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IR spectra of hydrogen fluoride solutions in *n*-propanol

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The densities of solutions of HF in *n*-PrOH were measured at different mole ratios of the components (from 1 : 12 to 3 : 1), and their IR spectra were recorded. The spectra of all the solutions exhibit absorption bands at 3500, 2600, and 1800 cm^{-1} and continuous absorption (CA) in the frequency range from 3500 to 1300 cm^{-1}. The intensities of these bands and CA increase in proportion to the concentration of HF in solution. The difference between the experimental solution density and the calculated additive sum of the densities of the solution components behaves analogously. The formation of heterocomplexes with a stoichiometric ratio greater than 3 : 1 in the HF solutions in propanol was revealed. These heterocomplexes have large identical structural fragments with the strong quasi-symmetric H-bond. The results of calculations of the stretching vibration frequencies and relative stability of different cyclic pentamers suggest that such a fragment is the most stable cyclic heteropentamer, $(HF)_2(nPrOH)_3$, in which the HF molecules occupy the neighboring positions.

Key words: solutions, hydrogen bond, hydrogen fluoride, complexes, vibrational spectra.

It has long been spectroscopically established that a characteristic feature of solutions of HF in organic solvents is the formation of new, virtually identical absorption centers, *viz.*, heterocomplexes with the natural frequencies of 3500, 2600, and 1800 cm^{-1}.[1—3] These frequencies were found to vary only slightly upon variation of the HF concentration in the solution. Therefore, a conclusion was drawn[3] that the new absorption centers represent the $[FHF]^-$ ions that are formed as a result of protonation of the solvent (Solv) molecules by hydrogen fluoride following the equation[4]

$$\text{Solv} + 2\,\text{HF} = [\text{SolvH}]^+ + [\text{FHF}]^- . \qquad (1)$$

During several decades the concept of proton transfer in solution remained unchanged,[5—7] while studies on the IR spectra of more simple complexes, such as Ar...HF, O_2...HF, CO_2...HF, *etc.*[8—18] have become the focus of research. For the most part, the shape of the ν_{HF} vibrational band, the rotational structure, and the dependence of the bandshape on temperature and on the state of aggregation of the compound under study were analyzed. Interest in the structure of heterocomplexes of HF with complex solvent molecules was rekindled only recently. In particular, the IR spectrum of the HF—PrOH (1 : 2) mixture was studied[19] and the results obtained were found to be close to those reported earlier.[3] However, the lack of information on the concentration dependences of the spectra did not allow one to use these data to draw definite conclusions about the molecular structure of the heterocomplexes formed in solutions.

The aim of this work was to study the IR spectra of the liquid mixtures of HF and PrOH over a wide concentration range to elucidate (i) do the heterocomplexes formed in solutions contain two HF molecules per solvent molecule and (ii) whether or not the structure and natural frequencies of these complexes depend on the initial solution stoichiometry.

Experimental

Hydrogen fluoride (99.95% purity according to GOST 12022-88) used in this work was additionally purified by redistillation and *n*-propanol of "chemically pure" grade was used as-received.

The solutions under study were prepared by mixing liquid HF and *n*-propanol in transparent 4MB fluoroplastic vessels. *n*-Propanol was introduced into frozen HF in small portions *via* a syringe at a temperature maintained at –100 °C to prevent HF from spontaneous boiling up. After the addition of each portion of *n*-propanol the mixture was defrosted, homogenized, and immediately cooled until solidification. The compositions of the solutions were controlled by weighing. This procedure was used for the preparation of solutions with the HF : PrOH mole ratios

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of 3 : 1, 2.5 : 1, 2 : 1, 1.5 : 1, and 1 : 1. The solutions with lower concentrations of HF (HF : PrOH = 1 : 12, 1 : 6, 1 : 3, 1 : 2.5, 1 : 2, and 1 : 1.5) were prepared by dissolving the 1 : 1 solution. The preparation of solutions with higher concentrations of hydrogen fluoride was impossible due to its high pressure over the solutions, which increased to 300—350 Torr at the HF : PrOH ratios from 5 : 1 to 7 : 1.

The solution densities (ρ) were determined by weighing at ~20 °C in a fluoroplastic picnometer of volume 25 cm^3; the error of measurements was ± 0.001 g cm^{-3}.

The IR absorption spectra of liquid mixtures of HF and PrOH were recorded on a Jasco IR-810 spectrometer attached to a personal computer in the frequency range from 4000 to 1300 cm^{-1} with an increment of 1 cm^{-1}. The solutions under study were placed in assembled CaF_2 cells 3.0 and 5.0 μm thick. A CaF_2 plate whose thickness was equal to the sum of the thicknesses of the cell windows was in the reference channel.

To reduce random errors, the IR spectra were smoothed. To make their comparison more convenient, all spectra were recalculated (in optical density units) to a layer thickness corresponding to the concentration of 4 μmol of *n*-propanol per square centimeter. It this amount of alcohol that contains within a layer 1 cm^2 in surface area and 3 μm thick at 20 °C. This procedure for the presentation of the spectra assured that the intensity of each band of the heterocomplex was proportional to its mole fraction in solution.

Results and Discussion

The results of our experiments (Fig. 1) indicate that the spectra of the solutions under study exhibit (i) the absorption bands characteristic of liquid propanol, (ii) the bands with maxima near 3500, 2600, and 1800 cm^{-1}, and (iii) continuous absorption (CA) in the frequency range from 3500 to 1300 cm^{-1}. The new bands are observed in the IR spectrum of the liquid mixture already when its components are taken in a mole ratio of 1 : 12 (see Fig. 1, *b*). For two of them (the bands at 2600 and 1800 cm^{-1}), the positions of maxima are shifted toward lower frequencies by 50 cm^{-1} as the concentration of HF increases from its minimum to maximum value. It is noteworthy that both the peak intensities of the new bands and the intensity of the background CA measured at 2200 cm^{-1} monotonically increase throughout the entire concentration range under study (Fig. 2). No decrease in the slope of the curves is observed even at the 75% mole fraction of HF, which is clearly seen for the absorption bands at 1800 and 3500 cm^{-1} (see Fig. 2, curves *1* and *2*, respectively).

The possibility for the $[FHF]^-$ ions to be formed in the solutions of HF and PrOH can be analyzed using the reported data.[20] The authors[20] have established that only the antisymmetrical vibration of the $[FHF]^-$ ion representing a symmetric hydrogen bridge can occur at a frequency higher than 1500 cm^{-1}. Hence, if the interaction between HF and *n*-propanol is described by Eq. (1), two stretching bands corresponding to ν_{OH} and ν_{FH} should be observed in the frequency range from 4000 to 1500 cm^{-1}.

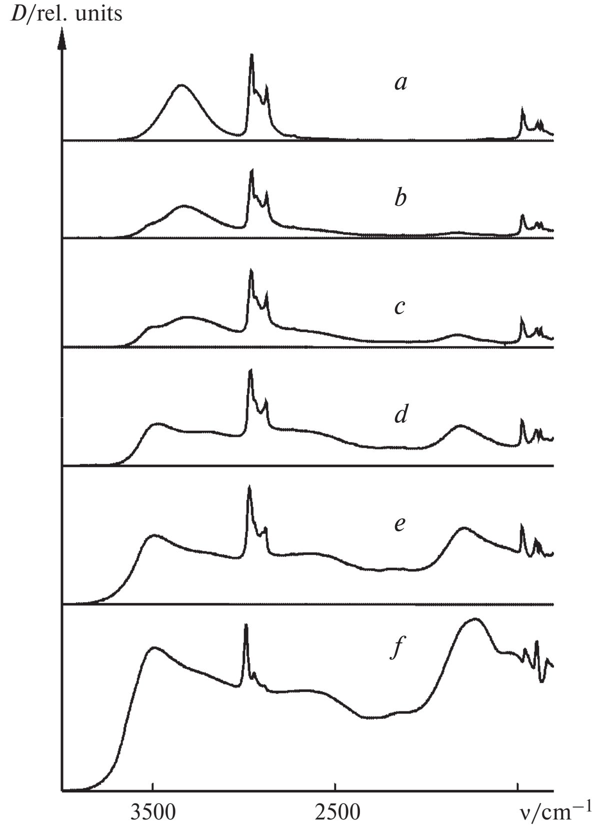

Fig. 1. Absorption spectra of HF—PrOH solutions. The mole ratio of the components: 0 : 1 (*a*), 1 : 12 (*b*), 1 : 3 (*c*), 1 : 1 (*d*), 2 : 1 (*e*), and 3 : 1 (*f*). The spectra were recalculated to the sample thicknesses corresponding to the concentration of 4 μmol of *n*-propanol per square centimeter.

The appearance of a larger number of bands in this region of the spectra of the solutions indicates that dissolution of

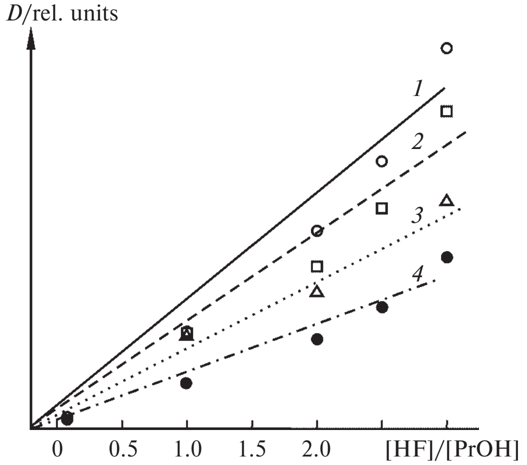

Fig. 2. Dependence of the reduced optical density (*D*) of the solution layer (4 μmol PrOH per square centimeter) on the mole fraction of HF added. Absorption band frequency/cm^{-1}: 1800 (*1*), 3500 (*2*), 2600 (*3*), and 2200 cm^{-1} (*4*).

HF in *n*-propanol produces molecular structures comprised of more than three atoms.

Analysis of the results obtained makes possible drawing some conclusions about the structure of the heterocomplexes formed in the liquid mixtures in question:

i) general invariable pattern of all the spectra under study suggests the retention of the basic structural fragment of the new absorption centers in the whole concentration range studied;

ii) an increase in the molar concentration of the heterocomplexes in solution up to the HF : PrOH ratio of 3 : 1 indicates that the mole ratio of the components in heterocomplexes is at least 3 : 1; and

iii) the appearance of CA (a characteristic spectral feature of strong quasi-symmetric hydrogen bond[20]) in the spectrum of the heterocomplex points to the presence of such a bond in the structure of the new absorption centers.

The solution density monotonically increases as the concentration of HF increases.

*m**	0 : 1	1 : 3	1 : 2	1 : 1.5	1 : 1
[HF] (vol.%)	0	8.5	12.2	15.7	21.8
ρ_{exp}/g cm^{-3}	0.807	0.826	0.837	0.847	0.863

m	1.5 : 1	2 : 1	2.5 : 1	3 : 1
[HF] (vol.%)	29.5	35.8	41.1	45.5
ρ_{exp}/g cm^{-3}	0.888	0.905	0.924	0.943

* *m* is the mole ratio of the components.

If the measured solution density differs from that calculated for a mixture of the same components using the additivity scheme, one can obtain information on the ratio of the HF and PrOH molecules in the heterocomplex. If the HF concentration in the liquid mixture is expressed in per cent by volume, the plot of the calculated density represents a straight line (Fig. 3, curve *2*). The plot constructed in the same coordinates for the experimental solution density is also nearly linear (see Fig. 3, curve *1*). The difference between the measured and calculated solution density monotonically increases in the concentration range studied. Hence it follows that the mole ratio of the components of the heterocomplex is greater than 3 : 1.

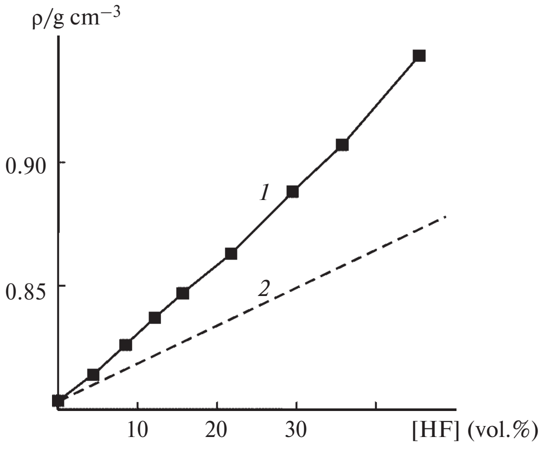

Fig. 3. Density (ρ) of the HF—PrOH liquid mixture plotted as function of the concentration of HF in solution: experiment (*1*) and calculations using the additivity scheme (*2*).

The ratio of components of the heterocomplex can be more correctly estimated by comparing the results obtained in this work with those reported[21] for solutions of methanesulfonic acid in 2-pyrrolidone. The authors[21] determined the densities (ρ) and optical densities (*D*) of solutions of methanesulfonic acid in 2-pyrrolidone and revealed the formation of 1 : 1 complexes based on the results of spectral studies. Using these results,[21] we calculated the ratio $(\rho_{exp} - \rho_{calc})/(N_{MSA} + N_{pyrrol})$ and plotted its values as function of $\ln(N_{MSA}/N_{pyrrol})$ (Fig. 4, curve *1*). As can be seen, this curve has a maximum at $\ln(N_{MSA}/N_{pyrrol}) \approx 0$, which corresponds to $N_{MSA}/N_{pyrrol} \approx 1$ and again confirms the 1 : 1 stoichiometry of the complex in the solution.[21] The curve for the HF solution in *n*-propanol plotted in the same coordinates (see Fig. 4, curve *2*) monotonically increases and has a nondecreasing derivative. Analysis of the shape of this curve suggests that it has a maximum at $\ln(N_{HF}/N_{PrOH}) \approx$ 1.5—2, which indicates the following relationship between the mole ratio of the solution components: $N_{HF}/N_{PrOH} \geq 5$—7. Therefore, the character of the concentration dependence of the solution density confirms the conclusion based on the results of spectroscopic studies, that is, the mole ratio of the components of the

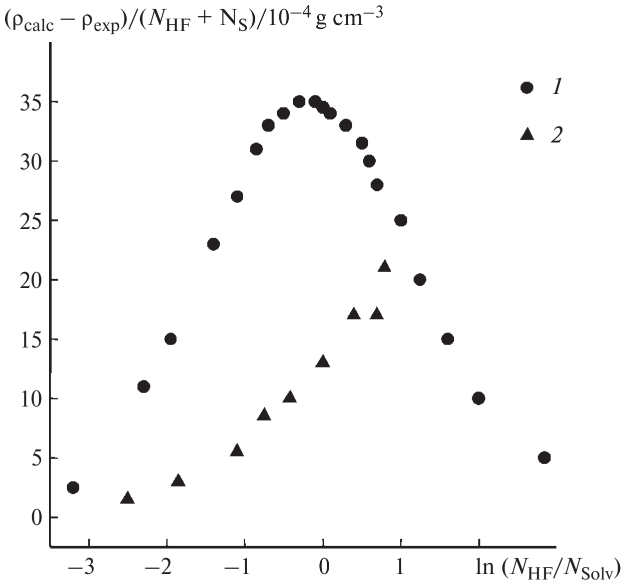

Fig. 4. The difference between the mixture density calculated using the additivity scheme and the experimental density, plotted as function of the component ratio (*N*) for methanesulfonic acid—2-pyrrolidone system (data were taken from Ref. 21) (*1*) and HF—PrOH system (*2*).

heterocomplex formed in solution of HF in PrOH is much larger than it was assumed earlier.[3]

Information on the stretching vibrations of the OH and FH groups and on the stoichiometries of the heterocomplexes $(HF)_m(PrOH)_n$ obtained in this work is insufficient for rigorous determination of the structure of these compounds by solving the inverse spectral problem. Structure determination is also precluded by the lack of data on the number and positions of individual components of the experimentally observed broad absorption bands, exact number of the HF and PrOH molecules in the complex, and on the mutual influence of H-bonds formed by the lone electron pairs of the same atom in branched molecular structures.

Nevertheless, the results obtained allowed us to perform approximate calculations (evaluation) and thus to make the first step toward the interpretation of the phenomenon under study. We started from the assumption that similarity of spectral features of the most abundant heterocomplexes (in solutions of any stoichiometry) points to a specific stability of the structural fragment that is common to these complexes. Judging from the results of the studies of the structure of the $(HF)_n$ associates formed in molecular beams and in the gas phase, most of them (>90%) represent five-membered rings to which the "tail" molecules are attached.[22,23] This suggests that the structure-forming fragment in the liquid mixture of HF and PrOH is also a cyclic pentamer.

To test this hypothesis, we calculated the frequencies and estimated the enthalpies of formation (ΔH) of all possible cyclic pentamers consisting of the HF and *n*-propanol molecules. Only isolated structures were considered, while the influence of the "tail" or surrounding solution molecules on the spectra was ignored. Calculations were carried out in the harmonic approximation using the known software.[24] We were interested only in the stretching vibration frequencies of the FH and OH groups involved in the cycle. These frequencies are independent of the bond lengths, therefore all the systems studied were assumed to have the same geometric parameters ($r_{\mathrm{OH(FH)}} = 0.96$ Å, $R_{\mathrm{H...O(H...F)}} = 1.80$ Å). The force constants and parameters characterizing the mutual influence of conjugated hydrogen bonds were calculated using the published experimental data[25—28] following a procedure that was described[29,30] and repeatedly used earlier.[22,23] The enthalpy of formation of each complex was estimated according to the Badger—Bauer rule[31] by calculating the sum of the differences of the force constants of the covalent FH(OH) bonds for a free HF(PrOH) molecule and for that considered as a constituent of the complex.

The relative enthalpies of formation of different heterocomplexes and their structural isomers are listed below.

Pentamer	ΔH_{rel} (%)	Pentamer	ΔH_{rel} (%)
$(PrOH)_5$	45	$(HF)_3(PrOH)_2$	85
$HF(PrOH)_4$	66	$(HF)_3(PrOH)_2$*	84
$(HF)_2(PrOH)_3$*	80	$(HF)_4PrOH$	72
$(HF)_2(PrOH)_3$	100	$(HF)_5$	64

* Structural isomers in which the HF molecules do not occupy neighboring positions.

As can be seen, replacement of a molecule in the *n*-propanol pentamer by the HF molecule leads to an ~1.5-fold increase in the enthalpy of formation of the complex. Heteropentamers formed by replacing two alcohol molecules by the HF molecules were found to be even more energetically favorable. The enthalpies of formation of two possible structural isomers differ appreciably (by 20%). More stable is the $(HF)_2(PrOH)_3$ complex in which the HF molecules occupy neighboring positions. It is noteworthy that further increase in the number of HF groups in the pentamer leads to a considerable decrease in the enthalpy of formation, the magnitude of the decrease being independent of the mutual arrangement of the molecules. On going from the $(HF)_5$ pentamer to complex $(HF)_4PrOH$ the energy of intermolecular interaction increases by more than 10%. By and large, the results presented in this work allow one to conclude that all kinds of the $(HF)_m(PrOH)_n$ heteropentamers are more stable than the $(HF)_5$ and $(PrOH)_5$ associates and unambiguously point to the most stable complex, $(HF)_2(PrOH)_3$, in which the HF molecules occupy neighboring positions. Marked difference between the enthalpy of formation of this heteropentamer and those of other systems studied suggests that it is these structures that are formed in the HF—PrOH mixtures even at low concentrations of each component.

The ν_{OH} and ν_{FH} ring vibration frequencies calculated for each of the pentamers are shown in Fig. 5. For convenience, we also present here the positions of maxima of the absorption bands observed in the spectra of the HF—PrOH mixtures (see Fig. 1).

The calculated stretching vibration frequencies of different pentamers differ appreciably from one another in both frequency range and mutual arrangement (see Fig. 5). At the same time, the spectra exhibit a common feature: the lowest-frequency vibration in all the heterocomplexes is due to the change in the H—F bond length in the O...HF bridge. It should be noted that the difference between the highest and lowest stretching vibration frequencies of the cycle for the heteropentamers with consecutive arrangement of the HF molecules ($(HF)_2(PrOH)_3$, $(HF)_3(PrOH)_2$, and $(HF)_4PrOH$) is nearly twice as large as that for other complexes. Only one, the most stable complex, $(HF)_2(PrOH)_3$, is characterized by a decrease in the lowest vibrational frequency, ν_{HF}, down to 1800 cm^{-1}. Such a strong decrease in ν_{HF} is

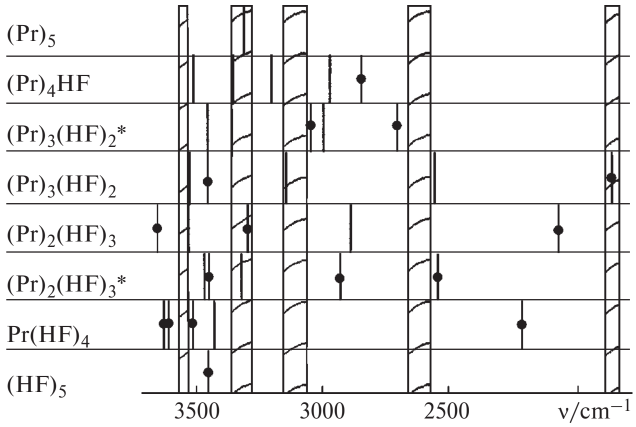

Fig. 5. Stretching vibration frequencies (ν_{OH} and ν_{FH}) calculated for cyclic pentamers $(HF)_m(PrOH)_n$ and observed in the IR spectra of liquid mixtures of HF and PrOH. Asterisked are the structural isomers in which the HF molecules do not occupy neighboring positions. Vertical linear segments denote the frequencies of the ν_{OH} vibrations, while vertical linear segments terminated by a circle denote the frequencies of the ν_{FH} vibrations. Shaded columns correspond to positions of the absorption bands observed in the IR spectra of liquid mixtures of HF and PrOH.

due to the reduction of the force constant of this HF bond down to the value that virtually coincides with the force constant of the neighboring O...H bond. In other words, a quasi-symmetric hydrogen bridge O...H...F characterized by CA is formed only in the most energetically favorable pentamer. No less important is the fact that all the stretching vibration frequencies of the cycle in this complex are in good agreement with the positions of maxima of the bands observed in the IR spectra of mixtures of HF and PrOH (see Fig. 5).

Comparison of the experimental and calculated data suggests a specific intermolecular interaction in the liquid mixture of *n*-propanol and HF. Probably, only more stable structural isomers of the cyclic complex $(HF)_2(PrOH)_3$ are present in the mixture under study starting from the lowest concentrations of HF. The ΔH values of these isomers are much larger than the enthalpies of formation of heteropentamers of different stoichiometry and structure. Such a concept provides an explanation for retention of virtually the same pattern of the IR spectra of HF—PrOH mixtures in the whole concentration range and for the main spectral features of the new absorption centers formed in solutions, namely, the positions of maxima of the absorption bands including the low-frequency band at 1800 cm^{-1} and CA.

Meanwhile, this assumption is valid only for those solutions studied that are characterized by the HF : PrOH mole ratio of at most 2 : 3. At higher concentrations of HF, branched molecular structures are necessarily formed. In this case, the effect of at least the molecules in the first solvation shell of the five-membered cycle on its vibrational properties should be taken into account. Information available at the moment is insufficient for quantitative estimation of this effect and determination of the structure of large branched complexes as well as for understanding the reasons for nearly identical patterns of the spectra of both dilute and concentrated solutions. Considerable progress in solving these problems can be achieved after experimental determination of the stoichiometries of branched heterocomplexes and all stretching vibration frequencies and after development of a procedure for the inclusion of mutual influence of hydrogen bonds formed by the lone electron pairs of the same atom.

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