Ion-molecular interactions in the HCl—isopropanol system

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Multiple Attenuated Total Reflectance (MATR) IR spectra of solutions of HCl in isopropanol, containing 0 to 43 mol. % HCl, were studied in the 900—4000 cm^{-1} range. The addition of HCl to Pr^iOH yields proton disolvates $(C_3H_7\underset{H}{O}...H...\underset{H}{O}C_3H_7)^+$ with strong symmetrical H-bonds. At high concentrations of HCl ($C^0_{HCl} > 5.7$ mol L^{-1}, $C^0_{Pr^iOH}/C^0_{HCl} < 2$), when the number of alcohol molecules is not enough to form disolvates with all of the protons present in the solution, $(Cl...H...Cl)^-$ ions are formed, in addition to $(C_3H_7OH)_2H^+$. The spectra of these ions have been assigned.

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

Nonaqueous solutions of strong acids are effective catalytic systems, whose activities are primarily determined by the compositions and structures of reactive species. In HCl—MeOH and HCl—EtOH binary systems, these are disolvates of protons with strong symmetrical H-bonds, $(Me\underset{H}{O}...H...\underset{H}{O}Me)^+$ and $(Et\underset{H}{O}...H...\underset{H}{O}Et)^+$, respectively.[1—3] However, in the case of the HCl—MeOH system, the relatively low solubility of HCl in methanol does not allow one to obtain solutions containing less than two methanol molecules per proton. It has been of interest to elucidate what happens to the HCl molecule in a solution that contains no "free" alcohol molecules, not incorporated into an ion with a strong symmetrical H-bond. For this purpose, we have chosen the HCl—isopropanol system, in which the solubility of HCl at ambient temperature is as high as 43 mol. %.

The purpose of the present work has been to study the solvation of a proton in the HCl—isopropanol system both with a substantial excess of the alcohol ($C^0_{Pr^iOH}/C^0_{HCl} > 2$) and in solutions with higher concentrations of HCl ($C^0_{Pr^iOH}/C^0_{HCl} < 2$) by MATR IR spectroscopy.

Experimental

The starting solution of HCl in isopropanol was prepared by saturating isopropanol of "chemically pure" grade with anhydrous gaseous hydrogen chloride. The concentration of water in the starting solution was no more than 0.1 mol L^{-1}. Previously we found that much greater quantities of water (up to 0.2 mol L^{-1}) have no effect on the IR spectral patterns, until absorption bands of complexes formed by alcohol molecules and protons with water are exhibited in the spectra.

Process solutions were prepared from the starting solution by diluting it with isopropanol (by mass). The concentration of HCl in the starting solution was determined by alkalimetric titration. To calculate molar concentrations of the solutions, their densities were measured (Table 1). Table 1 also presents the concentrations of the components in all of the solutions studied.

Multiple Attenuated Total Reflectance (MATR) IR spectra were recorded on a UR-20 spectrophotometer using an MNPVO-2 [MATR] unit produced at the Institute of Chemical Physics of the RAS and a Ge prism with an angle of incidence of 30° and a number of reflections of 8. The spectra were recorded with respect to air at 30 °C. The effective thickness of the absorbing layer determined from the spectra of water using its optical constants[4] was 3.10 μm at a frequency of 2000 cm^{-1}. The spectra of the solutions of HCl in isopropanol (0—8 mol L^{-1} of HCl) were recorded in the 900—4000 cm^{-1} range. The optical densities of bands were measured relative to base lines. In measuring the optical density of continuous absorption, absorption of the empty cell was taken into account.

Table 1. Compositions and densities (ρ) of solutions of HCl in Pr^iOH

C^0_{HCl} (mol. %)	C^0_{HCl} /mol L^{-1}	$C^0_{Pr^iOH}$ /mol L^{-1}	ρ /g cm^{-3}
0	0	13.08	0.768
9.80	1.39	12.80	0.820
15.72	2.34	12.56	0.840
18.87	2.89	12.41	0.851
20.31	3.14	12.34	0.856
20.77	3.22	12.30	0.857
22.36	3.52	12.23	0.863
24.41	3.91	12.11	0.870
25.80	4.16	12.01	0.874
27.40	4.44	11.93	0.879
28.40	4.70	11.84	0.883
33.55	5.79	11.48	0.901
35.19	6.16	11.35	0.907
37.05	6.58	11.18	0.913
39.34	7.29	10.97	0.925
42.83	8.00	10.67	0.933

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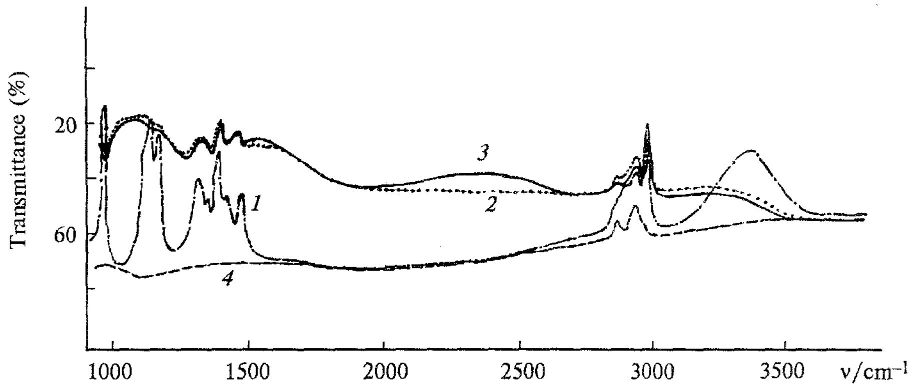

Fig. 1. MATR IR spectra of the HCl—isopropanol system: *1,* 100 % Pr^{i}OH; *2,* 5.79 mol L^{-1} of HCl ($C^0_{\mathrm{HCl}}/C^0_{\mathrm{Pr^iOH}}$ = 1 : 2); *3,* 8.68 mol L^{-1} of HCl; *4,* empty cell.

Results and Discussion

The IR spectra of the solutions studied are shown in Fig. 1. The spectrum of pure isopropanol exhibits a band at 955 cm^{-1} corresponding to ν(C—O) vibrations; a doublet at 1135 and 1160 cm^{-1} due to skeletal vibrations of the C_3H_7OH molecule; and bands at 1310 (δ(OH)), 1380 and 1465 ($\delta_s(CH_3)$ and $\delta_{as}(CH_3)$, respectively), 2880—2900 ($\nu_s(CH_3)$ and ν(CH)), 2980 ($\nu_{as}(CH_3)$), and 3355 (ν(OH)) cm^{-1}.

When HCl is added, the intensities of all of the absorption bands of isopropanol considerably decrease, and new smeared bands against the background of intense continuous absorption appear (see Fig. 1). When $C^0_{\mathrm{HCl}}/C^0_{\mathrm{Pr^iOH}} > 1 : 2$ (where C^0_{HCl} and $C^0_{\mathrm{Pr^iOH}}$ are stoichiometric concentrations of hydrochloric acid and isopropanol), the spectra contain a very broad band between 2100 and 2500 cm^{-1}.

The bands at 955 and 3355 cm^{-1} are the most convenient for quantitative measurements. The extinction coefficients at frequencies of 955 and 3355 cm^{-1} were determined from the spectrum of pure isopropanol. Using the values of D_{955} and D_{3355} for solutions of hydrochloric acid, the concentration of "free" isopropanol was determined. A comparison of the resulting value with the stoichiometric concentration of the alcohol, C^0_{PriOH}, indicates that each proton binds two isopropanol molecules (Table 2).

The changes occurring in the spectrum of isopropanol after the addition of HCl, when $C^0_{\mathrm{HCl}} < 5.7$ mol L^{-1} ($C^0_{\mathrm{HCl}}/C^0_{\mathrm{Pr^iOH}} < 1 : 2$), are similar to those previously observed in the spectra of ethanol and methanol after the addition of HCl. Intense continuous absorption (CA) and the absence of sharp bands corresponding to the proton disolvate are typical of ions with strong symmetrical H-bonds. The optical density of CA at a frequency of 2000 cm^{-1} is proportional to C^0_{HCl} with $C^0_{\mathrm{HCl}} < 0.5C^0_{\mathrm{PriOH}}$, *i.e.*, as long as free isopropanol is present in the solutions (Fig. 2). From the slope of this linear dependence the extinction coefficient of the proton disolvate at this frequency was found to be $\varepsilon_{2000} = 132\pm10$ L mol^{-1} cm^{-1}. This value is somewhat lower than the corresponding coefficients of CA of $H_5O_2^+$ ions and proton disolvates in MeOH ($\varepsilon_{2000} = 174\pm10$ L mol^{-1} cm^{-1} for $(MeOH)_2H^+$ and ~160—170 L mol^{-1} cm^{-1} for $H_5O_2^+$ and $(EtOH)_2H^+$).[1]

Notice that the spectral data indicate that HCl completely dissociates at $C^0_{\mathrm{HCl}} < 5.7$ mol L^{-1}. First, in this concentration region, each HCl molecule added releases the proton, which binds two molecules of the alcohol (see Table 2). Second, the optical density of the CA, which presents the spectrum of the proton disolvate

Table 2. Optical densities at 955 and 3355 cm^{-1}, concentrations of "free" and "bound" isopropanol, and the numbers of alcohol molecules (*n*) bound by one proton

C^0_{HCl} /mol L^{-1}	$C^0_{\mathrm{Pr^iOH}}$ /mol L^{-1}	D_{955}	$C^0_{\mathrm{Pr^iOH}}$* /mol L^{-1}	n_{955}	D_{3355}	$C^0_{\mathrm{Pr^iOH}}$** /mol L^{-1}	n_{3355}
1.39	12.80	0.545	9.43	2.4	0.209	10.28	1.8
2.34	12.56	0.418	7.24	2.3	0.150	7.41	2.2
3.14	12.34	0.296	5.13	2.3	0.108	5.33	2.2
3.22	12.30	0.308	5.33	2.2	0.106	5.23	2.2
4.18	12.01	0.189	3.27	2.1	0.067	3.29	2.1
4.44	11.93	0.177	3.07	2.0	0.066	3.24	2.0
4.70	11.84	0.150	2.60	2.0	0.059	2.89	1.9

* The concentration of "free" isopropanol determined from the optical density of the band at 955 cm^{-1}. ** The same for the band at 3355 cm^{-1}.

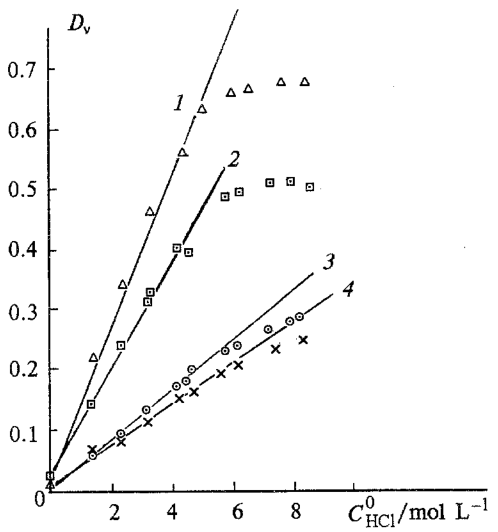

Fig. 2. Dependence of the optical densities at frequencies of 1030 cm^{-1} (*1*), 1520 cm^{-1} (*2*), 2000 cm^{-1} (*3*), and 2500 cm^{-1} (*4*) on the concentration of HCl.

in this region of concentrations, is proportional to C^0_{HCl}.

At $C^0_{HCl} > 5.7$ mol L^{-1}, the number of isopropanol molecules is not enough to form disolvates with each proton. The spectra of the system exhibit no sharp individual bands associated with the proton disolvate, which could have been used to follow the variations of its concentration occurring as the proportion of HCl in the solution increases. Therefore, we measured the concentration dependences of the optical densities of the CA on C^0_{HCl} over the whole frequency range studied. Figure 2 presents some of the resulting plots. The D_{1030} optical density is proportional to C^0_{HCl} up to $C^0_{HCl} = 5.7$ mol L^{-1}. In this concentration region, each HCl molecule being added binds two isopropanol molecules to give proton disolvate. At $C^0_{HCl} >$ 5.7 mol L^{-1} free alcohol is no longer present in the solution, and new disolvates cannot appear. Therefore, at $C^0_{HCl} > 5.7$ mol L^{-1}, the D_{1030} optical density virtually does not change. The optical density of the broad band at 1520 cm^{-1} associated with the $(C_3H_7\underset{H}{O}...H...\underset{H}{O}C_3H_7)^+$ ion depends on the HCl concentration in the same way (see Fig. 2).

One may assume that in the region of high HCl concentrations ($C^0_{HCl} > 5.7$ mol L^{-1}, $C^0_{HCl}/C^0_{Pr^iOH} >$ 1 : 2), $(ClHCl)^-$ ions are formed. Previously[5] these ions were detected in the DMF—HCl binary system; it was suggested that they possess a structure with a strong quasisymmetrical central H-bond. Therefore, at $C^0_{HCl} >$ 5.7 mol L^{-1}, the spectrum of CA is a superposition of the spectra of $(C_3H_7OH)_2H^+$ and $(ClHCl)^-$ ions, *i.e.*, for each frequency ν

$$D_\nu = (\varepsilon_{1\nu}l_\nu)C_1 + (\varepsilon_{2\nu}l_\nu)C_2, \qquad (1)$$

where D_ν is the optical density at frequency ν; C_1 and C_2 are the concentrations of the $(C_3H_7OH)_2H^+$ and $(ClHCl)^-$ ions, respectively; $\varepsilon_{1\nu}$ and $\varepsilon_{2\nu}$ are their extinction coefficients at this frequency; l_ν is the effective thickness of the absorbing layer. Since the absorption bands of isopropanol are missing from the spectrum at $C^0_{HCl} > 5.7$ mol L^{-1}, we will consider that the equilibrium

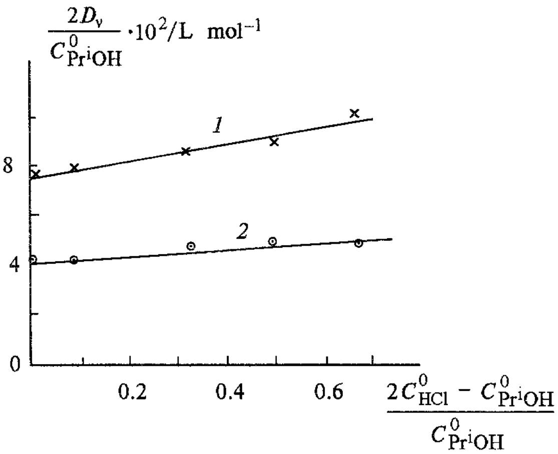

Fig. 3. Graphical solution of Eq. (4): ν = 1600 cm^{-1} (*1*); ν = 2000 cm^{-1} (*2*).

$$2\ C_3H_7OH + HCl \rightleftharpoons (C_3H_7OH)_2H^+ + Cl^-)$$

is completely shifted to the right, *i.e.*, at $C^0_{HCl} >$ 5.7 mol L^{-1}, all the alcohol is bound in proton disolvates and, consequently,

$$C_1 = 0.5C^0_{Pr^iOH}, \qquad (2)$$

$$C_2 = C^0_{HCl} - C_1 = C^0_{HCl} - 0.5C^0_{Pr^iOH}. \qquad (3)$$

From Eqs. (1)—(3) we obtain

$$2D_\nu/C^0_{Pr^iOH} = (\varepsilon_{1\nu}l_\nu) + (\varepsilon_{2\nu}l_\nu)(2C^0_{HCl} - C^0_{Pr^iOH})/C^0_{Pr^iOH}. (4)$$

Figure 3 presents the data for a number of frequencies, processed in terms of Eq. (4). The existence of linear dependences confirms that two sorts of ions, $(C_3H_7OH)_2H^+$ and $(ClHCl)^-$, are present in the solution.

For each frequency, the extinction coefficients were found. For the $(C_3H_7OH)_2H^+$ ion, they were determined both from Eq. (4) and the spectra at $C^0_{HCl} >$ 5.7 mol L^{-1} (see Fig. 2). For example, the ε_1 value, found from Eq. (4) for 2000 cm^{-1}, which is equal to 130 L mol^{-1} cm^{-1}, is identical to ε_1 found from Fig. 2 in the region of dilute systems. This also confirms the model suggested for ion-molecular interactions.

It is of interest to find out whether the ε_1 values obtained by different methods would be identical, if we chose another scheme of ion-molecular interactions at high concentrations of HCl. For example, let us assume that at $C^0_{HCl} > 5.7$ mol L^{-1}, mostly $C_3H_8O...H...Cl$

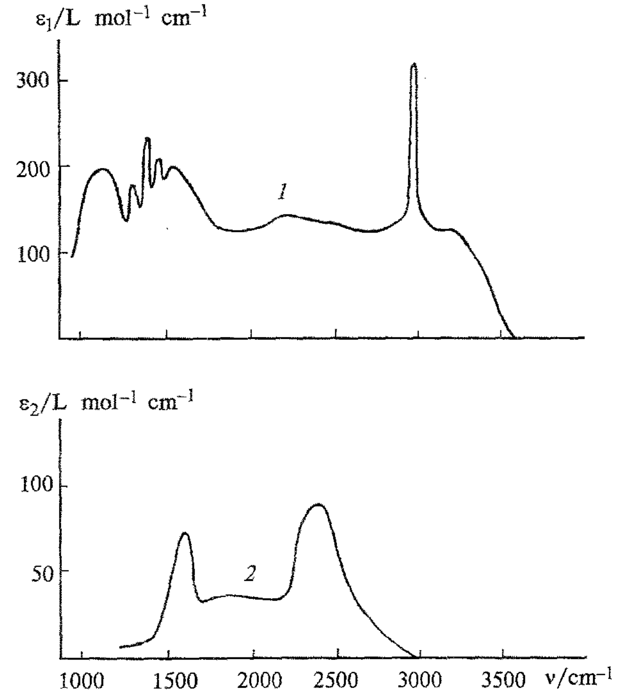

Fig. 4. Extinction spectrum of the proton disolvate $(C_3H_7OH)_2H^+$ (*1*) and the $(ClHCl)^-$ ion (*2*).

quasiionic pairs (see Ref. 6), rather than $(ClHCl)^-$ ions, are formed. Let us denote the concentration of the quasiionic pairs by C_3; then

$$C^0_{HCl} = C_3 + C_1, \quad (5)$$

$$C^0_{Pr^iOH} = 2C_1 + C_3, \quad (6)$$

$$D_{2000} = \varepsilon_1 l C_1 + \varepsilon_3 l C_3. \quad (7)$$

From Eqs. (5)—(7), it follows that

$$D_{2000}/C^0_{Pr^iOH} = (\varepsilon_1 - \varepsilon_3)l + (2\varepsilon_3 - \varepsilon_1)l(C^0_{HCl}/C^0_{Pr^iOH}). \quad (8)$$

Graphical solution of Eq. (8) gives: $\varepsilon_1 = 178\pm10$ L mol^{-1} cm^{-1} and $\varepsilon_3 = 130\pm10$ L mol^{-1} cm^{-1}. One can see that the absorption coefficients of the proton disolvates, $(C_3H_7OH)_2H^+$, determined for concentrated (ε_1 = 178 L mol^{-1} cm^{-1}) and dilute (ε_1 = 130 L mol^{-1} cm^{-1}) systems are substantially dissimilar. The value of the extinction coefficient of the quasiionic pair (ε_3 = 130 L mol^{-1} cm^{-1}) is also doubtful, since the ε values lying in the 50—80 L mol^{-1} cm^{-1} range have been found[6] for quasiionic pairs in other systems at 2000 cm^{-1}. Thus, we should conclude that no $C_3H_8O...H...Cl$ quasiion pairs are formed in the system under consideration.

Figure 4 presents the spectra of $(C_3H_7OH)_2H^+$ and $(ClHCl)^-$ ions obtained by processing the experimental data in terms of Eq. (4). As in the case of $(MeOH)_2H^+$,[7] the spectrum of the $(C_3H_7OH)_2H^+$ ion consists of low-intense smeared bands against the background of intense CA. This spectral pattern corresponds to the model of continuous absorption suggested by G. V. Yukhnevich.[8]

The spectrum of the $(ClHCl)^-$ ion (see Fig. 4) contains two very broad bands, which probably correspond to antisymmetrical stretching vibration and doubly degenerate deformation vibration of the $(Cl...H...Cl)^-$ ion. This spectrum coincides in appearance with the previously described[5] spectrum of the $(ClHCl)^-$ ion. However, the magnitudes of extinction coefficients obtained in this study are lower by a factor of 1.5—2 than the corresponding extinction coefficients published in the literature.[5] The difference between the intensities of the spectra of $(ClHCl)^-$ ions in the two different systems may be due to the interaction of these ions with the liquid medium.

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