of the constituent bands in scattered light of different polarizations. In proton-donor and proton-acceptor mixtures, the concentration dependence of the band width can pass through a maximum. What will be observed in the case of a more complex alcohol – tertiary butyl alcohol?

Our studies were carried out for the 750-cm^{-1} band of the alcohol (non-characteristic band). We investigated the RS spectra of TBA and its solutions with chloroform,

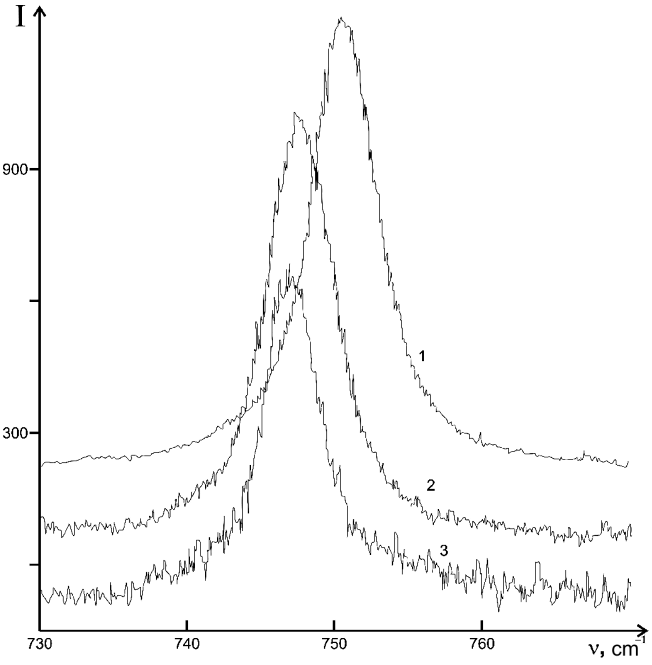

Fig. 1. 750-cm^{-1} band of TBA in solutions with chloroform at various alcohol contents: (*1* — pure liquid, *2* – 0.2 MF, *3* – 0.05 MF). Intensities hereinafter are not reduced to a single scale

hexane, and water. Along with experimental researches, we also performed quantum-chemical calculations of the dimer aggregation of alcohol molecules.

2. Experimental Part

The RS spectra of liquid TBA and its mixtures with chloroform, cyclohexane, and water were studied with the use of an automatized DFS-52 spectrometer with diffraction gratings having a 1800 l/mm line density. The scattering was excited by an LGN-503 argon laser with a wavelength of 488 nm and a power of 1 W. All measurements were performed at the 90-degree scattering geometry of linearly polarized exciting light. The polarization constituents of the scattered light bands were selected with the help of a polarization prism. The experiment was carried out with the use of chemically pure substances subjected to the additional vacuum distillation before measurements. The spectral width of the gap was equal to 1.8 cm^{-1} in all experiments. The errors of measuring the half-width and the relative position of the bands were equal to ±0.3 cm^{-1}. The investigations were performed at a temperature of 25 ± 3 °C. The concentration of the mixtures was determined in the units of molar fractions (MF).

3. Results and Discussion

Let us consider the behavior of the 750-cm^{-1} band of TBA in solutions. Figure 1 demonstrates the form of the bands of pure alcohol and some of its solutions in chloroform. In the case of pure alcohol, the band is strongly polarized with a maximum depolarization coefficient equal to 0.01. It was supposed in the experiments that the maximum of the polarization-undecomposed band coincides with that of the isotropic component. In the mixture with chloroform, a low-frequency shift of the band is observed (∼3 cm^{-1}). As one can see from the table, the concentration dependence of the width of the considered line in this mixture passes through a maximum at an alcohol content of ∼0.6 MF.

Such a behavior of the half-width as a function of the concentration should be explained in the following way. Alcohols belong to liquids, in which the intermolecular hydrogen bond determines, to a great extent, the properties of a substance. It is evident that the intermolecular hydrogen bond must be present in TBA as well. A special form of the molecules and their comparatively large dimensions must result in a different ratio of monomeric and aggregated molecules in pure TBA as compared to more low-molecular alcohols. However, the presence of aggregates of various compositions must lead to the complexity of the 750-cm^{-1} band, or rather it must consist of at least two lines corresponding to different most stable alcohol aggregates. Low-activity chloroform must destroy alcohol aggregates, which will result in the variation of the ratio of various aggregated formations due to the dilution of the alcohol.

Judging by the behavior of the band half-width, the shares of different most stable aggregates are equalized at an alcohol concentration of ∼0.6 MF. A further dilution of the alcohol results in an increase of the relative number of aggregates of one kind (possibly monomers). At the least alcohol concentration (0.05 MF), the aggregates remaining in the mixture are predominantly of one kind.

Similar results for the 750-cm^{-1} TBA band were also obtained in the case of another (completely neutral) solvent — cyclohexane. In the same way as in the "chloroform – alcohol" solution, the band shifts toward lower frequencies (∼3 cm^{-1} at a concentration of 0.03 MF). At low alcohol contents (0.2 MF), the band starts widening, by reaching 6.3 cm^{-1} at an alcohol concentration of 0.05 MF and then narrows to 5.0 cm^{-1} at the 0.01-MF alcohol content. In other words, the above-stated assumption about the role of chloroform in the destruction of alcohol aggregates proves to be correct. The small shift

Half-widths($\Delta\nu$, cm^{-1}) of the 667-cm^{-1} band of chloroform and the 750-cm^{-1} band of TBA in mixtures

C (MF)	$\Delta\nu$ (667 cm^{-1}) CHCl$_3$ in C$_4$H$_9$OH	$\Delta\nu$ (750 cm^{-1}) C$_4$H$_9$OH in chloroform	$\Delta\nu$ (750 cm^{-1}) C$_4$H$_9$OH in hexane	$\Delta\nu$ (750 cm^{-1}) C$_4$H$_9$OH in water
1.0	5.4	5.2	5.2	5.2
0.9	5.5	5.5	–	–
0.8	5.6	5.6	5.2	6.6
0.7	6.4	6.0	–	–
0.6	6.6	6.2	–	–
0.4	7.6	6.0	5.1	7.0
0.2	8.4	5.5	5.5	7.4
0.1	9.0	5.0	–	8.5
0.05	8.9	4.7	6.3	9.4
0.03	–	–	6.0	–
0.02	–	–	–	8.1
0.01	–	–	5.0	–

of the band both in CHCl$_3$ and in C$_6$H$_{12}$, as well as the comparatively low widening of the band, testifies that the splitting of bands of different aggregates is insignificant. The asymmetry observed in such cases is unnoticeable, and the complexity of the band can be judged about only by the behavior of its half-width.

In water solutions of tertiary butyl alcohol, its 750-cm^{-1} band widens with increasing dilution of the alcohol. The widening abruptly grows in the concentration range 0.2–0.05 MF. At concentrations lower than 0.05 MF, the band starts getting narrower.

It is worth to note that, in the same way as in [2–3], the maximum of the concentration line broadening coincides (within the error limits) with the maximum of the narrow intensity peak in the concentration dependence of the Rayleigh light scattering [1]. In water solutions, the 750-cm^{-1} band shifts toward lower frequencies (to 748 cm^{-1}); however, the rate of this shift changes, as the concentrations of solutions vary. In the concentration region, where the width changes insignificantly, a slight shift of the band is observed. This shift abruptly increases in the region of anomalous variation of the line width.

One can see from the presented results that the 750-cm^{-1} band of TBA analogously behaves itself with change in the concentration of the mixture in a neutral solvent, low-activity chloroform, and water. First, the band widens, reaches a widening maximum at some concentration, and then gets narrower at low concentrations.

It is worth noting that the concentration of the mixture corresponding to the widening maximum depends on the kind of the solvent. This fact can be explained as follows. Apparently, liquid TBA can include aggregates of various kinds. In liquid methanol, for example, there can exist monomers, dimers, trimers, and aggregates with a still larger number of molecules [8–9]. The stabilities of these aggregates must be different and depend on the energy of formation, form of molecules, and form of aggregates (in the case of methanol, there can exist cyclic formations as well). A similar picture is observed in ethanol [10]. For TBA, the multimeric aggregation is less probable, but the aggregation in the form of dimers, trimers, and monomers must be present. These aggregates must provide different bands in the Raman spectrum that weakly differ in maximum frequencies. That is why the RS bands of pure TBA must be complex (see below) and contain information about aggregates of various kinds. Depending on the energy gain, the concentrations of various aggregates in the liquid must be different. The largest contribution to the band intensity must be made by the most stable aggregates. Due to different stabilities of the aggregates, the variation of the alcohol temperature or its dissolution in some solvent must change the quantitative ratio between different aggregates, which will result in a variation of both the form of the band and its position. In the solution with hexane and low-activity chloroform, the destruction of low-stability aggregates firstly takes place. At some concentration, the contents of low-stability aggregates and more stable ones equalize, and the band widening reaches its maximum. At still lower alcohol concentrations, the further destruction of aggregates occurs. Finally, at the least concentration, the band corresponds to solely monomer molecules.

A similar picture is observed in water solutions. First, alcohol aggregates are destroyed, and “alcohol–water” ones are formed. In the region of the maximum widening (0.05-MF alcohol content), the amounts of “alcohol–water” and “alcohol–alcohol” aggregates equalize. At

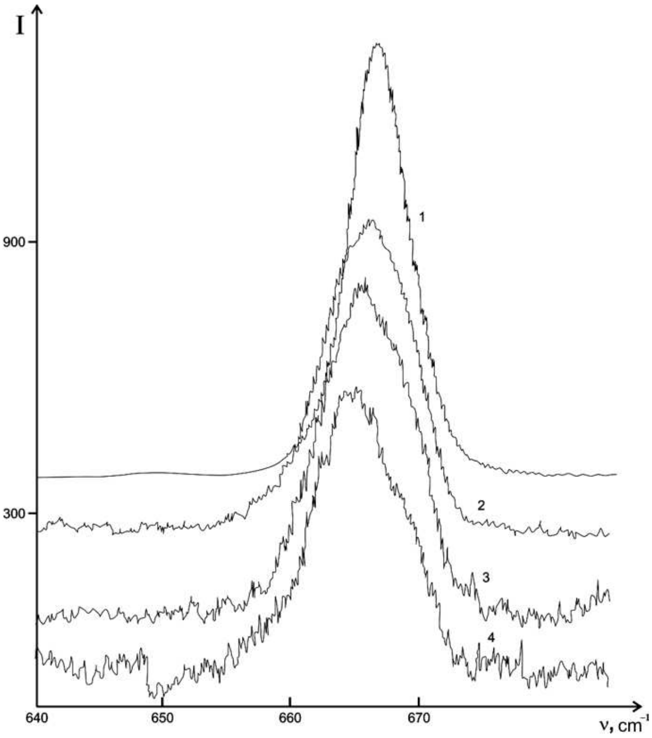

Fig. 2. 667-cm^{-1} band of chloroform in solutions with TBA at various chloroform contents (*1* – pure liquid, *2* – 0.2 MF, *3* – 0.1 MF, *4* – 0.05 MF)

lower concentrations, the relative number of "alcohol–water" aggregates prevails. The equilibrium of different aggregates ("alcohol–alcohol", "alcohol–water", and "water–water" ones) at small alcohol contents must result in the maximum development of structural fluctuations of the mixture, which results in the appearance of an additional intensity maximum in the Rayleigh isotropic light scattering.

It is worth saying several words about the data obtained for chloroform. It belongs to molecules that manifest weak proton-donor properties at the formation of intermolecular hydrogen bonds. However, some available spectroscopic data testify to the presence of such proton-donor properties that can be revealed in molecular spectra [4–5]. For example, in [11–13], one can find data on Raman scattering spectra of the C-H vibrational band of chloroform. This band behaves in a specific way in a mixture with proton-acceptor solvents, which was associated in [11] with the intermolecular hydrogen bond between chloroform and solvent molecules.

As is shown in a number of works and already mentioned above, the intermolecular hydrogen bond also has an effect on vibrations of atoms that do not directly participate in its formation (see, e.g., [6, 7]). It is very important to clarify if this phenomenon is also observed in the case of weakly proton-donor molecules, such as chloroform. In particular, it is due to the fact that the anisotropic and isotropic components of RS bands often serve as a basis for the determination of the relaxation time of orientation correlation and the vibrational relaxation time of molecules, respectively. It is evidently can be done only being sure that the form of the band is not complicated by the superposition of bands of the same vibrations in monomer molecules and aggregates. In the case of chloroform, these times can be, for example, determined from the anisotropic and isotropic components of the band at 667 cm^{-1} (that is related to vibrations of chlorine atoms in the molecule). We have investigated the concentration behavior of this band of chloroform in RS spectra in a proton-acceptor solvent (TBA).

In Fig. 2, one can see the vibrational (isotropic) component of the 667-cm^{-1} band of chloroform and its mixtures with alcohol. For gaseous chloroform, the wave number of the band is equal to 671 cm^{-1}, and the depolarization coefficient amounts to 0.04 [14]. The band half-width for pure liquid chloroform is 5.4 cm^{-1}. The dilution of chloroform in the alcohol results in the insignificant shift of the 667-cm^{-1} band toward lower frequencies (∼2 cm^{-1} at a content of 0.05 MF) and, which is most important, the band gets wider. The values of the band half-width are given in Table. The especially strong widening is registered, by starting from the 0.7-MF chloroform concentration. At 0.05 MF, the half-width amounts to 8.9 cm^{-1} (the half-width is everywhere given without regard for instrumental errors), which is higher than the half-width in pure liquid more than by a factor of 1.5.

Starting from the 0.2-MF chloroform content, some indications of the band complexity are observed: there appears an asymmetry on the low-frequency side of the band. At the 0.1-MF content of $CHCl_3$, this asymmetry shifts to the high-frequency side. At the 0.05-MF chloroform concentration, the band reveals a non-monotonicity that can be associated with the presence of low-frequency and high-frequency lines within the band. Unfortunately, we did not manage to investigate the band spectrum at lower chloroform concentrations in the mixture. In this case, it is worth expecting the narrowing of the band.

Judging by the concentration dependence of the band form, the high-frequency component is most probably related to monomer chloroform molecules. Their relative number must decrease, as chloroform is increasingly diluted. The low-frequency component belongs to "chloroform–alcohol" aggregates.

The Hartree–Fock approximation (RHF 6-31++G(d, p)) was applied to calculate the optimized structures for isolated molecules of tertiary butyl alcohol and its dimers [15].

According to our calculations, an isolated monomer of butyl alcohol has a rather complex structure (Fig. 3). In the RS spectra, the experimentally studied band well fits the calculated band at 798 cm^{-1} (scaled factor 0.94) with a depolarization coefficient of 0.01 (as was already noted, its experimental value was 0.01). This vibration is non-characteristic and involves all atoms of the molecule. The calculated dipole moments of TBA monomers are 1.77, whereas the tabular data yield 1.66 [16].

What do we have for the formation of dimers of alcohol molecules? An intermolecular hydrogen bond is formed between a hydrogen atom of the O–H group of one molecule and an oxygen atom of another molecule. The hydrogen bond length equals 2.068 Å (Fig. 3), moreover, the $\mathrm{O}^5\mathrm{H}^{30}\mathrm{O}^{20}$ angle is 171^o (the numbers of the atoms are the same as in the figure). The energy gain due to the formation of a dimer amounts to 19.7 kJ/mole. It is accompanied by some changes of the bond lengths (see Fig. 3) and the charge redistribution. These changes are especially noticeable for the molecule being a proton donor. The largest charge variations are registered for the O^5 and O^{20} atoms. Their negative charge grows both for the proton donor and acceptor (–0.563 and –0.548, respectively, whereas it is –0.521 for a monomer). The charge of the hydrogen atom participating in the formation of the H-bond increases almost by a factor of 1.5 (to +0.450, while this charge for a monomer equals +0.369). It is of interest that the charge of the hydrogen atom H^{15} of the O–H group not participating in the formation of the H-bond (proton acceptor) grows to +0.378. As one can see from the figure, the O^{20}–H^{30} distance somewhat grows as compared to the monomer molecule. The dipole moment of the aggregate is equal to 2.62 D.

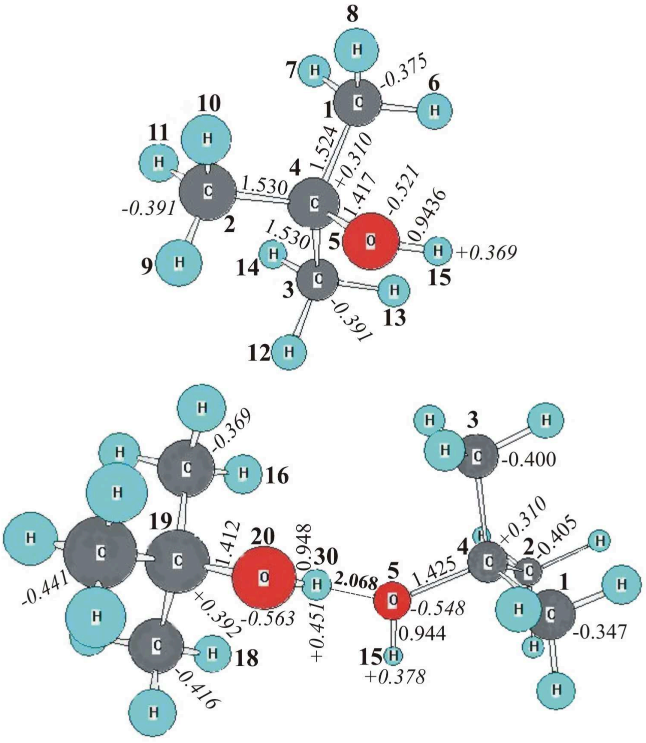

Fig. 3. Structure of isolated TBA aggregates. (Distances in Å, charges in units of the electron charge)

How does the formation of a dimer aggregate of TBA manifest itself in Raman scattering spectra? First of all, we are interested in the experimentally studied band at 750 cm^{-1}. In the case of the formation of a dimer aggregate, the indicated vibrations will be already coupled, that is why it is worth expecting a doublet splitting of the bands. This assumption is confirmed by the calculation. Instead of the band at 798 cm^{-1} calculated for a monomer, this vibration is now related to two bands at 796.7 cm^{-1} and 799.0 cm^{-1} with the depolarization coefficients equal to 0.009 and 0.007, respectively. The both bands are active in Raman scattering spectra and comparable in intensity. It is worth noting that the band at 796.7 cm^{-1} is mainly related to vibrations of atoms of the proton acceptor molecule. Though atoms of the proton donor are involved in this vibration, their shifts are small. For the band at 799.0 cm^{-1}, the picture is quite opposite: the vibration is realized with participation of atoms of the proton donor molecule. The shifts of the proton acceptor atoms are insignificant. As one can see, the splitting is small, only 2.3 cm^{-1}. The depolarization coefficients of superimposing bands slightly differ from one another. Therefore, it is not worth expecting noncoincidences of the frequencies of the band maxima in scattered light of different polarizations.

It should be noted that the calculated wave numbers correspond to isolated dimer formations, and their values are estimative due to the approximate character of the calculations. In the presence of aggregates of different numerical compositions, the band becomes still more complex. In addition, in real liquid media, the surrounding of molecules and aggregates must make some slight corrections. However, the tendency of variation of the quantities when passing from a monomer to aggregates must keep. Thus, for a dimer aggregate of tertiary butyl alcohol, we must observe at least a doublet splitting of the 750-cm^{-1} band. In real liquids at common temperatures, some equilibrium mixture of monomers, dimers, and possibly more complex aggregates must be obtained [8–10].

4. Conclusions

1. In the same way as in low-molecular alcohols, the presence of aggregates of various kinds in TBA makes the 750-cm^{-1} band to be complex and consisting of several superimposing lines with slightly differing vibration frequencies of atoms of different aggregates. The band acquires a simple form of a single line at a low TBA content in a neutral solvent.
2. In a strong proton-acceptor solvent, the 667-cm^{-1} band of chloroform appears complex due to the presence of monomeric and aggregated ($CHCl_3$-alcohol) formations in the mixture.

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МІЖМОЛЕКУЛЯРНИЙ ВОДНЕВИЙ ЗВ'ЯЗОК У ТРЕТИННОМУ БУТИЛОВОМУ СПИРТІ І ЙОГО РОЗЧИНАХ. СПЕКТРИ КОМБІНАЦІЙНОГО РОЗСІЯННЯ

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Резюме

У чистому третинному бутиловому спирті смуга з максимумом на частоті 750 см$^{-1}$ має складну структуру, яку можна інтерпретувати як результат накладання деяких тісно розташованих ліній, що належать різним агрегатам із молекул спирту. У нейтральних розчинниках концентраційна залежність ширини цієї смуги з розбавленням спирту проходить через максимум, що відповідає такій концентрації суміші, за якої в розчині склад різних найбільш стійких агрегатів порівняний. Квантово-хімічними розрахунками підтверджено складність структури смуги 750 см$^{-1}$ чистого спирту, зумовлена агрегацією молекул за допомогою водневого зв'язку. Розрахункові значення виграшу енергії при формуванні Н-зв'язку (димер) 19,7 Дж/моль, довжина водневого містка 2,068 Å.