Ions with a strong symmetrical H bond in the HCl—Bu^{i}OH system by IR spectroscopy data

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Ion-molecular interactions in the HCl—Bu^{i}OH system with different compositions (from neat isobutyl alcohol to 37 mol.% HCl) were studied by Multiple Attenuated Total Reflectance (MATR) IR spectroscopy at 30 °C. Proton disolvates (Bu^i(H)O...H...O(H)Bu^i)$^+$ with strong symmetrical H bonds are formed upon the addition of HCl to Bu^{i}OH. At high concentrations of HCl (C^0_{HCl} > 33 mol.%), (Cl...H...Cl)$^-$ ions are formed along with (Bu^{i}OH)$_2$H$^+$. The spectra of positively and negatively charged proton disolvates were compared to those of similar ions in the HCl—Pr^{i}OH and HCl—MeOH systems.

Key words: IR spectra; hydrogen bond; hydrogen chloride, isobutyl alcohol, solutions.

Non-aqueous solutions of strong acids are efficient catalytic systems, whose activity is determined first by the composition and structure of proton-containing species. In binary HCl—MeOH, HCl—EtOH, and HCl—Pr^{i}OH systems, these species are proton disolvates with a strong symmetrical H bond[1–4] (R(H)O...H...O(H)R)$^+$. In the HCl—Pr^{i}OH system at a ratio of components (acid : base) equal to 1 : 2, all isopropyl alcohol is bound as (Pr^{i}OH)$_2$H$^+$ ions forming ion pairs with Cl$^-$ ions. When the content of HCl increases further, the proton disolvates undergo no changes, and HCl molecules are transformed into (ClHCl)$^-$ anions with a strong symmetrical H bond.[4,5] The intensity of continuous absorption in the IR spectra of the HCl—Pr^{i}OH system is somewhat weaker than that in the spectra of methanol solutions of HCl.

In this work, we attempted to check whether the scheme of ion-molecular interactions established previously is applicable in the case of higher alcohols, for example, isobutyl alcohol, and to separate out the spectra of proton disolvates (Bu^i(H)O...H...O(H)Bu^i)$^+$ and (ClHCl)$^-$.

Experimental

A stock solution was prepared by saturation of isobutyl alcohol (reagent grade) with gaseous anhydrous HCl. The concentration of water in the stock solution was not higher than 0.1 mol L^{-1}. Working solutions were prepared from the stock solution by dilution with isobutyl alcohol. The concentration of HCl in each solution was determined by alkalimetric titration. Densities of solutions were measured for the calculation of molar concentrations (Table 1).

IR spectra were obtained on a UR-20 spectrophotometer with a Multiple Attenuated Total Reflectance attachment (MATR-2)[6] produced in the N. N. Semenov Institute of Chemical Physics of the Russian Academy of Sciences. A Ge prism with an incident angle of 30° and a number of reflection of 8 was used. The effective thickness of the absorbing layer at a frequency of 2000 cm^{-1} was 3.05 mm. Spectra were obtained at 30 °C.

Spectra of the Bu^{i}OH—HCl system were recorded in the composition region from 0 to 37 mol.% HCl (see Table 1) in

Table 1. Stoichiometric composition, densities of solutions of HCl in Bu^{i}OH, optical densities of the band at 1042 cm^{-1}, and concentrations of "bound" isobutyl alcohol at 30 °C

C^0_{HCl}	C^0_{HCl}	$C^0_{Bu^iOH}$	ρ	D_{1042}	$C^b_{Bu^iOH}/C^0_{HCl}$
(mol.%)	mol L^{-1}		/g cm^{-3}		
0	0	10.83	0.803	0.910	—
8.71	1.02	10.69	0.830	0.799	2.3
12.02	1.45	10.61	0.839	0.592	2.6
15.69	1.95	10.48	0.848	0.477	2.5
18.27	2.32	10.38	0.854	0.385	2.4
20.42	2.64	10.29	0.859	0.331	2.4
22.69	3.00	10.22	0.867	0.286	2.3
24.57	3.31	10.16	0.874	0.227	2.2
26.54	3.63	10.05	0.877	0.172	2.2
29.82	4.21	9.91	0.888	0.163	1.9
32.57	4.72	9.77	0.896	0.067	1.9
35.79	5.34	9.58	0.905	—	—
36.98	5.58	9.51	0.908	—	—

Note. $C^b_{Bu^iOH} = C^0_{Bu^iOH} - C_{Bu^iOH}$; $C_{Bu^iOH} = D_v/(\varepsilon_v l)$, where C_{Bu^iOH} and $C^b_{Bu^iOH}$ are the concentrations of "free" and "bound" Bu^{i}OH; $\varepsilon_v l$ is the absorption coefficient of "free" Bu^{i}OH, which was determined from the spectrum of neat Bu^{i}OH: $\varepsilon_v l = D_v/C^0_{Bu^iOH}$; the accuracy of determination of the $C^b_{Bu^iOH}/C^0_{HCl}$ value was 6—8%.

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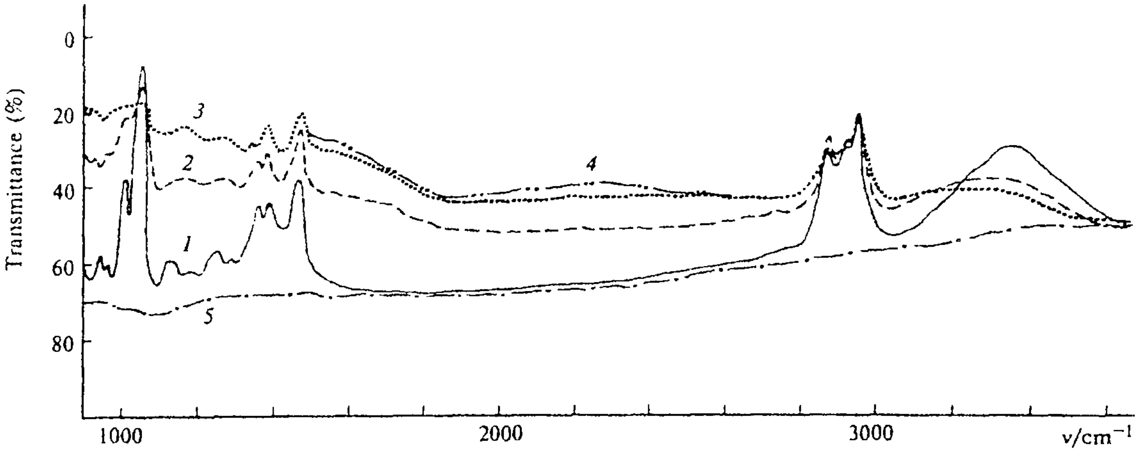

Fig. 1. MATR IR spectra of the Bu^{i}OH—HCl system: *1*, 100% Bu^{i}OH; *2*, 18.27; *3*, 32.57; *4*, 36.98 mol.% HCl; and *5*, empty cell.

the frequency range from 900 to 4000 cm^{-1}. Optical densities of the bands at 1042 and 3350 cm^{-1} were determined relative to base lines. Measurements at other frequencies were carried out against the empty cell. The accuracy of determination of the optical density was 3—5%.

Results and Discussion

The MATR IR spectra of the solutions under study are presented in Fig. 1. The spectrum of neat isobutyl alcohol[7] contains intense bands at 1042 (νCO) and 3350 cm^{-1} (νOH) and in the frequency region of 2800—3000 cm^{-1} (νCH, νCH$_2$, νCH$_3$), a medium-intensity band at 1467 cm^{-1} (δOH), and several weak bands of skeletal vibrations at 1100—1400 cm^{-1}.

The addition of HCl results in a considerable decrease in the optical densities of the bands of isobutyl alcohol at 1042 and 3350 cm^{-1}, and a new broad band at 1500—1900 cm^{-1} and an intense continuous absorption (CA) appear. No band of vibrations of the HCl molecule is observed.

The concentration of free, *i.e.*, unbound in complexes with HCl, isobutyl alcohol was determined from the optical density of the band at 1042 cm^{-1} (D_{1042}), which is most convenient for quantitative measurements. The absorption coefficient at 1042 cm^{-1} found from the spectrum of 100% Bu^{i}OH was used for calculations. The comparison of the concentrations obtained with the analytical concentration of isobutyl alcohol (see Table 1) at $C^0_{\mathrm{Bu^iOH}} : C^0_{\mathrm{HCl}} > 2$ ($C^0_{\mathrm{HCl}} < 33.3$ mol.%) shows that each acid molecule binds two isobutyl alcohol molecules. The same result was obtained from the analysis of the concentration dependences of optical densities of νCO and νOH bands for the MeOH—HCl and Pr^{i}OH—HCl systems[1,4] in which acid is completely dissociated and ions with a strong symmetrical H bond (MeOH)$_2$H$^+$ and (Pr^{i}OH)$_2$H$^+$ are formed. The intense band of CA characteristic of these ions and detected in the IR spectra of the Bu^{i}OH—HCl system indicates that proton disolvates (Bu^{i}OH)$_2$H$^+$ with a strong symmetrical H bond are also present in this system.

Let us consider the absorption spectrum of the (Bu^{i}OH)$_2$H$^+$ ions and compare it with the spectra of the proton disolvates (MeOH)$_2$H$^+$ and (Pr^{i}OH)$_2$H$^+$ obtained previously.[1,4] At $C^0_{\mathrm{HCl}} < 33.3$ mol.%, the optical densities in the spectra of the Bu^{i}OH—HCl system are the overall absorption of the proton disolvates (C_{l}) and molecules of free isobutyl alcohol ($C_{\mathrm{Bu^iOH}}$):

$$D_\nu = \varepsilon^\nu_{\mathrm{Bu^iOH}} l_\nu C_{\mathrm{Bu^iOH}} + \varepsilon^\nu_{\mathrm{l}} l_\nu C_{\mathrm{l}}, \qquad (1)$$

where D_ν is the optical density of absorption at the ν frequency, l_ν is the effective thickness of the absorbing layer at the ν frequency, $\varepsilon^\nu_{\mathrm{Bu^iOH}}$ and $\varepsilon^\nu_{\mathrm{l}}$ are the absorption coefficients of isobutyl alcohol and proton disolvates at this frequency, $C_{\mathrm{l}} = C^0_{\mathrm{HCl}}$, and $C_{\mathrm{Bu^iOH}} = C^0_{\mathrm{Bu^iOH}} - 2C^0_{\mathrm{HCl}}$.

From Eq. (1) we obtain

$$D_\nu/C_{\mathrm{Bu^iOH}} = \varepsilon^\nu_{\mathrm{Bu^iOH}} l_\nu + \varepsilon^\nu_{\mathrm{l}} l_\nu C_{\mathrm{l}}/C_{\mathrm{Bu^iOH}}. \qquad (2)$$

The dependences of $D_\nu/C_{\mathrm{Bu^iOH}}$ on $C_{\mathrm{l}}/C_{\mathrm{Bu^iOH}}$ are linear in the 1900—3600 cm^{-1} frequency region at $C^0_{\mathrm{HCl}} < 18$ mol.% and in the 1100—1900 cm^{-1} frequency region at $C^0_{\mathrm{HCl}} < 27$ mol.% (Fig. 2). The $\varepsilon^\nu_{\mathrm{l}}$ coefficients were determined from the linear regions of dependences (2).

The absorption coefficient at 2000 cm^{-1} is equal to 160±10 L mol^{-1} cm^{-1}. Such a high value corresponds to the absorption of positively charged complexes formed by a strong H bond.[8] For the (MeOH)$_2$H$^+$ and (Pr^{i}OH)$_2$H$^+$ ions, this coefficient is equal to 174 and 132 L mol^{-1} cm^{-1}, respectively.[1,4]

The spectra of the absorption coefficients of the (Bu^{i}OH)$_2$H$^+$ ion and proton disolvates formed by a strong symmetrical H bond studied previously[4,9] are presented in Fig. 3. The general view of the spectra of the (ROH)$_2$H$^+$ ions is independent of alcohol in the composition of the disolvate. They are characterized by a series of bands in the 900—1500 cm^{-1} frequency region of skeletal vibrations, a broad band at 1600—1700 cm^{-1}, an intense CA up to 3000 cm^{-1}, and a

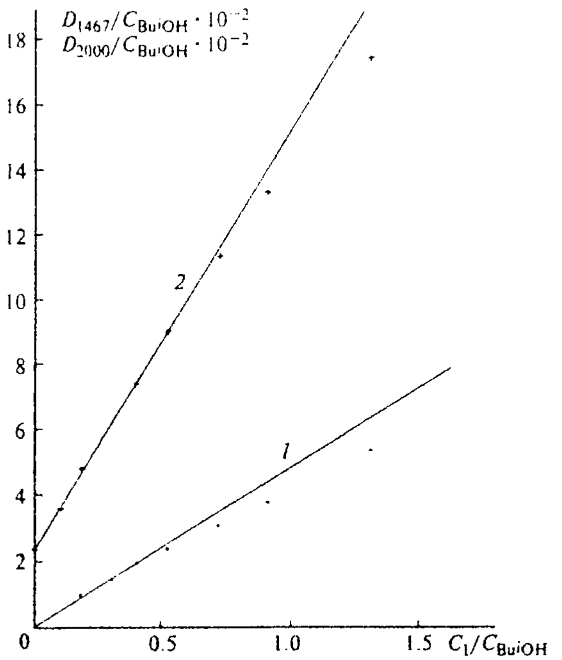

Fig. 2. Graphic solutions of Eq. (2) for frequencies 2000 (*1*) and 1467 (*2*) cm^{-1}.

broad band of stretching vibrations of the terminal OH groups of the proton disolvates at 3000—3300 cm^{-1}. Replacement of the methyl group in the proton disolvate by the isopropyl and then isobutyl group results in a noticeable weakening of mixing of νCH_3, νCH_2, and νCH vibrations with vibrations of the central proton involved in the strong symmetrical H bond. The spectrum of methyl groups in the 2800—3000 cm^{-1} region changes entirely when the $(Me(H)O...H...O(H)Me)^+$ ion is formed. The change in the spectrum of isopropyl groups is much weaker when the $(Pr^iOH)_2H^+$ disolvate is formed, the νCH_3, νCH_2, and νCH frequencies of vibrations of isobutyl groups remain unchanged, and their interaction with vibrations of the central proton results in a noticeable decrease (by 1.5 times) in the absorption coefficients of the corresponding bands only.

The optical densities of the νOH band at 3350 cm^{-1} in the spectrum of Bu^iOH also decrease according to Eq. (2), which indicates that two isobutyl alcohol molecules are bound to the proton disolvate. However, quantitative measurements of concentrations of "free" alcohol at this band are incorrect because of the superposition of absorption of the proton disolvate (see Fig. 1).

When the concentration of HCl increases, the intensity of the band of isobutyl alcohol at 1467 cm^{-1} decreases much more slowly than those of the bands at 1042 and 3350 cm^{-1}. This band is also observed in the spectrum of the proton disolvate. Dependence (2) for this band is linear in the concentration region from 0 to 25 mol.% HCl. This corresponds to the absorption at the given frequency of two forms: free isobutyl alcohol molecules and $(Bu^iOH)_2H^+$ ions. The absorption coefficient of the proton disolvate decreases in more concentrated solutions.

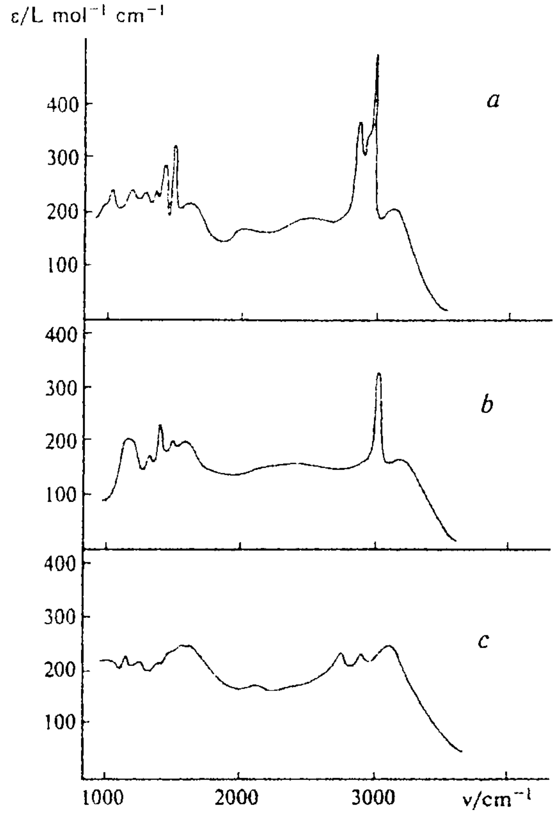

Fig. 3. IR spectra of proton disolvates: $(Bu^iOH)_2H^+$ (*a*), $(Pr^iOH)_2H^+$ (*b*), and $(MeOH)_2H^+$ (*c*).

Let us consider the reasons for a change in the absorption coefficients of the proton disolvates in concentrated solutions of HCl. The linear regions of dependences (2) for $\nu > 1900$ cm^{-1} correspond to the ratio of components Bu^iOH : HCl > 4—5. The same result has been obtained previously[1] for the MeOH—HCl system. Therefore, the spectrum of the proton disolvate is affected by its first coordination sphere. In the region of HCl concentrations where more than two alcohol molecules fall on each $(ROH)_2H^+$ ion, the structure of the proton disolvate is unchanged. In more concentrated solutions of HCl where the amount of alcohol is already insufficient for solvation of each $(ROH)_2H^+$ ion by two molecules, terminal OH groups of the proton disolvates appear, which form no hydrogen bonds with ROH molecules of the solvent and most likely interact with Cl^- anions. This corresponds to the formation of contact ion pairs $H(R)O...H^+...O(R)H \cdot Cl^-$, due to which absorption coefficients of the proton disolvates change.

IR spectra of ions with strong symmetrical H bonds are formed due to the superposition of a great number of combined bands.[10] Absorption coefficients change most strongly in the spectrum at $\nu > 1900$ cm^{-1}. This is explained by the fact that in this frequency region, combined bands forming the continuous spectrum contain vibrations of terminal OH groups of the proton disolvates interacting with molecules of the solvent. This results in minor differences between the spectra of proton disolvates, solvated alcohol molecules, and proton disolvates that form contact ion pairs with Cl^- at frequencies higher than 1900 cm^{-1}.

At the ratio of components Bu^iOH : HCl < 2 : 1, HCl added to the system already cannot form new proton disolvates. Studies in this region are restricted by the high elasticity of HCl vapor. Satisfactory spectra were obtained only below the ratio of component concentrations Bu^iOH : HCl equal to 1.7. In the spectra of concentrated solutions of HCl, no bands at 1042 and 3350 cm^{-1} are observed, a broad band at 2100—2500 cm^{-1} appears, and the absorption intensity at 1500—1600 cm^{-1} increases noticeably (see Fig. 1).

The $(Cl...H...Cl)^-$ anions with a strong symmetrical H bond are formed in concentrated solutions of HCl in isopropyl alcohol.[4,5] Their spectrum consists of two broad bands with maxima at 1600 and 2300 cm^{-1} (Fig. 4) corresponding to deformational and stretching antisymmetrical vibrations. The changes observed in the spectra of the Bu^iOH—HCl system at high concentrations of HCl are also evidence for the formation, along with the proton disolvate $(Bu^iOH)_2H^+$, of a new species containing a strong symmetrical H bond, *i.e.*, $(ClHCl)^-$ anion.

Under the condition of complete binding of alcohol and acid molecules, the optical densities of absorption at $C^0_{HCl} > 33.3$ mol.% are the sum of the absorptions of the $(Bu^iOH)_2H^+$ (C_1) and $(ClHCl)^-$ (C_2) ions:

$$D_\nu = \varepsilon^\nu{}_1 l_\nu C_1 + \varepsilon^\nu{}_2 l_\nu C_2, \qquad (3)$$

where $\varepsilon^\nu{}_2$ is the absorption coefficient of the $(ClHCl)^-$ ions at the ν frequency.

The equilibrium concentrations of $(Bu^iOH)_2H^+$ and $(ClHCl)^-$ ions are determined by the following equations:

$$C_1 = C^0{}_{Bu^iOH}/2, \; C_2 = C^0{}_{HCl} - C^0{}_{Bu^iOH}/2.$$

From Eq. (3) we obtain

$$\varepsilon^\nu{}_2 = (D_\nu - \varepsilon^\nu{}_1 l_\nu C_1)/(l_\nu C_2). \qquad (4)$$

The absorption coefficients $\varepsilon^\nu{}_2$ in the 1100—2700 cm^{-1} frequency region were calculated by Eq. (4) from the IR spectra of solutions with a concentration of HCl of 5.34 and 5.58 mol L^{-1}. The values of $\varepsilon^\nu{}_1$ coefficients were determined from the spectrum of a solution with the ratio of components Bu^iOH : HCl = 2, *i.e.*, the solution that contains only the proton disolvates. The $\varepsilon_2(\nu)$ spectrum coincides in the shape and intensity with that of the $(ClHCl)^-$ anions obtained[4] by the analysis of the IR spectra of the Pr^iOH—HCl system. Some differences in the spectra are likely related to differences in the interaction of the $(ClHCl)^-$ anions with the Bu^i and Pr^i groups of the $(ROH)_2H^+$ proton disolvates in different systems.

The results obtained in this and previous[1,4,9] works indicate that the same scheme of acid-base interaction takes place during dissolution of HCl in lower alcohols. The $(ROH)_2H^+$ cations and $(ClHCl)^-$ anions formed by the strong symmetrical H bond are the main forms of the solvated proton. The $(ClHCl)^-$ anions are formed in solutions where for each acid molecule there are less than two alcohol molecules.

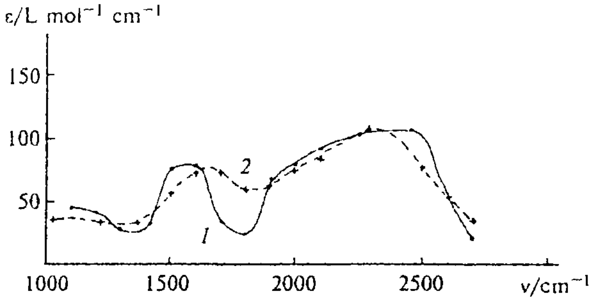

Fig. 4. IR spectra of the $(ClHCl)^-$ ion in Bu^iOH—HCl (*1*) and Pr^iOH—HCl (*2*) systems.

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