Physical Chemistry

Structural properties of liquid formamide—*N*,*N*-dimethylformamide mixtures

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Monte Carlo simulations of formamide—*N*,*N*-dimethylformamide mixtures in the whole range of compositions were carried out at 298 K. Structural properties were investigated by calculating the atom-atom spatial distribution functions, generalized spatial distribution functions, concentrations of closed cycles of H-bonds, and other properties of the system of hydrogen bonds. It was found that local spatial regions with the structure of pure components are conserved in a wide range of concentrations. The regularities of manifestation of solvophobic effects have been established.

Key words: organic solvents, binary mixtures, amides, formamide, *N*,*N*-dimethylformamide, structure of liquid, intermolecular interactions, hydrogen bonds; computer simulation of liquids, Monte Carlo method.

Investigation of interactions of the simplest amides of carboxylic acids, considered as model systems, establishment of regularities of the formation of H-bonds, and isolation of specific stable associates in the liquid phase are of great importance for determining the mechanisms of molecular recognition and formation of the spatial structure of biopolymers. That is why the appearance of a large number of recent studies[1—5] dedicated to investigation of amide systems is not accidental. Liquid amides are of interest not only for biological disciplines, but also for the modern physical chemistry of solutions since they exhibit a number of specific properties.

It was established[1] that the aggregation of heterofunctional molecules exists not only in water and that hydrophobic effects should be considered as a particular case of more general solvophobic effects. Peculiarities of structural and thermodynamic properties of aqueous solutions of non-electrolytes are due to the presence of the network of hydrogen bonds in water. A complex system of H-bonds also exists in formamide (FA). Condensed states of FA are characterized by a specific way of spatial ordering of the molecules. They can form cyclic dimers and chain associates.[6]

Among tertiary amides, *N*,*N*-dimethylformamide (DMF) is the simplest aprotic solvent. Despite the fact that the DMF molecules have relatively large dipole moments, packing factors have the major effect on their spatial arrangement in the liquid.[7] Since the FA and DMF molecules contain carbonyl groups, they can form heteroassociates involving H-bonds with the participation of both *cis*- and *trans*-protons of the amino groups of FA.

Aqueous solutions of DMF are characterized by hydrophobic effects and a distinct tendency for the mixture to be separated on the molecular level, or microheterogeneity of the solution.[8,9] It can be expected

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that similar transformations of the spatial structure and properties of the system of H-bonds will also occur in the FA—DMF system as the composition of the mixture changes. This work is dedicated to revealing general regularities and specific features of these processes in liquid mixtures consisting of strongly and weakly associated components and is a continuation of investigation of structural properties of amide systems.[6—8]

Calculation procedure

Calculations were carried out by the Monte Carlo method in the *NVT*-ensemble at 298 K using the standard Metropolis sampling algorithm. A unit cell containing 125 molecules was used. In addition to pure solvents, we simulated mixtures of compositions X_D = 0.1, 0.3, 0.5, 0.7, and 0.9 mole fraction of DMF. Periodic boundary conditions and spherical cut-off of the potential functions were used. The intermolecular interactions were described by the OPLS system of the potential functions.[10] In each simulation the total length of the Markovian chain exceeded $30 \cdot 10^6$ configurations, of which the portion of accepted ones was ~50%.

Experimental

The enthalpies of mixing were measured on a hermetic isothermic-shell swinging calorimeter[11] at 298.15 K in the whole range of compositions. The relative error did not exceed 1%. Formamide of "pure" grade and DMF of "extra pure" grade were used. The solvents were purified according to the known procedures.[12] Preliminarily frozen FA was vacuum distilled with sampling of the medium fraction followed by drying for 72 h over freshly calcinated molecular sieves (3A, Aldrich). Then FA was vacuum distilled again. DMF was vacuum distilled twice with drying of the intermediate product over molecular sieves (4A, Aldrich). The content of water in purified solvents determined by titration with the Fischer reagent was less than 0.03 wt.%, and the refractive indices of the solvents were in good agreement with the reference data.[12]

Experimental values of the enthalpies of mixing were approximated using the Redlich—Kister equation:

$$H^E = X_F X_D \sum_{n=1}^{4} C_n (X_F - X_D)^{n-1},$$

where X_F is the mole fraction of FA and X_D is the mole fraction of DMF. The following coefficients were obtained: C_1 = −5168.9, C_2 = −1673.7, C_3 = 223.56, and C_4 = 49.24.

Results and Discussion

Concentration changes of the structure of a mixed solvent can be considered from several points of view. In the framework of the system-structural approach, it is first necessary to define the *system* in the matter of investigation, *i.e.*, a set of related elements chosen according to a certain criterion. By the *structure* of the system we assume the totality of stable connections, relations between the elements.[13,14] The atom-atom spatial structure (statistical arrangement of the atoms of molecules in liquid) is usually described using the radial distribution functions (RDF). Some of the calculated RDF for the FA—DMF system are shown in Figs. 1 and 2. Hereafter the composition of the mixture is expressed as mole fractions of DMF (X_D) or FA (X_F).

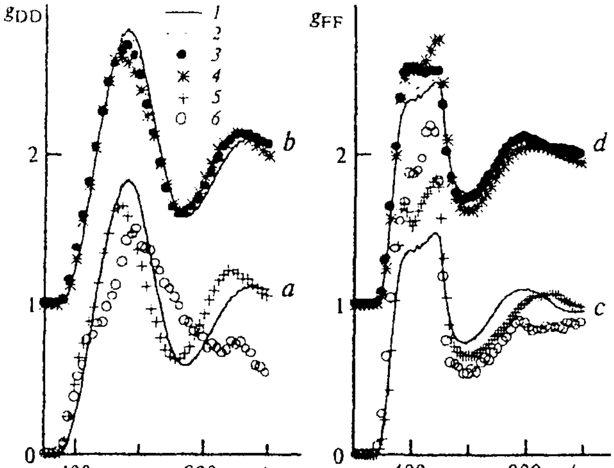

Fig. 1. Radial distribution functions of N atoms of DMF $g_{DD}(r)$ (*a*, *b*), and FA $g_{FF}(r)$ (*c*, *d*) molecules. The plots *b* and *d* are shifted along the coordinate axis. X = 0 (*1*), 0.1 (*2*), 0.3 (*3*), 0.5 (*4*), 0.7 (*5*), and 0.9 (*6*). $X = X_F$ (*a*, *b*), X_D (*c*, *d*).

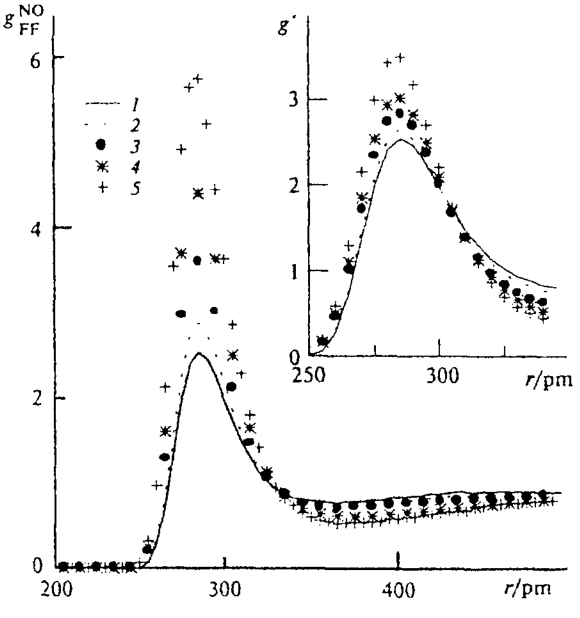

Fig. 2. Radial distribution functions of O atoms relative to N atoms of FA molecules $g_{FF}^{NO}(r)$. X_D = 0 (*1*), 0.1 (*2*), 0.3 (*3*), 0.5 (*4*), and 0.7 (*5*). Functions renormalized using formula (4) are shown in the inset.

It can be pointed out that a slight smooth decrease in the height of the first peak and an increase in the height of the second peak of the RDF of nitrogen atoms of DMF $g_{DD}(r)$ is observed as X_F increases in the range $0 < X_F < 0.5$ (see Fig. 1, *b*). At large X_F (especially at $X_F = 0.9$, see Fig. 1, *a*), the shape of the function changes significantly, which indicates the destruction of the proper spatial structure of DMF. Another behavior is characteristic of the RDF of nitrogen atoms of FA $g_{FF}(r)$: the height of the first peak increases, whereas the height of the second peak decreases to a certain extent as X_D increases.

By definition, the RDF is the ratio of the numerical local density of atoms in the spherical layer $\rho(r)$ to the average density ρ:

$$g(r) = \rho(r)/\rho = [dN(r)/dV]/\rho, \quad (1)$$

where $dN(r)$ is the number of atoms in the spherical layer of radius r, thickness dr, and volume dV surrounding the given atom. For a mixture of two sorts of molecules, the density ρ can be expressed through the density of one pure component, *e.g.*, the first component. Then we have

$$g(r,X_2) = [dN(r,X_2)/dV]/[\rho(0)\cdot(1 - X_2)\cdot V(0)/V(X_2)], \quad (2)$$

where X_2 is the mole fraction of the second component, and $V(0)$ and $V(X_2)$ are the unit cell volumes for the pure first component and solution. If the condition $g(r,X_2) = g(r,0)$ is fulfilled in a certain range of values of the parameters, then the following relationship is valid:

$$dN(r,X_2) = dN(r,0)\cdot(1 - X_2)\cdot V(0)/V(X_2) \approx dN(r,0)\cdot\varphi, \quad (3)$$

where φ is the volume fraction of the first component in the mixture.

This means that for a given range of concentration and spatial region the number of atoms in the spherical layer is determined by the factor characterizing the structure of the pure component and by the volume fraction of the component. In our case, this means that at $X_D > 0.5$ the N atoms of FA molecules replace the N atoms of DMF surrounding a given DMF molecule in proportion to the volume fraction of FA in solution without appreciable change in the proper structure of DMF at all intermolecular distances as the content of FA in the mixture increases. The same conclusion can also be drawn concerning the replacement of N atoms of FA by N atoms of DMF at distances over 700 pm, since at $X_F > 0.5$ the equality $g_{FF}(r,X_D) = g_{FF}(r,0)$ is valid. Hence, interpenetrating microregions with undistorted structure of pure DMF and FA should be conserved in a wide concentration range.

The first peak of the FA RDF $g_{FF}^{NO}(r,X_D)$ shown in Fig. 2 reflects statistical regularities of the arrangement of H-bonded molecules. The increase in its height observed with an increase in the DMF concentration is explained by the change in the density of the solution and by the increase in the volume unit cell used in simulation $V(X_D)$. In fact, the simple renormalization of the function using the formula

$$g'(r,X_D) = [V(0)/V(X_D)]\cdot g(r,X_D) \quad (4)$$

compensates for its increase and results in close heights of the first maxima of g' in a wide concentration range. From exact equality of the functions g' and g, it follows that

$$dN(r,X_D) = dN(r,0)\cdot(1 - X_D). \quad (5)$$

This means that the number of O atoms of a FA molecule in the nearest environment of the N atom of FA is proportional to that characteristic of pure FA and to the mole fraction of FA. As follows from Fig. 2, a one-to-one replacement of O atoms of FA by O atoms of DMF occurs as X_D increases to 0.3 for $r_{NO} < 330$ pm. Incomplete compensation of the increase in the function g' indicates a tendency to increased self-association of FA molecules. Renormalization of the nitrogen RDF g_{FF} using formula (4) results in a decrease in the height of the first maximum, which reflects the incomplete correspondence between the shapes of FA and DMF molecules and suggests a slight spatially localized distortion of the structure of pure FA.

Since in the liquid phase each FA molecule, acting simultaneously as both a donor and acceptor of protons, can form four H-bonds (ignoring bifurcated bonds) with neighboring molecules, from the behavior of the RDF it follows that spatial regions with almost non-distorted structure of pure FA are conserved at $X_F > 0.7$. The increase in the maxima of the functions is explained by the "effect of excluded volume" observed in the experimental[15] and computer[9] studies of aqueous systems (in particular, an H_2O—DMF mixture). Thus, a certain similarity in structural transformations of strongly associated liquids (water, FA) is traced in the range of low and medium concentrations of an aprotic solvent.

More detailed information on the regularities of the mutual arrangement of molecules in the liquid can be obtained using generalized functions of the spatial distribution of atoms.[6,7] Suppose that the quantity $\rho(r)$ in formula (1) is defined in the volume element of arbitrary shape. Then, by definition

$$g_{ab}(x,y,z) = [dN_{ab}(x,y,z)/dxdydz]/\rho, \quad (6)$$

where dN_{ab} is the number of species of the type b in the volume element $dxdydz$ at a distance $r(x,y,z)$ from a species of the type a. By fixing one of the coordinates we get a function of two variables that can be depicted on a plane. Previously,[6,7] we have established the regularities of the spatial arrangement of the molecules in pure components of the mixture under study using generalized functions. The volume element used in our calculations had the shape of a rectangular parallelepiped with a 15 pm length of the side of square base and a 400 pm height.

Let us consider the manner in which the molecules of the components of an equimolar mixture are spatially ordered. We calculated the statistical distribution of the

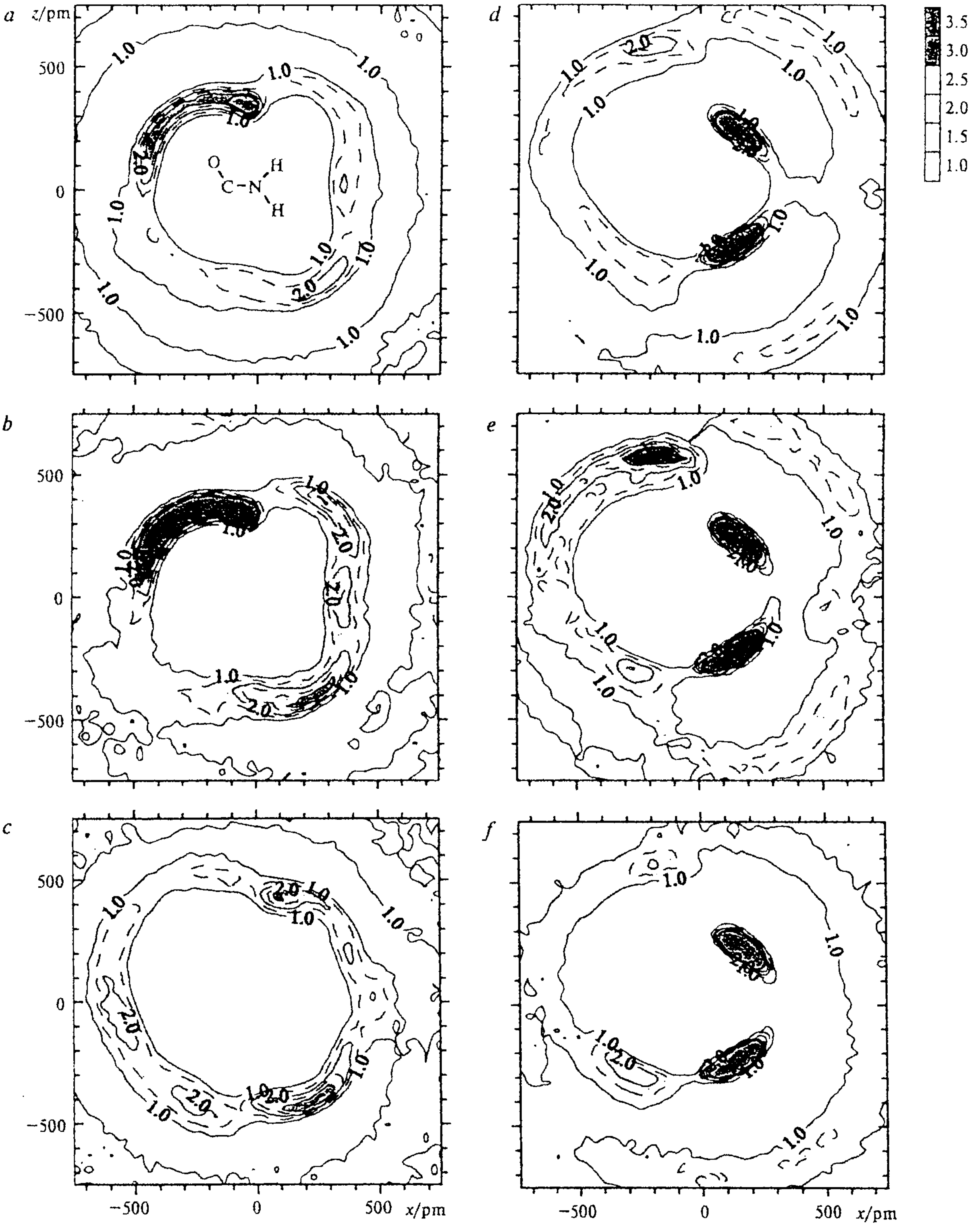

Fig. 3. Generalized $g(x,0,z)$ functions of spatial distribution of N (*a—c*) and O (*d—f*) atoms relative to FA molecule: FA atoms at X_D = 0 (*a*, *d*) and 0.5 (*b*, *e*), and DMF atoms at X_D = 0.5 (*c*, *f*). Contour lines are drawn with an increment of 0.5 starting from 1.

atoms of molecules in a layer parallel to the plane of a given molecule assuming that the N atom is at the origin. The normalized spatial distributions of local densities (6) of N (*a—c*) and O (*d—f*) atoms relative to FA

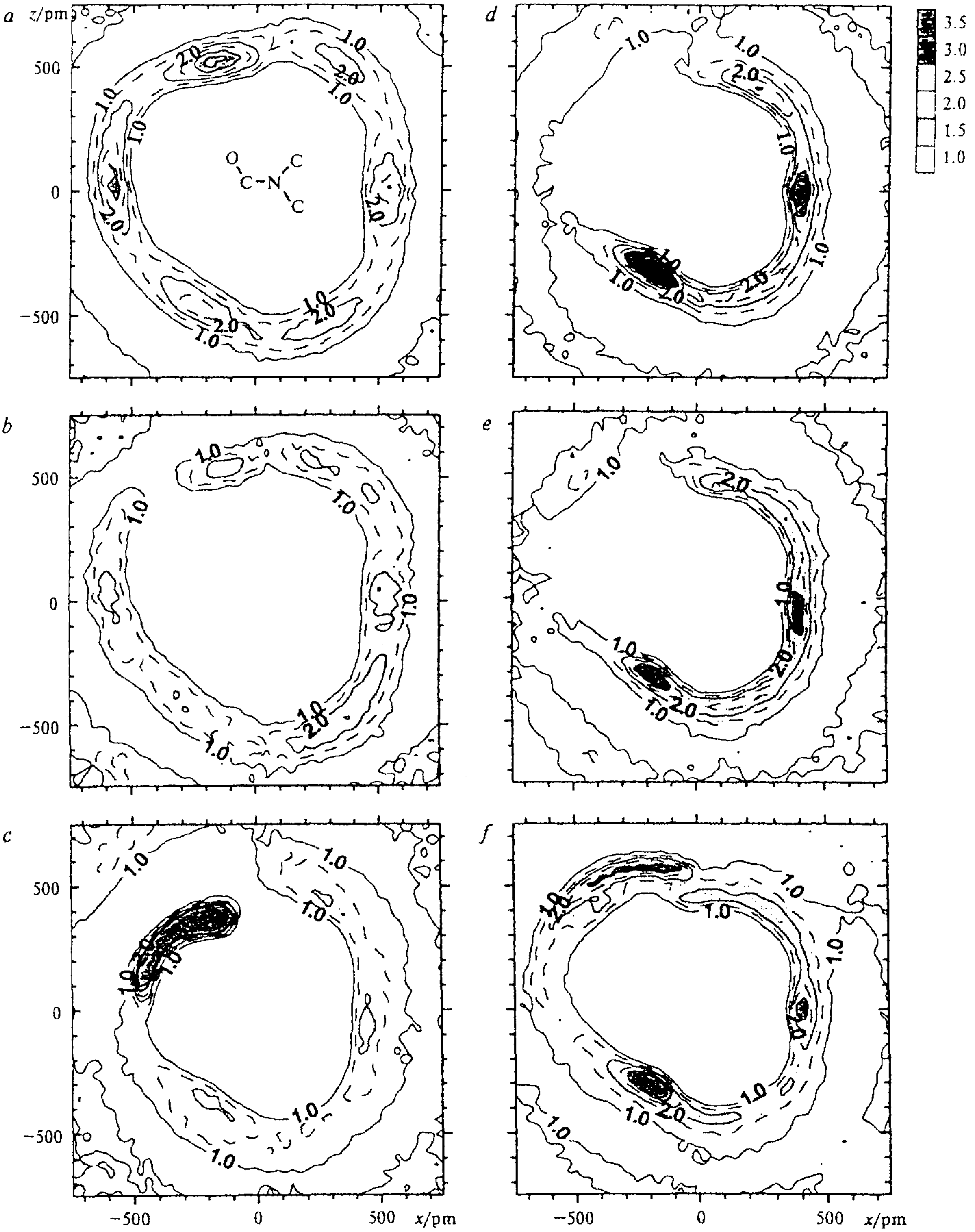

Fig. 4. Generalized $g(x,0,z)$ functions of spatial distribution of N (*a—c*) and O (*d—f*) atoms relative to the DMF molecule: DMF atoms at X_F = 0 (*a*, *d*) and 0.5 (*b*, *e*), and FA atoms at X_F = 0.5 (*c*, *f*). Contour lines are drawn with an increment of 0.5 starting from 1.

and DMF molecules are shown in Figs. 3 and 4, respectively. Anisotropy of the distributions is observed within the first coordination shell of the molecules. The similarity of the plots *a* and *b* (and, analogously, that of the plots *d* and *e*) in Fig. 3 indicates that the main features of the spatial structure of pure FA are conserved in the mixture. An analogous conclusion that the regularities of the mutual ordering of DMF molecules are conserved can be drawn by comparing the plots (*a* and *b*, and *d* and *e*) shown in Fig. 4. As in the case of the atom-atom RDF, a slight decrease in the correlations of DMF atoms (see Fig. 4, *b*,*e*) and an increase in the correlations of FA atoms (see Fig. 3, *b*,*e*) occurs in the mixture.

The mutual arrangement of FA and DMF molecules is shown on the plots *c* and *f*. The regions with increased concentration of N and O atoms of FA are clearly seen in the region where the O atom of DMF is located (see Fig. 4, *c*,*f*); the shape of these regions is similar to that of the regions characterizing the mutual arrangement of FA molecules (see Fig. 3, *a*,*b* for N atoms and Fig. 3, *d*,*e* for O atoms). At the same time, the arrangement of N and O atoms of DMF in the region of protons of the amino group is the same as that of N and O atoms of FA (see Fig. 3, *c*,*f*).

Thus, not only integrated RDF that can be affected by the effects of density redistribution and mutual compensation of contributions within spherical layers, but also generalized distribution functions reflect structural regularities characteristic of pure components in the mixture. Due to the presence of the same functional groups, a partial interchange of FA and DMF molecules in the nearest environment of each given molecule is observed. A smooth transition from one type of spatial ordering to another type occurs as the composition of the mixture changes. Thus, a more detailed picture of mutual ordering of the molecules in the mixture, which confirms the conclusions drawn from analysis of the atom-atom RDF, was obtained using generalized distribution functions.

The functions of the atomic density distribution characterize the local spatial structure of the substance. To describe the supramolecular structure, the structural elements should be defined and the regularities of their interrelations should be established. The molecules linked by H-bonds into closed cycles can serve as elements of a supramolecular structure, while the spatial distributions and the ratios of concentrations of the cycles can be considered as system relations.[6–8] By averaging of statistical functions over the ensemble it is possible to obtain a set of stable relations that characterize the topological properties of the system of H-bonds and the supramolecular structure of the liquid.

Unfortunately, there is no criterion that makes it possible to establish the existence of H-bonds between the FA molecules unambiguously.[5,10] In this work, we used the energetic and geometrical criterion[6,10] when determining homo- and heteromolecular H-bonds. It was assumed that two molecules form an H-bond if the energy of their interactions is less than -18.83 kJ mol^{-1} and the O...H distance is no longer than 280 pm. It is natural that the choice of criterion will first affect quantitative characteristics of the system of H-bonds and to a lesser extent its qualitative characteristics (relative values).

Table 1. Concentrations of closed cycles of H-bonds in the FA—DMF system

X_D	Type of cycle	n	C_2	C_3	C_4	C_5	C_6	C_7
0	—	2.59	10.30	0.69	3.56	1.83	2.99	2.86
0.1	*A*	2.19	9.45	0.35	2.83	1.03	2.24	1.84
0.3	*A*	1.44	6.91	0.54	1.31	0.67	0.67	0.19
0.5	*A*	0.79	3.73	0.34	0.45	0.22	0.08	0.02
0.1	*B*	2.42	10.46	0.38	3.14	1.14	2.48	2.03
0.3	*B*	2.05	9.81	0.77	1.86	0.95	0.95	0.27
0.5	*B*	1.56	7.40	0.66	0.89	0.44	0.15	0.04

Note. C_i is the number of cycles per 100 molecules of the mixture (*A*) of per 100 FA molecules (*B*), i is the number of vertices in cycle, X_D is the mole fraction of DMF, and n is the average number of bonds per molecule.

The data on changes in the concentration of closed cycles of H-bonds on going from pure FA to its mixtures with DMF are listed in Table 1. Two types of cycles, *A* and *B*, were considered. Cycles of the type *A* were built of any molecules, and those of the type *B* were built only of FA molecules. In both cases, the connectedness parameter n (the number of H-bonds per molecule) decreases as the DMF content increases. Cycles having four to seven vertices break down rapidly. The concentration of three-membered cycles is low; therefore unambiguous conclusions about its change can hardly be made. On the contrary, cyclic dimers are main structural elements and can be built only of FA molecules. The number of dimers decreases very slowly, while in the case of type *B* at $X_D = 0.1$ it increases to a certain extent despite a decrease in the connectedness parameter.

The RDF of geometric centers of dimers $G_{22}(r)$ are shown in Fig. 5. They were calculated using formula (1), where $dN(r)$ is the number of centers of cycles in the spherical layer of thickness dr at a distance r from the specified center defined as the arithmetic mean of the coordinates of the atoms of N molecules forming the cycle.[6] The broad peak of the function at about 500 pm is split into two peaks as X_D increases; the height of the first peak increases appreciably, while that of the second peak decreases after a small increase and the peak is shifted towards longer distances. Such a behavior of the function can be explained by an increase in the degree of association, stabilization of certain types of dimers, and by breakdown of chains of H-bonds.[6] At $X_D = 0.5$, the unit cell contains, on the average, 4.6 cycles and the calculated RDF has appreciable statistical noise.

Thus, conservation of basic regularities of the formation of the system of H-bonds at low and medium DMF concentrations is accompanied by stabilization[6] of spatially localized fragments of the supramolecular structure of pure FA. Conservation of a considerable number of cyclic dimers indicates a tendency for increased self-

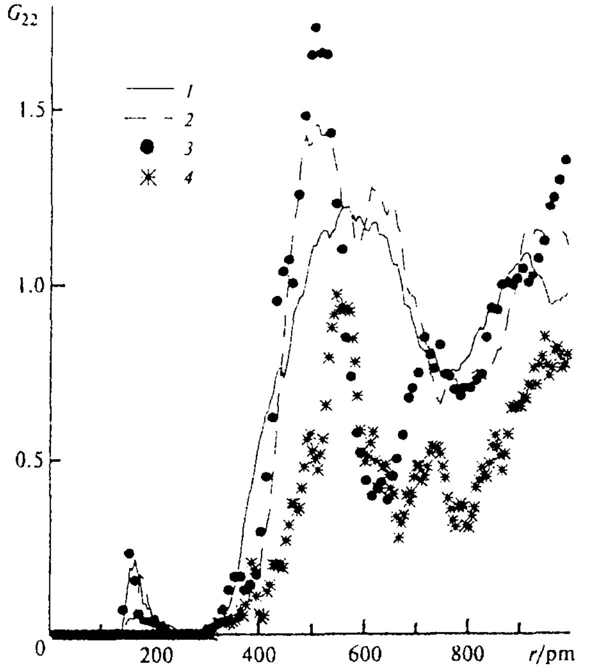

Fig. 5. Radial distribution functions of geometric centers of FA cyclic dimers $G_{22}(r)$ at X_D = 0 (*1*), 0.1 (*2*), 0.3 (*3*), and 0.5 (*4*).

association of FA molecules, whereas the larger number of cycles with even numbers of vertices compared to that of cycles with odd numbers of vertices reflects a tendency for association of dimers.

As is known, in liquid FA the bonds formed with participation of *cis*-proton differ substantially from *trans*-bonds.[6] The concentration dependences of the portions of free protons of amino groups (M_3) and of the protons participating in homocomponent (M_1) and heterocomponent (M_2) H-bonds are shown in Fig. 6. Comparison of the values obtained shows that, on the average, a larger number of H-bonds is formed with participation of *trans*-proton. In both cases, slight deviations from the additive behavior are observed as the composition of the mixture changes. The replacement of FA—FA bonds by FA—DMF bonds occurs and the portion of free H atoms decreases as the DMF content increases. The FA—FA *cis*-bonds, due to which cyclic dimers are formed, break down more slowly than *trans*-bonds as X_D increases, which indicates an increased stability of dimers.

Let us consider the totality of intercomponent H-bonds whose relative portion among all the bonds is given by the M_2 value. Let us divide FA and DMF molecules into three types: molecules forming no intercomponent bonds (N_3) and those forming one (N_1) or two (N_2) intercomponent bonds. The portions of each type of the molecules for FA and DMF are shown in Fig. 6, *c* and Fig. 6, *d*, respectively. The ways the molecules form heteroassociates can be described by the formulas FA · *m*DMF and DMF · *m*FA, where *m* = 1, 2. Homo- and heteroassociates, as well as cycles, can serve as structural elements, and along with the ratios (relations) determine the system possessing the supramolecular structure. Here, the concentrations of associates can be considered as system relations.

As follows from the dependences shown in Fig. 6, several types of heteroassociates are present in the solution. The portion of molecules forming no intercomponent bonds decreases almost linearly as the content of the second component increases in the mixture. Molecules forming one heterocomponent H-bond (FA · DMF) are predominant in a wide range of compositions of the mixture. At equal concentrations (X_F = X_D), the number of FA · 2DMF complexes formed is larger than that of DMF · 2FA complexes.

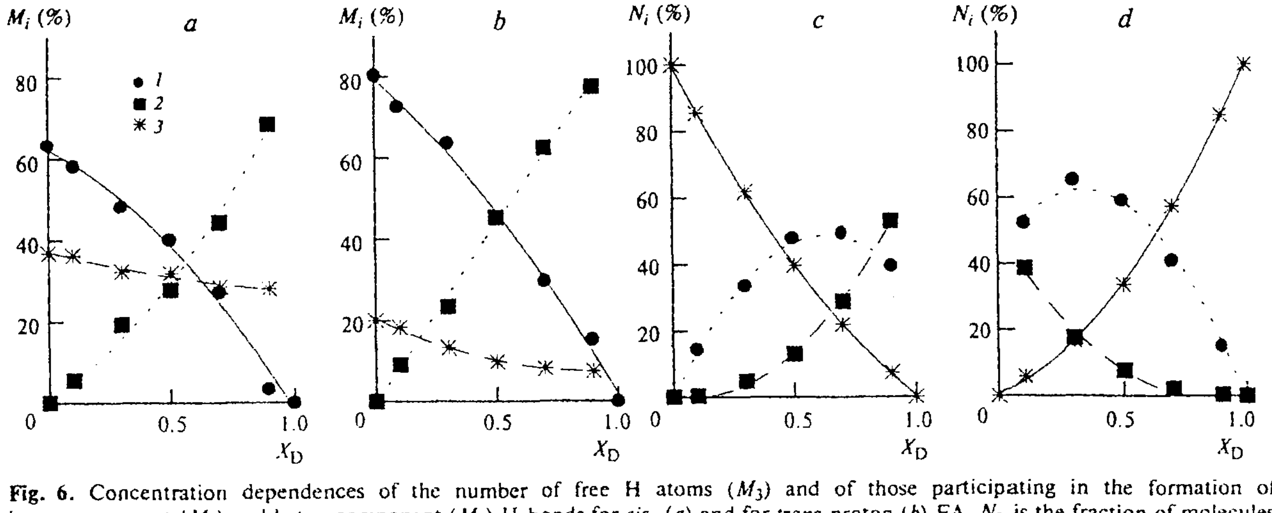

Fig. 6. Concentration dependences of the number of free H atoms (M_3) and of those participating in the formation of homocomponent (M_1) and heterocomponent (M_2) H-bonds for *cis*- (*a*) and for *trans*-proton (*b*) FA. N_3 is the fraction of molecules forming no heterocomponent H-bonds, N_1 is the fraction of molecules forming one heterobond, and N_2 is the fraction of molecules forming two heterobonds: *c*, for FA, and *d*, for DMF.

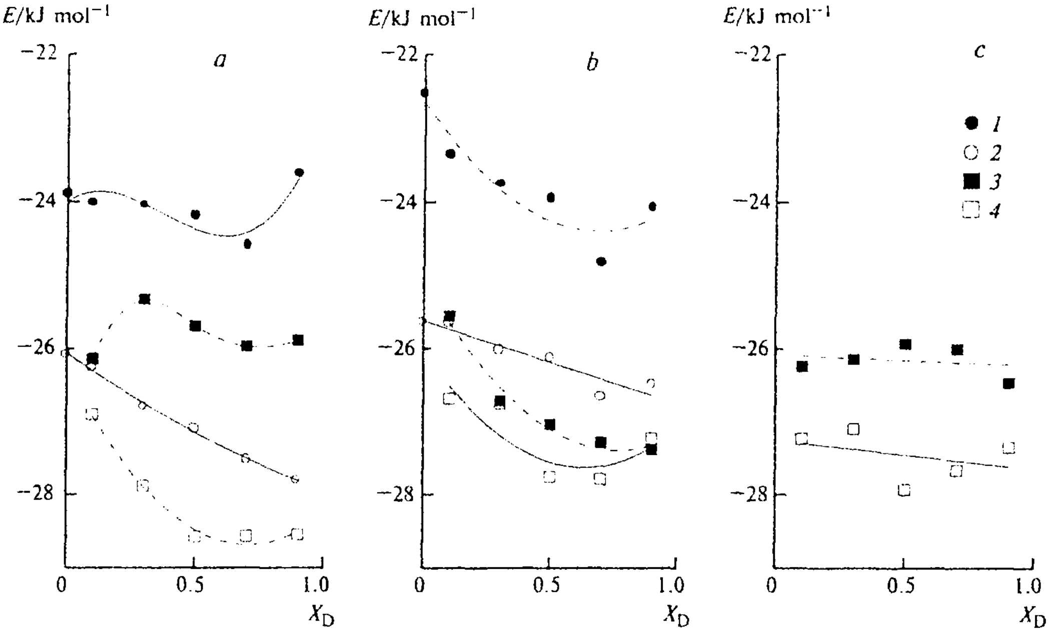

Fig. 7. Average energies of the H-bond formation in associates: *a*, *cis*-FA · FA (*1*), *trans*-FA · FA (*2*), *cis*-FA · DMF (*3*), and *trans*-FA · DMF (*4*); *b*, FA · 2FA (*1*), FA · FA (*2*), FA · 2DMF (*3*), and FA · DMF (*4*); *c*, DMF · 2FA (*3*), and DMF · FA (*4*).

The concentration dependences of the average energy of the formation of H-bond are shown in Fig. 7. From the behavior of the functions shown in Fig. 7, *a* it follows that in the whole range of compositions the bonds weaken in the following order: *trans*-FA · DMF, *trans*-FA · FA, *cis*-FA · DMF, and *cis*-FA · FA. Irrespective of the type of bond, the average energy of the bond formation for FA molecules forming one H-bond is more negative than for FA molecules forming two H-bonds (the bond is stronger), while heterocomponent bonds are stronger than homocomponent ones (see Fig. 7, *b*). A slight strengthening of homocomponent bonds is observed as X_D increases, which is mostly due to stabilization of *trans*-FA · FA bonds. Analysis of bonds formed between DMF and FA molecules shows that even in this case the bonds in complexes of composition DMF · FA (see Fig. 7, *c*) are the most thermodynamically stable.

Thus, despite the fact that *cis*-bonds FA · FA are the weakest, their increased stability in cyclic dimers (see above) is explained by structural, packing factors. It should be noted that in a wide range of concentrations the associates considered exist not separately but in the system of H-bonds that threads the whole accessible space at $X_D \leq 0.1$ since it is above the percolation threshold. The increase in the DMF concentration results in breakdown of chains of H-bonds and formation of clusters differing in shape and composition.[6]

Previously,[16] an attempt was made to obtain quantitative information on the molecular association and intermolecular interactions based on the study of the FA—DMF system by ^{1}H NMR spectroscopy. The concentration dependences of chemical shifts for *cis*- and *trans*-protons as well as the values we calculated using the formula

$$\delta(X_D) = \sum_i \delta_i M_i(X_D),$$

where δ is the chemical shift and M_i are the portions of free protons and protons participating in the formation of homo- and heteroassociates (see Fig. 6), are shown in Fig. 8. Three parameters δ_i and three functions $M_i(X_D)$ were used to fit the experimental dependence.[16] This problem belongs to the class of incorrect mathematical problems[17] and has no unambiguous solution. Moreover, the authors made an unverified assumption that the number of *cis*-bonds and that of *trans*-bonds are equal.

It was natural that the $M_i(X_D)$ dependences we found when processing the results of computer simulation differ strongly from those determined previously.[16] The three unknown free parameters δ_i were fitted by the least squares method (LSM). It was found that the chemical shifts of free *trans*-protons, of those formed self-associates, and of those in complex with DMF are 2.12, 7.44, and 6.75 ppm, respectively. The following values of the chemical shifts were obtained for *cis*-protons: 1.63, 9.47, and 8.77 ppm. It should be pointed out that the choice of the criterion of the H-bond formation can strongly affect these characteristics.

It is also important to note that small trial variations of $M_i(X_D)$ values appreciably changed δ_i values. This means that even at three free parameters the system of LSM equations is an ill-posed system. Nevertheless,

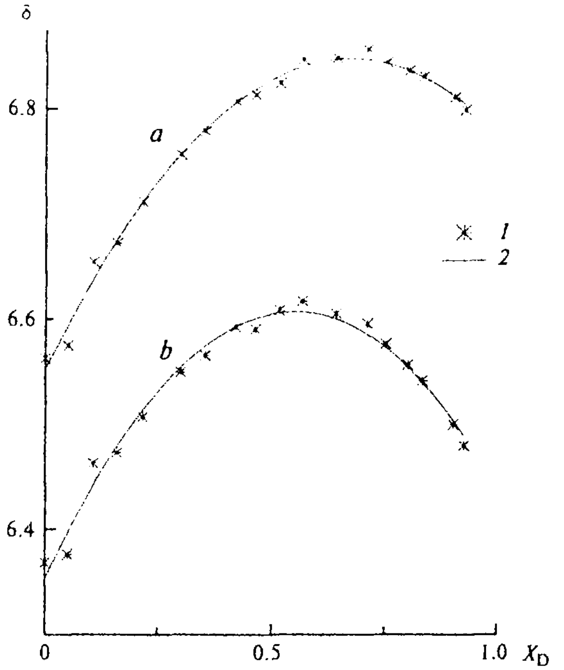

Fig. 8. Concentration dependences of chemical shifts of the protons of the formamide amino group for *cis*- (*a*) and *trans*-proton (*b*): experiment (*1*) [16] and calculations (*2*).

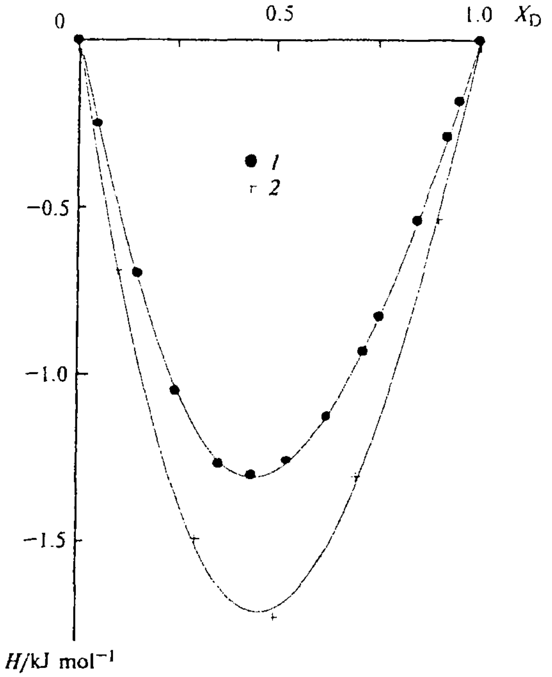

Fig. 9. Excess enthalpies of mixing of FA with DMF: experiment (*1*) and calculations (*2*).

good agreement between experimental and calculated concentration dependences of the chemical shifts suggests that at the qualitative level our calculations reproduce well the structural changes in the FA—DMF system and that methods of computer simulation can be successfully used for the interpretation of the experimental NMR spectra.

The calculated and experimental excess enthalpies of mixing FA with DMF are shown in Fig. 9. The theoretical dependence adequately reproduces the sign of the effect and the shape of the experimental curve. The observed deviation does not exceed 0.5 kJ mol^{-1}, which is a fairly good result taking into account the rather rough description of interparticle interactions, the small number of species in the unit cell, and the limited length of the generated Markovian chains. As is known, the values of excess thermodynamic functions are poorly reproduced by methods of computer simulation.[18] The qualitative agreement between the calculated and experimental values is evidence for the adequacy of the description of the FA—DMF mixture on both microscopic and macroscopic levels.

Let us compare the concentration changes in the structural properties of a non-aqueous mixture and H_2O—DMF and H_2O—acetone binary solutions in the range of low and medium concentrations of the aprotic component.[8] The observed conservation of a considerable number of supramolecular structural elements, the stabilization of spatially localized fragments of the structure of the pure strongly associated component, the increase in coordination of the arrangement of the structural elements, and the decrease in the energies of formation of H-bonds are a specific indication of the manifestation of solvophobic effects and indicate altogether that transformations of the local spatial and supramolecular structures of these liquid mixtures obey unified regularities.

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