Coordination polyhedra of hydration shells of Na^+ and K^+ cations in aqueous solutions

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Simulation of the hydration of Na^+ and K^+ cations in dilute solution was performed by the Monte Carlo method. A novel approach to structural analysis of hydration shells of ions was developed. Specific sets of coordination polyhedra formed by water molecules of the first coordination sphere were found. Structural and energy characteristics of hydration were calculated. The effect of Na^+ and K^+ cations on the structure of the network of H-bonds and mobility of water molecules in hydration shells was studied.

Key words: hydration, cations, structure, coordination polyhedra, hydrogen bonds, simulation, Monte Carlo method, aqueous solutions.

To gain an insight into the mechanisms of various physicochemical processes in solutions and develop realistic models of hydrated ions, detailed information on the structure of their water shells is required. Studies in this area are associated not only with computational difficulties, but also with semantic problems that are common to description of the structure of amorphous solids. Definitions of the concept of the "structure of liquids" that is widely used in scientific practice are too subjective and are of a rather philosophical nature.[1,2] In essence, structural analysis implies a search for specific variants of realization of "spatial ordering" postulated by definitions and establishment of corresponding quantitative characteristics.

For instance, one-, two-, or three-layer shells of water molecules, revealed by various experimental methods, are usually mentioned for ions in solutions. Depending on the procedure used, the hydration number or the coordination number (*CN*) serve as measured structural characteristics. More detailed information on the structure of hydration shells of ions in solutions cannot be obtained by traditional methods. Further progress in this area requires a close interrelation of experimental methods and theoretical approaches using computer simulation.

In recent decades, computational methods of statistical-geometric analysis have been widely used in studies of the structure of liquids and amorphous solids.[3] In this case Voronoi polyhedra or Delaunay simplexes are constructed to perform the structural analysis of a system of points corresponding to the centers of mass of atoms or molecules. This type of approach is indispensable in studies of the properties associated with the shape and size of the cavities occupied by species. At the same time, only indirect information on regularities of the mutual arrangement of water molecules around the ion can be obtained using these methods.

A method we have developed for studying the spatial organization of aqueous solutions and clusters is based on the statistical-geometric analysis of representative samples of molecular configurations generated using the Monte Carlo or molecular dynamics procedures. In this case each configuration is associated with a general graph whose vertices and edges correspond to solvent species and lines connecting adjacent species, respectively. The latter are determined using a geometric criterion based on the radial distribution functions. Previously,[4] this approach was successfully used in studies of conformational peculiarities of double helix DNA in aqueous solution. To describe the structure of hydration shells of ions (and, in the future, also simple molecules), we suggest using sets of structural elements ordered according to their statistical weights, *viz.*, coordination polyhedra (CP) and their fragments, which explicitly represent the topology of intermolecular contacts in the hydration shell of the ion.

Calculation procedure

Simulation of hydration of Na^+ and K^+ cations. Computer experiments were performed using model systems containing a cation (a Na^+ or K^+ cation) and 256 water molecules in a cubic unit cell with an edge length of 19.72 Å or 19.734 Å for Na^+ or K^+ cations, respectively.[5] The cation was located at the cube center. Periodic boundary conditions were imposed only on the water molecules. The energies of "water—water" and "water—cation" interactions were calculated using the atom-atom potential functions specially developed[5,6] for this type of systems. The contributions of "water—water" and "water—cation" interactions between adjacent cells were estimated by the minimum image prescription.[7] The interactions between cations located in neigh-

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boring cells were ignored, since their positions remained unchanged in the course of calculations.

The energy and structural characteristics of hydration of the cations were calculated using representative samples of molecular configurations of the unit cell obtained by applying the Monte Carlo sampling algorithm.[8] In practice, the procedure was as follows. At a given temperature T (in this work, at $T = 300$ K), a random change in the position of a water molecule (elementary trial) resulting in a change in the system energy from E_1 to E_2 was accepted provided that $E_2 \le E_1$ or, otherwise, that $\exp[(E_1 - E_2)/(kT)] > \xi$, where ξ is a random number uniformly distributed on the (0,1) interval and k is the Boltzmann constant. If the trial state was rejected, the preceding configuration of water molecules was again included in the sample.

The elementary trial consisted of a displacement of a water molecule by a value of $\delta(1 - 2\alpha_i)$ Å along each of the coordinate axes (i) and its rotation about a randomly chosen axis passing through the center of the O atom by an angle of $\gamma(1 - 2\beta)$ rad, where α_i and β are random numbers uniformly distributed on the (0,1) interval. The δ and γ values were chosen in such a way that no more than half of new configurations could be rejected in the course of trials. For the systems under consideration, $\delta = 0.125$ Å and $\gamma = 0.125$ rad. By repeated use of this procedure a totality of configurations was generated that would form a canonical Gibbs ensemble (in our case, the NVT-ensemble) in the limiting case ($n \to \infty$, where n is the number of trials). For this totality of configurations, the probability of the choice of a configuration with an energy E is proportional to the Boltzmann factor, $\exp[-E/(kT)]$, and transitions between configurations have the properties of Markovian chains.

Each computer experiment was performed in two stages. First, the initial fraction of the Markovian chain of 50 thousand trials (per water molecule) required to achieve thermal equilibrium for the systems under study was excluded from consideration. Then, Markovian chains of 2 million trials per water molecule were generated and the energy and structural characteristics were calculated.

Software and algorithms. The main program consists of the main module used for generating molecular configurations according to the Monte Carlo algorithm, the module A that is used for analyzing the structure of a hydration shell of a cation, and the service module B that operates as the simplest database for storage and processing of structural information.

Operations in module A:

1. Selection of the water molecules that form the first coordination sphere (FCS) of the ion using a geometric criterion (falling within a sphere of radius R_1 circumscribed about the ion). The R_1 value corresponds to the position of the first minimum of the radial distribution function (RDF).*

2. Finding pairs of vertices that form the CP edges. The formation of a list of adjacent vertices using a geometric criterion (the molecules in the FCS located at distances no longer than the limiting distance (R_c) at which the vertices are considered to share an edge) and determination of the vertex multiplicity (the number of issuing edges) for each vertex.

3. Construction of a numerical index for the found CP. The numerical index is an array of numbers in which the first element is the number of vertices of multiplicity 0, the second element is the number of vertices of multiplicity 1, *etc.* For instance, the indices for a prism, an octahedron, and a cube are 0006, 00006, and 0008, respectively.

Operations in module B:

1. Checking the CP index of a newly accepted configuration for coincidence with the CP indices for previously processed structures.

2. Writing of a record with information on a new CP in the case of noncoincidence.

3. An increment of the counter for the given CP by 1.

4. Activation of an additional database containing information on the CP fragments. This database was specially designed for correct processing of data in those very rare cases where the CP is disintegrated into several isolated fragments.

The program output is the list of CP indices sorted according to their statistical weight factors in the computer experiment.

Unfortunately, this procedure has some drawbacks. For instance, the algorithm of the search for the edges can miss a pair of vertices sharing an edge longer than R_c or, *v.v.*, include lines inside the CP in the list of edges. The results appeared to be more sensitive to the choice of the R_1 rather than the R_c parameter. For instance, decrease in R_1 from 3.68 Å (*CN* 8.52) to 3.4 Å for systems containing K$^+$ cations leads to the *CN* 7.7, which is closer to the data obtained for crystal hydrates; however, the number of incomplete structures (the absence of one vertex is clearly seen in computer visualized models) among the CP sharply increases in this case. In addition, in some instances the indexing algorithm can not distinguish topologically inequivalent structures. As was shown by repeated experiments, these situations are very rare and make no appreciable corrections.

For each new type of CP, the coordinates of the vertices are stored in a special file for controlling the operation of the program and for visual analysis of the structure. Using an additional software module, it is possible to display the model of each CP or to use the corresponding data stored in the PDB format as input data for molecular graphics software.

Results and Discussion

Coordination numbers and coordination polyhedra. One of the key concepts of the theory of electrolyte solutions is the coordination number of ions, *i.e.*, the number of solvent molecules forming the FCS. Usually, the *CN* is defined as the average number of water molecules in a sphere of radius R_1 circumscribed about the ion. The RDF parameters for real solutions are determined using diffraction methods. For the systems described above this function can be easily calculated in the course of computer simulation (Fig. 1).

As can be seen in Fig. 1, the region of the first RDF minimum is a rather lengthy (>0.5 Å) plateau. For the Na$^+$ cation the RDF values in this region are close to zero and at $R_1 = 3.19$ Å the *CN* is 6.7±0.15. For the K$^+$ cation the RDF values in the vicinity of the first minimum are rather high; therefore, the error of the *CN* determination can amount to 11% (at R_1 = 3.68 Å the *CN* is 8.52±0.9). Analogous conclusions can be drawn based on the data of X-ray analysis of crystal hydrates (see, *e.g.*, references in the recently reported study[5]), *viz.*, usually, the *CN* (taking into account nonaqueous ligands) for Na$^+$ cations is 6, whereas *CN* values of 6 and 8 are most characteristic of K$^+$ cations.

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* Physical meaning of the RDF is the relative probability of location of the O atom of a water molecule at a distance R from the ion.

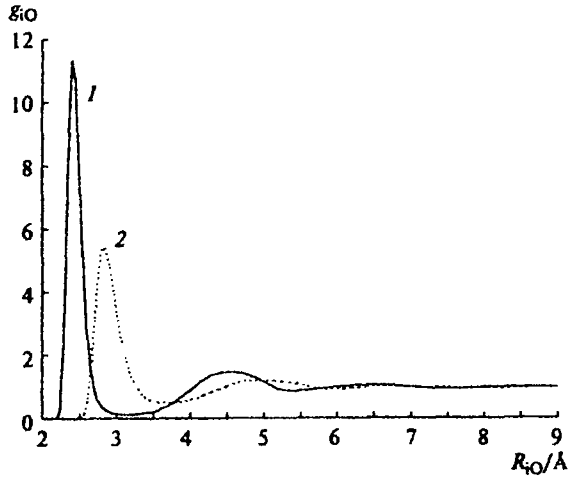

Fig. 1. Radial distribution functions (g_{iO}) of oxygen atoms of water molecules around Na^+ (*1*) and K^+ (*2*) ions.

Knowing the *CN* of an ion, it is impossible to confidently reconstruct the spatial arrangement of the atoms (molecules) in its FCS even for crystal hydrates. In such cases, it is convenient to use the concept of a "coordination polyhedron" of the ion. The oxygen atoms of water molecules (O_w) or other ligands and the lines connecting the adjacent vertices are associated with CP vertices and edges, respectively. The choice of criterion for revealing the edge is nontrivial and is based on the analysis of the distance distribution between O_w atoms of the water molecules forming the FCS.

The families of such distributions for Na^+ and K^+ ions calculated using representative samples for different *CN* are shown in Fig. 2, *a* and 2, *b*, respectively. As can be seen, the distances between adjacent vertices (CP edges) are localized in the range from 2.5 Å to R_c. The R_c values for Na^+ and K^+ cations are 4.44 and 4.68 Å, respectively. The R_c values were chosen taking into account first of all the distributions of the most often realized *CN* values (6—7 for Na^+ and 8—9 for K^+ cations). A peak in the range of short distances corresponds to the formation of hydrogen bonds (H-bonds) between neighboring water molecules in the FCS.

According to the data of X-ray analysis of crystal hydrates, an octahedron is the most typical CP for the Na^+ cation; for the K^+ cation it is an octahedron and a cube (often a cube "twisted" by 45°). In solution, the *CN* of an ion continuously changes due to thermal motion. Because of this, the description of the structure of the cation hydration shell requires enumeration of a variety of CP having whimsical shapes, most of which will occur very rarely. Computer simulation makes it possible to analyze hundreds of millions of molecular configurations in a reasonable time and to reveal the *CN* and CP that are the most characteristic of a given cation.

Sets of coordination polyhedra. In the course of computer experiments we established that there are more than 180 types of CP for Na^+ and over 1700 types of CP for K^+ cations in the sets of CP in the FCS of hydration shells of these cations. However, more than two thirds of these CP are realized for less than 15% of the configurations corresponding to high *CN* (Tables 1 and 2). Visual analysis of several dozen models of CP using molecular graphics software revealed that many of them differ only in positions of pseudoedges (the lines connecting pairs of vertices are inside the CP). At the same time, it was established that several types of CP are realized much more often than other CP types. This

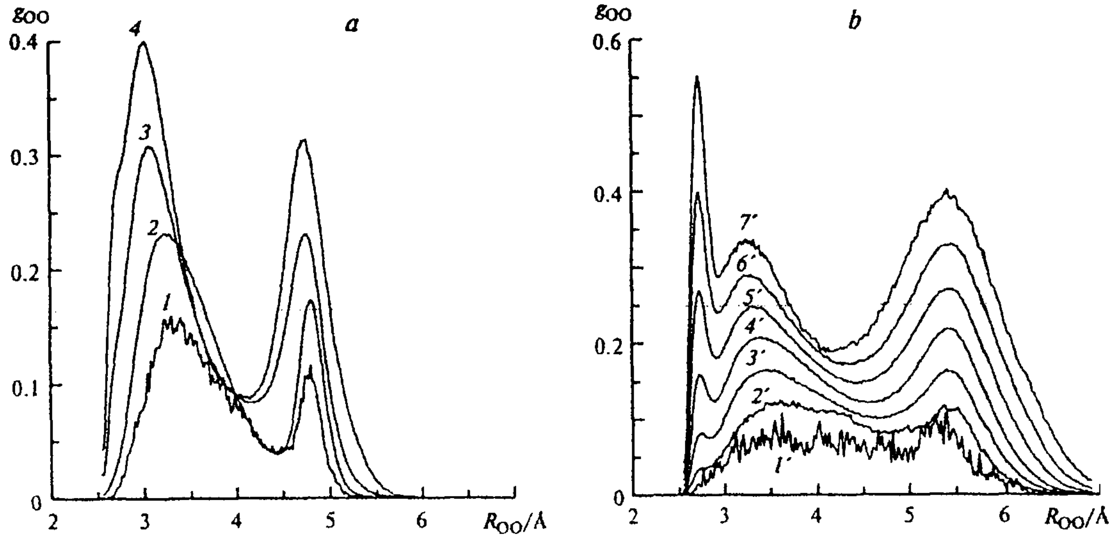

Fig. 2. Families of distributions (g_{OO}, for different *CN*) of distances between the oxygen atoms of water molecules (R_{OO}) forming the FCS of Na^+ (*a*) and K^+ (*b*) cations: *CN* = 5 (*1*, *1'*); 6 (*2*, *2'*); 7 (*3*, *3'*); 8 (*4*, *4'*); 9 (*5'*); 10 (*6'*); and 11 (*7'*).

Table 1. Structural characteristics of the FCS of the Na$^+$ cation

Parameter	Values for different *CN*				
	5	6	7	8	9
P (%)	0.15	35.3	56.6	8.3	0.1
N_{CP}	7	19	49	59	49
R_{iO}/Å	2.44	2.46	2.52	2.56	2.63
R_w/Å	3.54	3.45	3.37	3.29	3.20
D	7.93	11.79	15.26	19.0	23.0
F	5.93	7.79	10.26	13.0	16.0
H	0.11	0.38	1.62	3.34	5.18
H/D (%)	1.4	3.2	10.6	17.6	22.5

Note. P is the fraction of the FCS configurations for a given *CN*; N_{CP} is the number of revealed CP types; R_{iO} is the average distance between the ion and the O atom of the water molecule in the FCS; R_w is the average distance between the O atoms of water molecules in the FCS of the cation; D is the average number of CP edges; F is the average number of CP faces; and H is the average number of H-bonds between the water molecules in the FCS.

Table 2. Structural characteristics of the FCS of the K$^+$ cation

Parameter	Values for different *CN*							
	5	6	7	8	9	10	11	12
P (%)	0.1	1.4	12.5	36.0	34.5	13.4	2.2	0.1
N_{CP}	13	41	92	199	326	446	447	251
R_{iO}/Å	2.88	2.91	2.95	2.99	3.03	3.07	3.11	3.12
R_w/Å	3.89	3.74	3.68	3.62	3.56	3.52	3.49	3.45
D	5.98	9.27	12.67	16.36	20.3	24.35	28.71	33.06
F	2.98	5.27	7.67	10.36	13.3	16.35	19.71	23.06
H	0.11	0.53	1.13	2.16	3.55	5.15	6.97	8.83
H/D (%)	1.8	5.7	8.9	13.2	17.5	21.1	24.3	26.7

Note. For the notations of the parameters, see note to Table 1.

conclusion was confirmed by additional calculations of chains of 2 million trials per water molecule performed twice for each cation.

Four types of CP in the set of coordination polyhedra of the FCS of the Na$^+$ cation have the highest statistical weight factors. Water molecules are most often arranged to form pentagonal bipyramids (Fig. 3, *b*, 37% of configurations, *CN* 7) or octahedra (Fig. 3, *a*, 27% of configurations, *CN* 6). Coordination polyhedra of the type "trigonal prism+tetragonal pyramid" (Fig. 3, *c*, *CN* 7) occur much less often (9% of configurations) and the structures shown in Fig. 3, *d* are very rare (3.5% of configurations, *CN* 8).

The set of coordination polyhedra of the FCS of the K$^+$ cation is larger than in the preceding case. There occur a "twisted cube+pyramid" (Fig. 3, *g*, 13% of configurations, *CN* 9); the CP shown in Fig. 3, *d* (12% of configurations, *CN* 8); a "prism+two pyramids" (Fig. 3, *e*, 9% of configurations, *CN* 8); a "prism+three pyramids" (Fig. 3, *h*, 6% of configurations, *CN* 9); a "hexahedron+two pyramids" (Fig. 3, *i*, 4% of configurations, *CN* 10); a "trigonal prism+tetragonal pyramid" (Fig. 3, *c*, 3% of configurations, *CN* 7); a pentagonal bipyramid (Fig. 3, *b*, 2% of configurations, *CN* 7); and a cube "twisted by 45°" (Fig. 3, *f*, 1% of configurations, *CN* 8).

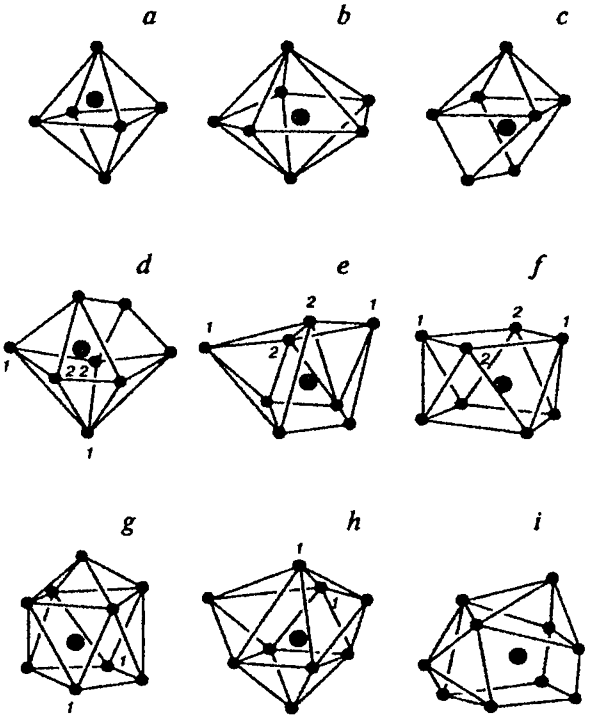

Fig. 3. Models of the most typical CP (*a*—*i*, see text). The O atoms of water molecules (connected by lines) and cations at the centers are shown.

The configurations shown in Fig. 3 reflect only statistical regularities of the spatial arrangement of the O atoms of water molecules in the FCS. At certain instants one type of CP is transformed into other types due to thermal motion of solution components. Two types of such transformations can be distinguished, *viz.*, transformations occurring with and without change in the *CN*. It was found that the first type (transformation of the octahedron into the pentagonal bipyramid *via* the formation of the intermediate structure shown in Fig. 3, *c*) is mainly realized in the hydration shell of Na$^+$ cations, whereas both these types are equiprobable for K$^+$ cations. This means that in the case of Na$^+$ cations the cycle of CP transformations describes a possible mechanism of exchange of water molecules between the first and second hydration shells. The monomolecular type of exchange process for the hydration shell of Na$^+$ cations was also pointed out in the study concerned with hydration simulation by the method of molecular dynamics.[9]

For the K$^+$ cation, changes in the CP structure often occur with conservation of *CN*. For instance, the structures shown in Figs. 3, *d—f* are easily transformed into one another as the *1—1* and *2—2* distances between pairs of O_w atoms vary, while the CP shown in Fig. 3, *g* is transformed into structure 3, *h* as the *1—1* distance varies. In turn, transformations with a change in the *CN* occur due to addition of one more vertex (*e.g.*, structure 3, *g* is formed from 3, *f*, while structure 3, *h* is formed from 3, *e*) or even two more vertices simultaneously, which in the case of the K^+ cation is favored by high (in contrast to the Na^+ cation) probability of the presence of water molecules of the second hydration sphere at distances close to R_c.

If the *CN* and the corresponding average number of CP edges ($D = (CN \cdot D_l)/2$, where D_l is the average multiplicity of a CP vertex) are known, it is possible to estimate the average number of CP faces (*F*) for a given *CN* ($V = CN$, *i.e.*, the number of CP vertices) using the Euler formula ($V - D + F = 2$). The *F* values thus calculated (see Tables 1 and 2) are in good agreement with the number of faces for coordination polyhedra in the corresponding CP sets shown in Fig. 3. It should be noted that the use of the Euler formula is not quite correct for high *CN* (over 8 and 10 for Na^+ and K^+, respectively), since the CP contain relatively large numbers of internal edges. In addition, underestimated (as compared to corresponding values for the Na^+ cation) values of the number of faces in coordination polyhedra characterized by low *CN* (7 and lower) for the K^+ cation indicate a considerable fraction of "incomplete" polyhedra. A detailed analysis has shown that most of these structures are artifacts, which is explained by errors of the selection of the nearest neighboring species when using the geometric criterion (see Calculation procedure). At the same time, the fraction of configurations corresponding to nontypical *CN* for a given cation is insignificant (see Tables 1 and 2); therefore, the use of geometric criteria makes it possible to obtain quite reliable results.

Peculiarities of the structure of hydration shells of cations and hydration. The average ion—O_w distance (R_{iO}) monotonically increases (see Tables 1 and 2) and the distance between neighboring water molecules (R_w) in the FCS monotonically decreases as the *CN* of an ion increases. It should be noted that the root-mean-square deviations for corresponding groups of distances (0.1 and 0.2 Å for the R_{iO} distance and 0.5 and 0.6 Å for the R_w distance for Na^+ and K^+ cations, respectively) are much larger than the increase (or decrease) in the R_{iO} or R_w values due to changes in the *CN*. Such large root-mean-square deviations for the R_w distances indicate a possibility of large fluctuations of the local density of the water molecules in the FCS (*e.g.*, at a certain instant the number of molecules on the left of the ion can be twice as large as that on the right). In addition, the fraction of short (shorter than 3 Å) CP edges substantially increases as the *CN* increases, which is particularly clearly seen in Fig. 2, *b*. As was shown by statistical-geometric analysis, this is associated with the increase in the probability of the formation of H-bonds* between the water molecules in the FCS of the cation.

The average numbers of H-bonds (*H*) in the CP and their proportion (*H/D*) in the average number of CP edges (*D*) at corresponding *CN* are listed in Tables 1 and 2 for different *CN* of Na^+ and K^+ cations. Noteworthy is that the *H/D* value for the Na^+ cation is, as a rule, larger than for the K^+ cation at the same *CN* despite the stronger electrostatic field that causes perturbations in the FCS in the vicinity of Na^+ cations, which is noticeable for *CN* 5 or 6. The higher ability of K^+ cations to destroy the network of H-bonds in the FCS that manifests itself in such a way is due to a purely geometric factor, *viz.*, the radius of the defect surrounded by water molecules is so large that the R_w distances between the neighboring species in the FCS rarely fall within the limits corresponding to the length of the H-bond. On the quantitative level, the situation is quite the reverse, *viz.*, the average number of H-bonds in the FCS of the Na^+ cation is 1.33, whereas it is equal to 3.0 in the FCS of the K^+ cation because of the fact that the average *CN* of the K^+ cation (8.52) is substantially larger than that of the Na^+ cation (6.7).

Analysis of the topology of the network of H-bonds in the FCS of cations performed using the calculation procedure described above showed that 29% of the FCS configurations of the Na^+ cation have no H-bonds, one H-bond is formed in 31% of cases, two H-bonds are formed in 24% of configurations (slightly more than half of them are formed by different pairs of water molecules and the remaining fraction consist of chains of three molecules), and three H-bonds are realized in 11% of configurations (among them, half consist of those containing simultaneously a chain of three molecules and a pair of molecules and 23% are chains of four water molecules). At the same time, for the K^+ cation no H-bonds were found only in 5% of the FCS configurations, one H-bond is formed in 15% of configurations, two H-bonds are formed in 22% of configurations (2/3 of them are formed by different pairs of molecules and 1/3 are formed by chains of three molecules), three H-bonds are formed in 22% of configurations (about half of them are formed by structures of the "pair+chain of three molecules" type, 21% of bonds are formed by three individual H-bonds, and 18% of them are formed by chains of four molecules), four H-bonds are formed in 16% of configurations (by structures of the "chain of three molecules+two individual bonds" type (28%), "one bond+chain of four molecules" type (23%), and by sets of two individual chains of three molecules (12%)), 10% of configurations contain five H-bonds, six H-bonds are formed in 5% of configurations, *etc.*

The calculations also showed that each water molecule in the FCS of Na^+ cation forms, on the average, 0.4 bond with neighboring species in the CP (67% of

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* The H-bonds were revealed using the geometric criterion.[6]

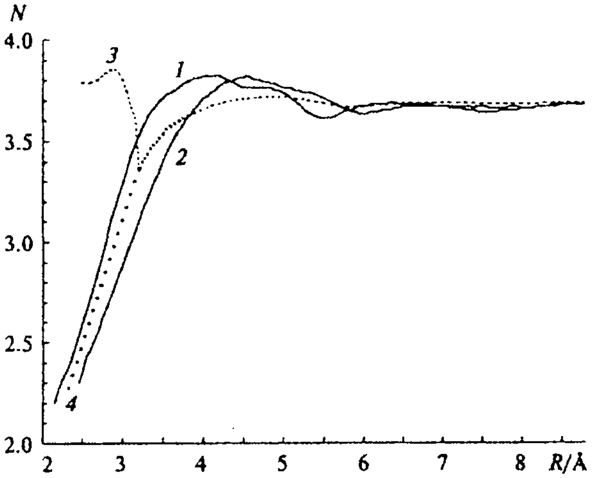

Fig. 4. Dependences of the average number (N) of hydrogen bonds formed by a water molecule on the distance (R) from a Na$^+$ (*1*) or K$^+$ (*2*) cation or on the distance from another molecule in pure water (*3*). Hypothetical extrapolation of curve *3* (*4*).

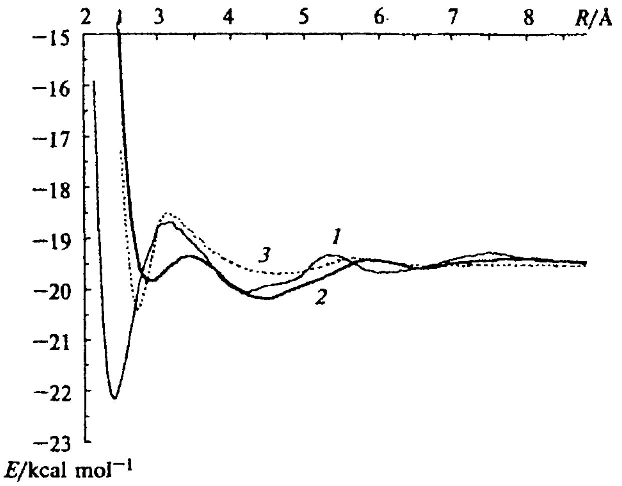

Fig. 5. Dependences of the potential energy (E) of a water molecule on the distance (R) from a Na$^+$ (*1*) or K$^+$ (*2*) cation or another water molecule (*3*).

molecules form no H-bonds at all, 27% of molecules form one H-bond, and 4% of them form two H-bonds). For the FCS of the K$^+$ cation this value is equal to 0.7 (46% of molecules form no H-bonds with one another, 40% of molecules form one H-bond, and 12% of molecules form two H-bonds). The water molecules that form the FCS are characterized by intense formation of hydrogen bonds with the molecules of the second coordination sphere (SCS). As can be seen in Fig. 4, the total number of H-bonds formed by one water molecule (N) never is less that 2.2 even in the case of shortest distances to the cation. It is noteworthy that, according to this plot, water molecules in the FCS and SCS are indistinguishable and occupy a common space (of radius 5.5 or 6.1 Å for Na$^+$ or K$^+$ cations, respectively) containing up to 26 or 33 molecules around the Na$^+$ or K$^+$ cation, respectively.

For comparison, the dependence of the number of H-bonds formed by one water molecule located at a distance R from another water molecule in the system without ions is also shown in Fig. 4. At short R, this curve drastically differs from corresponding curves for the systems with cations, which is due to the formation of an additional H-bond with the water molecule located at the origin. Otherwise the curve of "self-hydration" of the water molecule is very similar to the dependences for hydration shells of cations. Moreover, by extrapolating N values to the region of short R in a hypothetical case where the central molecule is forbidden to contribute to the N value we found a line passing between the dependences for the cations. The fact that the curves for Na$^+$ and K$^+$ in this case appear to lie on opposite sides of this "ideal" line is not accidental but fundamental by its nature. These cations are the classical pair to illustrate the phenomena of positive (Na$^+$) and negative (K$^+$) hydration.[10]

The dependences of the potential energy of a water molecule (with inclusion of "water—cation" and "water—water" interactions) on the distance R from the cation (or another H_2O molecule) are shown in Fig. 5. As can be seen, the average activation energy of transfer of a water molecule from the first coordination sphere to the second coordination sphere (the energy difference between the first maximum and the first minimum) for the Na$^+$ cation is ~1.5 kcal mol^{-1} higher, while for the K$^+$ cation it is ~1.5 kcal mol^{-1} lower, than for pure water. Moreover, the energy barrier to the transfer between the coordination spheres of the K$^+$ cation is close to the average kinetic energy of the water molecule at $T = 300$ K (based on the $3RT$ value), which, in turn, favors increasing mobility of water molecules in the hydration shell of K$^+$ cations. These distinctions, on the whole, reflect two types of behavior of water molecules in the vicinity of ions.

In conclusion it should be noted that it is the ratio of the contributions of "water—cation" and "water—water" interactions that is the reason for such different structural and energy properties of hydration shells of Na$^+$ and K$^+$ cations.

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