Physical Chemistry

Structural peculiarities of particle solvation in *N,N*-dimethylformamide

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Monte Carlo computer simulation of infinitely dilute solutions of Cs^+ and I^- ions and Xe atoms in *N,N*-dimethylformamide (DMF) was performed. Peculiarities of intermolecular interactions and structural properties of the solutions were investigated. The solvation enthalpies of cations and anions are close, but the energies of the ion-solvent and solvent-solvent interactions differ appreciably. The solute particles affect the energy and structural properties of DMF only in spatially localized domains. The second solvation shell of the solute particles was not structurally allocated. Two structurally and energetically differing states of DMF molecules (with normal and anomalous orientation of the dipole moments) exist in solution of Cs^+ cations. The anomalous orientation of DMF molecules is due to the solvation steric effect, packing, and kinematic factors.

Key words: organic solvents, amides, *N,N*-dimethylformamide, ionic solvation, structure of liquid, intermolecular interactions; computer simulation of liquids, Monte Carlo method.

Various experimental and theoretical methods are widely used for comprehensive study of solvation in liquids.[1—4] The most objective information on the structural properties of solutions is obtained by X-ray structural analysis, neutron diffraction, and spectroscopy. Thermochemical and physicochemical characteristics reflect overall changes in the interactions and regularities of mutual arrangement of the molecules which occur at the formation of a solution. The complicated structure of liquid makes rigorous theoretical description of its properties difficult.

Investigation of ionic solvation is a special division of physical chemistry of solutions. Since electrostatic interactions are stronger than those in non-electrolyte solutions, the effects observed on dissolution of ions appear to be much more pronounced, which increases the accuracy of their measurements. Thermodynamic, physicochemical, and structural characteristics of solvation are closely related. They are due to solute—solvent and solvent—solvent interactions of a complex nature, which makes it possible to consider these interactions as a sum of individual contributions; however, this division is ambiguous. Determination of dominating interactions, which control the structure formation, mutual orientation, and molecular motions is a topical problem of physical chemistry of solutions.

Phenomenological analysis of thermodynamic functions characterizing ionic solvation includes separation of the contributions of cavity formation in the solvent, electrostatic interactions between the ion and solvent molecules, as well as those due to changes in the structural and energy properties of the solvent.[1—4] This scheme is rather conditional. Several approximate methods for assessing individual contributions have been

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developed.[2] However, formulas used for taking into account the properties of the ion and solvent molecules are numerous and contain fitting parameters. Correct calculations can be carried out[2] only if discrete properties of the solvent are determined.

In the mean sphere approximation (MSA), which is one of the most theoretically substantiated approximations, the contribution of electrostatic interactions is calculated using the multipole expansion.[2,5,6] As a rule, only the ion-dipole and dipole-dipole interactions are taken into account. Calculations of thermodynamic functions require setting the size of the spheres approximating the ion and the solvent molecule, the dipole moment and polarizability of the molecule, the dielectric constant, the density of the solution, and several fitting parameters. Obviously, description of solvation in the MSA model is highly inadequate because of using inexact equations based on tentative initial assumptions concerning structural and energy properties of the solution. Of crucial importance is that several parameters used in this model cannot be objectively determined.

The interaction between solvent molecules, which determines the spatial structure of the solvent, manifests itself most pronouncedly in the course of complexation. The results obtained in the studies[7] of the energy and structural properties of the solutions of divalent transition-metal ions in several solvents made it possible to suggest the existence of solvation steric effects. Depending on how the coordination number of the ion changes on going from *N,N*-dimethylformamide (DMF) to another solvent, it was proposed[7] to distinguish between a strong and weak steric solvation effect.

Division of thermodynamic characteristics of a stoichiometric mixture into ionic contributions is a separate problem of the ionic solvation theory.[1,2] Most often, the division procedure used implies equality of the thermodynamic functions of solvation of large cations and anions. However, the assumption that all microscopic and macroscopic properties of anion and cation solvation are the same in all solvents is characteristic of primitive schemes only. Usually, scales corresponding to large organic ions are used for calculating the enthalpies of transfer of individual ions from one solvent (most often, water) to another. Calculations of solvation enthalpies require information on the sublimation enthalpies of the crystals of organic salts. Unfortunately, only a few studies[8] on experimental determination of crystal lattice enthalpies have been reported. The accuracy of the results obtained was rather low.

Currently, many problems of the ionic solvation theory can be consistently solved by comparing the experimental properties of solutions with the results of computer simulation. The Monte Carlo and molecular dynamics methods are widely used in the studies of ionic solvation.[3,4] Numerous studies have been dedicated to investigation of structural, thermodynamic, and kinematic aspects of hydration of simple and polyatomic ions. Solutions of ions in non-aqueous and mixed solvents have been less studied.[9—15]

Based on the results of computer simulation, in this work we made an effort to answer the following questions. How are the methods for division of thermodynamic characteristics of a stoichiometric mixture of ions into components theoretically substantiated? Is consideration of multipole interactions only sufficient to perform correct calculations of the electrostatic component of thermodynamic functions? What is the role of the repulsive interactions and the spatial structure of the solvent in ionic solvation? What are the peculiarities of steric solvation effect in the case of particles of the same size but carrying different charges?

The choice of the objects studied in this work is due to the fact that liquid DMF is a typical representative of the wide class of aprotic solvents. Its molecule has a relatively large dipole moment. Hence, ion-dipole interactions make an appreciable contribution to thermodynamic functions. Studies on the solvation of Cs^+ and I^- ions are of importance for establishing the regularities of structural and energy transformations in solutions. In one of the scales (see above) these particles are considered[1,2] as reference points when dividing thermodynamic functions of a stoichiometric mixture of ions into particular contributions. Relatively large ion size leads to weakening of electrostatic fields near the ions, weakening of polarization effects, and small structural distortions of solvent molecules.

In this work, the solvation of particles was studied by the Monte Carlo method. Computer simulation of a liquid is based[4] on knowledge of the analytical form of the effective potential of intermolecular interactions and on the approximate numerical solution of rigorous equations of statistical physics. Calculations are carried out to obtain the lists of particle coordinates (*I*-ensemble), which makes it possible to analyze not only the averaged structural properties, but also the arrangement and the energy characteristics of the interacting particles in individual molecular configurations.

Prior to performing computer experiments, we must introduce some simplifying assumptions.[4] The main parameters of the model are the parameters of the effective potential of interparticle interactions. The particular form of the potential is determined by reproducibility of actual properties of the solution taking into account the data of quantum-chemical calculations of the energy and geometry of molecular complexes. As a rule, there are several parametrizations of the potential for the same substance.

To eliminate the influence of surface effects and to pass to the thermodynamic limit, it is assumed[4] that the entire space is filled with identical cells containing *N* particles each. Then, one out of several possible procedures for calculation of intermolecular interactions in a quasi-infinite system is specified. In the simplest case, spherical cutoff of the potential is used.[4] Of course, this introduces an error in the energy of the system obtained in the studies of ionic solvation, since the Coulomb interactions decrease slowly as the distance increases. A particular problem is associated with ergodicity of simulation. Nevertheless, it has been shown[4] that by taking into account the above-mentioned drawbacks of the method and by using the procedures developed to reduce the errors it is possible to achieve a correct qualitative and quantitative reproduction of several properties of solutions. The use of the methods of computer simulation allows one to establish the most probable picture of the phenomenon.

Based on the topological analysis of the networks built of lines connecting the nearest molecules, it has been shown[15—18] that electrostatic interactions have the smallest effect on the regularities of mutual spatial arrangement of molecules in several organic solvents and solutions of ions, which is first of all determined by the molecular shape, universal interactions, and molecular packing factors. In particular, it has been established[17] that the mutual arrangement of the molecules in liquid DMF can to a first approximation be considered as an arrangement of molecules in a random closely packed system of soft spheres (SS). This conclusion is virtually independent of both the procedure for simulation and the parametrization of the potential. Therefore, it is reasonable to suppose that the results presented in this work give the most plausible qualitative picture of the phenomenon under study.

Calculation procedure

Calculations were carried out using the standard Monte Carlo method in the *NVT*-ensemble at $N = 125$ (see Ref. 4). The conditions of the computer simulation of DMF corresponded to a density of 0.9443 g cm^{-3} and to $T = 298$ K. Periodic boundary conditions were used. The intermolecular interactions were chosen in accord with the OPLS system of potential functions.[17,19] The structure of a DMF molecule is shown in Fig. 1. Solvation effects in the model infinitely dilute solutions of three types of spherically symmetric isoelectronic particles (Cs^+ cation, Xe atom, and I^- anion) were studied. When simulating the solutions, one DMF molecule in the unit cell was replaced by a solvated particle. The volume of the system was considered constant.

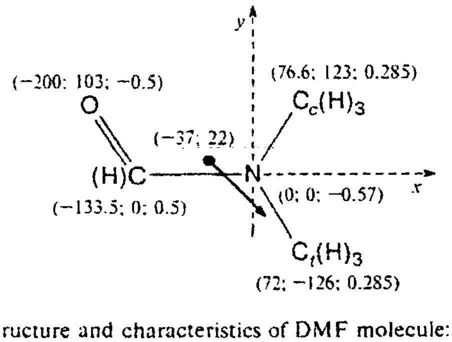

Fig. 1. Structure and characteristics of DMF molecule: C_c and C_t are the atoms in *cis*- and *trans*-position with respect to the O atom, respectively; atomic coordinates (*x*/pm, *y*/pm) and charges (*q*/e) are given in parentheses (*x*; *y*; *q*); the center of gravity of the molecule is shown by a filled circle, and the direction of the dipole moment vector $\mathbf{d}$ ($|\mathbf{d}| = 4.4$ D) is shown by an arrow.

The size of an ion is one of its most important characteristics. The problem of ionic radii is a moot question.[1] When interpreting the results of thermodynamic studies, the ionic radii are used as fitting parameters. Usually, crystal-chemical systems of radii are used, which virtually are structural parameters of the crystal lattices of the corresponding salts. However, representation of an ion as a solid sphere of the same size both in the crystal and in solution has not been theoretically substantiated. More preferable are the systems of radii that correlate with the distances between the electron density maxima.[20] In the crystallographic system,[1] the difference between the radii of Cs^+ and I^- ions is 55 pm according to Goldschmidt or 47 pm according to Pauling, whereas in the orbital system[20] it is only 14.4 pm ($r_{Cs^+} = 92.1$ pm, $r_{I^-} = 106.5$ pm).

Computer simulation is performed using the effective potentials, which take into account both the energies of interparticle interaction obtained from quantum-chemical calculations and the experimental properties of condensed phases of matter. In this work, we focussed our attention on consideration of the peculiarities of solvation of particles carrying different charges. The radii of the particles were assumed to be equal to the radius of the Xe atom ($r_{Xe} = 98.6$ pm). The parameters of the Lennard-Jones (12—6) potential were set to $\sigma = 425.4$ pm and $\varepsilon = 213.54$ K [21] for the Xe atom, while those for the particles interacting with DMF molecules were calculated using the combination rules $\sigma_{ai} = (\sigma_a + \sigma_i)/2$ and $\varepsilon_{ai} = (\varepsilon_a \cdot \varepsilon_i)^{0.5}$. Here, the *a* and *i* indices label the particle and the interacting center of the molecule (an atom or atomic group), respectively. Spherical cutoff of the potential was used, according to which the interaction energy was assumed to be zero if the distance from the N atom of the DMF molecule to the solvated particle or to the N atom of another DMF molecule was longer than half the unit cell edge length (1262 pm). In each simulation, Markovian chain of a total length of about 50—70 · 10^6 configurations was generated, of which the portion of accepted configurations was ~50%.

Results and Discussion

Solvation effects manifest themselves as changes in the structural, energy, kinetic, and other properties of the solvent under the action of solute. Initially, let us assess the adequacy of our simulation of solutions. The solvation enthalpies, ΔH_{solv}, of particles characterize the overall changes in the interactions caused by the transfer of 1 mole of the substance from the gas phase to solution. Computer simulation of liquids is performed to obtain sets of molecular configurations with known coordinates and energies of the interaction of all particles in the unit cell. The ΔH_{solv} values are calculated using the standard formulas[2—4]

$$\Delta H_{solv} = \Delta E_{solv} + P\Delta V_{solv} - RT,$$

$$\Delta E_{solv} = E_{SX} + E_{SS} - E^*_{SS} = E_{SX} + \Delta E_{SS},$$

where ΔV_{solv} is the change in the volume of the liquid; E_{SX} is the average energy of the interaction between the particle (X) and the solvent molecules (S); E_{SS} and E^*_{SS} are the energies of the interaction between the solvent molecules in solution and in pure solvent, respectively; and ΔE_{SS} is the reorganization energy of the solvent. The error of determination of ΔH_{solv} depends on the accuracy of all types of interactions taken into account using the effective potentials, as well as on the size and shape of the unit cell, procedure for calculations of long-range interactions, convergence, and ergodicity of the simulation.[4] First of all, we were interested in studying the structural aspects of particle solvation. Therefore, the accuracy of reproduction of thermodynamic characteristics of dissolution received little attention, which made it possible to simplify the algorithm used and to reduce the computational cost of calculations. Nevertheless, the results obtained are in good agreement with experimental data.

The calculated thermodynamic functions of the solutions of particles in DMF are listed in Table 1. The ΔH_{solv} values of the Cs^+ and I^- ions are close; however, the individual contributions to these overall values are strongly different. Compared to the anion, the cation has a stronger effect on the energy characteristics of solvent molecules, thus increasing the energy of intermolecular interaction. At the same time, this solution is characterized by a lower energy of the interaction between the solvent molecules and the ion, E_{SX}. Therefore, the energy properties of the solution are strongly dependent on the magnitude and sign of the charge of the solvated particle. Calculations using phenomenological equations[2] with multipole expansion of electrostatic interactions and spherical approximation of the molecular shape give incorrect contributions to the solvation enthalpy.

Ambiguity of the procedure for division of the solvation enthalpy of a stoichiometric mixture of ions into components precludes direct comparison of calculated and experimental values. Depending on the division procedure and method of extrapolation to infinite dilution, one can obtain $\Delta H_{solv}(I^-)$ values of −138,[22] −259,[23] and −299 [23] kJ mol^{-1}. The overall effect determined in this work differs from that calculated from experimental data (ΔH_{solv}(CsI) = −611 kJ mol^{-1})[24] only by 7%. Fairly good agreement between the results suggests that our simplifying assumptions are insignificant and that the models used correctly reproduce the main structural and energy properties of solutions.

Table 1. Thermodynamic functions of dilute solutions of particles in DMF

Particle	E_{SX}	ΔE_{SS}	ΔE_{solv}	ΔH_{solv}
	kJ mol^{-1}			
Xe	−28.7	37.4	8.7	6.2
Cs^+	−518.3	241.2	−277.1	−279.6
I^-	−444.1	157.8	−286.3	−288.8

Note. E_{SX} is the energy of interaction between the particle and the solvent molecules, ΔE_{SS} is the solvent reorganization energy, ΔE_{solv} is the solvation energy, and ΔH_{solv} is the solvation enthalpy.

If the solvated particle has a spherical shape, then, at the first glance, it seems to be reasonable to compare the properties of the solvent in spherically symmetric solvation shells of the particle.[1] Strong interactions in the system suggest that the properties of the solvent near the dissolved particle will be substantially changed. With increasing distance from the particle, the state of the solvent should approach that characteristic of the pure solvent. As a rule, these propositions are used in phenomenological description of solvation effects. It is common practice to distinguish between the boundaries of incomplete, short-range, and long-range solvation.[1] However, the real picture of the phenomenon can differ significantly from that discussed above. This can be illustrated taking the solutions studied in this work as examples.

The radial distribution functions (RDF), $g(r)$, characterize the spatial arrangement of the atoms in the liquid. By definition, the $g(r)$ function is equal to the ratio of the local density of atoms $\rho(r)$ in a spherical layer to the average density ρ:

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

where $dN(r)$ is the number of atoms in the layer surrounding the given atom, and r and dV are the radius and the volume of the layer, respectively. Knowing the RDF, the number of atoms in the sphere of radius r, $N(r)$, can be found with ease using formula (1).

The N atom is near the center of mass of the DMF molecule (see Fig. 1). To a first approximation, the position of the center of mass of the molecule can be chosen as its geometric center. The plots of the $g_{AN}(r)$ and $N(r)$ curves characterizing the arrangement of N atoms of DMF molecules with respect to solvated particles are shown in Fig. 2. The behavior of the functions is to a great extent dependent on the particle charge. The distinction between the ionic solvation and the solvation of the Xe atom manifests itself as an increase in the height of the first $g_{XeN}(r)$ peak and a narrowing of the first $g_{XeN}(r)$ peak, which indicates strengthening of the spatial coordination of solvent molecules in the first solvation shell (FSS) of the ions. It is conventional to assess the FSS size from the position of the first RDF minimum. The FSS boundary cannot be rigorously allocated because of thermal motion of the molecules and a relatively weak coordinating effect of the particle field.

The behavior of the integrated quantity $N(r)$ is to a lesser extent dependent on the charge of the solvated particle. We can argue that the number of DMF molecules in a spherical layer of thickness ~100 pm (550 pm < r_{AN} < 650 pm) in the solutions of the ions is larger than that in the analogous layer of the solvation shell of the Xe atom. Here, the molecules are more closely packed. However, the values of the $N(r)$ functions nearly coincide already at r_{AN} > 700 pm. For definiteness, we assumed that the FSS of the particles in all systems under study contained 12 solvent molecules, which corresponded

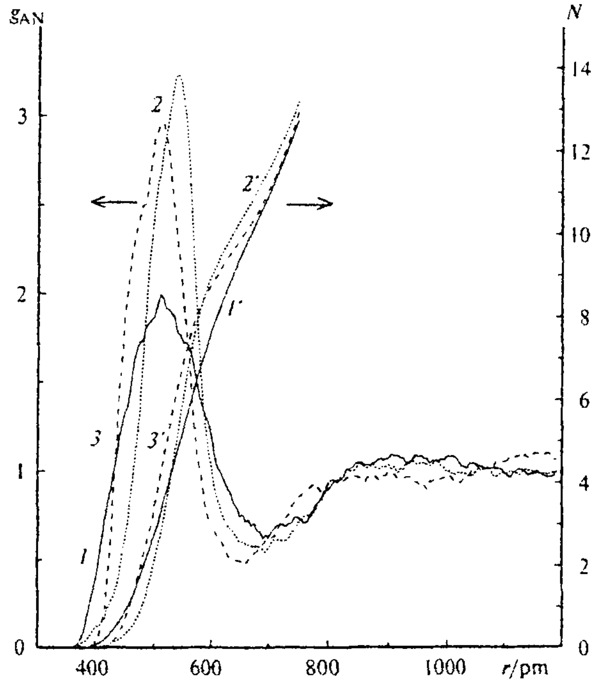

Fig. 2. Radial distribution functions, $g_{AN}(r)$, of nitrogen atoms of DMF molecules with respect to solvated particle A (*1—3*) and the dependences of the number of molecules within the sphere of radius r, $N(r)$ (*1'—3'*), on r. A = Xe (*1*, *1'*); Cs^+ (*2*, *2'*); I^- (*3*, *3'*).

to a shell radius of 730 pm for Xe and I^- solutions and of 710 pm for Cs^+ solution. At r_{AN} > 800 pm, the g_{AN} functions do not oscillate and their values are close to unity. At these distances, the local and average densities of N atoms coincide. From this an important conclusion follows that the second solvation shell in the systems studied cannot be structurally allocated. In spite of strong interactions between the molecules and ions, changes in the solvent structure are of local nature.

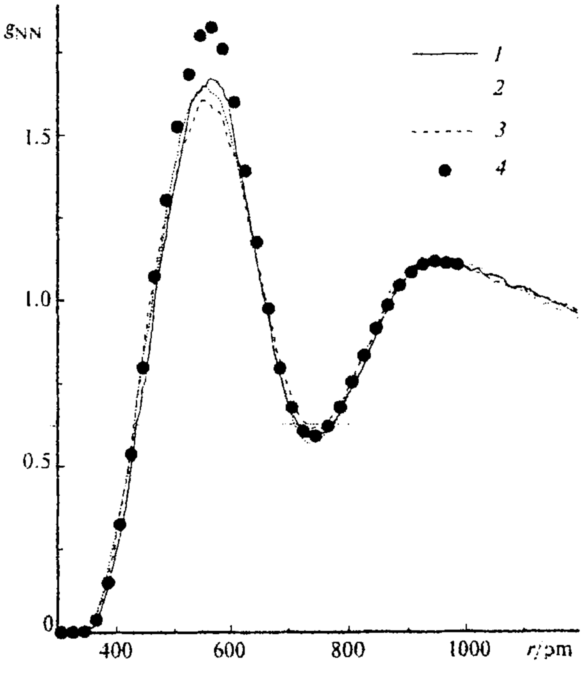

Fig. 3. Radial distribution functions of nitrogen atoms of DMF molecules, $g_{NN}(r)$, in the FSS of Xe atoms (*1*), Cs^+ (*2*) and I^- (*3*) ions, and in pure DMF (*4*).

This conclusion is also confirmed by the plots of the $g_{NN}(r)$ RDF of the N atoms of the DMF molecules constituting the FSS of particles (Fig. 3). Distinctions between the pure liquid and solutions manifest themselves in a small decrease in the height of the first maximum of the curves in the narrow range of intermolecular distances. Similar behavior of the $g_{NN}(r)$ function of DMF was also observed[25,26] for liquid DMF—formamide and DMF—water mixtures. Taking into account that for most of the molecules in the FSS the distance from the solvated particle is 500—700 pm, it is possible to give a simple explanation for the above-mentioned decrease in the peak height.[25,26] Each dissolved particle replaces a DMF molecule without changing the regularities of the arrangement of N atoms and, likely, the character of the packing of other solvent molecules.

The plots of the $g_{XeA}(r)$ functions characterizing the arrangement of the atoms of DMF molecules with respect to the Xe atom are shown in Fig. 4. Positions of

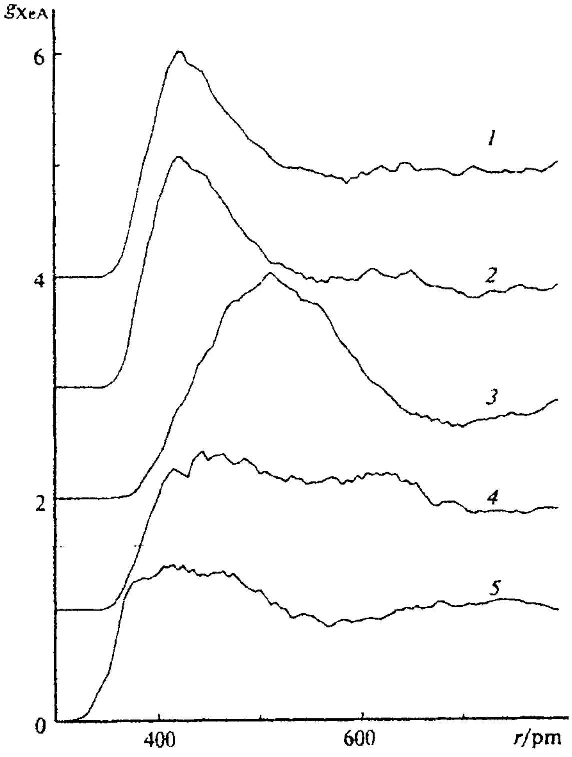

Fig. 4. Radial distribution functions of the atoms (A) of DMF molecules, $g_{XeA}(r)$, with respect to the Xe atom: A = C_t (*1*), C_c (*2*), N (*3*), C (*4*), and O (*5*). For clarity, the plots are shifted along the ordinate axis.

the first maxima of the RDF of the O, C, C_c, and C_t atoms virtually coincide. They are shifted toward shorter distances as compared to the first maximum of the g_{XeN} function. Tangential orientation of DMF molecules is the most probable in the FSS of the particle. This means that the molecular planes are perpendicular to the vector r_{XeN} connecting the particle and the N atom. Librations near the centers of mass of the molecules bring the solvated particle closer to the peripheral atoms. Therefore the first g_{XeN} peak is shifted toward long distances. Higher peaks of the RDF of the C_c and C_t atoms compared to those of the O and C atoms indicate preferable orientation of the methyl groups toward the solvated particle.

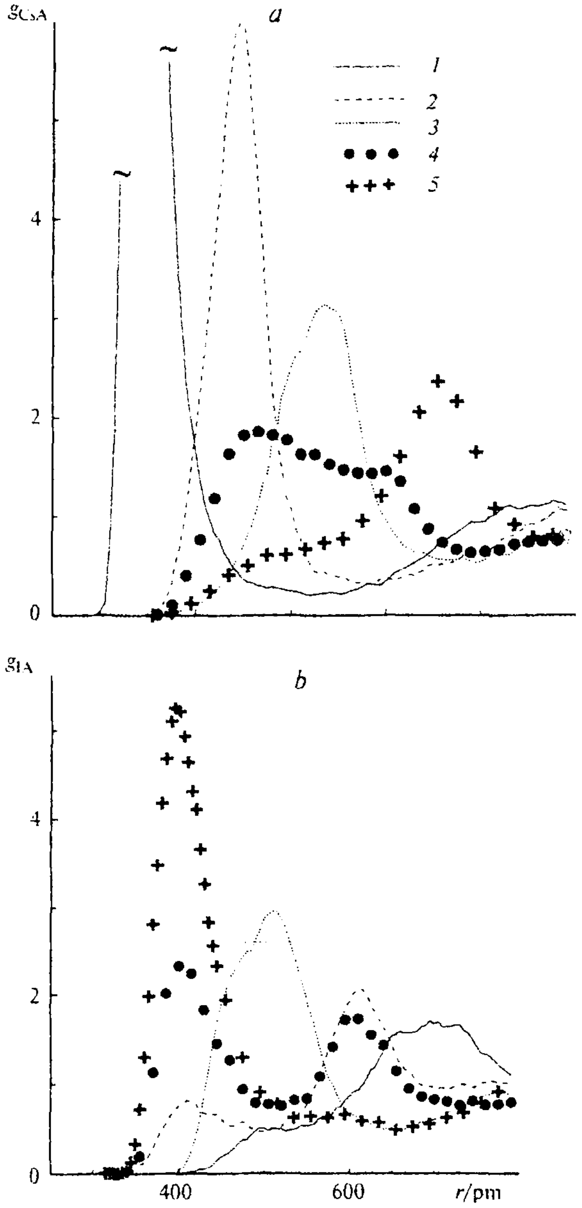

Fig. 5. Radial distribution functions of the O (*1*), C(*2*), N(*3*), C_c (*4*), and C_t (*5*) atoms of DMF molecules with respect to the Cs^+ (*a*) and I^- (*b*) ions.

The plots of the RDF characterizing the arrangement of the atoms of the DMF molecule with respect to the ions are shown in Fig. 5. The electrostatic field of the ions affects the orientation of the solvent molecules. The atoms of the nearest molecules in the FSS of the cation are situated as follows: O, C, and N as the distance from the cation increases. Mention should be made of the unexpected behavior of the RDF of positively charged methyl groups, which can be at relatively short distances (~400 pm) from the Cs^+ ion. To a greater extent this is characteristic of the *cis*-Me groups of the molecules. The positions of maxima of the g_{CsA} functions of the C and C_c atoms virtually coincide. In the first case, it can be assumed that the orientation of DMF molecules is determined by ion-dipole interactions; however, in the second case we have to accept that the dipole moments of a fraction of the molecules are directed antiparallel to the vector of the electrostatic field strength (the like charges are at shorter distances than the unlike charges). This unexpected result has to be clarified.

No anomalous orientations of solvent molecules were observed for the I^- ion. The probabilities for positively (C_t, C_c, C) and negatively charged atoms (N, O) to be at short distances are strongly different. The dipole moments of most of the molecules in the FSS are actually oriented along the direction of the field strength vector. A smaller number of molecules are characterized by "correctly" oriented dipole moments of the $N-C_c$ bonds. These two most probable types of the arrangement of the molecules with respect to the anion manifest themselves as two more or less pronounced extrema on each of the curves shown in Fig. 5, *b*. Mention may be made that some molecules are oriented so that the C atom of the carbonyl group is directed toward the ion.

Yet another important characteristic of the orientation of DMF molecules with respect to the dissolved particle is the *S*(*r*) function calculated using the formula

$$S(r) = \langle \cos (\alpha(r)) \rangle,$$

where α is the angle between the dipole moment vector of the solvent molecule (***d***) and the vector (***r***) between the particle and the N atom ($r = |\boldsymbol{r}|$, angular brackets denote averaging over ensemble). The plots of the *S*(*r*) functions are shown in Fig. 6.

The values of the *S*(*r*) function calculated for the Xe solution are close to zero, which can be explained by the fact that the ***d*** and ***r*** vectors are perpendicular to each other and, hence, their scalar product is equal to zero. At distances corresponding to the FSS of the I^- anion, the values of the *S*(*r*) function are negative and the orientation of molecules is determined by the ion field. However, two states of the molecules, which differ in orientation, can be distinguished in the FSS of the Cs^+ cation. At short distances, the dipole moments of the molecules are mostly oriented along the field strength vector, whereas at 600 < r_{CsN} < 850 pm they are oriented in the opposite direction. Here, the overall effect of the molecules with anomalous orientation of dipole moments exceeds that of the "correctly" oriented molecules, which manifests itself in negative values of the $S(r)$ function.

Polarization of a dissolved particle is determined by the polarization coefficient and field strength. The nearest solvent molecules have the most pronounced effect on the particle. As can be seen in Fig. 6, polarizations of the cation and anion are different. Anisotropic distribution of molecular orientations suggests that the polarization effects should play a more important role in the case of solvation of the Cs^+ ion.

Let us establish the reason for the anomalous orientation of DMF molecules in the FSS of the Cs^+ ion. In Fig. 7, we present the dependences of the energy of intermolecular interaction (U) on the distance r from the ion:

$$U(r) = U_{SX}(r) + U_{SS}(r),$$

where U_{SX} and U_{SS} are the contributions of the ion—solvent and solvent–solvent interactions, respectively.

Near the Cs^+ ion (at $r < 600$ pm), strong electrostatic interactions of the ion with DMF molecules compensate the increase in the U_{SS} term. The U_{SX} contribution increases, whereas the U_{SS} term decreases substantially as the distance increases. At 620 pm $< r <$ 820 pm, the energy of interaction between the DMF molecules and Cs^+ ion is positive ($U_{SX} \approx 5$—10 kJ mol^{-1}); however, this is completely compensated by strengthening of DMF—DMF interactions. Thus, anomalous orientation of DMF molecules causes no increase in the average total energy of their interaction. In the case of solvation of the I^- anion, the energy changes are less pronounced and the U_{SX} values are negative at all distances.

Using Monte Carlo simulation, it is impossible to study actual motions of the molecules of a liquid. However, lower potential energy values of the solvent molecules in the FSS of ions compared to the corresponding asymptotic values at long distances (ΔU ~$4RT$ for Cs^+ cation and ~$1RT$ for I^- anion) suggest that the

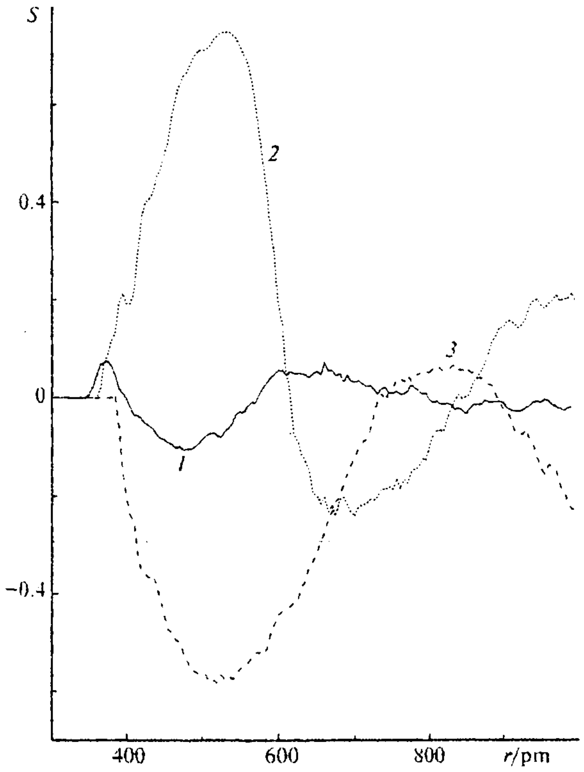

Fig. 6. Functions $S(r)$ characterizing the orientation of the molecular dipole moments with respect to the r_{AN} vector: A = Xe (*1*); Cs^+ (*2*); and I^- (*3*).

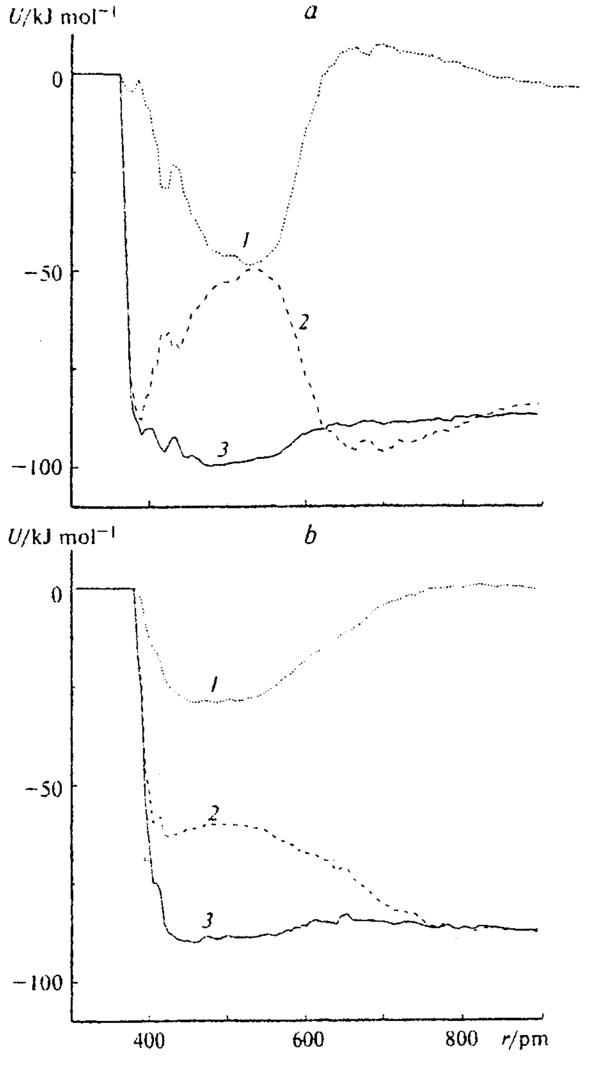

Fig. 7. Dependences of the energies of molecular interactions on the distance from the Cs^+ (*a*) and I^- ions (*b*); average energies of ion-molecule interactions, $U_{SX}(r)$ (*1*), and solvent-solvent interactions, $U_{SS}(r)$ (*2*); and their sum, $U(r)$ (*3*).

ions are positively[1] solvated. It is likely that about 8 DMF molecules are involved in cooperative motion with the Cs^+ ion. The solvent molecules with anomalous orientation, which are constituents of the FSS, are not involved in this motion. As a result of thermal motion of the solvated cation, a fraction of the solvent molecules penetrate the FSS (in accordance with the principle of close packing). As a consequence, these molecules can have any orientation (including anomalous orientation) with respect to the Cs^+ cation.

Usually, phenomenological models of solvation take into account[2] only the ion-dipole and dipole-dipole interactions. However, the multipole expansion is valid at distances that much exceed the size of the molecules, *i.e.*, it is inapplicable to the molecules in the FSS of ions. In fact, based on this concept, one cannot expect a large number of molecules with anomalous orientation that would be capable of forming a structural microphase.

The presence of two structurally and energetically different states of DMF molecules in the FSS of the cation is clearly seen in the behavior of the $W(E_{SS})$ function, which, by definition, is equal to the fraction of molecules with a specified value of the energy of solvent—solvent interaction (E_{SS}). The plots of the $W(E_{SS})$ dependences calculated for the solvation shells of particles and for a DMF molecule (considered as a solvated particle) are shown in Fig. 8. In all cases, except for the cation, the curves have a unimodal Gaussian shape. These dependences can be approximated by the function

$$W(E_{SS}) = C\exp\{-0.5[(E_{SS} - E_m)/\sigma]^2\}, \qquad (2)$$

where E_m is the position of the maximum, C is the height, and σ is the dispersion (width) of the distribution. The $W(E_{SS})$ function calculated for the molecules in the FSS of the Cs^+ cation has a more complex shape. It can be approximated by a sum of two Gaussians of the type (2).

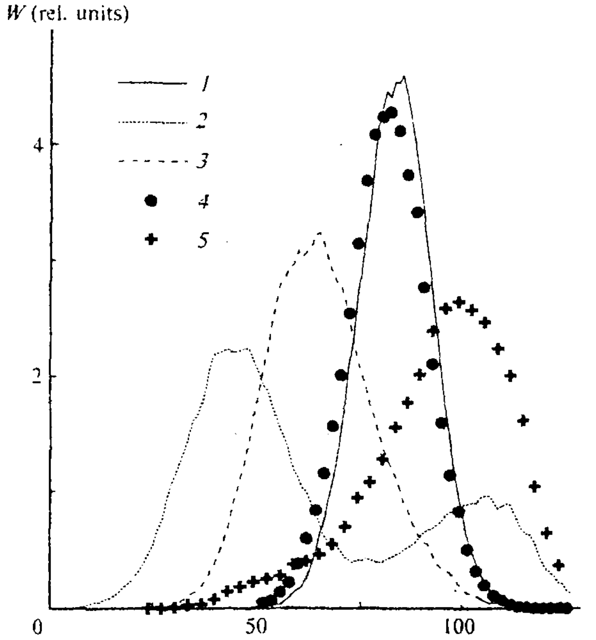

Fig. 8. Relative fractions W of the molecules in the FSS of Xe atoms (*1*), Cs^+ (*2*) and I^- (*3*) ions, DMF molecules (*4*), and around the Cs^+ ion in the spherical layer at 650 pm < r_{CsN} < 750 pm (*5*).

The coefficients in expression (2) for the molecules in the solvation shells of the particles and DMF molecule are listed in Table 2. As should be expected, in the Xe solution outside the FSS the distribution parameters coincide with the corresponding values calculated for pure DMF. Therefore, the spatial domain of the effect of the Xe atom is confined to the FSS size. Compared to pure DMF, the position of the maximum of the distribution for the FSS of the Xe atom is shifted toward higher energies (taking into account the sign), on the average, by ~4 kJ mol⁻¹. At the same time, the maximum value is ~2 kJ mol⁻¹ lower than the E_m values found for the FSS of the DMF molecule. Therefore, replacement of a Xe atom by one of the solvent molecules leads to a strengthening of the interaction between the DMF molecules nearest to the particle, which is responsible for stabilization of the solvent.

Unlike the neutral Xe atom, the ions also affect the energy characteristics of the molecules outside the FSS boundaries. The average interaction energy (E_m) and dispersion of the distribution increase. The strongest destabilizing field effect is observed in the FSS of ions. However, the E_{SS} energy of a fraction of DMF molecules in Cs^+ solution is appreciably lower than that in pure solvent. This is one of the reasons why the molecules in the FSS of the cation have an anomalous orientation. In fact, the low-energy states are characteristic of molecules in a spherical layer of thickness 100 pm (650 pm < r < 750 pm). It is these states that

Table 2. Parameters of function (2) approximating the distribution of DMF molecules over energy

Particle	Variant*	$-E_m$	σ	C
		kJ mol⁻¹		
DMF	*1*	81.77(3)	9.70(4)	4.29(1)
	2	87.72(2)	9.02(2)	4.61(1)
Xe	*1*	83.76(4)	9.04(4)	4.61(2)
	2	87.74(4)	9.00(4)	4.64(1)
I^-	*1*	64.2(2)	13.1(2)	3.17(2)
	2	87.61(4)	9.79(4)	4.25(1)
Cs^+	*1*	45.2(2), 102.2(3)	12.5(2), 14.9(4)	2.27(2), 0.93(2)
	2	86.32(4)	10.04(4)	4.12(1)

Note. The errors of determination of the last significant digit are given in parentheses. The distribution of molecules in the FSS of the Cs^+ cation was approximated as the sum of two Gaussians (2).

* Calculated for molecules in the FSS of particles (*1*) and for other DMF molecules (*2*).

make the major contribution to the minimum of the $U_{SS}(r)$ function and to the additional maximum of the $W(E_{SS})$ function of the cation (see Figs. 7 and 8). This confirms the assumption of the existence of a spatially localized domain with anomalous orientation of DMF molecules (see above).

Irrespective of their positions relative to the Cs^+ ion, on the whole, 10.4 out of 124 DMF molecules in each molecular configuration have low energies ($E_{SS} < -100$ kJ mol^{-1}). We have determined the structural and energy properties of this molecular subsystem. From the behavior of the functions shown in Fig. 9 it follows that the increased local densities of the molecules are concentrated in the range $550 < r_{CsN} < 850$ pm (see Fig. 9, *a*). Correlations in the spatial arrangement of the molecules nearest to one another increase as compared to pure DMF (see Fig. 9, *a*), which is due to a closer packing of these molecules. The subsystem under study is characterized by positive energies of the interaction with the cation (see Fig. 9, *b*). Therefore, in a dilute Cs^+ solution, the structural and energy properties of this subsystem differ from the properties of the vast majority of molecules.

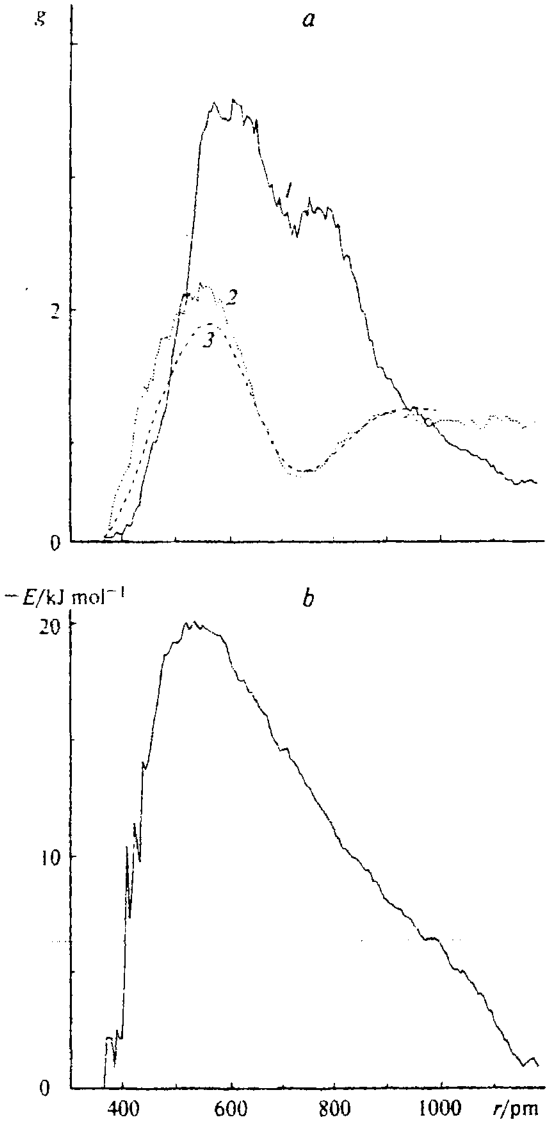

Fig. 9. Functions characterizing molecular subsystems with low energies of intermolecular interactions in Cs^+ solution ($E_{SS} < -100$ kJ mol^{-1}). Radial distribution functions (*a*): $g_{CsN}(r)$ (*1*) and $g_{NN}(r)$ (*2*, for low-energy molecules; and *3*, for all molecules); average energy of ion-molecule interaction (*b*).

The functions considered above characterize the *D*-structure of liquid. They were calculated using averaging over the ensemble. In the framework of the Monte Carlo method, it is also possible to analyze instantaneous molecular configurations (lists of coordinates). The scheme of possible arrangement of DMF molecules with anomalous orientation with respect to the Cs^+ ion is shown in Fig. 10. For an arbitrarily chosen molecular configuration in the FSS of the cation (*0*), we specified a molecule (*1*) of this type. Other molecules with anomalous orientation shown in Fig. 10 (*2*—*4*) are constituents of the nearest environment of molecule (*1*) and, taken together, form a spatially localized "domain." Like the first molecule, the second molecule (*2*) also belongs to the FSS of the cation (r_{02} = 619 pm). The distances between the third and fourth molecules and the cation are 838 and 910 pm, respectively.

The results of our analysis suggest that solvation cannot be adequately described only on the basis of the concept of successive changes in the structural and energy properties of the solvent in solvation shells. Even if one could allocate the solvation shells using any subjective criterion, the molecules formally belonging to

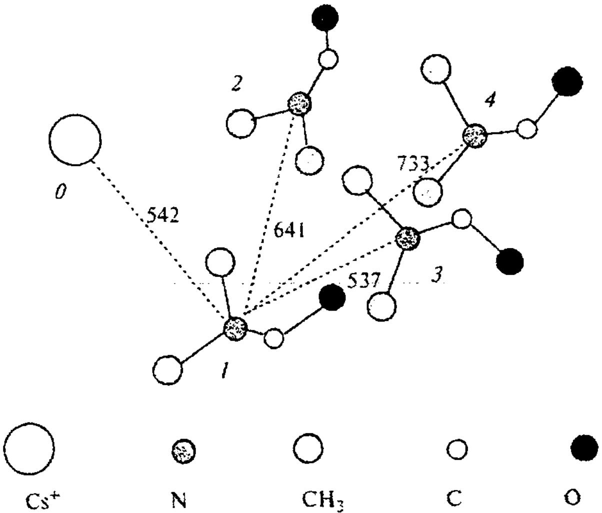

Fig. 10. Scheme of the arrangement of several DMF molecules with anomalous orientation with respect to the Cs^+ ion: Cs^+ ion (*0*) and DMF molecules (*1*—*4*). Figures denote the distances (*r*/pm) between the atoms connected by dotted lines.

different layers can have identical properties and form a spatially localized supramolecular subsystem.

As was mentioned above, anomalous orientation of the molecules with respect to the cation is explained by a gain in the energy of the DMF—DMF interaction and by peculiarities of the motion of the solvated ion. However, these reasons are not principal. Previously,[17] it has been shown that the structure of liquid DMF is first of all determined by the molecular shape and packing factors. Electrostatic interactions affect mainly the mutual orientation of the molecules. We will show that the spatial ordering of molecules in solutions is also due to their packing. Studies of solvation steric effects require knowledge of the supramolecular structure of the liquid. The results of calculations of molecular and energy distributions are inapplicable in this case, since they only indirectly characterize the peculiarities of molecular packing.

Methods of statistical geometry are widely used for analyzing the supramolecular structure of the liquid.[27—30] All space of a disordered system is divided into Voronoi polyhedra or Delaunay simplices. Rigorous mathematical treatment and unambiguity should be considered the advantages of these methods. However, the procedure for constructing the Voronoi polyhedra and analyzing their geometric characteristics is rather complicated, while the polyhedra obtained can have various shapes. It is known[28] that hundreds of topological types of polyhedra can be distinguished in the space of liquid. Periodic boundary conditions used in computer simulation methods can strongly affect statistical distribution of their geometric characteristics. The procedure for dividing the space into Delaunay simplices also has some drawbacks, since in the three-dimensional space the simplices are topologically equivalent tetrahedra. Primitivity of shape substantially reduces the number of possible structural characteristics.

Yet another procedure for analyzing the configurations of random closely packed systems has been proposed.[27] According to this procedure, the nearest particles were connected by lines and then characteristic polyhedra were distinguished in the three-dimensional network thus obtained. It turned out that only five types of polyhedra exist in such systems. These are tetrahedron, semioctahedron, trigonal prism, antiprism, and tetragonal dodecadeltahedron.

The above-mentioned methods of analysis of molecular configurations are based on the results obtained in studies of statistical distributions and topological properties of polyhedra, which are complex supramolecular aggregates. Closed cycles of "bonds," built of lines connecting neighboring molecules, are simpler elements of the supramolecular structural network. Each initial structural element comprises a small number of molecules united to form a cycle. Relative simplicity and topological diversity of the cycles facilitate calculations and interpretation of the results obtained. In addition, errors due to specific features of simulation procedure are decreased.

We compared topological properties of the networks built of lines connecting the nearest N atoms of DMF molecules in the FSS of the particles. The fluid of soft spheres (SS) was chosen as a system for comparison.[17] The interaction between SS was described by the Lennard-Jones (12—6) potential with parameters $\varepsilon = 16.72$ kJ mol^{-1} and $\sigma = 800$ pm. Previously,[17] it has been shown that the RDF of the SS system and those of the N atoms of DMF molecules ($g_{\mathrm{NN}}(r)$) are close.

The network of bonds was considered as a connected graph in which the cycles of bonds can be specified and enumerated. A cycle was taken as any closed circuit connecting adjacent vertices of the graph. According to calculations, topological parameters of the network, which occupies all space of the unit cell, remain virtually unchanged in solutions. Dissolved particles affect the supramolecular structure of the solvent in spatially localized domains. Therefore, we determined the properties of the networks built in the FSS of particles.

The scheme of the arrangement of the N atoms of the DMF molecules nearest to the cation in a randomly chosen molecular configuration is presented in Fig. 11. The lines connecting the nearest atoms form a polyhedron with triangular and quadrangular faces. Triangular cycles sharing an edge are united to form cycles with a larger number of vertices. A fragment of dodecadeltahedron consisting of five triangular cycles can be seen in the foreground. Each cycle can be assigned a point, namely, the geometric center of the cycle defined as the mean value of the coordinates of the vertices. Previously,[15—18,25,26] it has been shown that the concentrations of cycles and the RDF of their centers characterize topological properties of the network.

The properties of the networks were compared at an arbitrarily chosen value of the connectivity parameter of the network ($n = 3.66$), which determines the average

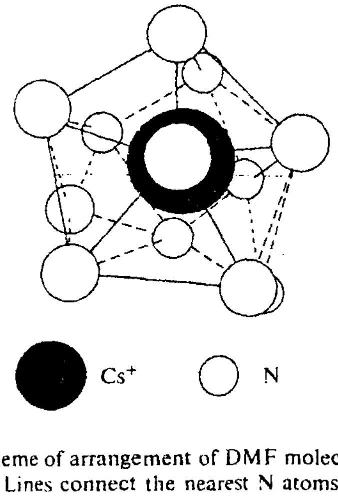

Fig. 11. Scheme of arrangement of DMF molecules in the FSS of particles. Lines connect the nearest N atoms.

Table 3. Concentrations of closed cycles in the networks built of lines connecting the nearest N atoms of DMF molecules (or spheres in the SS model) in the FSS of particles

Particle	r_{NN}/pm	c_3	c_4	c_5	c_6
DMF	710	0.70	0.76	1.28	2.63
MC	678	0.69	0.75	1.23	2.68
Xe	659	0.67	0.75	1.27	2.78
Cs^+	657	0.67	0.71	1.18	2.65
I^-	670	0.69	0.78	1.26	2.58

Note. c_i is the number of cycles per DMF molecule, r_{NN} is the distance between N atoms; at $r_{NN}^{exp} < r_{NN}$, the N atoms were considered bonded.

number of bonds per molecule. It should be noted that a too large n value leads to a drastic increase in the computing time, whereas a small n value leads to an increase in the statistical error. According to our experience, the choice of this parameter has virtually no effect on qualitative regularities of the formation of supramolecular structure.

The concentrations of closed cycles in the networks of bonds are listed in Table 3. They differ insignificantly for different models, which is evidence for closely related topological properties of the networks of solvation shells of particles (including DMF molecules) and the random closely packed system of SS. By definition (1), the RDF characterizes the degree of changes in the local numerical density of points (atoms, centers of cycles) in spherical layers with respect to a specified point. The molecule or the geometric center of the cycle is not at the FSS center. If only the points in a confined spatial domain (the FSS of solvated particles) are taken into account, their distribution in spherical layers will be anisotropic by construction. Hence, the RDF cannot be correctly normalized in this case. Nevertheless, if the functions are calculated using Eq. (1) under the same conditions, their relative changes will characterize peculiarities of the structure of the solvation shells.

The plots of the RDF of the centers of cycles, $G_{ij}(r)$, are shown in Fig. 12. Here, the indices denote the type of the cycle (the number of its vertices) for which the functions were calculated. Previously,[16] it has been shown that the positions of the RDF maxima correspond to the distances between the cycles in five polyhedra, while the individual contributions dependent on the mutual arrangement of the cycles can be judged from the ratio of their heights. For instance, the first G_{33} peak, which is less pronounced than the second peak, reflects domination of the octahedral and dodecadeltahedral types of coordination of triangular cycles over tetrahedral coordination. Without going into detailed analysis of the functions, mention may be made of the identical shape of all the curves presented, which is not accidental. The differences observed are minimum, while the greatest distortions of the shape of the G_{ij} functions characteristic of the pure solvent are observed upon solvation of the I^- ion.

It should be noted that all calculated topological parameters of the networks of the solvation shells of particles and of the SS system are close. The charge of solvated particle has the smallest effect on the topological properties of the network. The arrangement of DMF molecules in the solvation shells of particles is the same as that of soft spheres in the FSS of the central particle. Hence, structural properties of the solvation shells of particles are determined by the packing, whereas solvation steric effects play a dominating role in the formation of these shells.

The DMF molecule has no spherical symmetry. The principle of close packing imposes restrictions[17] on the distribution of the parameters characterizing mutual orientation of the molecules. This is the main reason for the appearance of molecules with anomalous orientation in the solvation shell of the Cs^+ ion. In the DMF molecule, the negatively charged N atom is shielded on three sides by positively charged C, C_t, and C_c atoms. There are three types of orientation of the solvent molecules in the FSS by the I^- anion and two types of their orientation by the Cs^+ cation. The probability of realization of each orientation type is mainly determined by the requirement of close packing of molecules. Strong electrostatic interactions between the ions and solvent molecules have little effect on the spatial arrangement of their centers (their packing).

Thus, computer simulation of Xe, Cs^+, and I^- solutions in DMF showed that the structural and energy manifestations of ionic solvation are much more complicated than those usually considered and taken into account in phenomenological models. Calculations based on the representation of thermodynamic functions as sums of the contributions of the components of the interaction potential do not always correctly reflect actual structural properties of a solution. Each solution is characterized by specific structural changes, which are determined both by the type of solvated particle and by the properties of the solvent. In phenomenological solvation models the repulsive interactions and kinematic and packing factors are inadequately taken into account.

Division of thermodynamic characteristics of a stoichiometric mixture into ionic components, which is based on the assumption of equal solvation enthalpies of large ions, is likely not always valid. Close values of solvation enthalpies of Cs^+ and I^- ions in DMF are due to mutual compensation of substantially different contributions of particular types of interactions in solutions.

Taking the solvation of Cs^+ ion as an example, we showed that the orientation of a fraction of solvent molecules in the nearest environment of the ion contradicts the existing ideas of the role of ion-dipole interactions in solutions. Two structurally and energetically different molecular subsystems were allocated. The presence of several structural states of the molecules makes it impossible to describe solvation phenomena in terms of the *D*-structure with unimodal distribution of parameters.

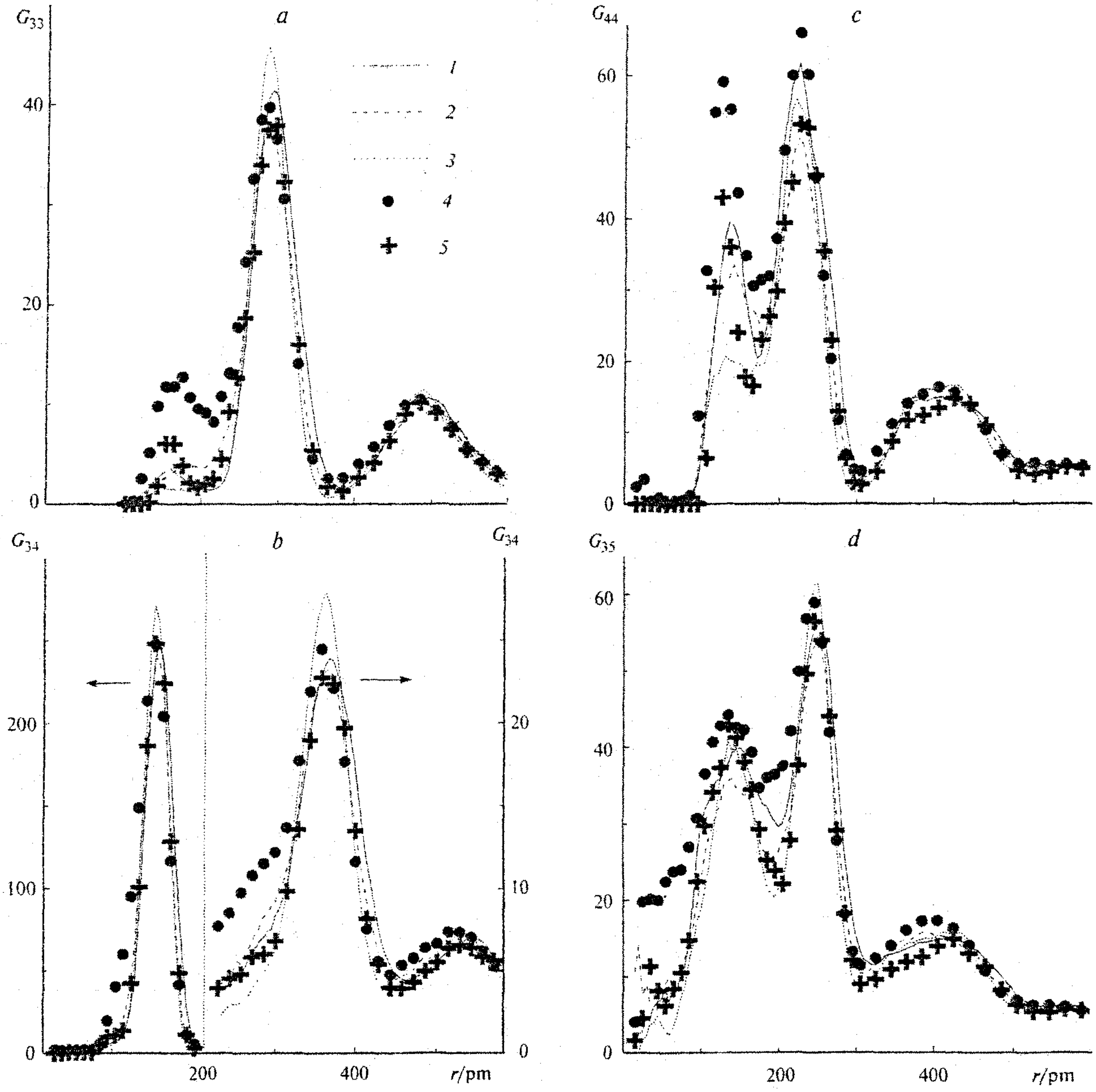

Fig. 12. Radial distribution functions $G_{ij}(r)$ of geometric centers of the closed cycles of bonds in the networks of nearest neighbors in the FSS of particles (*i,j* are the numbers of vertices in the cycle) *ij* = 33 (*a*), 34 (*b*), 44 (*c*), 35 (*d*): DMF (*1*); Xe (*2*); Cs^+ (*3*); I^- (*4*); and SS (*5*).

In this work, taking the solutions studied as examples, we have shown that the assumptions of gradual change in the solvent properties in the sequence of solvation shells are contrary to facts. No indication was found that makes it possible to allocate the second solvation shell of particles. The dissolved particle affects structural properties of the solvent in a spatially localized domain. For the Cs^+ ion, the distribution of solvent molecules belonging to different structural states is not spherically symmetrical. Solvation steric effects and packing factors affect the molecular arrangement in the solvation shells of particles to the greatest extent and are the reasons for the appearance of two structural states of DMF molecules in the solvation shell of the Cs^+ ion. The charge of the particle determines the energy and kinematic rather than structural characteristics of solvation.

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