Composition and structure of heteroassociates formed in the HF—*N*,*N*-dimethylformamide binary liquid system

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The concentration dependence of the normalized (to the total number of moles of the components per liter) absorbance of HF solutions in DMF in ratios from 1 : 12 to 7 : 1 was analyzed. In the binary liquid system (BLS) under consideration, there are molecular complexes with stoichiometric ratios of 1 : 1 and ≥10 : 1 along with heteroassociates (HA) with the HF to DMF ratio of 4 : 1, which have been found earlier. For each HA, the concentration range, in which HA is formed in BLS, was estimated, and the positions of the stretching bands of HF were determined. The optimal configurations and the vibrational frequencies of the molecular complexes $(HF)_m \cdot (DMF)_n$ ($m = 1, 2, 4, 8$; $n = 1, 2$) with different topologies were calculated using the density functional theory (B3LYP/6-31++G(d,p)). The relative stability and structural features of the latter complexes were investigated. The complex formation in the HF—DMF system was analyzed. The structures of HA with stoichiometric ratios of 1 : 1 and 4 : 1 were determined by comparing the results of calculations and experimental data.

Key words: binary liquid system, IR spectroscopy, hydrogen bond, heteroassociates, hydrogen fluoride, dimethylformamide.

Hydrogen fluoride has the unique ability to form solvates and complexes.[1] Its molecules are involved in numerous stable heteroassociates (HA) with different structures,[1—32] which determine the chemical, physicochemical, and spectroscopic properties of HF-containing systems. Comprehensive studies of these HA are of fundamental and practical interest due, in particular, to the fact that some HA can act as fluorinating agents.[1,3—6,14,18]

One of important goals in the solution chemistry is to determine the composition, structures, and the mechanism of the formation of stable hydrogen-bonded molecular complexes $(HF)_m \cdot (Solv)_n$ (Solv is an organic solvent) in the liquid phase. Chemical and physicochemical methods,[1,3—6,14,18,25—30] IR spectroscopy,[2,22,26—32] X-ray diffraction, and differential thermal analysis[12,13] are employed to obtain relevant information.

The structural features and conditions of the formation of heteroassociates $(HF)_m \cdot (Solv)_n$ in binary liquid systems (BLS) were considered in experimental and computational studies having common logic.[25—32] In these studies, new methodological approaches were developed. For example, two procedures adequate to the law of mass action[33] were developed for the determination of the stoichiometric HF : Solv ratios in these HA.[25,26] One of these procedures is based on measurements of the concentration dependences of the normalized (to the total number of moles of the components of BLS per liter of the solution) excess density of the solution ($\Delta\rho/N$, g mol^{-1}) and the fact that, according to the law of mass action, the maximum in this dependence will be observed at the molar ratio of the components in the binary mixture corresponding to the stoichiometric composition of HA. An alternative procedure[26] involves measurements of a series of normalized absorbance of solutions (A/N, L mol^{-1}), the determination of the frequency regions, in which the absorption of molecular complexes is observed, and the analysis of the concentration dependences of A/N constructed for the frequencies characterizing the vibrations of these complexes (hereinafter, referred to as analytical frequencies). In this analysis, the allowance for the law of mass action is needed.[33]

Studies with the use of these procedures showed that up to four types of stable* HA containing from 0.5 to ~12 HF molecules per Solv molecule can be formed in HF—Solv binary mixtures (see, for example, Refs 28—32). Each type of HA exists in a wide concentration range. Hence, at

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* The presence of strong hydrogen bonds in the heteroassociates under consideration is confirmed by (a) strong (up to 1600 cm^{-1}) low-frequency shifts of the stretching vibration bands of HF molecules involved in HA with respect to the absorption band of liquid hydrogen fluoride and (b) a substantial increase in the real density of the HF—Solv solution compared to the additive density.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 79—86, January, 2011.

certain molar ratios of the components, all types of HA are simultaneously present in solution.

First data on the structures of molecular complexes that are formed in HF—Solv BLS were reported in the recent works.[31,32] It was shown by an example of HF—CH_3CN and HF—$(C_2H_5)_2O$ solutions that the structures of all such complexes can be determined in these solutions, except for the largest complexes. For this purpose, the following four problems should be successively solved: (1) the determination of the number of different types of HA that are present in BLS, the evaluation of the stoichiometric ratio of the molecules in each HA, and the estimation of the concentration ranges, in which these associates are formed in solution; (2) the determination of the positions of the stretching vibration bands of HF molecules (ν_{HF}) involved in each HA, whose structure should be determined; (3) the application of the density functional theory to calculate the configurations and frequencies ν_{HF} of stable associates with different structures, in which the HF : Solv ratios are equal to those determined experimentally and the investigation of the relative stability of these associates; (4) the determination of the structures of HA under consideration by comparing the results of calculations and experimental data.

The aim of the present study was to determine the structures of HA that are formed in HF—DMF BLS. For this purpose, it was necessary to solve the above-mentioned problems making use of experimental data[27] according to the procedure described earlier.[26]

Experimental data processing

The absorbance (A) spectra of nine HF—DMF solutions with the molar ratio of the components varying from 1 : 12 to 7 : 1 were used as the starting spectra.[27] Data on the HF : DMF ratios in HA under consideration were obtained according to the known procedure[26] taking into account the concentration dependences of A/N at twenty frequencies in the range of 3600—1850 cm^{-1}. This allowed us to study in detail the absorption of hydrogen-bonded complexes throughout the range suitable for the choice of analytical frequencies, *i.e.*, in the spectral regions, where the concentration dependence of A/N for solutions shows a maximum at each frequency.

The graphical representation of the plots of A/N approximated by Lorentzian functions was made by plotting the logarithm of the molar ratio of the solution components on the abscissa. In the case that only one type of HA shows absorption at the frequency under consideration, this representation of the results provides an adequate description of the dependence of A/N by the Lorentzian function, whose maximum is observed at the HF : DMF molar ratio equal to the stoichiometric ratio of the molecules in HA. A considerable asymmetry of the experimental curve or the presence of several extreme points in this curve is indicative of the absorption of different associates at this analytical frequency. The stoichiometric ratios of the molecules corresponding to these HA were evaluated by the decomposition of the A/N dependence into Lorentzians, whose number was determined by the character of the curve.

The concentration range, in which HA exist in the HF—DMF system, was estimated based on the results of the decomposition of the experimental A/N dependences into Lorentzians and employing the following criterion, which has been formulated and used for the first time earlier:[29] the boundaries of the range of the values $\ln(N_{HF}/N_{Solv})$, in which the presence of a particular HA in solution is detected by IR spectroscopy, are the abscissa values of the points in the Lorentzian curve corresponding to this associate, whose y coordinates make up one-fifth of the peak intensity. The range of the existence of molecular complexes evaluated based on this criterion is the bottom-up estimate.

The positions of the stretching bands of HF molecules involved in relevant HA were determined according to the procedure, which has been described and used for the first time earlier.[31] According to this procedure, the absorbance spectrum of each solution was normalized to the number of Solv molecules per square centimeter of the layer under study (S). Then the A/S spectrum of a solution of the lower concentration was subtracted from the spectrum of each subsequent concentration (which is of interest for a particular consideration). The $\Delta A/S$ difference spectra thus obtained fairly clearly reflect the concentration changes in the absorption of HF molecules per solvent molecule. Since the search for the ν_{HF} values characterizing the $(HF)_m \cdot (Solv)_n$ HA is a difficult problem for unbiased reasons, all A/S spectra and several series of $\Delta A/S$ spectra were analyzed in detail.

Results and Discussion

The normalized absorbance spectra of a series of HF—DMF solutions are shown in Fig. 1. To simplify the understanding of the results, we represent only the spectra, which most clearly show the concentration changes in A/N. As can be seen from Fig. 1, the frequencies outside the strong absorption regions of DMF (3000—2800 and 1750—1500 cm^{-1}) can be used as analytical frequencies.

A decrease in the molar fraction of the solvent in the region of 3800—2300 cm^{-1} leads to substantial changes in the envelope of the vibrational bands of HF molecules that form hydrogen bonds of different strength. The strongest band with a maximum at 2800—2750 cm^{-1} and a half-width of at least 200 cm^{-1} is observed in the spectra of solutions with compositions varying from 1 : 12 to 3 : 1. It was impossible to determine these parameters with higher accuracy because the band under consideration overlaps with the stretching bands of the CH_3 groups of the DMF

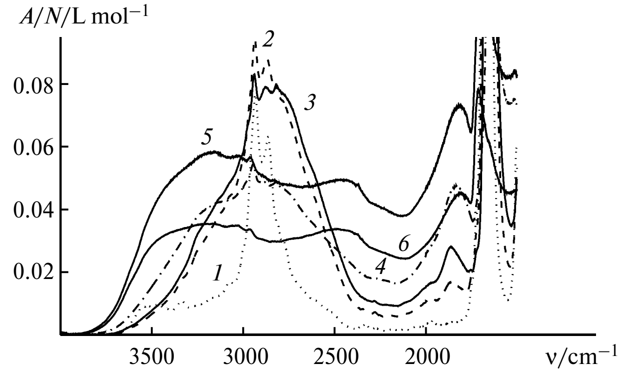

Fig. 1. Absorbance spectra of HF—DMF solutions normalized to the total number of the moles of the components per liter of the solution (results of the study[27]). The molar ratio of the components: 1 : 12 (*1*), 1 : 2 (*2*), 1 : 1 (*3*), 2 : 1 (*4*), 4 : 1 (*5*), and 7 : 1 (*6*).

molecule. The highest intensity ($A/N \approx 0.08$ L mol^{-1}) was observed for an equimolar binary mixture. In the spectrum of the 4 : 1 solution, diffuse maxima dominate at 3200 and 2450 cm^{-1}. At higher concentrations, the spectra of the solutions show an additional strong absorption in the region of 3550—3300 cm^{-1}.

In the most transparent region of the HF—DMF binary mixture (2300—2000 cm^{-1}), the characteristic spectroscopic evidence of HA is observed. It involves the continuous absorption (CA), which monotonically increases with increasing molar ratio of the solution components to 4 : 1 and then decreases as the HF content further increases. Against the background of this absorption, starting with the lowest concentrations, there is an additional evidence of the formation of $(HF)_m \cdot (Solv)_n$ associates in solutions, *viz.*, the band at 1900—1800 cm^{-1}, whose intensity changes in parallel with the intensity of CA. At the molar ratios of the solution components from 1 : 12 to 1 : 1, the maximum of this band is observed at 1863 cm^{-1}, and then it slowly shifts to longer wavelengths.

To find the stoichiometric ratios of the molecules in HA prevailing in HF—DMF binary mixtures, we chose twenty analytical frequencies. Seven of these frequencies exactly (3200, 2450, and 1863 cm^{-1}) or approximately (2750, 2700, 2550, and 2400 cm^{-1}) correspond to the experimentally observed absorbance maxima of the solutions. Six frequencies (3600, 3560, 3500, 3150, 3100, and 3050 cm^{-1}) occur in the strong absorption region, which is difficult to interpret (and which is partially unsuitable for the interpretation*). The other seven frequencies (taken with a step of 50 cm^{-1}) lie in the region of relative transparency (2200—1900 cm^{-1}).

Table 1. Stoichiometric ratios of molecules in heteroassociates $(HF)_m \cdot (DMF)_n$ determined from the concentration dependences of A/N at analytical frequencies

ν/cm^{-1}	HF : DMF		
3600	—	4.0 : 1	8.0 : 1
3560	—	3.9 : 1	7.3 : 1
3500	—	4.0 : 1	12.0 : 1
3200	0.9 : 1	4.1 : 1	—
3150	0.8 : 1	4.0 : 1	—
3100	0.8 : 1	3.9 : 1	—
3050	0.8 : 1	3.9 : 1	—
2750	0.7 : 1	4.1 : 1	—
2700	0.7 : 1	4.3 : 1	—
2550	0.8 : 1	4.5 : 1	—
2450	0.9 : 1	4.5 : 1	
2400	0.9 : 1	4.5 : 1	
2200	—	4.2 : 1	
2150	—	4.2 : 1	
2100	—	4.1 : 1	
2050	—	4.0 : 1	
2000	—	3.9 : 1	
1950	—	3.8 : 1	
1900	—	3.6 : 1	
1863	—	3.5 : 1	

The concentration dependences of the normalized absorbance constructed at all analytical frequencies in the region of 3200—2400 cm^{-1} have two pronounced maxima. Due to this fact, each dependence can be described with high accuracy by two Lorentzians, whose extreme points correspond to the molar ratios of the solution components equal to 1 : 1 and 4 : 1 (Table 1). Now we can consider the results obtained at 3150 (Fig. 2, *a*), 2750 (Fig. 2, *b*), and 2400 cm^{-1} (Fig. 2, *c*) as an example. From the ratios of the peak intensities in three pairs of Lorentzians, it follows that the band at ~2800—2750 cm^{-1} can be assigned to vibrations of 1 : 1 HA (see Fig. 2, *b*),* whereas 4 : 1 associates make a major contribution to the strong absorption on both sides of this band (see Fig. 2, *a* and *c*).

It should be emphasized that the results presented in Fig. 2, *c* suggest that larger species (which cannot be characterized based on the available data) make a contribution to the absorption at 2400 cm^{-1} in more concentrated solutions. Actually, the mutual arrangement of the experimental points at molar ratios of the solution components higher than 3 : 1 is such that the maximum of the second Lorentzian is shifted to larger values $\ln(N_{HF}/N_{Solv})$ and corresponds to the 4.5 : 1 stoichiometric ratio of the molecules.** The earlier studies[30,31] have shown that such a considerable deviation from the 4 : 1 ratio may be a consequence of the absorption of large HA, which was not directly detected.

The presence of these HA in the HF—DMF binary mixture is most clearly manifested in the analysis of the concentration dependences of A/N constructed for the three highest analytical frequencies (3600, 3560, and 3500 cm^{-1} (the latter is presented in Fig. 3 as an example).

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* The character of the mutual arrangement of experimental points in the dependences $A/N(\ln(N_{HF}/N_{Solv}))$ constructed for the frequencies in the range of 3450—3250 cm^{-1} is such that it is impossible to correctly apply the procedure of the decomposition into Lorentzians.

* Hereinafter, for the sake of brevity, we will write 1 : 1 HA instead of "heteroassociates with the stoichiometric ratio of the molecules equal to 1 : 1".

** Similar results were obtained in the study of the concentration dependence of the normalized absorbance of HF—DMF solutions at 2450 and 2550 cm^{-1} (see Table 1).

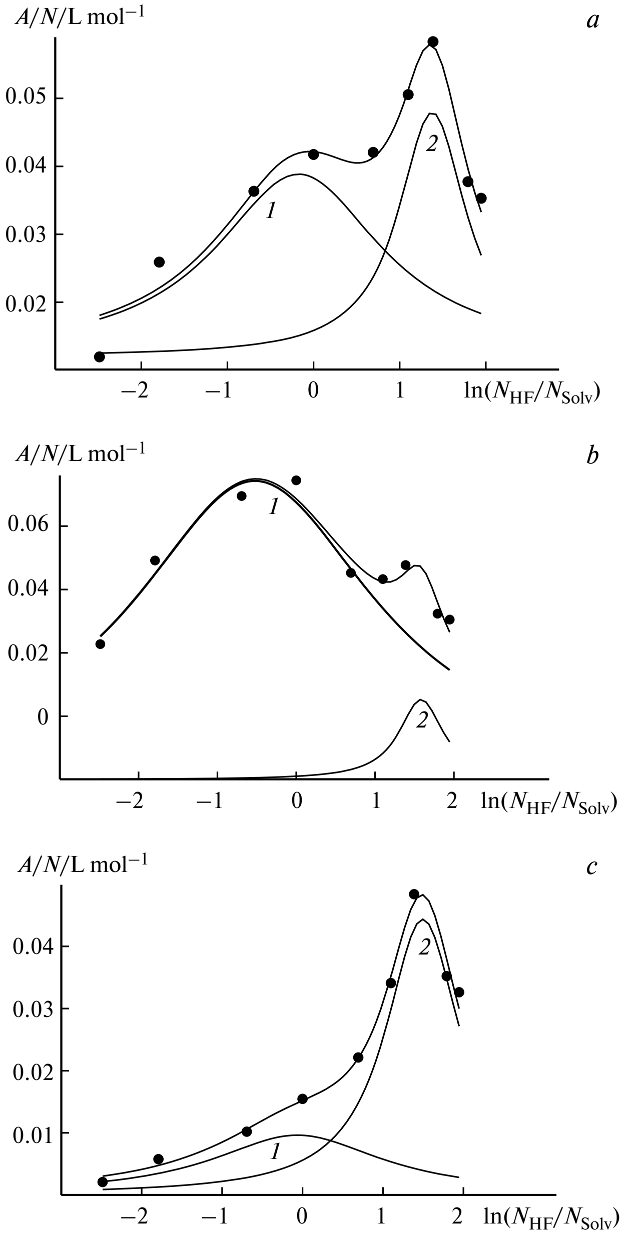

Fig. 2. Concentration dependences of the normalized absorbance of HF—DMF solutions at 3150 (*a*), 2750 (*b*), and 2400 cm^{-1} (*c*). The experimental curves are described by two Lorentzians, whose maxima correspond to the HF : DMF stoichiometric ratios equal to 1 : 1 (*1*) and 4 : 1 (*2*).

The decomposition of these dependences into two Lorentzians provides an estimate of the stoichiometric ratio of molecules in a large associate (see Fig. 3 and Table 1). This estimate ((7.3—12) : 1) is rough for unbiased reasons (the absence of the *A*/*N* values for solutions with molar ratios of the components ≥8 : 1). Accordingly, for the correct determination of each maximum in the dependences of $A/N(\ln(N_{HF}/N_{Solv}))$ it is necessary to know the *A*/*N* values at molar ratios of the solution components on the abscissa on both sides of the target N_{HF}/N_{Solv} value.

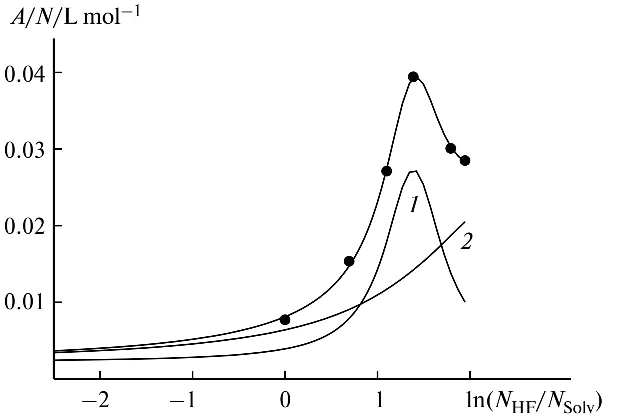

Fig. 3. Concentration dependence of the normalized absorbance of HF—DMF solutions at 3500 cm^{-1}. The experimental curve is described by two Lorentzians, whose maxima correspond to the HF : DMF stoichiometric ratios equal to 4 : 1 (*1*) and 12 : 1 (*2*).

Nevertheless, based on the above estimate of the mutual arrangement of the points corresponding to the 4 : 1, 6 : 1, and 7 : 1 compositions of the solutions in the experimental dependences (see Fig. 3) and the results of investigation of the complex formation in some other HF—Solv BLS,[29—31] it can be concluded that the stoichiometric ratio of the molecules in the largest HA that is present in the HF—DMF binary mixture is ≥10 : 1.

The concentration dependences of the normalized absorbance in the frequency range of 2200—1863 cm^{-1} differ from those considered above but are similar to each other. Each dependence can be adequately described by one Lorentzian, whose maximum is indicative of the formation of 4 : 1 HA in the solutions under consideration (see Table 1).

On the whole, the results obtained in the analysis of the *A*/*N* spectra suggest that three different types of HA are formed in HF—DMF BLS (with ratios of 1 : 1, 4 : 1, and ≥10 : 1). For each type of HA, we evaluated the concentration range, in which this type of associates exists in the solution in amounts detected by IR spectroscopy. In the former two cases, the estimation was performed by a conventional method[29] based on the results of the decomposition of the dependences of $A/N(\ln(N_{HF}/N_{Solv}))$ into Lorentzians. As a results, it was shown that 1 : 1 and 4 : 1 HA are present in the binary mixture at molar ratios of the components from 1 : 12 to 6 : 1 and from 1 : 1 to 10 : 1, respectively.

In the case of ≥10 : 1 HA, the data needed for the use of the above-mentioned procedure[29] are lacking and, consequently, the composition of the solution, at which the absorption of this associates begins to be manifested, was determined by the analysis of the concentration changes in the normalized absorbance spectra (see Fig. 1).

The shift of the band at 1863 cm $^{-1}$ to lower frequencies and a considerable enhancement of the absorption at 3600—3400 cm^{-1} were considered as evidence of the appearance of ≥10 : 1 HA. These spectral manifestations of large HA (which have been observed in different studies[2,26—30] of HF—Solv BLS) are clearly seen in the spectra of solutions with a high HF content starting with the 2 : 1 composition.

Therefore, each stable molecular complex found in the HF—DMF binary mixture exists in a wide concentration range, and all three types of HA are simultaneously present in the solution at molar ratios of the components from 2 : 1 to 6 : 1. It is necessary to take into account these data when searching for absorption bands of HF molecules involved in different HA.

For this purpose, the absorbance spectra of HF—DMF BLS were normalized (according to the procedure reported earlier[31]) to the number of solvent molecules per square centimeter of the solution layer under consideration. As a result, we obtained a series of A/S spectra (Fig. 4) having a "diffuse" character. Due to this fact coupled with the observation described above that almost all the spectra under consideration include (in different proportions) the total absorption of two—three HA, the determination of ν_{HF} is a difficult problem. To solve this problem, all A/S spectra and several series of the difference spectra were analyzed in detail.

Figure 5 shows the most informative series of $\Delta A/S$ spectra derived from the spectra of the pure solvent and the spectra of solutions containing components in a molar ratio equal (or, in the case of ≥10 : 1 HA, very similar) to the HF : DMF ratios in the three HA that are formed in BLS. An analysis of these results considering the characteristic features in the changes of the $\Delta A/S$* spectra indicates that the vibrational frequency ν_{HF} of 1 : 1 HA is observed at 2800—2750 cm^{-1} (see Fig. 5, the maximum of curve *1* and the minimum of curve *2*). The stretching vibration bands of the 4 : 1 associate occurred near 3400, 2400, and 1863 cm^{-1}, and the absorption maxima of ≥10 : 1 HA are observed in the vicinity of 3600, 3050, and 2550 cm^{-1}.

More than twenty difference spectra were analyzed in a similar way. The estimates of ν_{HF} obtained from these spectra were compared with the above values and with the results of the analysis of the A/S spectra. Finally, we were able to find the positions of most of the stretching bands of HF molecules involved in HA with an error of 50—100 cm^{-1} typical of these studies. The most probable target frequencies are as follows: 2750±50 (HA 1 : 1), 3380±100, 3100±100, 2400±100 and 1863±10 (HA 4 : 1), 3560±50, 3050±100 and 2530±50 cm^{-1} (HA ≥10 : 1).

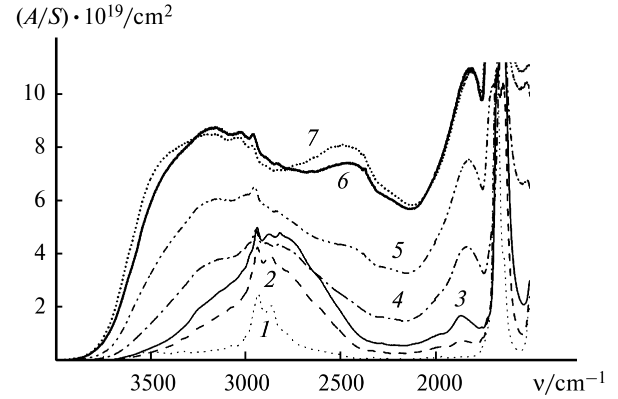

Fig. 4. Absorbance spectra of HF—DMF solutions normalized to the number of DMF molecules per square centimeter of the solution layer under consideration (*S*). The molar ratio of the components: 1 : 12 (*1*), 1 : 2 (*2*), 1 : 1 (*3*), 2 : 1 (*4*), 3 : 1 (*5*), 4 : 1 (*6*), and 7 : 1 (*7*).

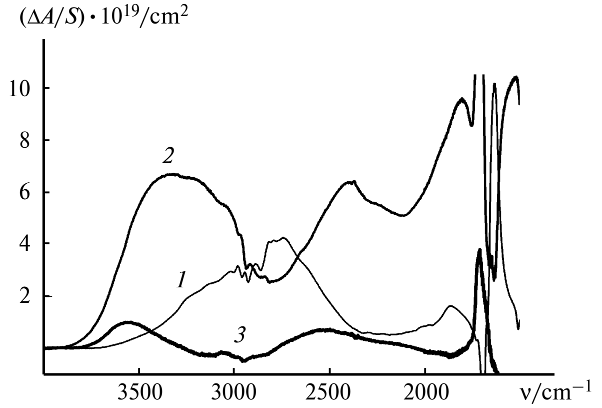

Fig. 5. Difference absorbance spectra of HF—DMF solutions normalized to the number of DMF molecules per square centimeter of the solution layer under consideration (*S*). The difference between the *A/S* spectra of solutions with ratios of 1 : 1 and 0 : 1 (*1*), 4 : 1 and 1 : 1 (*2*), 7 : 1 and 4 : 1 (*3*).

Quantum chemical calculations of heteroassociates $(HF)_m\cdot(DMF)_n$ (m = 1, 2, 4, 8; n = 1, 2)

To obtain data on the stretching vibration frequencies ν_{HF} of relatively small HA (1 : 1 and 4 : 1) containing HF and DMF molecules, ten hydrogen-bonded $(HF)_m\cdot(DMF)_n$ complexes (m = 1, 2, 4, 8, n = 1, 2) with different topologies (Table 2, **3**—**12**) were studied by the density functional theory (B3LYP/6-31++G(d,p)). Three of the systems under consideration (one system contain-

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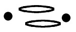
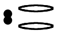
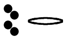
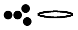
* The nature of these changes, which have been comprehensively considered in the study,[31] is as follows. If an increase in the concentration of the solution leads to a substantial shift of the equilibrium between HA that are formed in the solution toward larger associates, their relative contribution to the absorption of the solution per solvent molecule strongly increases and, correspondingly, the contribution of smaller HA decreases. As a result, the intensity of the bands of the smaller associate in the subtracted spectrum is substantially higher than that in the spectrum from which the former spectrum is subtracted, and the absorption minima are observed in the $\Delta A/S$ spectrum instead of the maxima of these bands.

Table 2. Calculated total energies (E/au), the enthalpies of formation of heteroassociates (ΔH/kcal mol^{-1}), the enthalpies of formation of HA per HF molecule ($\Delta H/m$/kcal mol^{-1}), the bond lengths of the O...HF bridge ($R_{O...H}$, r_{HF}, Å), and the vibrational frequencies of HF molecules ($\nu_{HF}(i)$ (i = 1—4), cm^{-1})

System		$-E$	ΔH	$\Delta H/m$	$R_{O...H}$	r_{HF}	$\nu_{HF}(1)$	$\nu_{HF}(2)$	$\nu_{HF}(3)$	$\nu_{HF}(4)$
HF (**1**)		100.449919	—	—	—	0.928	4068	—	—	—
DMF (**2**)		248.533596	—	—	—	—	—	—	—	—
$HF \cdot DMF$ (**3**)		349.005797	14.0	14.0	1.589	0.963	3323	—	—	—
$(HF)_2 \cdot (DMF)_2$ (**4**)		698.030981	40.1	20.1	1.459	0.995	2774	—	—	—
$(HF)_2 \cdot (DMF)_2$ (**5**)		698.025186	36.5	18.2	1.367	1.028	2251	3370	—	—
$(HF)_4 \cdot DMF$ (**6**)		650.419799	54.3	13.6	1.229	1.113	1203	2571	3071	3431
$(HF)_4 \cdot DMF$ (**7**)		650.415203	51.4	12.8	1.112	1.245	1601	2820	3351	3656
$(HF)_4 \cdot DMF$ (**8**)		650.415095	51.3	12.8	1.076	1.319	2032	2822	3409	3437
$(HF)_4 \cdot DMF$ (**9**)		650.412761	49.9	12.5	1.114	1.244	1187	2059	3316	3726
$(HF)_4 \cdot DMF$ (**10**)		650.407092	46.3	11.6	1.083	1.303	1982	3424	3623	3710
$(HF)_8 \cdot (DMF)_2$ (**11**)		1300.853241	117.1	14.6	1.053	1.359	1843	2484	2972	3474
$(HF)_8 \cdot (DMF)_2$ (**12**)		1300.844619	111.7	14.0	1.212	1.124	1220	2486	3015	3401

ing one DMF molecule and two systems containing two DMF molecules each) are 1 : 1 HA (**3—5**). Seven associates (five associates with one DMF molecule each (**6—10**) and two associates with two DMF molecules each (**11** and **12**)) are characterized by the 4 : 1 stoichiometric ratio of the molecules.

The calculations of the optimal configurations of all the HA under consideration and of free HF and N,N-dimethylformamide molecules were carried out with the use of the GAUSSIAN-98 program.[34] The calculated total energies (E), enthalpies of formation (ΔH), bond lengths of the O...H—F bridge, and frequencies ν_{HF} are presented in Table 2. Table 2 gives also the enthalpies of formation of the complexes per hydrogen fluoride molecule ($\Delta H/m$), which provide estimates of the relative stability of HA of different compositions and with different structures.

From the results of the present study it follows that interactions between HF and DMF molecules can lead to the formation of stable isomers with different structures: cyclic (**4—6**, **11**, and **12**), chain (**3**), and branched (**7—10**). In the first group of conformers ($m = n = 2$), the heterotetramer with the C_{2h} symmetry consisting of alternating HF and DMF molecules (**4**) is much more stable than the tetramer with the C_1 symmetry (**5**). In the second group (m = 4, n = 1), the molecular complex with the cyclic structure (**6**) is more stable than HA containing not only cyclic but also tail molecules (**7—10**). Based on these results (which are consistent with the results of the corresponding calculations for the $(HF)_m \cdot (CH_3CN)_n$ (see Ref. 31) and $(HF)_m \cdot ((C_2H_5)_2O)_n$ systems[32]), only centrosymmetric $(HF)_8 \cdot (DMF)_2$ associates consisting of cyclic moieties were considered in the third group. A comparison of the enthalpies of formation of the associates of interest showed that the associate that is formed by the binding of two $(HF)_3$ chains, which are closed through the hydrogen atoms of the methyl groups, to the C_{2h}-symmetry tetramer (**11**) are much more stable than purely cyclic HA (**12**).

It should also be emphasized that the proton transfer to the carbonyl oxygen atom occurs in all molecular complexes containing branches (**7—11**) (see Table 2). The proton transfer is accompanied by a substantial electron density redistribution on the HF molecules and the formation of the characteristic pyramidal structural moiety consisting of three H...F bonds, whose vertex is occupied by the fluorine atom bearing a charge of approximately −0.8 au. This explains the difference between the mechanism of the complex formation in the HF—DMF system and the corresponding mechanism in the HF—CH_3CN binary mixture.[31] According to the results of quantum chemical calculations,[32] there is an intermediate case in the HF—$(C_2H_5)_2O$ system, where the proton transfer to the solvent molecule occurs in certain branched structures, whereas no proton transfer is observed in other structures.

The rigorous explanation of this phenomenon, which requires the use of the concept of the "transferring" ability of the molecule (see Ref. 35) and the detailed consideration of the structural features of particular HA, is beyond the scope of the present study. To a first approximation, the differences in the mechanism of the complex formation in the three HF—Solv systems of interest can be attributed to the difference in the proton affinity of acetonitrile (191.5 kcal mol^{-1}), diethyl ether (201.9 kcal mol^{-1}), and DMF (214.2 kcal mol^{-1}) molecules.[36]

The relative stability of the molecular complexes of different compositions and with different structures was estimated by comparing the calculated $\Delta H/m$ values (see Table 2). In the branched associates (**7—10**), $\Delta H/m$ are 11.6—12.8 kcal mol^{-1}; in the cyclic associates (including the heteroassociate $(HF)_8 \cdot (DMF)_2$ consisting of three rings), $\Delta H/m$ are 14.0—20.1 kcal mol^{-1}. The largest enthalpy of complex formation per HF molecule (20.1 kcal mol^{-1}) was found in the tetramer $(HF)_2 \cdot (DMF)_2$ with the C_{2h} symmetry (**4**), which served as the basis for the formation of the most stable ($\Delta H/m$ = = 14.6 kcal mol^{-1}) 4 : 1 associate (**11**). Now, we can couple these results with the fact that the hydrogen-bonded $(HF)_m \cdot (Solv)_n$ complexes, which are most stable of all HA with the same stoichiometric ratio of the molecules, are formed in HF—$(C_2H_5)_2O$ and HF—CH_3CN solutions. It can thus be hypothesized that the 1 : 1 and 4 : 1 HA experimentally observed in HF—DMF BLS have the structures described above.

To unambiguously determine the structures of these HA, the experimental vibrational frequencies ν_{HF} and their mutual arrangement were compared with the corresponding characteristics of the calculated spectra of the molecular complexes with the compositions 1 : 1, 2 : 2, 4 : 1, and 8 : 2. It was taken into account that, in some cases, the corresponding experimental and calculated frequencies might be determined with a large error (up to 100—120 and 150—200 cm^{-1}, respectively).

From the vibrational frequencies of HF molecules in the $HF \cdot DMF$ and $(HF)_2 \cdot (DMF)_2$ heteroassociates (**4** and **5**) given in Table 2, it follows that the results of calculations of the C_{2h}-symmetry cyclic heterotetramer agree well with the experimental data ($\Delta\nu_{HF} = \nu_{HF}{}^{exp} - \nu_{HF}{}^{calc} = -24$ cm^{-1}). The differences in the corresponding values in the case of the linear dimer ($\Delta\nu_{HF} = -573$ cm^{-1}) and the C_1-symmetry tetramer ($\Delta\nu_{HF}(1) = -620$ cm^{-1}, $\Delta\nu_{HF}(2) = 499$ cm^{-1}) are much higher than the error of the calculations of $\nu_{HF}{}^{calc}$. Therefore, the above data provide evidence that the dissolution of HF in DMF affords centrosymmetric cyclic 2 : 2 HA (Fig. 6, *a*).

To improve the reliability of the conclusions drawn from a comparison of the calculated and measured spectra of 4 : 1 HA, the following parameters were analyzed: the rms deviations of the calculated frequencies from the experimental values (δ), the centers of gravity of the spectra of stretching vibrations of HF in molecular complexes of different compositions and with different structures, the frequency ranges (Δ), where the vibrational bands ν_{HF} are observed, and the mutual arrangement of these bands. It appeared that the frequencies $\nu_{HF}{}^{calc}$ of heterodecamer **11** (Fig. 6, *b*) are most similar to those determined from the experimental data. The value of δ (60 cm^{-1}) calculated for heterodecamer **11** is smaller than the calculation and experimental errors. The rms deviations for the other six associates are ~3—7 times larger than this value.

The detailed analysis of other spectral characteristics of HA also provided strong evidence that the agreement with the results of measurements is achieved only for the molecular complex $(HF)_8 \cdot (DMF)_2$ (**11**). Thus, the center of gravity of the spectrum of vibrations ν_{HF} is observed at 2686 cm^{-1}, and the calculated center of gravity for this HA is at 2693 cm^{-1}. In the other cases, the deviations of the calculated data from the experimental results are 114—499 cm^{-1}. The spectral range containing four absorption bands of HF molecules based on the results of measurements is 1517 cm^{-1}. The calculated values most similar to this value were obtained for HA **11** (1631 cm^{-1}) and **8** (1405 cm^{-1}). The values of Δ calculated for molecular complexes **6**, **7**, **9**, **10**, and **12** are substantially (by 211—711 cm^{-1}) larger than 1517 cm^{-1}.

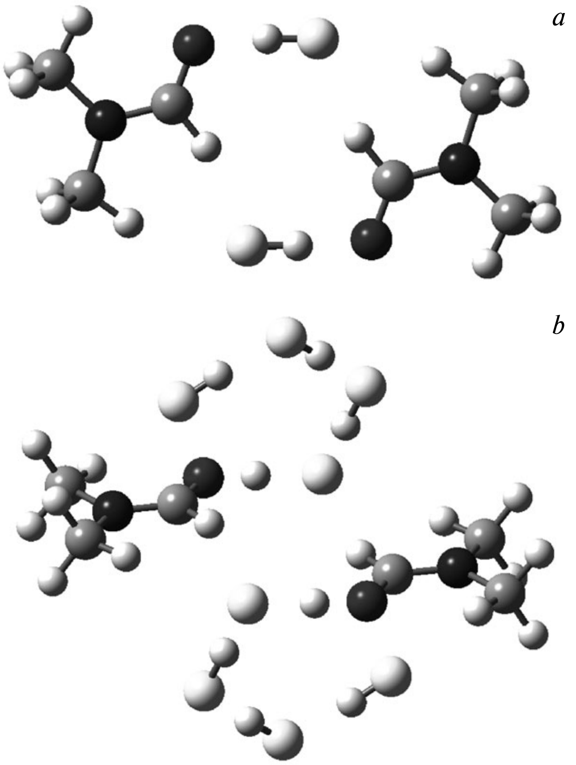


Fig. 6. Structures of stable heteroassociates containing molecules in stoichiometric ratios of 1 : 1 and 4 : 1 that are formed in HF—DMF solutions: $(HF)_2 \cdot (DMF)_2$ (*a*) and $(HF)_8 \cdot (DMF)_2$ (*b*).

The mutual arrangement of the bands in the range under consideration, whose value was assumed to be 100%, was characterized by the distances between the adjacent pairs of the ν_{HF} bands (starting with the low-frequency band) expressed in percentage. The relative distances thus determined are 35, 46, and 19% in the experimental spectrum, and 39, 30, and 31% in the calculated spectrum of heterodecamer **11**. In the overwhelming majority of the molecular complexes, the mutual arrangement of the bands ν_{HF} differs much more substantially from the results of measurements (for example, the distances under consideration in the calculated spectrum of associate **8** are 56, 42, and 2%). The exception is heteropentamer **9** (the relative distances are 34, 50, and 16%). However, the low stability of this associate ($\Delta H/m$ = 12.5 kcal mol^{-1}) and the inconsistency of the experimental data with the most reliable and characteristic spectroscopic parameters (δ = 287 cm^{-1}, Δ = 2539 cm^{-1}) show that the good agreement of the relative distances between the bands ν_{HF} with experimental data is accidental.

The following conclusions were drawn in the present study.

— Heteroassociates containing molecules in 1 : 1, 4 : 1, and ≥10 : 1 stoichiometric ratios are formed in the HF—DMF binary liquid system. Each HA exists in a wide concentration range. At molar ratios of the components from 2 : 1 to 6 : 1, all three types of HA are simultaneously present in solution.

— The positions of the absorption bands of HF molecules involved in various HA were found from the absorbance spectra of a series of HF—DMF solutions.

— The optimal configurations and the vibrational frequencies of the molecular complexes $(HF)_m \cdot (DMF)_n$ (m = 1, 2, 4, 8, n = 1, 2) with different topologies were calculated using the density functional theory (B3LYP/6-31++G(d,p)); the relative stability and structural features of these complexes were studied.

— A comparison of the results of calculations and experimental data showed that the following hydrogen-bonded complexes most stable of all HA with the same stoichiometric ratio of the molecules are formed in solutions of HF in DMF: the C_{2h}-symmetry cyclic heterotetramer $(HF)_2 \cdot (DMF)_2$ and the heterodecamer $(HF)_8 \cdot (DMF)_2$ formed based on this heterotetramer by the binding of two $(HF)_3$ moieties.

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Received June 7, 2010