Physical Chemistry

Structural properties of dilute aqueous solutions of dimethylformamide and acetone based on computer simulation

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The Monte Carlo simulation of molecular configurations for aqueous solutions of *N,N*-dimethylformamide and acetone was carried out. The atom—atom radial distribution functions were determined. The topological properties of the H-bond system were investigated. The concentrations of closed H-bond cycles and the radial distribution functions of their geometric centers were found. It was shown that the local arrangement of molecules and supermolecular assemblies typical of the H-bond network in neat water is retained in the solutions studied.

Key words: structure of water, aqueous solutions, hydration; computer simulation of liquids, network of H-bonds.

Determination of the structure, types of interaction, and dynamic characteristics of the molecular configurations in solution is an important objective of the physical chemistry of liquids. Binary aqueous solutions of organic nonelectrolytes are of considerable interest, because, on the one hand, the role of water in biological and technological processes cannot be overestimated, and on the other hand, experimentally determined characteristics of aqueous solutions possess some specific features that are not observed in nonaqueous solutions.[1] Thus the concentration dependences of some properties exhibit extreme points in the $X = 0.1$—0.3 range (from here on, X is the mole fraction of the organic component in the mixture). According to the character of interaction with water, hydrophilic and hydrophobic groups are conventionally distinguished in molecules of nonelectrolytes. The specific character of the concentration dependences of the properties of aqueous solutions of nonelectrolytes are explained by the mutual influence of the hydration shells of these groups.

Several viewpoints on the nature of these phenomena have been discussed in the literature. Some authors believe that the specific features of these systems are due to the formation of water—nonelectrolyte complexes.[2,3] Other researchers confirm the occurrence of intense interaction between components of the solution and

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conclude that the structure of water is strengthened through the formation of quasi-clathrate species.[4,5] Based on the data of IR spectroscopy, X-ray diffraction analysis, and thermochemical measurements, the model of microheterogeneous structure of mixtures of water with nonelectrolytes has been proposed and developed.[6,7] For dilute electrolyte solutions, the principle of the least possible change in the structure of water was formulated.[8] It has also been shown that this principle is valid for solutions of both electrolytes and nonelectrolytes over a broad concentration range.[9—11] The results of more recent neutron diffraction studies[12] of dilute aqueous solutions of alcohols and tetraalkylammonium salts indicate that the three-dimensional ordering of water molecules in solutions is not increased compared to that in neat water and that the nonpolar parts of molecules of dissolved substances occupy vacancies of the network of H-bonds occurring in water.

The purpose of this work is to determine the structural properties of aqueous solutions of acetone and DMF in the region of existence of the H-bond network and to elucidate the general and specific features of the influence of functional groups of molecules on this network. The studies were carried out by Monte Carlo computer simulation, which allowed direct analysis of large arrays of coordinates of molecules.

These particular systems were chosen for several reasons. Data on the potentials of intermolecular interaction in these systems have been reported in the literature, and some properties and structural characteristics of these solutions have been determined;[13,14] thus, it was not necessary to consider here the problems of agreement between the calculated and experimental results. The hydrophobic groups in the molecules of DMF and acetone are similar in their type and geometry. Therefore, it can be assumed that the structural features of dilute aqueous solutions are mostly determined by hydrophilic groups. Unlike the authors of previous studies, we described the structural changes over a broad range of compositions of mixed solvents using the topological characteristics of H-bond networks.

Simulation procedure

The simulation was carried out by the Monte Carlo method according to the standard Metropolis algorithm in the NVT-ensemble at $N = 125$, $T = 298.15$ K, and $X = 0$, 0.05, 0.1, 0.2, and 0.4. Periodic boundary conditions and spherical cutting-off of the areas of action of the intermolecular interaction potentials were used. The energy for water was calculated using the TIP4P potential, that for DMF was found with the OPLS potential,[13,14] and for acetone a previously developed potential with a somewhat changed molecular geometry (the C—C—O angle equal to 120°) was used.[15,16] The parameters of inter-component interaction potentials were calculated according to the combination rules. The lengths of the Markov chains in the simulation reached 40—70 million of configurations. The beginning of the equilibrium section was detected from the average energy of interaction and correlation functions. The procedure for calculation of the topological characteristics of networks was reported previously.[17,18] The rings formed by bond chains, self-closed due to the use of the periodic boundary conditions, were not taken into account.

Results and Discussion

Information on the mutual spatial arrangement of atoms in liquids is normally obtained from X-ray and neutron scattering data. However, for the majority of water—nonelectrolyte mixtures the experimental results cannot be unambiguously interpreted.[1,12,19] The presence of several types of atoms with slightly different sizes and scattering abilities, the great number of possible mutual arrangements of molecules in solution, and the ambiguity of the mathematical processing of experimental data preclude the possibility of determining the full set of orientational and atom—atom radial distribution functions (RDF). However, using computer simulation methods, which make it possible to obtain lists of atomic coordinates, one can easily calculate the atom—atom RDFs from standard relationships:

$$g(r) = \rho(r)/\rho = [\mathrm{d}N(r)/\mathrm{d}V]/\rho = (1/4\pi r^3\rho)\cdot[\mathrm{d}N(r)/\mathrm{d}r], \quad (1)$$

where $\rho(r)$ is the numerical density of atoms in a spherical layer with thickness $\mathrm{d}r$ and volume $\mathrm{d}V$ at distance r from the chosen atom, ρ is the average numerical density, and $\mathrm{d}N(r)$ is the number of atoms in the spherical layer.

Previously,[1,6,7] it has been shown experimentally that up to high concentrations of solutes, whose molecules contain hydrophobic groups, a peak typical of neat water is retained on the angular dependence of the scattering intensity. The increase in the RDF maxima at small intermolecular distances observed in both real and computer experiments has often been interpreted as "strengthening of the structure of water" or as a specific manifestation of hydrophobic hydration.[12]

Figure 1 shows the RDFs of the O atoms that we obtained for two mixtures. In both systems, as the content of the organic component increases, the height of the first peak of the function for the water subsystem increases, while at distances larger than 30 Å, the changes are slight (see Fig. 1, *a*,*b*).

If the atom—atom RDF does not depend on the composition of the mixture X over some range of r values

$$g(r,X) = g(r,0), \quad (2)$$

then, having taken N as the number of particles in a unit cell with volume $V(X)$, we obtain

$$g(r,X) = [\mathrm{d}N(r,X)/\mathrm{d}V]/[\rho(0)\cdot(1-X)\cdot V(0)/V(X).$$

From condition (2), it follows that

$$\mathrm{d}N(r,X) = \mathrm{d}N(r,0)\cdot(1-X)\cdot V(0)/V(X) \approx \mathrm{d}N(r,0)\cdot\phi, \quad (3)$$

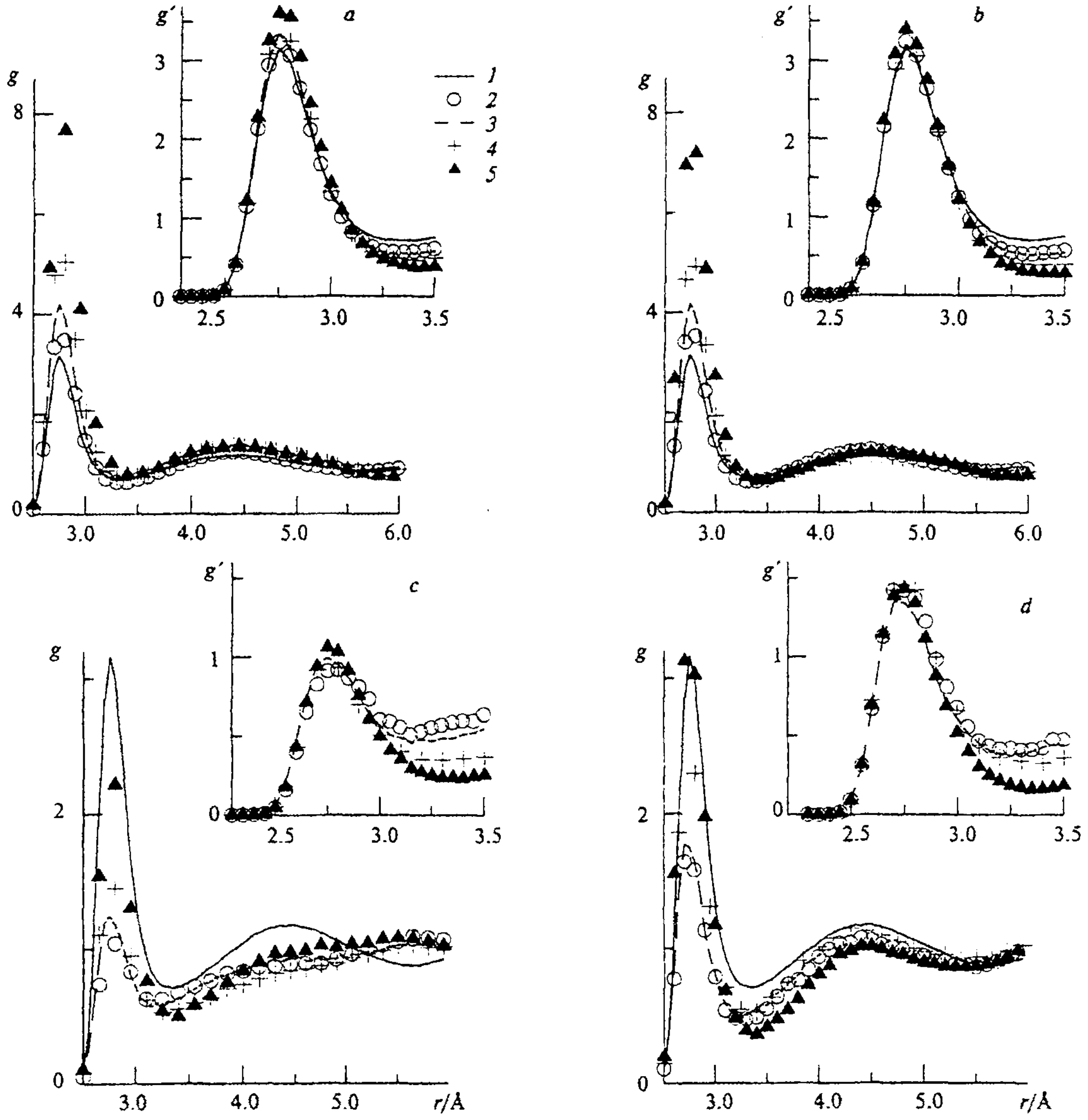

Fig. 1. Radial distribution functions $g(r,X)$ for the O atoms of water in mixtures with acetone (*a*) and DMF (*b*); of acetone (*c*) and DMF (*d*) in relation to water; r is interatomic distance; X is the mole fraction of the organic nonelectrolyte in the mixtures: $X = 0$ (*1*), 0.05 (*2*), 0.1 (*3*), 0.2 (*4*), 0.4 (*5*). The insets show the functions normalized according to formula (4).

where $V(0)$ and $V(X)$ are the unit cell volumes for water and solution, respectively, and ϕ is the volume fraction of water in the solution.

If the relationship

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

holds, we obtain

$$dN(r,X) = dN(r,0) \cdot (1-X). \qquad (5)$$

In both cases, the number of particles in a spherical layer with thickness dr is determined by the concentration of water and by a factor characterizing the spatial structure of neat water.

As shown in the insets in Fig. 1, *a*,*b*, after normalization in terms of Eq. (4), the $g'(r,X)$ functions at $r < 30$ Å and $0 \leq X \leq 0.4$ almost completely coincide. This means that equality (5) is fulfilled. Therefore, in the local environment of the chosen O atom of a water molecule, a molecule of an organic nonelectrolyte replaces only one neighbor. The mutual arrangement of the rest of the O atoms does not change.

Thus, the regularities in the arrangement of molecules, characteristic of neat water are locally retained. At large distances, the number of O atoms falling into the spherical layer is proportional to the volume fraction of water and to the factor characterizing the distribution

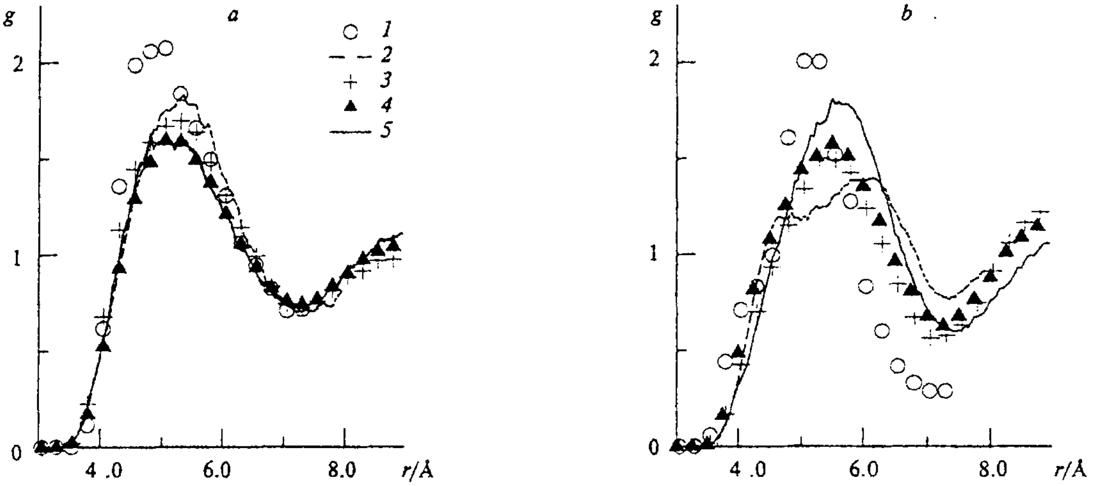

Fig. 2. Radial distribution functions $g(r,X)$ for the carbonyl C atoms of acetone (*a*) and the N atoms of DMF (*b*) in mixtures of nonelectrolytes with water: $X = 0.05$ (*1*), 0.1 (*2*), 0.2 (*3*), 0.4 (*4*), 1.0 (*5*).

of molecules in neat water. This manifestation of the "effect of excluded volume"[12] is possible only provided that areas with unchanged spatial structure of water are retained.

A similar behavior is observed for the functions characterizing the mutual arrangement of the O atoms of the components of the mixture (see Fig. 1, *c,d*). It can be said that molecules of an organic compound are built in the H-bond network of water by replacing neighbors of O atoms. In the case of solutions of DMF, a second maximum of the function is clearly manifested at about 4.5 Å, indicating a tetrahedral arrangement of the second neighbors; at $X = 0.4$, the function resembles most closely that of pure water (see Fig. 1, *d*). For mixtures of water with acetone, specific features in the behavior of RDFs can be observed: the peaks are much less intense, and the second of them is shifted to longer distances (see Fig. 1, *c*). It can be claimed that the incorporation of the hydrophilic parts of DMF distorts the spatial structure of the H-bond network of water to a lesser degree.

The functions $g_{\rm CC}$ and $g_{\rm NN}$ (C is the carbonyl carbon atom in an acetone molecule, N is the nitrogen atom in DMF), shown in Fig. 2, characterize the regularities of the arrangement of the central atoms of the molecules, and, hence, the hydrophobic groups as well. At $X = 0.4$, the $g_{\rm CC}(r)$ function coincides with the corresponding function for pure acetone and obeys relation (3), where ϕ is the volume fraction of the organic component. Thus, at a given composition of the mixture, microareas with nondistorted structure of the pure organic component are retained, and water molecules replace its molecules in accordance with the volume fraction of water. When X decreases, the first peak of the function increases and shifts to shorter distances. In the case of solutions of DMF, the first peak of $g_{\rm NN}$ first slightly decreases, while at $X = 0.05$, it sharply increases, as in the case of acetone. The enhanced correlation in the mutual arrangement of molecules and the increased concentration fluctuations, observed experimentally at small X values, are associated with the hydrophobic interaction of nonelectrolyte molecules.[1]

The behavior of the atom—atom RDFs makes it possible to judge the correlations in the mutual arrangement of molecules; however, virtually nothing can be said about the supermolecular spatial structure (regularities in the arrangement of groups of molecules). It is known that in the network of H-bonds of water, closed cycles can be found, which characterize its topological structure.[17,18]

It has been shown[20] that in the network of H-bonds of neat water, the concentration of closed cycles C_i obeys an exponential dependence on the probability of formation of a bond, p:

$$C_i = a_i \cdot p^i, \tag{6}$$

$$\ln C_i = \ln a_i + i \ln p, \tag{7}$$

where i is the number of apices in the cycle. Since it is impossible to propose a physically justified energetic or energetic-and-geometric criterion for the occurrence of an H-bond, the dependence of the properties of the system of bonds on its parameters is usually studied.

We chose the threshold energy criterion. Let us assume that two molecules form an H-bond if the energy of their interaction is smaller than a fixed negative value $E_{\rm HB}$. Successive decrease in the threshold value leads to a decrease in the connectivity parameter of the network n (the average number of bonds per

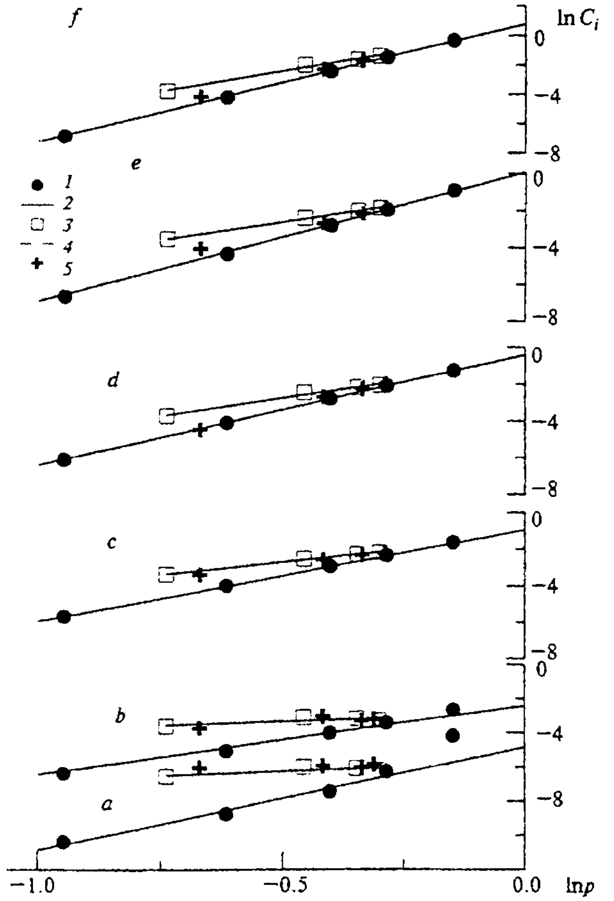

Fig. 3. Dependences of the concentrations of closed structures (C_i) on the probability of formation of a bond (p); i (the number of apices in the cycle) is 3 (*a*), 4 (*b*), 5 (*c*), 6 (*d*), 7 (*e*), 8 (*f*); calculation for water (*1*); approximation in terms of Eq. (7) (*2*); calculation for mixtures of water with acetone (*3*); linear approximation (*4*); calculation for mixtures of water with DMF (*5*).

molecule), and, hence, in the probability of formation of the bond, $p = n/4$. This means that weak bonds are gradually excluded from consideration.

It can be seen in Fig. 3 that for neat water, according to expression (7), the points fit in straight lines over a broad range of p values. At $p \to 1$, the number of bifurcated bonds sharply increases (molecules forming five or more bonds appear in the network); this results in deviations from relations (6) and (7). The a_i values can be found by least squares based on expression (6) or (7), which, reasonably, leads to somewhat dissimilar results. Using the TIP4P potential and expression (7), the following coefficients a_i were obtained: $a_3 = 0.0078$, $a_4 = 0.087$, $a_5 = 0.378$, $a_6 = 0.664$, $a_7 = 1.09$, and $a_8 = 2.20$. Here, the concentration was defined as the average number of cycles per water molecule.

It follows from the data presented in Fig. 3 that on dissolution of bifunctional compounds in water, the topological properties of the network built of both components change. Although the bond threshold remains constant ($E_{\rm HB} = -13$ kJ mol^{-1}), the bond network is successively destroyed with increase in X, which is manifested as a decrease in the p value. However, the number of triangular and quadrangular cycles remains almost constant. For solutions of acetone, the concentrations of all types of cycles markedly increase compared to that in neat water at the same p value, *i.e.*, for water with stronger H-bonds. In the case of DMF, this statement is valid only for cycles with numbers of apices of less than six. In the networks of mixtures, the total numbers of all cycles is larger than that in the network of water at the corresponding p value. Hence, the networks become more openworked due to a decrease of the proportion of noncyclic structures, *viz.*, "tree" fragments.

In addition to relations (6) and (7), which were obtained for the water network of bonds by simulation with pair-additive interaction potentials, the binomial distribution of molecules over the number of H-bonds they form is obeyed with high accuracy (for the TIP4P potential, the deviation does not exceed 0.7%)

$$w_m = \{4!/[(4-m)!m!]\}\cdot p^m\cdot(1-p)^{4-m}, \qquad (8)$$

where w_m is the fraction of molecules with m bonds, p is the probability of formation of a bond. This means that the bonds are formed randomly and independently of one another, *i.e.*, a "cooperative" effect is not involved. This assumption forms the basis of the percolation model of the H-bond network in water.[21]

In the configurations obtained by computer simulation, for the network of the water subsystem (only water—water bonds are taken into account), relation (8) holds with a sufficiently high accuracy up to high concentrations of the organic nonelectrolyte.[22] Thus in the case of acetone at $X = 0.4$, the maximum deviation from the binomial distribution is equal to 8% (for a solution of DMF, it is 4%) and is observed for molecules that form two bonds. The fraction of these molecules in solutions is larger than that typical of the network of neat water at the same parameter p. Thus, the network of H-bonds in the water subsystem of solutions is qualitatively similar to that of pure water. The construction of cyclic and extended chain structures requires molecules that form no less than two bonds. Hence, these network fragments are stabilized.

Now we consider how many bonds are formed, on the average, between a nonelectrolyte molecule and water molecules ($E_{\rm HB} = -13$ kJ mol^{-1}). The dependences shown in Fig. 4 imply that at small X values, the molecules of acetone are mostly involved in one H-bond with water molecules, and DMF molecules participate in one or two H-bonds with water. It follows from the symmetry of the curves that as the mole fraction of DMF increases, some of the doubly bound molecules are converted into singly bound ones. Calculations show that the average energy needed to cleave the H-bonds between water molecules (the magnitude of the interac-

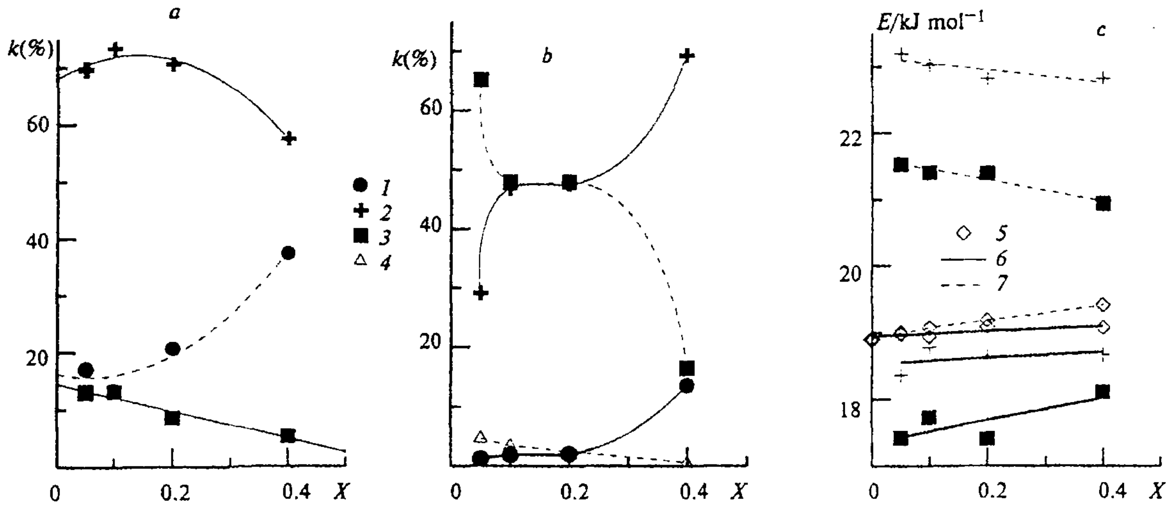

Fig. 4. Dependences of the proportion of nonelectrolyte molecules k forming m H-bonds with water molecules on the composition of the mixture X: m = 0 (*1*), 1 (*2*), 2 (*3*), 3 (*4*); *a* and *b*, calculations for mixtures of water with acetone and DMF, respectively; *c*, dependences of the mean energy of an H-bond (E) on the composition: calculation for water (*5*); approximation for water—acetone (*6*) and water—DMF (*7*) systems.

tion energy) somewhat increases upon the addition of nonelectrolytes pointing to a slight stabilization of the water subsystem. However, the average energy of acetone—water bonds is smaller and that of DMF—water bonds is larger than the energy of water—water bonds. Therefore, the formation of highly stable acetone—water complexes of composition 1 : 1 or 1 : 2 is relatively unlikely, whereas in the DMF—water system, these complexes can be found, together with a small amount of 1 : 3 complexes. It should be borne in mind that water molecules are incorporated in a common network of bonds, because in the concentration range under consideration, the system of H-bonds does not pass the percolation threshold, $p > 0.4$.

Figure 5 shows the dependences of the average numbers of H-bonds per nonelectrolyte molecule and per water molecule on the composition of the mixture. In addition to the above-noted energy stabilization of the bonds between water molecules, positive deviations from the additive mean value are observed; this implies a relative increase in the connectivity in the water subsystem. The average number of the nonelectrolyte—water bonds decreases as the X value increases. Linear extrapolation to the zero concentration of the nonelectrolyte shows that in an infinitely dilute solution, a molecule of acetone forms an average of one bond, and a DMF molecule forms an average of 1.8 bonds with water molecules. The latter value coincides with the value found by the simulation of an infinitely dilute solution.[14]

Thus, it follows from Figs. 4 and 5 that molecules of DMF, incorporated into the network of bonds *via* their O atoms, can occur in cyclic or chain-like structures. Since no more than 14% of the acetone molecules form two bonds with water molecules, it might be expected that the content of cycles in the network would decrease. However, their concentration in water—acetone mixtures increases to a larger extent than in water—DMF mixtures. The water—water bonds are stronger than water—acetone bonds, and this is the driving force of the spontaneous closure of chains consisting of water molecules. The role of hydrophilic groups of organic nonelectrolytes can be clearly followed.

The mutual spatial arrangement of the cycles in solution networks can be described using the RDF of

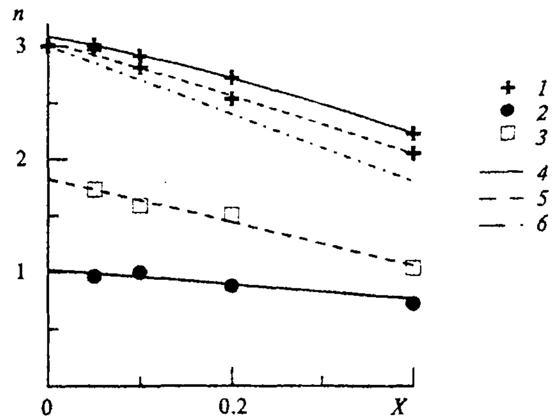

Fig. 5. Dependences of the average number of H-bonds (n) on the composition of the mixture X: calculations for the water—water system per water molecule (*1*), acetone—water system per acetone molecule (*2*), DMF—water system per DMF molecule (*3*); approximation for water—acetone (*4*) and water—DMF (*5*) mixtures; calculation for an additive system (*6*).

their geometric centers, $G_{ij}(r)$, where ij is the number of apices in a cycle. For this purpose, it is only needed to substitute the arithmetic mean of the coordinates of the O atoms of molecules incorporated in a closed cycle formed by H-bonds into Eq. (1), instead of the coordinates of atoms, which were used in the determination of the atom—atom RDF. In this particular case, the RDF is the ratio of the local density of the cycle centers in a spherical layer to the statistical mean value. The plots of the $G_{ij}(r)$ functions for neat water exhibit a characteristic set of distances corresponding to the maximum correlations. At short distances, the peaks correspond to certain associates of cycles, *i.e.*, pairs of cycles sharing one, two, or three edges.[17,18]

From the plots of the $G_{ij}(r)$ functions for solutions of organic nonelectrolytes in water, it can be seen that the height of peaks substantially increases with increase in X. As in the case of atom—atom functions, this can be explained by the "effect of excluded volume." In fact, if we assume that the relation

$$G'(r,X) = [V(0)/V(X)]\cdot G(r,X) = \\ = [V(0)/V(X)]\cdot[\mathrm{d}N(r,X)/\mathrm{d}V]/\rho(X) = G(r,0), \qquad (9)$$

holds, then, taking into account that

$$\rho(X) = NC(X)/V(X)$$

we obtain

$$\mathrm{d}N(r,X) = [\mathrm{d}N(r,0)/C(0)]\cdot C(X).$$

Thus, the number of cycle centers in a spherical layer of thickness dr is determined by the factor characterizing the structure of neat water and by the concentration of cycles in the cell at a given composition of the mixture.

Figure 6 shows the plots of the functions $G'(r,X)$, which contain almost invariable peaks, despite the fact that the concentration of the nonelectrolyte has increased to $X = 0.4$. At this composition, the volume fraction of water in its mixture with acetone is 27%, and that with DMF is 26%. Nevertheless, the solution network still contains areas with structure nearly identical to that of pure water.

The concept of formation of quasi-clathrate structures states that near the hydrophobic parts of nonelectrolytes in aqueous solutions, cells that structurally resemble clathrates are formed from water molecules. In

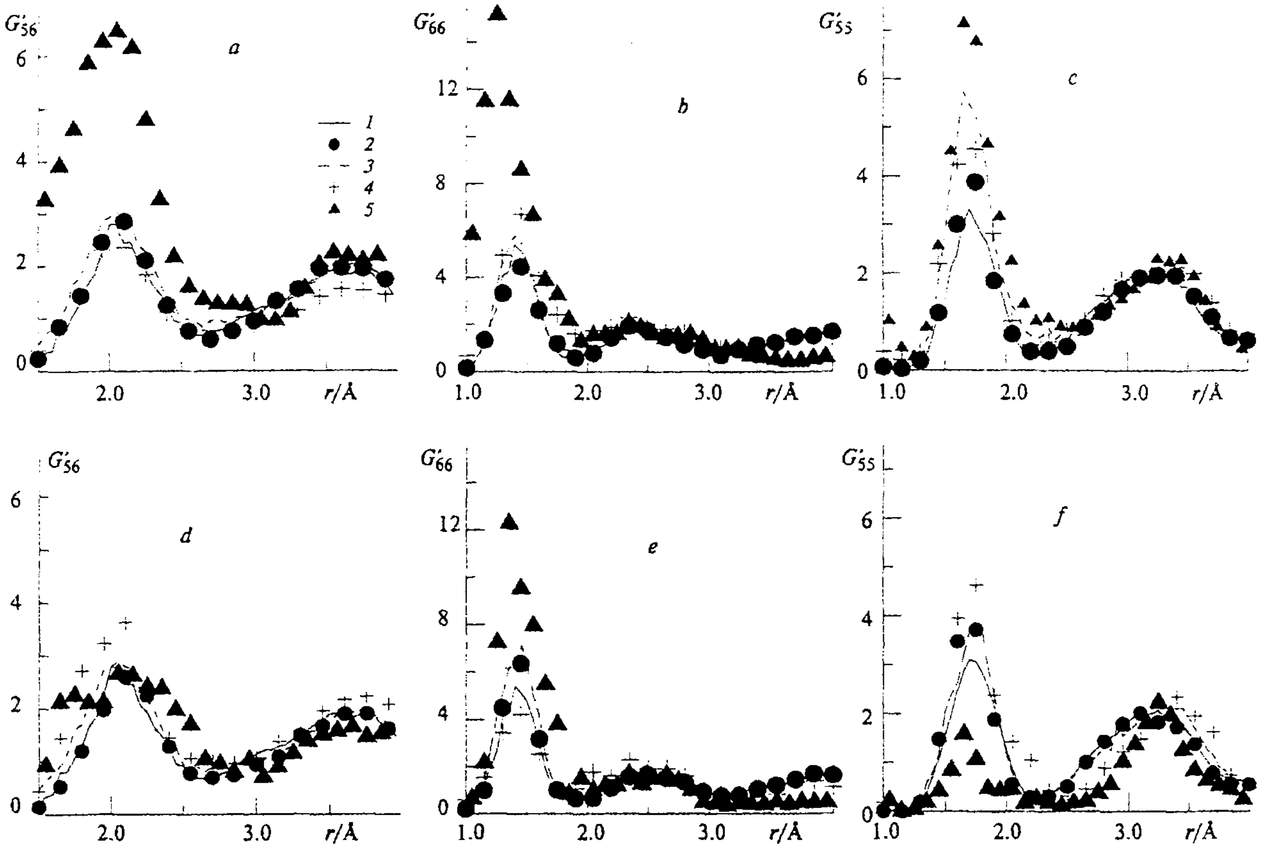

Fig. 6. Radial distribution functions for the geometric centers of closed cycles of H-bonds, $G'_{ij}(r)$ (*9*) for water—acetone (*a*—*c*) and water—DMF (*d*—*f*) mixtures; r is the distance between the cycles; i,j are the numbers of apices in the cycles; $X = 0$ (*1*), 0.05 (*2*), 0.1 (*3*), 0.2 (*4*), 0.4 (*5*).

clathrate compounds[23] (including those of acetone[24]), H-bonds form a set of convex polyhedral frameworks with planar pentagonal and hexagonal faces in such a way that neighboring cycles share an edge and their centers are located at strictly specified distances.

It follows from Fig. 6 that for aqueous solutions of acetone, the $G'_{55}(r,X)$ function does not undergo any changes in the $2.5 < r < 3.7$ Å range. The distance of 3.3 Å corresponds to an associate of two planar pentagons sharing one edge; this is a typical fragment of a clathrate cell. For solutions of DMF, the variations of the function in this range are insignificant. Whereas at the assumed bond criterion, every 100 molecules in the water network incorporate, on the average, 9.4 rings, in the case of a mixture with acetone at $X = 0.05$, the concentration of pentagons increases to 10.8, and in the case of DMF, it is 10.6, which is obviously insufficient for a clathrate-like structure to arise. This is not at variance with the results of previous studies, which support the concept of the formation of quasi-clathrate structures, because fragments of clathrate cells are present in a noticeable concentration even in the network of bonds of neat water.

Despite the qualitative similarity of the bond networks in a solution and in water, some specific features of solution networks can also been noted. As follows from Fig. 6, in solutions of acetone, the concentration and the spatial coordination of pentagons sharing two edges markedly increases. This construction corresponds to the peak of $G'_{55}(r,X)$ at $r = 1.79$ Å. In the case of the $G'_{66}(r,X)$ function, which characterizes the distribution of hexagons, at $X = 0.4$, the maximum at 1.47 Å corresponding to associates of "twist-boats" increases, whereas in the plot of $G'_{56}(r,X)$, this X value corresponds to an increase in the peak at 2.12 Å, which is the distance in the assembly of a pentagon and a hexagon with two common edges.[18]

Thus, compact structures rather than open extended structures are stabilized. In the case of mixtures of water with DMF, topological properties of the bond network change but these changes are less pronounced. The average coordination of cycles in the existing water-like areas is higher than that in the network of neat water.

As the content of a nonelectrolyte in a mixture increases, the network of bonds is gradually destroyed. As this takes place, the concentration of closed and chain-like structures becomes higher than that in the network of neat water at the same connectivity parameter. At the accepted bond criterion, the system of the H-bonds in both solutions does not pass the percolation threshold in the concentration range studied, *i.e.*, the common network running through the whole available bulk is retained. In this case, it looks like "trees" with groups of cycles hanging from them.

Here, an analogy can be drawn with the experimentally observed inhomogeneity of the structure of network polymers; with some reservation, water can be placed in this category. Theoretically, the inhomogeneity can apparently be attributed to the fact that the conformation entropy of the structures formed is larger than that of structures like regular lattices.[25] The competition between the processes of destruction of the network and an increase in its openwork character and the appearance of interconnected local fragments with slightly distorted water structure account for the experimentally observed extreme points on the concentration dependences of microscopic properties.

Thus, the results of computer simulation of aqueous solutions of nonelectrolytes at $X \leq 0.4$ demonstrated that not only the local spatial ordering in the arrangement of molecules typical of pure water is retained (which is in agreement with the results of the latest neutron diffraction experiments), but the fragments of the supermolecular structure of water are also retained. The principle of the least possible change in the structure of water was confirmed. However, the concepts of formation of quasi-clathrate structures and "strengthening of the structure of water" were not confirmed (these effects can occur in solutions but in these particular cases, they play a minor role). It was found that in DMF solutions, complexes of the composition DMF—nH$_2$O ($n = 1$—3) incorporated into the common bond network are energetically distinguished.

The theory of microheterogeneous structure of solutions was partly supported; solutions are concentrationally inhomogeneous and contain water-like areas, but the size and shape of these areas considerably differ from those predicted theoretically. However, the limitations of the simulation technique caused by the small number of species in a unit cell should also be taken into account.

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References

1. Yu. M. Kessler and A. L. Zaitsev, *Sol'vofobnye effekty. Teoriya, eksperiment, praktika* [*Solvophobic Effects. Theory, Experiment, Practice*], Khimiya, Leningrad, 1989, 312 pp. (in Russian).
2. A. Luzar, *J. Chem. Phys.*, 1989, **91**, 3603.
3. A. M. Zaichikov and G. A. Krestov, *Zh. Fiz. Khim.*, 1995, **69**, 389 [*Russ. J. Phys. Chem.*, 1995, **69** (Engl. Transl.)].
4. D. N. Glew, *J. Phys. Chem.*, 1962, **66**, 605.
5. F. Franks and D. J. G. Ives, *Q. Rev.*, 1966, **20**, 1.
6. V. I. Korsunskii and Yu. I. Naberukhin, *Zh. Strukt. Khim.*, 1976, **18**, 587 [*Russ. J. Struct. Chem.*, 1976, **18** (Engl. Transl.)].
7. M. Klose and J. I. Naberuchin, *Wasser. Structur und Dynamik*, Akademieverlag, Berlin, 1986, 176 pp.
8. O. Ya. Samoilov, *Struktura vodnykh rastvorov elektrolitov i gidratatsiya ionov* [*Structure of Aqueous Solutions of Electrolytes and Hydration of Ions*], Izd Akad. Nauk SSSR, Moscow, 1957, 182 pp. (in Russian).
9. A. K. Lyashchenko, *Zh. Strukt. Khim.*, 1968, **9**, 781 [*J. Struct. Chem. USSR*, 1968, **9** (Engl. Transl.)].

10. A. K. Lyashchenko, P. S. Yastremskii, and V. S. Khar'kin, *Zh. Fiz. Khim.*, 1984, **58**, 2750 [*Russ. J. Phys. Chem.*, 1984, **58** (Engl. Transl.)].
11. A. K. Lyashchenko, *Zh. Fiz. Khim.*, 1992, **66**, 167 [*Russ. J. Phys. Chem.*, 1992, **66** (Engl. Transl.)].
12. J. Tuner and A. K. Soper, *J. Chem. Phys.*, 1994, **101**, 6116.
13. W. L. Jorgensen and C. J. Swenson, *J. Am. Chem. Soc.*, 1985, **107**, 569.
14. W. L. Jorgensen and C. J. Swenson, *J. Am. Chem. Soc.*, 1985, **107**, 1489.
15. M. Ferrario, M. Haughney, I. R. McDonald, and M. L. Klein, *J. Chem. Phys.*, 1990, **93**, 5156.
16. P. Jedlovszky and G. Palinkas, *Mol. Phys.*, 1995, **84**, 217.
17. Yu. G. Bushuev and A. K. Lyashchenko, *Zh. Fiz. Khim.*, 1994, **68**, 525 [*Russ. J. Phys. Chem.*, 1994, **68**, 470 (Engl. Transl.)].
18. Yu. G. Bushuev and A. K. Lyashchenko, *Zh. Fiz. Khim.*, 1996, **70**, 416 [*Russ. J. Phys. Chem.*, 1996, **70**, 380 (Engl. Transl.)].
19. A. K. Soper, *J. Chem. Phys.*, 1994, **101**, 6888.
20. Yu. G. Bushuev, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 928 [*Russ. Chem. Bull.*, 1997, **46**, 888 (Engl. Transl.)].
21. H. E. Stanley and J. Teixeira, *J. Chem. Phys.*, 1980, **73**, 3404.
22. Yu. G. Bushuev, T. A. Dubinkina, and V. P. Korolev, *Zh. Fiz. Khim.*, 1997, **71**, 113 [*Russ. J. Phys. Chem.*, 1997, **71**, 106 (Engl. Transl.)].
23. Yu. A. Dyadin, I. V. Bondaryuk, and L. S. Aladko, *Zh. Strukt. Khim.*, 1995, **36**, 1089 [*Russ. J. Struct. Chem.*, 1995, **36** (Engl. Transl.)].
24. Yu. A. Dyadin, Yu. M. Zelenin, S. G. Bezuglov, and I. V. Bondaryuk, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* [*Bull. Sib. Branch USSR Acad. Sci.*], 1978, **3**, 70 (in Russian).
25. B. G. Ozol'-Kalnin and Ya. A. Travitis, *Vysokomol. Soedin., Ser. B*, 1982, **24**, 329 [*Polym. Sci. USSR, Ser. B*, 1982, **24** (Engl. Transl.)].

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