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Composition of heteroassociates formed in HF—pyridine and HF—formamide binary liquid systems

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The IR spectra and the densities of solutions in HF—pyridine and HF—formamide binary liquid systems were measured over a wide range of mole ratios HF : Solv (Solv is the organic solvent). The composition of heteroassociates (HA) formed in these systems was determined by analysis of the concentration dependences of normalized (to the total number of moles per 1 L) optical density in the IR region and the excess density of the binary mixtures under study. The HA with the stoichiometric ratio 3 : 1 are present in the HF—Py system at all studied mole ratios of the components (from 1 : 12 to 20 : 1). The 1 : 2 HA were found in the dilute solutions, whereas the >6 : 1 HA were revealed in the concentrated solutions. The HA with the stoichiometric ratio 4 : 1 were found in HF—formamide system. The results obtained were compared with the known data on the composition of HA formed in the binary liquid systems HF—DMF, HF—Me_2CO, and HF—MeCN.

Key words: binary liquid system, IR spectroscopy, density of solution, hydrogen bond, heteroassociates, hydrogen fluoride, pyridine, formamide.

The composition and structure of self- and heteroassociates (HA) of molecules composing solid, liquid, and gaseous systems are actively studied by various experimental methods.[1—7] The composition of species formed in molecular beams detected by the vibrational pre-dissociation spectroscopy method is determined by mass spectrometric measurements[4,5] or using the theory of vibrational spectra.[6] In several cases, for instance, in determination of the stoichiometric ratio of molecules in HA existing in solution, it is substantially difficult and sometimes impossible to obtain the desired data from the experimental results. For example, when IR spectroscopy is traditionally used, to determine parameters of the particle under study, one should select its absorption bands from the spectrum of the solution and solve the inverse spectral problem.[8] For physicochemical analysis of binary liquid systems (BLS), the composition of HA can be estimated only in the presence of strong intermolecular interactions by measuring the excess (compared to the additive sum of densities of the components) density of the solution $\Delta\rho$.[7]

Fundamental and practical significance of many HF—Solv solutions (Solv is organic solvent) was a reason for investigation of the molecular structural parameters of associates composing these systems by physicochemical,[9] differential thermal, and X-ray diffraction analyses,[10,11] NMR[12] and IR spectroscopy.[13,14] Increasing interest in HF—Solv systems stimulated the search for reliable original procedures of determination of the composition of H-bonded complexes prevailing in BLS. The results of this search are published.[15,16] The first of these publications is devoted to the correction of the known method for determination of the composition of associates formed in two-component mixtures,[7] and a basically new method was developed in the second study. The appearance of these methods extended appreciably possibilities for finding stoichiometric ratios of molecules in HA. Therefore, let us characterize briefly each method.

The excess density of a binary mixture was shown[15] to be determined by both the fraction of molecules composing stable HA (this concept makes a basis for the traditional approach[7]) and the total number of molecules per volume unit. The allowance for the latter requires the transition from an analysis of the excess solution weight per volume unit ($\Delta\rho$, g L^{-1}) to the consideration of the excess weight in the volume occupied by one mole of the solution ($\Delta\rho/N$, g mol^{-1}). Here N is the total number of moles of the components of BLS in 1 liter. Due to this normalization, on going from one concentration to another, the effect stops depending on the

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change in the molecules in the volume unit, because $\Delta\rho/N$ is determined only by the composition of the solution. According to the law of mass action,[17] the maximum in the curve of the $\Delta\rho/N$ concentration plot is observed at the mole ratio of the components of the solution corresponding to the stoichiometric composition of HA.

The method for finding the HA composition based on an analysis of the concentration dependence of the IR spectra and adequate to the law of mass action was proposed[16] and tested for three BLS (HF—DMF, HF—Me_2CO, and HF—MeCN). This method is more universal than that considered above,[15] because is makes it possible to determine the composition of HA with both strong and weak intermolecular bonds and to study two-component systems in the liquid, solid, and gaseous phases. Its essence is as follows. To determine the composition of HA prevailing in a mixture of any two substances, one should find the mole ratio for which the content of these associates is maximum. IR spectroscopy is used for the experimental detection of HA and estimation of their amount. The starting material is a series of absorption spectra of the binary mixture recorded in a broad interval of concentrations containing frequency regions, whose absorption is due to only (or predominantly) associates. The contribution of HA to the total optical density (A) can reliably be estimated also in the case when their bands are completely overlapped with the bands of the initial components of the mixture and differ substantially from them in half-width.

When searching for the maximum in the concentration plot of A of any of the bands of HA chosen as the analytical one, it is taken into account that the intensity of this band in the spectra of mixtures with different mole ratios, measured at the same thickness of the samples, depends on the mole fraction of associates in the mixture and also on the change in the total number of particles in the volume unit with a change in the concentration. The normalization similar to that described above is performed for the intensity of the analytical bands of HA to be a function only of the mole ratio of the components: the A spectrum of a mixture of each concentration measured at the sample thickness single for the whole series is divided by the total number of moles (N) of compounds in 1 L of this mixture.

The purpose of the present work is to determine using two independent methods[15,16] the stoichiometric ratio of molecules in HA formed in HF solutions in pyridine and formamide and to compare the results with similar data for HF—DMF, HF—Me_2CN, and HF—MeCN binary mixtures.[16] When choosing the objects, we took into account both the structure and proton affinity of solvent molecules, which are of interest in searching for the relationship of the properties of a Solv molecule to the HA structure, and practical significance of the both systems, especially Olah´s reagent widely used in nucleophilic halo- and hydrofluorination.

Experimental

Two series of binary mixtures were studied: HF—Py (1 : 12—20 : 1) and HF—$HCONH_2$ (1 : 12—20 : 1). Liquid hydrogen fluoride (99.95%, GOST 14022-88), pyridine (analytical pure grade), and formamide (Acros) were used for the preparation of the mixtures. Hydrogen fluoride was additionally purified by recondensation.

Highly concentrated solutions were prepared by mixing HF with Py or $HCONH_2$ in vessels tailored from transparent 4MB fluoroplastic. The solvent was introduced into frozen (existing in the solid phase) HF by small portions (to prevent boiling up) using a medical syringe at the temperature exceeding the melting point of the solvent by 1—2 °C. The composition of the solution was monitored gravimetrically on a VLE-1 electronic laboratory balance (measurement error ±0.01 g). Binary mixtures with a lower HF content were obtained by the dilution of concentrated solutions with the corresponding solvent. The densities of the solutions were measured at 20 °C by gravimetry in a picnometer tailored from 4MB fluoroplastic. The volume of the picnometer was 25 cm^3, and the measurement error was ±0.001 g cm^{-3}.

The IR spectra of eleven HF—Py (1 : 12—10 : 1) and nine HF—$HCONH_2$ (1 : 12—6 : 1) solutions in the frequency region 4000—1000 cm^{-1} were recorded on a Philips PU9804 FTIR spectrometer with the step-by-step detection providing a high accuracy of processing of the primary experimental data. The sample was placed in a dismountable fluorite cell with a constant thickness (3.7±0.2 μm), transparent in the visible spectral range (which made it possible to monitor the completeness of filling its working field) and rather chemically resistant to HF. The design of the cell[18] provided simplicity and reliability of its washing. The optical density of the solution in the IR region was determined by the subtraction of the spectrum of cell windows from the spectrum of the cell filled with the solution.

Data on the composition of HA formed in the BLS under study were obtained from the $\Delta\rho/N$ and A/N concentration dependences using earlier described procedures.[15,16] For graphical presentation of the both dependences, the logarithm of the mole ratio of components of the binary mixture was put in the abscissa. The experimental values of the normalized excess density of the solution and its optical density were approximated by the Lorentz functions. This method of presenting results is clear and convenient for detailed analysis. If HA of the same composition are formed in the concentration range under study, all curves of the $\Delta\rho/N$ and A/N plots are symmetric, which makes it possible to determine exactly positions of their maxima and interpolate any their regions.

Results and Discussion

The spectra of the normalized optical density of components of the solutions under study, including the spectrum of liquid HF measured with a high accuracy,[19] are shown in Fig. 1. It can be seen that liquid HF absorbs in the whole studied frequency region; however, the

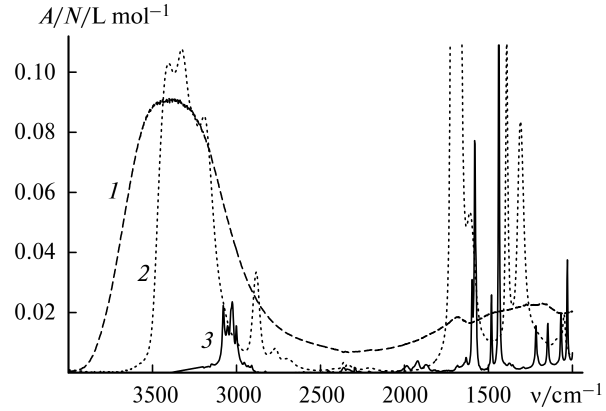

Fig. 1. Spectra of the normalized optical density of the components of solutions: *1*, liquid HF (according to published data[19]); *2*, $HCONH_2$, and *3*, Py.

A/N values (0.007—0.010 L mol^{-1}) in the region of relative transparency (2500—2000 cm^{-1}) are substantially lower than those at the maximum of the band of stretching vibrations of HF (0.091 L mol^{-1}). The spectra of the both solvents contain wide transparency regions (4000—3600 and 2650—2000 cm^{-1}), totally composing ~1/3 of the frequency interval under study. The features mentioned for the absorption curves of HF, $HCONH_2$, and Py should be taken into account when searching for analytical frequencies to plot the concentration dependences of A/N, which are used to determine the composition of HA.

The spectra of the normalized optical density of HF—Py and HF—$HCONH_2$ binary mixtures are presented in Figs 2 and 3. To facilitate perception of the results, each figure contains the spectra of not all solutions under study but only those that are most characteristic to illustrate the phenomenon considered. It follows from them that the concentration changes in A/N of the BLS under study have common features along with substantial distinctions. For instance, a decrease in the mole fraction of the solvent at 4000—2500 cm^{-1} is accompanied by the smooth change in the envelope of vibrational bands of the HF molecules forming H-bonds of different strength. The continuous absorption and a relatively narrow band at 1800 cm^{-1}, whose intensities depend on the concentration, are observed in the interval of the highest transparency of the both components of the system.

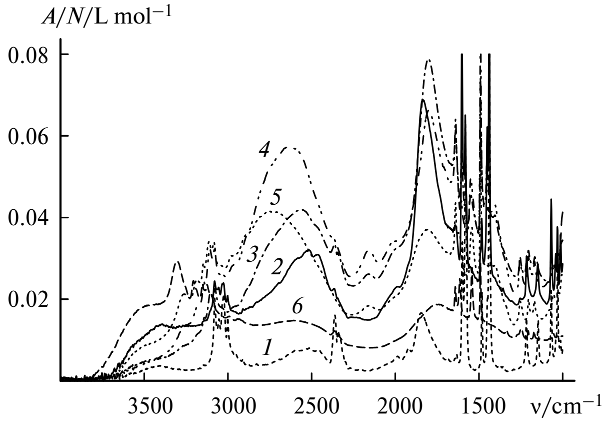

Fig. 2. Spectra of the normalized optical density of HF—Py solutions with the mole ratio of the components 1 : 12 (*1*), 1 : 2 (*2*), 2 : 1 (*3*), 3 : 1 (*4*), 4 : 1 (*5*), and 10 : 1 (*6*).

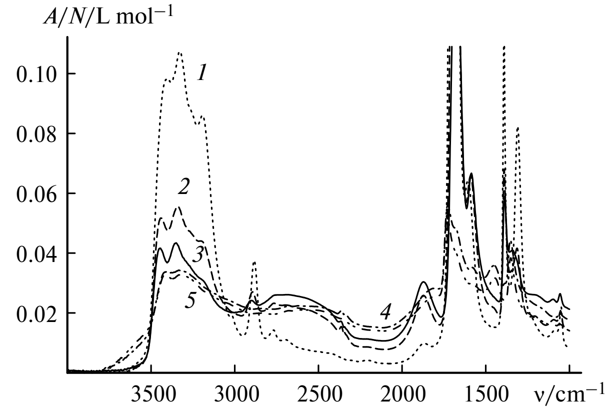

Fig. 3. Spectra of the normalized optical density of HF—$HCONH_2$ solutions with the mole ratio of the components 1 : 12 (*1*), 1 : 2 (*2*), 1 : 1 (*3*), 4 : 1 (*4*), and 6 : 1 (*5*).

These changes are typical of the HF—Solv BLS,[13,14,16] and only the A/N spectra of an HF—MeCN solution are substantially different.[16] However, it should be mentioned that in the earlier studied binary mixtures the intensities of the band at ~1800 cm^{-1} and continuous absorption, which is traditionally measured at 2100±100 cm^{-1} (see, *e.g.*, Ref. 20), change in parallel with an increase in the fraction of HF.[16] Therefore, the HA composition determined from the A/N concentration plots at these frequencies is the same. In the spectra of HF solutions in pyridine and formamide, the A/N values in the vicinity of frequencies 2100 and 1800 cm^{-1} pass through a maximum at different HF : Solv ratios, which can be a consequence of different factors.

Detailed analysis of the spectra of the HF—Py system (see Fig. 2) made it possible to distinguish the regions of HA absorption optimal for choosing the analytical frequencies. This is an interval of 2300—2100 cm^{-1} in which the background absorption is most pronounced, the band with a maximum shifting (with increasing the mole fraction of HF) from 1844 to 1742 cm^{-1}, and the region 1650—1000 cm^{-1} containing more than twenty narrow bands. The concentration run of the latter can distinctly be monitored. The basis for choosing these frequency intervals was the fact that the normalized optical density in the first two of them increases monotonically, reaches the maximum value at some HF : Solv ratio, and then decreases gradually. The intensities of the bands in the 1650—1000 cm^{-1} interval caused by vibrations of the Py molecules composing HA change similarly (Table 1).

Table 1. Concentration dependence of the $A/N \cdot 10^3$ values (L mol^{-1}) in the IR spectra of the HF—Py system with different mole ratios at the analytical frequencies (ν) in the spectra region 1650—1000 cm^{-1}

ν/cm^{-1}	HF : Py									
	1 : 12	1 : 4	1 : 2	1 : 1	2 : 1	3 : 1	4 : 1	6 : 1	8 : 1	10 : 1
1641	1.7	5.1	9.4	9.4	16.2	20.4	16.2	11.9	8.5	6.0
1615	—	—	—	—	—	2.1	8.8	12.3	10.2	8.5
1604	26.4	48.5	57.8	33.2	23.0	4.3	1.7	—	—	—
1548	—	0.7	1.3	3.0	9.4	12.8	11.9	—	—	—
1491	—	—	7.7	17.0	38.3	54.4	34.0	23.8	19.1	13.6
1449	11.9	25.5	34.0	22.1	12.8	2.6	—	—	—	—
1270	—	—	—	—	—	0.4	1.2	1.4	1.4	0.7
1253	0.2	0.4	1.4	2.8	4.3	6.4	3.9	2.1	0.7	0.4
1242	—	—	—	—	—	—	1.4	3.9	3.6	2.5
1205	0.4	0.7	1.8	3.2	5.0	8.5	6.0	3.6	2.8	2.0
1168	0.4	0.7	1.8	2.5	4.6	7.3	5.2	3.6	2.8	2.0
1043	3.2	7.1	10.7	5.0	1.8	—	—	—	—	—
1012	4.3	10.7	14.2	7.8	3.6	—	—	—	—	—

Thus, the curve of the dependence of A/N on the concentration of the solution at any analytical frequency has a maximum.

We chose five frequencies in the analytical region 2300—2100 cm^{-1} (with an increment of 50 cm^{-1}) to enhance the accuracy of determination of the composition of associates formed in the HF—Py system. The A/N values at these frequencies found for all studied mole ratios of the solution components are presented in Fig. 4, *a*. The mutual arrangement of points corresponding to different concentrations show that the A/N dependence in the frequency interval considered cannot be described by one Lorentz function. This is a distinction of the HF—Py binary mixture from the earlier studied solutions of HF in DMF, acetone, and acetonitrile.[16] Mathematical processing of the obtained experimental data showed that they are the sum of two Lorentz functions (see Fig. 4, *a*). The positions of maxima of these functions correspond to the HF : Solv stoichiometric ratios, being ~3 : 1 and ~1 : 2 (Table 2).

In the BLS under study, the A/N values in the region of continuous absorption and near the band at ~1800 cm^{-1} are the highest at different concentrations of the solution. The reason for this effect remains unknown so far but the results obtained show that the effect is objective in character and cannot be due to measurement errors. A consequence of the effect is the fact that the concentration plots of A/N at the frequencies 1844, 1806, and 1742 cm^{-1} resemble much those presented in Fig. 4, *a* but have maxima at the mole ratios of the solution components 2 : 1 and 1 : 2 (see Table 2). Based on the available data, we can only state that two molecular associates with different compositions absorb in the considered frequency region. Spectral manifestations of one of them (with the stoichiometric ratio 1 : 2) are also observed in other analytical frequency intervals.

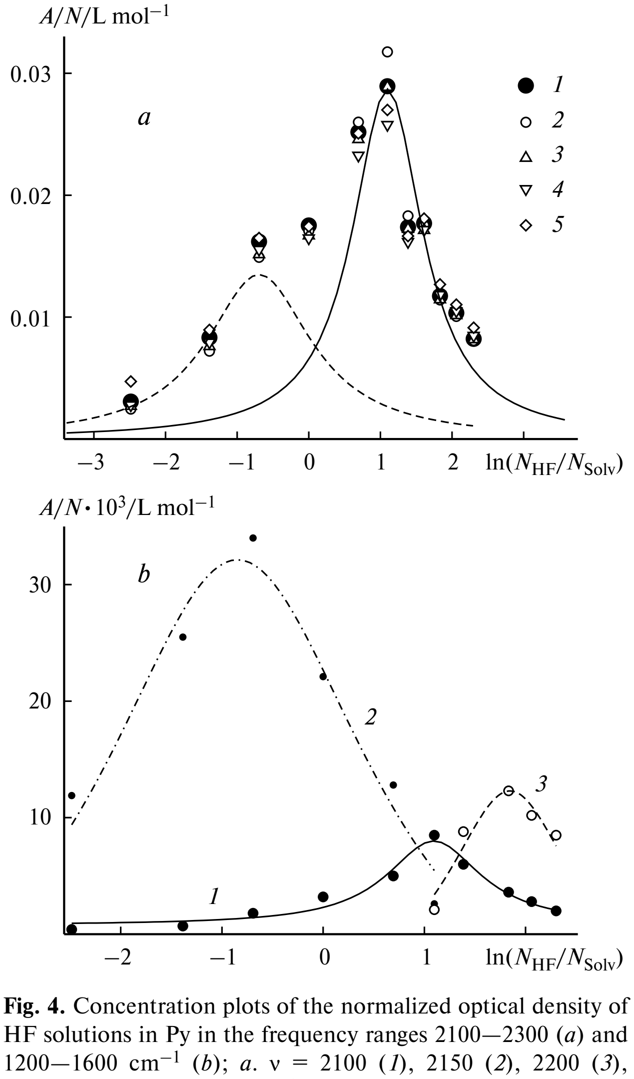

Fig. 4. Concentration plots of the normalized optical density of HF solutions in Py in the frequency ranges 2100—2300 (*a*) and 1200—1600 cm^{-1} (*b*); *a*. ν = 2100 (*1*), 2150 (*2*), 2200 (*3*), 2250 (*4*), and 2300 (*5*) cm^{-1}; *b*. ν = 1205 (*1*), 1449 (*2*), and 1615 cm^{-1} (*3*).

Table 2. Stoichiometric ratio of molecules in the heterocomplexes formed in HF—Solv binary liquid systems*

HF—Py		HF—HCONH$_2$		HF—DMF		HF—Me$_2$CO		HF—MeCN	
ν/cm^{-1}	HF : Solv	ν/cm^{-1}	HF : Solv	ν/cm^{-1}	HF : Solv	ν/cm^{-1}	HF : Solv	ν/cm^{-1}	HF : Solv
2300—2100	~3 : 1, ~1 : 2	2200	4.09 : 1	2200	4.25 : 1	2200	6.01 : 1	1706	4.42 : 1
1844—1742	~2 : 1, ~1 : 2	2150	3.99 : 1	2150	4.23 : 1	2150	6.52 : 1	1619	4.07 : 1
2163	2.75 : 1	2100	3.71 : 1	2100	4.13 : 1	2100	6.18 : 1	1241	4.08 : 1
1641	2.73 : 1	2050	4.40 : 1	2050	4.03 : 1	2050	6.05 : 1	1216	4.22 : 1
1615	6.34 : 1	2000	3.11 : 1	2000	3.89 : 1	2000	5.88 : 1	1165	4.20 : 1
1604	1 : 2.76	1447	4.88 : 1	1950	3.82 : 1	1950	5.39 : 1	—	—
1548	3.17 : 1	1352	4.29 : 1	1900	3.64 : 1	1900	5.00 : 1	—	—
1491	2.79 : 1	—	—	1850	3.55 : 1	1850	5.06 : 1	—	—
1449	1 : 2.33	—	—	1830	3.60 : 1	1830	5.42 : 1	—	—
1270	6.19 : 1	—	—	1800	3.71 : 1	1800	6.34 : 1	—	—
1253	2.61 : 1	—	—	—	—	—	—	—	—
1242	6.83 : 1	—	—	—	—	—	—	—	—
1205	2.98 : 1	—	—	—	—	—	—	—	—
1168	3.01 : 1	—	—	—	—	—	—	—	—
1043	1 : 2.36	—	—	—	—	—	—	—	—
1012	1 : 2.37	—	—	—	—	—	—	—	

* Determined using the A/N concentration dependences; using the $\Delta\rho/N$ concentration dependence for the HF—Py, HF—HCONH$_2$, HF—DMF, HF—Me$_2$CO, and HF—MeCN systems the following HF : Solv ratios were obtained: 2.93 : 1, 4.34 : 1, 4.17 : 1, 7.06 : 1, and 4.17 : 1, respectively.

The composition of HA that are present in the HF—Py system was additionally estimated by analysis of the concentration run of the normalized optical density of fourteen particular narrow lines. To determine the intensity of each line, the background absorption was subtracted from the peak A/N value. The maximum of the first of the bands observed in a restricted concentration range (1 : 1—5 : 1) lies at 2163 cm^{-1} in the continuous absorption region. The HF : Solv ratio obtained at this frequency from the A/N dependence is close to 3 : 1 (see Table 2).

The other thirteen analytical absorption bands lie at 1650—1000 cm^{-1}. The data in Table 1 show that in this frequency interval the spectral manifestations of HA are distinctly grouped as follows. The first group contains the bands detected, as a rule, in the whole studied interval of solution concentrations and having the maximum intensity at the mole ratio of components 3 : 1. The second group is composed of the bands present in the spectra of dilute solutions (from 1 : 12 to 2 : 1—4 : 1). For them the maximum of A/N values is observed at the HF : Solv ratio equal to 1 : 2. The third, least spectrally pronounced group is formed of the bands observed only at a high HF content (beginning from the mole ratio 3 : 1) and the most intense in the spectrum of 6 : 1—8 : 1 solutions.

The stoichiometric ratios of molecules in HA determined from the concentration dependences of A/N at all analytical frequencies in the interval 1650—1000 cm^{-1} are presented in Table 2. As should be expected, these ratios obtained for the first, second, and third groups of bands are close to 3 : 1, 1 : 2, and ~6 : 1, respectively. The A/N dependences plotted for one of the frequencies of each group, namely, 1205, 1449, and 1615 cm^{-1}, are shown as an example in Fig. 4, *b*. In all cases, the experimental results are well described by the Lorentz function. The first curve corresponds to the stoichiometric ratio 3 : 1, the second curve corresponds to the 1 : 2 ratio (which agrees completely with the data in Fig. 4, *a*), and the third curve suggests that HA in which at least six HF molecules fall per one solvent molecule are also formed in the HF—Py system.

This assumption is confirmed by results of measurements of the density of HF solutions in pyridine. The $\Delta\rho/N$ values obtained at different concentrations of components according to an earlier described procedure[15] are presented in Fig. 5, *a*. It is seen that at the HF : Py mole ratios exceeding 6 : 1 these values stop to lie on the Lorentz curve, whose maximum position indicates that the 3 : 1 HA prevails in the system. The systematic deviation of the experimental points from the symmetric curve indicates that the solutions under study also contain stable associates with the stoichiometric ratio of molecules >6 : 1. The absence of any specific features (maximum, inflection, *etc.*) in the curve of the concentration dependence of $\Delta\rho/N$ in the region of low HF concentrations suggests that the 1 : 2 HA observed by IR spectroscopy contain H-bonds that result in no noticeable changes in the average distance between molecules in solution.

This conclusion agrees with the results of calculation of the Py molecule, Py$_2$ dimer, and HF$\cdot$Py$_n$ complexes (n = 1, 2). The calculation was performed by the density

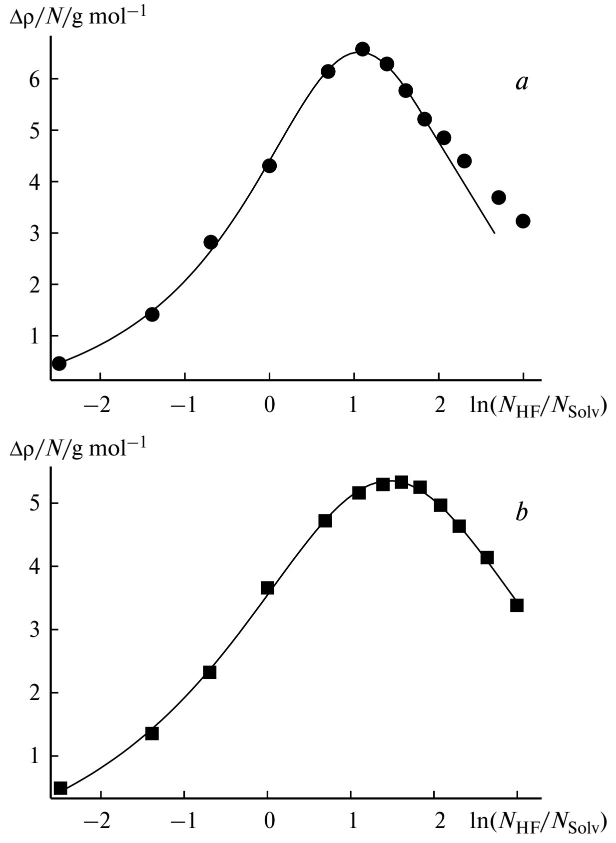

Fig. 5. Concentration plots of the normalized excess density of solutions in HF—Py (*a*) and HF—HCONH$_2$ (*b*) systems.

functional method (B3LYP/6-31++G(d,p)) using the GAUSSIAN-98 program package.[21] The purpose of this calculation was to estimate the lengths and energies of intermolecular bonds in the 1 : 2 HA consisting of three molecules: $C_5H_5N\cdots HF\cdots HC_5H_4N$. Associates with the same stoichiometric ratio but containing six or nine molecules were not considered in the present work. The calculated total energy values of the studied molecular systems, energies of their H-bonds, and distances between the atoms of hydrogen bridges are given in Table 3. The estimations of the strength of H-bonds were performed under assumption, according to which the total energy of the complex can be presented as the sum of energies of particular fragments and bond energies between the fragments.

The calculation showed that the average bridge length in the heterotrimer (2.945 Å) is by ~20% less than that in the $(C_5H_5N)_2$ dimer (3.587 Å). Thus, even in a solution with a high content of the HF • Py$_2$ complexes (which simultaneously contains, as can be seen from experiment, appreciable amounts of 3 : 1 HA and "free" Py molecules) their contribution to the excess density can be insignificant. The data obtained (see Table 3) make it possible to estimate to which extent the interactions between the HF and Py molecules are stronger than those between the Py molecules. For example, the strength of the H-bond in the N...HF bridges of the heterodimer and trimer is higher by 7.4 and 8.5 times, respectively, than that in the Py$_2$ self-associate. In this case, the energy of the second H-bond ($E_{\text{F...H}}$) in the HF • Py$_2$ complex 1.4-fold exceeds the $E_{\text{N...H}}$ value in the Py$_2$ dimer.

In the case of the HF—HCONH$_2$ BLS, the concentration changes in the vibrational spectrum (see Fig. 3) are much less intricate than the corresponding changes in the spectrum of the HF—Py mixture (see Fig. 2). The most convenient for choosing analytical frequencies are the regions 2200—2000 cm^{-1}, 1873—1800 cm^{-1}, and the low-frequency interval 1500—1300 cm^{-1} containing two narrow rather intense vibrational bands of HA. As in the above examined system, the concentration dependences of *A*/*N* in the continuous absorption region are plotted on five frequencies with an increment of 50 cm^{-1}. All the curves obtained are similar and well described by the Lorentz functions, reaching a maximum at the mole ratios close to 4 : 1 (see Table 2). This is exemplified by the *A*/*N* plot corresponding to a frequency of 2100 cm^{-1} in Fig. 6. An analogous concentration run of the normalized optical density of HF—HCONH$_2$ solutions is observed at 1447 and 1352 cm^{-1} (see Table 2).

In the region of the band at ~1800 cm^{-1} the highest intensity was detected for the 3 : 1 mixture (see Fig. 3). This exhibits a distortion of the symbate character of concentrations changes in *A*/*N* in the regions near 2100 and 1800 cm^{-1}, which is objective as in the case of the HF—Py system. It follows from the *A*/*N* dependence at any frequency of the 1873—1800 cm^{-1} interval (within which

Table 3. Parameters of the optimal configurations of the Py molecule, Py$_2$ dimer, and HF • Py$_n$ associates (n = 1, 2)*

System	$-E_{\text{tot}}$/au	*E*/kcal mol^{-1}		*R*/Å			
		N...H	F...H	N...H	H—F	F...H	H—C
Py	248.303464	—	—	—	—	—	1.086
Py$_2$	496.610365	2.1	—	2.499	—	—	1.088
HF • Py	348.777719	15.8	—	1.612	0.975	—	—
HF • Py$_2$	597.085321	18.2	2.9	1.571	0.985	2.247	1.086

* The total energy (E_{tot}), energies of H-bonds (*E*), and distances between the atoms of the hydrogen bridges (*R*).

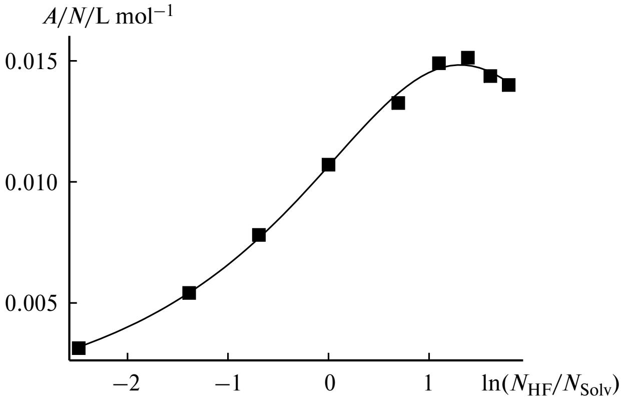

Fig. 6. Concentration plot of the normalized optical density of HF solutions in HCONH$_2$ at the frequency 2100 cm^{-1}.

the band maximum shifts with an increase in the HF fraction) that HA of two different compositions absorb in this interval. However, since the vibrational bands of these associates in the region considered overlap on the shoulder and, possibly, on the steep slope of the most intense band of formamide at 1694 cm^{-1} (see Figs 1 and 3), correct determination of their compositions turned out to be impossible. Based on the available data, we can only assume that the stoichiometric ratios of molecules in these HA are 1 : 1 and 4 : 1.

The concentration dependence of the excess density of solutions in the HF—HCONH$_2$ system is shown in Fig. 5, *b*. It is seen that all experimental points fall on the Lorentz curve, whose maximum corresponds to the stoichiometric ratio of molecules 4 : 1 (see Table 2). This result is completely consistent with the data on the composition of HA prevailing in HF solutions in formamide, which were obtained in the analytical frequency intervals 2200—2000 and 1500—1300 cm^{-1}.

The present study extended concepts on the composition and conditions of formation of HA that are present in HF solutions in organic solvents. A comparison of the obtained results with published data[16] (see Table 2) allowed us to reveal several interesting regularities. For instance, in each HF—Solv mixture under study we found stable molecular associates existing (and, as a rule, predominant) in the whole studied concentration interval (from 1 : 12 to $\geq$20 : 1). The composition of these associates is characteristic: in them from three to six HF molecules fall on one solvent molecule. In some BLS, HA with the substantially different ratio of molecules are formed along with the predominant HA: 1 : 2(1) in solutions with a low HF content and $\geq$6 : 1 in highly concentrated solutions. In this case, unlike the "major" HA, intermolecular interactions in them should not necessarily be strong.

Thus, in this work the IR spectra and densities of solutions were measured in HF—Py and HF—formamide binary liquid systems in a wide range of changing the HF : Solv mole ratio. The composition of HA formed in the binary mixtures under study was determined by analysis of the concentration dependences of the normalized (to the total number of moles in 1 L) optical density and excess density of these mixtures. It is shown that the HF—Py system at all studied component ratios (1 : 12—20 : 1) contains HA with three HF molecules per one pyridine molecule. In dilute solutions, 1 : 2 associates are present along with the above HA, whereas concentrated solutions contain, most likely, associates of $\geq$6 : 1. Heteroassociates with the stoichiometric ratio of molecules 4 : 1 were found in the HF—HCONH$_2$ system.

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