

BRIEF COMMUNICATIONS

MOLECULAR STRUCTURES AND STRATIFICATION
IN A 2-BUTANOL–WATER SYSTEM

V. F. Korolev and O. Ya. Shmelev*

UDC 535.14:539.193

The results of investigation of the spectra of 2-butanol in CCl₄, pure 2-butanol, and a 2-butanol–water mixture in the region of the second overtone of the stretching O–H vibration are presented. The assignment of the bands of the overtones is performed. The role of various associates in the processes of stratification in the 2-butanol–water system is discussed.

Keywords: *absorption spectrum, overtone, 2-butanol–water, stratification, O–H stretching vibration.*

Introduction. Characteristic of a 2-butanol–water mixture (just as of an *n*-butanol–water one) is the presence of the dependence of the stratification curves on the strength of the hydrogen bond (H-bond) between the molecules of water and alcohol [1–4]. The question of the formation of critical points and stratification curves in the case of association between the molecules of water and alcohol through the H-bond (including the 2-butanol–water system and *n*-butanol–water one) has been considered fairly thoroughly theoretically in [3, 4].

It is well known that alcohols and water are highly associated liquids [5]. Taking into consideration that the study of the overtone region of the spectra of alcohols and their associates with other liquids gives fairly complete structural information, we have investigated the spectra in the region <1 μm.

Experimental. The spectra were registered by an SF-16 spectrophotometer (LOMO, USSR) with cylindrical cuvettes of length 5 cm (pure 2-butanol and a 2-butanol–water mixture) and 10 cm (2-butanol in CCl₄) [6]. For the analysis, analytical-grade alcohols and bidistilled water were used.

Discussion of Results. Having studied the concentration dependence of the spectra of the O–H stretching vibration of 2-butanol in CCl₄ (Fig. 1), we have assigned the 0.96-μm band to a monomer, the 0.91 μm one — to dimers, and the 1.02-μm band — to polymer forms. According to [5], when an H-bond is formed, the frequency of the stretching vibration is usually shifted towards lower values, and a band that accounts for coupled O–H vibrations appears.

It is well known that in highly diluted solutions only the bands of nonassociated O–H groups are observed. Therefore, the assignment of the 0.96-μm band to a monomer is related to the fact that at a concentration of 0.1 M of 2-butanol in CCl₄ it is just this band which is the most intense one. The relative intensity of this band is considerably decreased on increase in the concentration. Moreover, its width is smaller than that of other bands observed. In pure 2-butanol (Fig. 2), the intensity of the 0.96-μm band is very low, which fits in with the concept of alcohols as highly associated liquids.

In accordance with the results of investigations of the overtones of methanol and butanol, the band of free O–H groups is found at 10,440 cm⁻¹ (0.960 μm) for methanol and at 10,320 cm⁻¹ (0.968 μm) for *tert*-butanol [7]. Pauling [8] points to the band of free O–H vibrations in methanol at 10,440 cm⁻¹ and emphasizes its small width. There is an empirical formula (which may not, of course, be reckoned as universal) for the vibrational term [9]:

*To whom correspondence should be addressed.

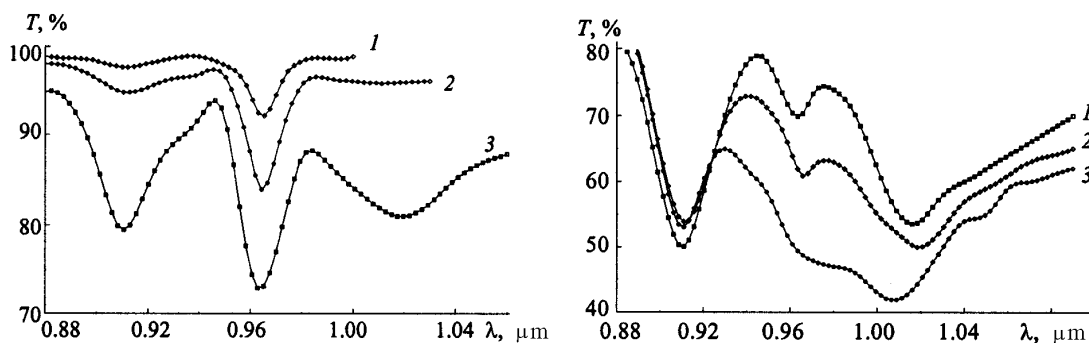


Fig. 1. Absorption spectrum of 2-butanol [0.1 (1), 0.5 (2), and 2.0 M (3)] in CCl_4 at $T = 23^\circ\text{C}$.

Fig. 2. Absorption spectra of pure 2-butanol (1), mixtures: 2-butanol–water (3M H_2O) (2) and 2-butanol–water (12 M of H_2O) (3) at $T = 24^\circ\text{C}$.

$$E(\text{OH}) = 3735(V + 1/2) - 82(V + 1/2)^2 [\text{cm}^{-1}], \quad (1)$$

where V is the vibrational quantum number.

The calculation by formula (1) gives a value of $0.978 \mu\text{m}$ for the frequency of the 2nd overtone of the monomer.

The band assigned by us to the dimer is explained in [8] to be a result of the strengthening of the O–H bond and, according to Badjer's rule [10], applied in different spectroscopic calculations (see, e.g., [11]), has a frequency which is higher than that of the monomer.

We suggest the increase in the frequency to be explained by partial compensation for the anharmonism, meaning the following. The potential coupling curve can be represented as [12]

$$V = (1/2)kQ^2 + k_3Q^3 + k_4Q^4, \quad (2)$$

where the first term is the harmonic potential (higher terms account for the mechanical anharmonicity); k , k_3 , and k_4 are the constants of the potentials of the harmonic, cubic, and fourth orders; Q is the normal coordinate. As is shown in [12], the perturbing potential is selected (in the second order of the perturbation theory) in the form

$$H' = k_3Q^3 + k_4Q^4. \quad (3)$$

The vibrational terms (in the Morse curve approximation) are obtained to be

$$G_V = \omega_e(V + 1/2) - X(V + 1/2)^2, \quad (4)$$

where ω_e is the harmonic frequency; X is the anharmonicity constant.

The frequency of the second overtone can be calculated using formula (4):

$$\nu_{03} = 3\omega_e - 12X. \quad (5)$$

The quantity X may be written as [12]

$$X = \frac{15k_3^2}{4\omega_e} - \frac{3}{2}k_4. \quad (6)$$

A situation is possible where the formation of the H-bond results in an increase in k_4 with respect to k_3 , and the quantity X determined from (6) is decreased. Therefore, ν_{03} approaches $3\omega_e$ in value, which is treated by us as a

"partial compensation for the anharmonism" (in fact, this does not imply a decrease in the real vibration anharmonism). The probability of such an effect is pointed out in [12], and it was observed experimentally in [13]. At the same time, a decrease in the quantity X is possible when the H-bond is formed due to the decrease in all the constants of the anharmonic potential, which seems to be highly improbable.

The slightly larger width of the 0.91- μm band in comparison with the monomer band and the increase in its intensity at concentrations larger than 0.1 M of 2-butanol in CCl_4 (here the concentration only of the monomer band manifested itself) permits us to assign this band to a dimer.

The 1.02- μm band is assigned by us to the polymer forms because of the large width and because it appears in the spectrum of 2-butanol in CCl_4 at concentrations higher than 0.5 M, as well as due to the high intensity and large width in the spectrum of pure 2-butanol.

Our assignments for the bands of the second overtone of the O–H stretching vibration of 2-butanol do not contradict the similar results for different associated forms of other monatomic alcohols, which were obtained in [7, 8, 12–14].

From Fig. 1 it follows that the shift of the band corresponding to the polymer forms is about 560 cm^{-1} . The 1.02- μm band becomes significantly more asymmetrical with increase in the concentration of alcohol than the bands at 0.91 and 0.96 μm , which seems to point to the manifestation of conformational rearrangement [15].

The study of the spectra of the 2nd overtone of the O–H stretching vibration in the 2-butanol–water mixture shows that with an increase in the concentration of H_2O in 2-butanol the monomer frequency experiences a slight shift towards smaller values in comparison with the spectrum of pure alcohol. Moreover, a quasi-isobestic point is observed at 0.925 μm , which is usually related to the change in the concentration of associated forms. The intensity of the monomer of 2-butanol at 12 M of H_2O in 2-butanol is infinitesimally low as compared to pure alcohol. At the same time, the frequency of the alcohol dimer (0.91 μm) does not experience a visible shift, which is related by us to the presence of a considerable amount of ring-type dimers, because their O–H end groups are closed and cannot form the H-bond. The frequency of a polymer form (at 1.02 μm) virtually does not undergo a shift on increase in the concentration of water, but the absorption maximum turns out to be somewhat extended.

In connection with the possible influence of water, which did not enter into the H-bond with alcohol, on the absorption spectrum of the broad band of the second overtone of the O–H stretching vibration, we registered the spectrum of the 2-butanol–water system (10 M H_2O in 2-butanol) and subtracted from it the water spectrum in this region. The reference cuvette was filled with 10 M of H_2O . The spectrum is essentially identical to the spectrum of pure 2-butanol (the spectrum is not presented). However, the band corresponding to the monomer is practically invisible in it, which may be interpreted as:

- 1) formation of associates of the polymer water forms with alcohol monomers and the virtual disappearance of molecules of the alcohol monomer at the concentrations under study;
- 2) impossibility for the alcohol dimers to enter into the H-bond with water because of the presence of dimers predominantly of closed type (ring-shaped);
- 3) significant presence of polycyclic alcohol self-associates which do not enter into the H-bond with water.

Conclusions. It is evident from the analysis of the data obtained in the region of the investigated concentrations of water in 2-butanol that further mutual solubility (at temperatures of the experiment) due to the formation of the H-bond is limited.

REFERENCES

1. J. D. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.*, **5**, 896–899 (1937).
2. J. A. Barker and W. Fock, *Discuss. Faraday Soc.*, **15**, 188–202 (1953).
3. J. S. Walker and C. A. Vause, *J. Chem. Phys.*, **79**, No. 6, 2660–2668 (1983).
4. J. S. Walker and C. A. Vause, *Sci. Am.*, **256**, No. 5, 620–626 (1987).
5. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* [Russian translation], Mir, Moscow (1964).
6. S. I. Dergunov, V. F. Korolev, and V. F. Nozdrev, in: *Ultrasound and Thermodynamic Properties of Substances* [in Russian], Collection of Papers, KGPI, Kursk (1990), pp. 86–89.
7. C. Bourderon and C. Sandorfy, *J. Chem. Phys.*, **59**, No. 5, 2527–2536 (1973).

8. L. Pauling, *The Nature of the Chemical Bond* [Russian translation], GNTI Khim. Lit., Moscow–Leningrad (1947).
9. M. V. Vol'kenshtein, *Structure and Chemical Properties of Molecules* [in Russian], Izd. AN SSSR, Moscow–Leningrad (1955).
10. R. M. J. Badger, *Chem. Phys.*, **3**, 710–712 (1935).
11. V. F. Korolev and V. I. Tyulin, *Vestn. MGU, Ser. 2, Khimiya*, **29**, No. 2, 143–147 (1988).
12. C. Sandorfy, *Can. J. Spectrosc.*, **17**, No. 1, 24–37 (1972).
13. S. Detoni, D. Hadzi, and M. Juranji, *Spectrochim. Acta*, **A30**, 249–252 (1974).
14. W. A. P. Luck and W. Ditter, *Ber. Bunsenges. Phys. Chem.*, **72**, 365–368 (1968).
15. E. T. G. Luts and J. H. van der Maas, *Spectrochim. Acta*, **A34**, No. 1, 915–917 (1978).