Atom-atom potential functions for simulation of DNA—counterion interaction in aqueous solution

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A system of atom-atom potential functions for computer simulation of aqueous solutions of DNA fragments and counterions was developed. Hydration of Na^+, K^+, and dimethyl phosphate (DMP^-) ions was simulated by the Monte Carlo method. The obtained energy and structural characteristics of the solutions reproduce well the experimental data and are in good agreement with the results of *ab initio* calculations carried out by other authors.

Key words: potential functions, computer simulation, DNA, ions, solution, hydration, Monte Carlo method.

Computer simulation is widely used in studying various physicochemical processes on the atomic-molecular level. Nevertheless, such program packages as AMBER [1] are better suited for studying complex molecular systems since large sets of coefficients of the potential functions (hereafter PFC) are used to take into account all kinds of pair combinations of the atoms. At the same time, the use of the PFC sets specially designed for simulation of certain types of molecules (*e.g.*, fragments of nucleic acids) yields more reliable results. Thus, the system of atom-atom potential functions[2] for simulation of hydration of nucleic acids we developed in 1984 has been successfully used currently.[3] In this work we extended this set of PFC by including potentials of the interaction with the phosphate anion and Na^+ and K^+ ions.

The DNA interaction with ions is one of the most important factors determining the local structure and general conformation of the DNA double helix in solution and *in vivo*. Therefore, the potential functions used in computer simulation must reproduce the known experimental data with high accuracy. Like previously,[2,3] the PFC development for each new subsystem includes two stages. First, the potential functions are tested using the methods of potential energy minimization and the Monte Carlo method on bimolecular systems (one ion and one water molecule, one ion and one nitrogen base, *etc.*). This allows one to reliably control the agreement between the calculated and experimental values of interatomic distances and energy. Then, the Monte Carlo simulation of diluted aqueous solution is carried out to obtain the values of coordination numbers, hydration energies, *etc.*, and compare them with experimental values.

Calculation procedure

The parameters of carbonyl oxygen atom[4] and those of aromatic carbon atom[4] were used as the first approximation for Na^+ and K^+ ions, respectively. Only the coefficients describing the interactions between the ions and oxygen and pyridine nitrogen atoms (N3, Table 1) were changed in further refinement.

The geometry of molecules of water and nitrogen bases (9-methyladenine, 9-methylguanine, 1-methylthimine, 1-methylcytosine), partial charges on their atoms, and the PFC were described previously.[2,3] The *N*-methylated nitrogen bases were chosen since the corresponding nitrogen atom in nucleotides is *N*-glycosylated. The dimethyl phosphate anion (DMP^-) was taken as a convenient prototype for investigating the properties of the structural unit of charged polynucleotide sugar-phosphate backbone.[5] The fixed *gg*-conformation[6,7] corresponding to the geometry of the sugar-phosphate backbone of the DNA double helix was chosen for DMP^-. The atomic charges of the phosphate group[8] and PFC[4] were used as the first approximation.

The Monte Carlo simulations of the hydration of individual ion (including DMP^-) at infinite dilution was performed at 300 K using the standard procedure described previously[2,3] (using the Metropolis algorithm in the NVT ensemble). The water—cation systems contained 256 water molecules in the unit cell while water—DMP^- systems contained 400 water molecules. To ensure the proper density of each system, the unit cell volume was calculated as the sum of partial volumes of all its components at given temperature and at a pressure of 1 atm. The values of partial volumes for water molecule, Na^+ ion, K^+ ion, and DMP^- anion used in the calculations were 30 Å^3, −11 Å^3, 5 Å^3, and 100 Å^3, respectively. The experimental data for the cations reported in Ref. 9 are −11.69 Å^3 (Na^+) and 5 Å^3 (K^+) (recalculated from mL mol^{-1}). The same value (−11 Å^3) for Na^+ was used in Ref. 10. The partial DMP^- volume was found as the difference between the corresponding volumes of the Na^+—DMP^- ionic pair (53.1 mL mol^{-1})[5] and the Na^+ ion. The hydrated ion was

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located at the center of unit cell. Periodic boundary conditions were imposed on the system; the minimum image prescription was used for energy calculations. The initial fraction of the Markovian chain of 50 thousand trials (calculated per water molecule) was excluded to achieve the thermodynamic equilibrium for each system under study. After this procedure, the average energies and structural characteristics of systems for chains of length 2 million (ion+256 water molecules) or 500 thousand (DMP^-+400 water molecules) trials per water molecule were calculated.

The dependences of various energy characteristics of the systems on the ion—water distance, DMP^-—water distance, *etc.* (Figs. 1 and 2) were plotted using the values averaged in the course of the Monte Carlo procedure over short (0.02 Å for water—cation systems and 0.05 Å for other systems) successive intervals. The binary (radial) distribution functions were calculated using an analogous approach.

Results and Discussion

Water—ion systems

The interaction between the water oxygen (O_w) and the Na^+ ion was described using the potential functions of the type 1—12—10:

$$U_{ij} = q_i q_j / r_{ij} + B_{ij} / r_{ij}^{12} - A_{ij} / r_{ij}^{10},$$

while all the other (O_w—K^+ and H_w—ion)* interactions were described using those of the type 1—12—6:

$$U_{ij} = q_i q_j / r_{ij} + B_{ij} / r_{ij}^{12} - A_{ij} / r_{ij}^{6}.$$

* O_w and H_w are oxygen and hydrogen atoms of a water molecule.

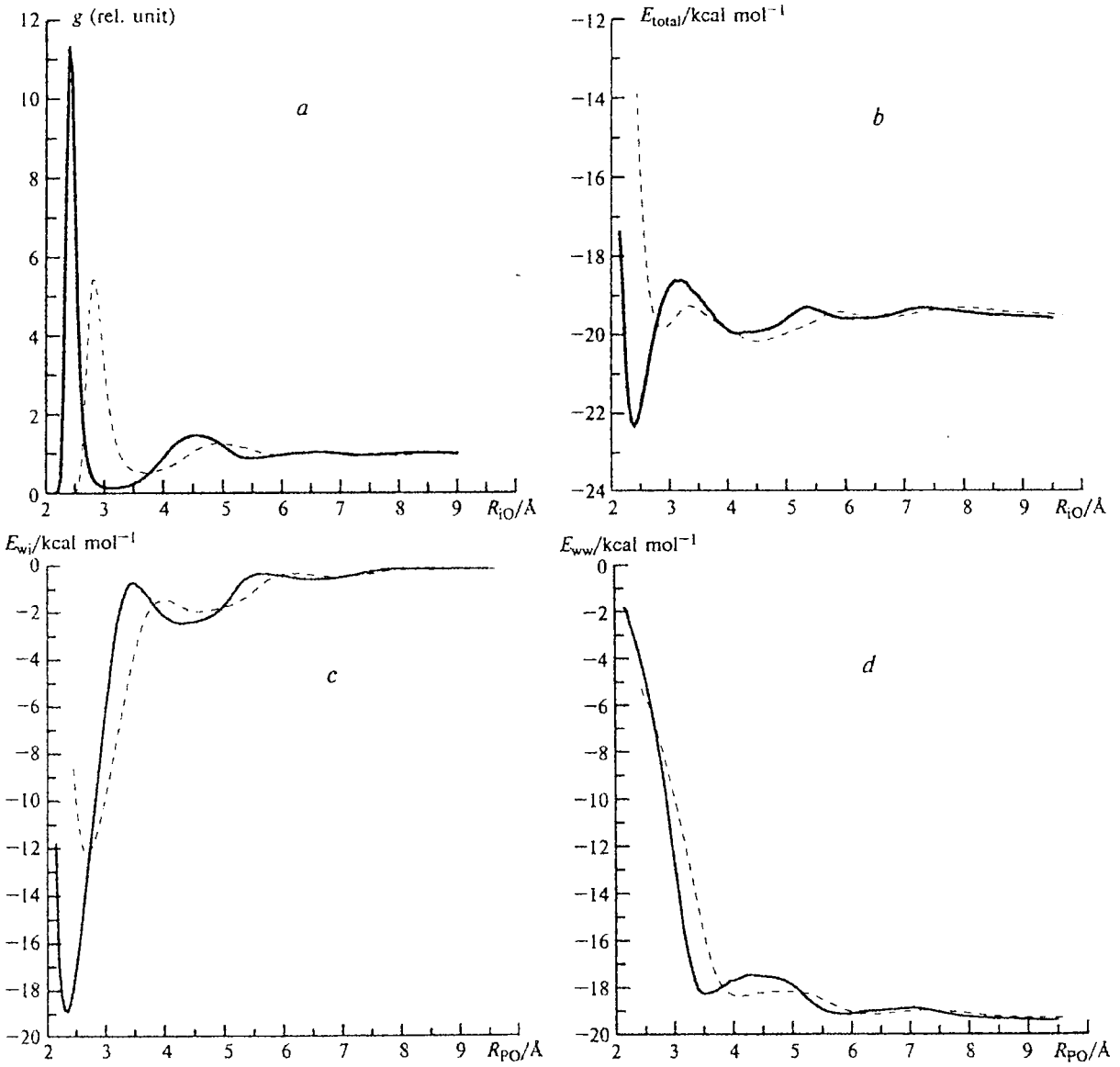

Fig. 1. Radial distribution functions (g) of water oxygen atoms surrounding the ion (*a*). Dependences of the total potential energy E_{total} of water molecule (*b*) and contributions of water—ion E_{wi} (*c*) and water—water E_{ww} (*d*) interactions on the distance R_{iO} between the ion and water O atom. Solid line represents the data for Na^+ and dashed line represents the data for K^+.

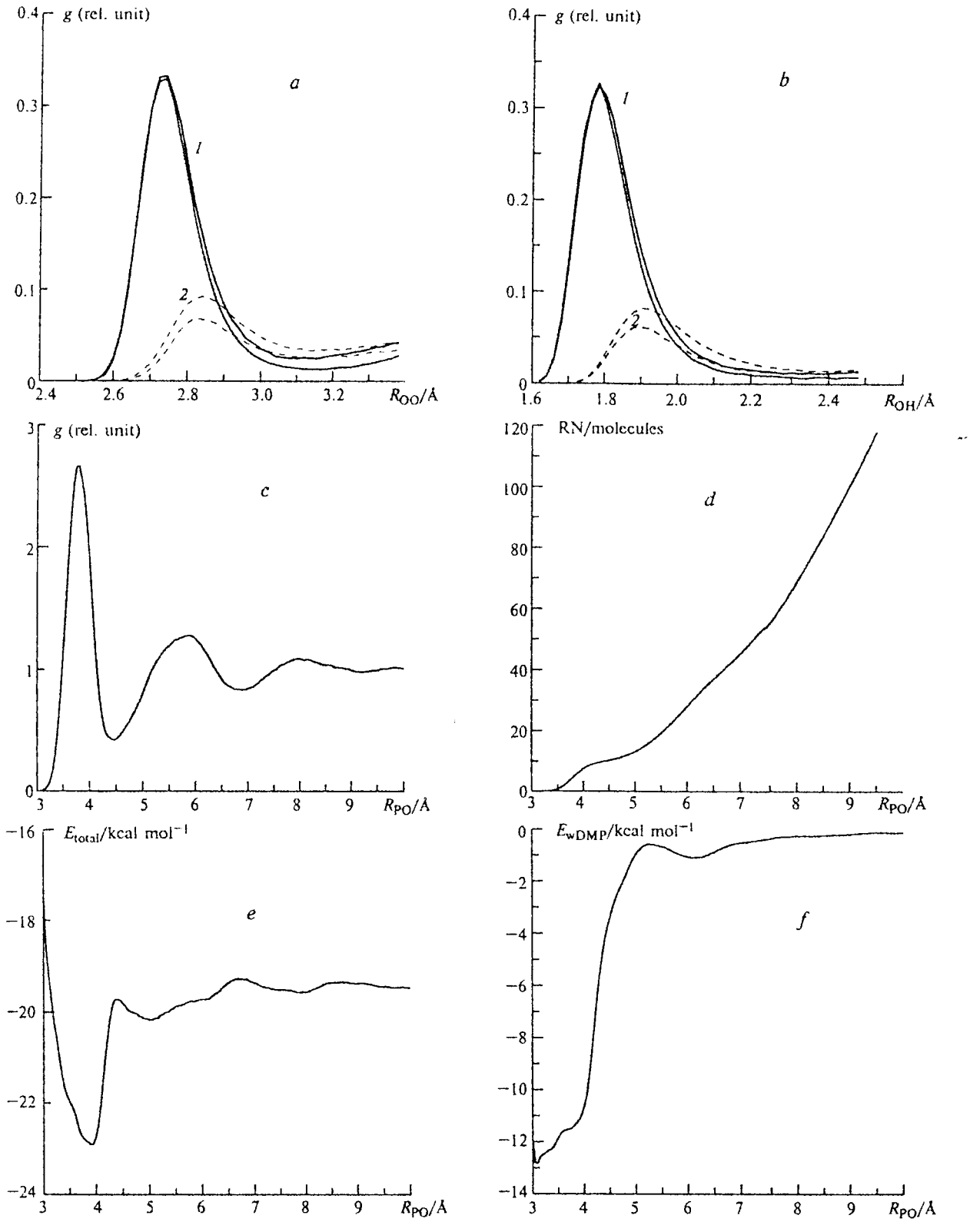

Fig. 2. Radial distribution functions (RDF) of O_w—O_{DMP} (*a*) and H_w—O_{DMP} (*b*) distances: *1*, anionic oxygen atoms (O^-), and *2*, ether oxygen atoms (O_e). RDF (*g*) of water oxygen atoms surrounding the DMP^- phosphorus atom (*c*). Dependence of the number of water molecules within a sphere of radius R_{PO} (*d*). Dependence of the total potential energy E_{total} of water molecule (*e*) and contribution of water—DMP^- interactions E_{wDMP} (*f*) on the distance R_{PO} between the phosphorus atom and water O atom.

Table 1. Coefficients of potential functions

Atom	Na^+		K^+	
	A	B	A	B
H1	121	17800	126	27300
H2	121	17800	126	61700
H3	121	42200	126	81600
C1	305	349000	316	601000
C2	385	406000	400	704000
N1	327	317000	334	544000
N2	391	366000	400	630000
N3	190000*	1095000	2147	1153000
O1	129000*	688000	1674	701000
O2	129000*	688000	1674	701000
O3	169000*	954000	3220	1730000
P	1182	1352000	1156	2195000
O_w	150840*	830200	1954	954000
	O_w		$H_w(H1)$	
O3	326	531400	6225*	15900

Note. Types of atoms: H1, H2, and H3 are hydrogen atoms bonded to N or O atoms, those bonded to aromatic carbon atom, and those bonded to aliphatic carbon atom, respectively; C1 and C2 are aliphatic and aromatic carbon atoms, respectively; N1 is nitrogen atom of amino group, N2 and N3 are pyrrole and pyridine nitrogen atoms, respectively; O1, O2 and O3 are ether, carbonyl, and anionic oxygen atoms, respectively; P is phosphorus atom; O_w is water oxygen atom; and H_w is water hydrogen atom. The values marked by asterisks were calculated using the potential functions of the type 1—12—10.

Here q_i is the charge of species i and the coefficients A and B determine the non-Coulomb interactions. Their values are listed in Table 1.

Small water clusters containing an ion. The study of such simple systems containing from one to six water molecules directly contacting the ion is the preliminary stage of the PFC selection, since our goal is to develop the potential functions for simulation of solutions. Selected structural and energy parameters of water-ion clusters calculated in this work as well as the experimental data[11] and the results obtained from *ab initio* calculations[12] are listed in Table 2. As can be seen from the data in Table 2, the results obtained using our PFC are rather close (especially, for large clusters) to both the experimental and *ab initio* data despite the fact that the model of water molecule with fixed geometry and charge distribution used in our calculations was developed for simulation of bulk medium.[2]

Ion in diluted solution. The diluted solution was simulated using a system consisting of 256 water molecules and one ion and forming a cubic unit cell (with an edge length of 19.72 Å for Na^+ and 19.734 Å for K^+) and periodic boundary conditions. The most important results of simulation are shown in Fig. 1 and listed in Table 3. As can be seen in Fig. 1, the first and the second peaks of the radial distribution functions* of the water oxygen atoms surrounding the cation (Fig. 1, *a*) are clearly defined for both Na^+ and K^+ cations. The corresponding minima of the dependence of the total energy (E_{total}) of the water molecule on the distance to the ion (Fig. 1, *b*) are also clearly seen. The first maxima of the radial distribution functions for Na^+ and K^+ ions correspond to distances of 2.42 Å and 2.84 Å, respectively. This is in good agreement with the values obtained[13] for distributions of distances between the ion and the water oxygen atom in Na^+ and K^+ crystal hydrates calculated from X-ray structural data (2.38 Å for Na^+ and 2.8 Å for K^+). Information on the distance

* Radial distribution function (g) is the ratio of the number of O or H atoms of water in a spherical layer 0.05 Å thick located at a given distance to the number of corresponding atoms in the same volume of bulk water.

Table 2. Characteristics of ion-containing water clusters $M^+(H_2O)_n$

n	ΔE	ΔH	$\Delta H^{298}{}_{exp}$	R_{MO}	
				This work	*ab initio*
			Sodium		
1	−20.93	−21.53	−24.0	2.39	2.21
2	−19.85	−20.45	−19.8	2.39	2.25
3	−18.10	−18.70	−15.8	2.40	2.29
4	−16.17	−16.77	−13.8	2.41	2.31
5	−13.30	−13.90	−12.3	2.42	2.32
6	−10.80	−11.40	−10.7	2.43	2.42
			Potassium		
1	−14.51	−15.11	−17.9	2.77	2.58
2	−13.69	−14.29	−16.1	2.77	2.68
3	−12.54	−13.14	−13.2	2.78	2.70
4	−11.09	−11.69	−11.8	2.80	2.72
5	−9.72	−10.32	−10.7	2.81	2.73
6	−9.44	−10.04	−10.0	2.82	2.80

Note: n is the number of water molecules in the cluster. The increments of energy ΔE and enthalpy ΔH (kcal mol^{-1}) at 300 K for the reaction of addition of one water molecule $M^+(H_2O)_{n-1} + H_2O \rightarrow M^+(H_2O)_n$ are listed. The ΔH values were obtained by subtracting the value $\Delta A = p\Delta V \approx 0.6$ kcal mol^{-1} (the expansion work of 1 mole of the ideal gas of water molecules at 300 K) from the corresponding ΔE values. The $\Delta H^{298}{}_{exp}$ values were taken from Ref. 11. The R_{MO} and $R_{MO}{}^{ab\ initio}$ values are the average distances (Å) between the ion and water oxygen atom found from the Monte Carlo and *ab initio* calculations,[12] respectively.

Table 3. Hydration characteristics of Na^+ and K^+ ions

Ion	E_{total}	E_{wi}	ΔE_{hyd}	ΔH_{hyd}	CN
			kcal mol^{-1}		
Na^+	−2609	−188	−108	−101—106	6.68
K^+	−2584	−151	−83	−81—86	7.67

Note. E_{total} is the total energy of the system consisting of an ion and 256 water molecules, E_{wi} is the contribution of water—ion interactions, ΔE_{hyd} is the energy of ion hydration, and CN is the coordination number of ion. ΔH_{hyd} is the experimental enthalpy of hydration[15,14] at 298 K. The expansion work of 1 mole of the ideal gas of water molecules at 300 K (0.6 kcal mol^{-1}) should be added to ΔH_{hyd} when comparing with ΔE_{hyd} values.

Table 4. Characteristics of water—DMP^- interaction *in vacuo*

Position[a]	This work			*Ab initio*[17]		MM		
	E	R_{HwO^-}	R_{HwOe}	E	R_{HwO^-}	E[17]	R_{HwO^-}[17]	E[b 18]
1	−19.04	1.90	—	−22.19	2.10	−19.40	1.87	−19.0
2	−16.05	1.83	2.06	—[c]	—[c]	—[c]	—[c]	−16.0
3	−16.00	1.83	2.06	—[c]	—[c]	—[c]	—[c]	−17.0
4	−15.51	1.76	—	−18.82[d]	1.75	14.55	1.72	—[c]
5	−13.22	—	1.95	—[c]	—[c]	—[c]	—[c]	—[c]

Note. E is the energy of water—DMP^- interaction (kcal mol^{-1}); R_{HwO^-} and R_{HwOe} are the distances (Å) between the water H atom and the O^- atom (or the ether O_e atom) of DMP^- anion (for the data for the O_w atom of water molecule, see text); and MM denotes calculations by the method of molecular mechanics.

[a] The position numbers describing the relative position of a water molecule, see Fig. 3.

[b] Data for $H_2PO_4^-$.

[c] No data.

[d] Averaged for two values (−19.68 and −17.95) reported in Ref. 17.

distribution between the ion and the water oxygen atom and the dependence of E_{total} on this distance were used for evaluating the coordination number (CN) of the ion. We defined the CN of the ion as the average number of water molecules located around the ion within a sphere of radius R_{CN}. The R_{CN} value corresponding to the positions of the first E_{total} maxima (3.1 Å for Na^+ and 3.4 Å for K^+) were used in calculations. The coordination numbers of ions obtained (see Table 3) are in good agreement with the experimental values.[13,14]

The hydration energy of ion ΔE_{hyd} (see Table 3) was calculated as the difference between the potential energies of the system containing an ion and the system without ion ($\Delta E_{hyd} = E$(ion+256 water molecules) $- E_{aq}$, where E_{aq} is the potential energy of the system consisting only of 256 water molecules (−2501 kcal mol^{-1})). The calculated hydration energies are in good agreement with experimental values[9,14,15] (see Table 3).

The dependence of E_{total} on the distance between the ion and the water oxygen atom clearly demonstrates the different character of hydration for Na^+ and K^+ ions. As can be seen in Fig. 1, *b*, the potential energy of water molecule in the first hydrate shell of Na^+ ion (the first minimum of the E_{total} curve) is about 2.5 kcal mol^{-1} lower than its energy away from the ion. At the same time, this gain is insignificant for water molecules from the first hydrate shell of K^+ ion while the molecules in the second layer are even in more favorable conditions. Such differences in the properties of water shells of Na^+ and K^+ ions clearly demonstrate the idea[16] of the positive (Na^+) and negative (K^+) hydration of ions.

Water—phosphate interactions

To reduce the differences in the charges on ether and ionized ("anionic") atoms oxygen, the negative partial charges on DMP^- atoms were somewhat changed as compared to those proposed in Ref. 8. The final charges on the phosphorus, anionic O^-, ether O_e, carbon, and hydrogen atoms of DMP^- used in this work were +0.802, −0.730, −0.313, −0.039, and +0.060, respectively (all values in |e| units). The interaction between the water hydrogen atom and phosphate oxygen atoms was described using the potential functions of the type 1—12—10 while all other interactions were described using those of the type 1—12—6. The PFC of hydroxyl O atom (see Ref. 3) were used to simulate the ether oxygen atoms. The parameters for anionic oxygen atoms were calculated anew.

Bimolecular complex water—DMP^-. The global minimum of the potential energy of this system (−19.04 kcal mol^{-1}, Table 4) corresponds to a "water bridge" between the anionic O^- atoms (see Fig. 3, position 1; the O_w...O^- distance is 2.72 Å). We call the water molecule that forms hydrogen bonds (H-bonds) with two proton-acceptor atoms a bridge. The other two minima with energies 3 kcal mol^{-1} higher than that of the global minimum correspond to the formation of a water bridge between the ether and anionic oxygen atoms (see Fig. 3, positions 2 and 3; the O_w... O^- and O_w... O_e distances are 2.68 Å and 2.84 Å, respectively). The formation of H-bonds with one of the DMP^- oxygen atoms is even less energetically favorable (see Fig. 3, positions 4 and 5; the O_w... O^- and O_w... O_e distances are 2.71 Å and 2.79 Å, respectively, see Table 4). As can be seen from the data in Table 4, our results are in good agreement with those reported in the literature.[17,18]

DMP^- in diluted solution. A system containing a DMP^- anion and 400 water molecules in a cubic unit cell with an edge of 22.956 Å was simulated. The calculated radial distribution functions of O_w and H_w atoms of water molecule surrounding the DMP^- oxygen atoms are shown in Fig. 2, *a*, *b*. The curves corresponding to the $O(1)^-$ and $O(2)^-$ oxygen atoms have distinct first maxima at 2.75 Å for O_w and at 1.79 Å for H_w. The average number of H-bonds with water molecules formed

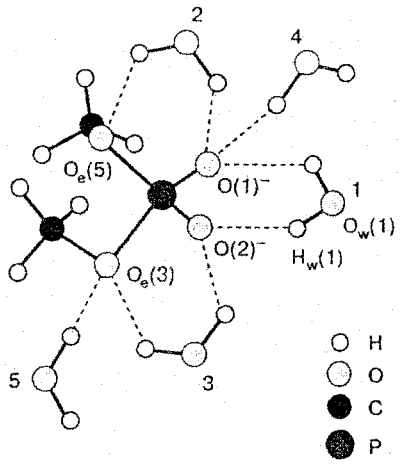

Fig. 3. Scheme of binding sites for the water—DMP^- pair *in vacuo*.

by one O^- atom calculated using the geometric criterion[2] is 3.3. As to the H-bonds between water molecules and ether $O_e(3)$ and $O_e(5)$ atoms, they are rarely formed (0.9—1.2 bonds per oxygen atom) while their geometric parameters vary over a wide range (see Fig. 2, *a*, *b*; the first maxima of radial distribution functions of O_w... O_e and H_w...O_e distances correspond to distances 2.85 and 1.92 Å, respectively). This is in good agreement with the experimental data for nucleotide crystal hydrates and their analogs. For instance, in the crystal hydrate $5'$-$dCMP^{2-} \cdot Na^+_2 \cdot 7H_2O$ [19] two of the three anionic oxygen atoms each form three H-bonds with water molecules, while the third O^- atom forms two H-bonds. In this case the average O_w...O^- and H_w... O^- distances are 2.77±0.06 Å and 1.84±0.1 Å, respectively.

The dependence of the local water density (normalized to a bulk water density of 1 g cm^{-3}) on the distance between the phosphorus atom and the water O_w atom shown in Fig. 2, *c* adequately depicts the multilayer structure of DMP^- water shell. In particular, it is possible to isolate the first coordination sphere of radius 4.45 Å containing 10 water molecules (see the number of water molecules in the sphere of radius R_{PO} in Fig. 2, *d*). The average number of H-bonds with water molecules formed by four DMP^- oxygen atoms is 8.7. There is a distinct minimum on the dependence of the total (with inclusion of water—water interactions) potential energy of individual water molecule E_{total} on the distance between the phosphorus atom and the water O_w atom (see Fig. 2, *e*). This minimum corresponds to the formation of water—phosphate H-bonds (see the average energy of interaction between water molecule and DMP^- in Fig. 2, *f*) and its energy is 3.4 kcal mol^{-1} lower than that corresponding to large distance from P atom. Water bridges between the oxygen atoms of the phosphate group are the main structural elements of the DMP^- water shell. "Two-water" $O(1)^-$...W...W...$O(2)^-$ and O_e...W...W...O^- bridges (57 and 25% configurations, respectively) and three-water bridges between the same pairs of oxygen atoms (100 and 37% configurations, respectively) (here dots denote an H-bond and W denotes a water molecule) were most often revealed in the course of Monte Carlo simulations. The value 100% means that in some instances the anionic oxygen atoms can be simultaneously connected by two different three-water bridges. "One-water" (O...W...O) bridges (corresponding, as was mentioned above, to energy minima) as well as bifurcated H-bonds are very rare (less than 3% of configurations).

The calculated hydration energy of DMP^- (the difference between a potential energy of aqueous system with the anion of −4001.3 kcal mol^{-1} and that of the aqueous system without the anion of −3908 kcal mol^{-1}) is −93.3 kcal mol^{-1}. This value is very close to that of −92.5 kcal mol^{-1} found by the Monte Carlo method for the NPT ensemble.[6] The average energy of the interaction of DMP^- with water molecules is −181.7 kcal mol^{-1}.

Ion—phosphate and ion—nitrogen base interactions

DMP^-—counterion pair *in vacuo*. The interaction between the Na^+ ion and the phosphate oxygen atoms was described using potential functions of the type 1—12—10 while all other interactions were described using those of the type 1—12—6 (including the PFC for K^+). Only the PFC for ion—oxygen atom interactions were refined. The global minimum of the potential energy of the ionic pair (−139.7 kcal mol^{-1} for Na^+ and −120.3 kcal mol^{-1} for K^+) corresponds to the ion position on the bisectrix of the $O(1)^-PO(2)^-$ angle (Fig. 4, position 1); at the same time, the ionic "bridges" between the ether and anionic oxygen atoms (Fig. 4, positions 3, 4) are not local minima (the values of the interaction energy are 26 kcal mol^{-1} (for Na^+) and 19 kcal mol^{-1} (for K^+) higher than the minimum energy). It should be noted that the ions (in particular, Na^+) in crystal hydrates occupy positions 3 and 4 very rarely. The ion ...O^- distances corresponding to the global minimum are 2.38 and 2.79 Å for Na^+ and K^+, respectively. The shortest distances between the ion and the O^- atom (2.31 Å for Na^+ and 2.6 Å for K^+) correspond to the ion positions in a narrow (±10°) cone coaxial to the PO^- bond (Fig. 4, position 2). The distances corresponding to the formation of an ionic "bridge" between the ether and anionic oxygen atoms (Fig. 4, positions 3 and 4) vary in the range 2.38—2.52 Å for Na^+ (if the O_e... Na^+ distance is 2.38 Å, then the O^-...Na^+ distance is 2.52 Å and *v.v.*) and are 2.76 Å for K^+. The calculated geometric parameters are in very good agreement with the X-ray structural data for crystal hydrates. For instance, the distances between the ion and the O^- atom lie in the range 2.30—2.46 Å for Na^+ [20—23] and 2.6—3.2 Å for K^+,[24—26] while the ion—O_e distances are 2.50—2.58 Å for Na^+ [22] and 2.84 Å for K^+.[27]

Ion—nitrogen base interactions *in vacuo*. The interactions between the Na^+ ion and the oxygen atoms of car-

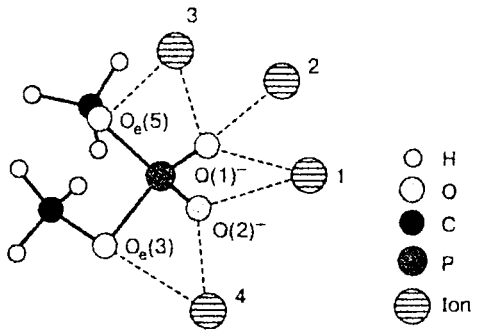

Fig. 4. Scheme of binding sites for the ion—DMP^- pair *in vacuo*.

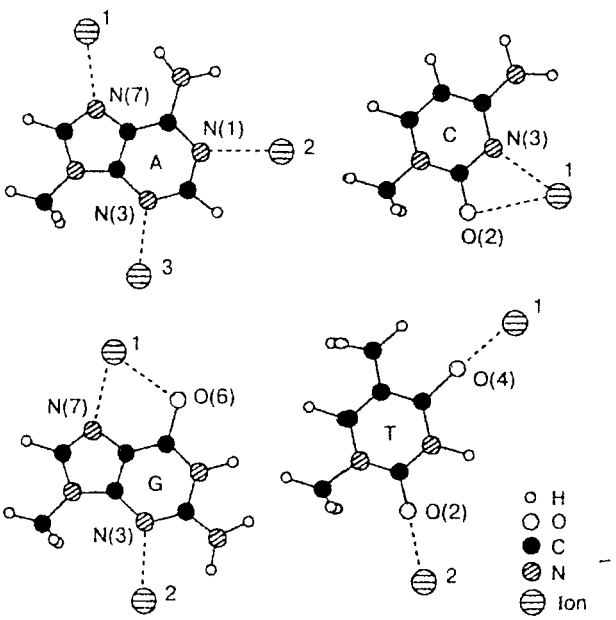

Fig. 5. Scheme of binding sites for the ion—nitrogen base systems *in vacuo*.
A is 9-methyladenine, G is 9-methylguanine,
C is 1-methylcytosine, and T is 1-methylthimine.

bonyl groups and pyridine nitrogen atoms were described using the potential functions of the type 1—12—10 while all other interactions were described using those of the type 1—12—6 (including all functions for K^+). Only the PFC for ion—oxygen atom and ion—pyridine nitrogen atom interactions were refined. The positions of local minima of the potential energy of the ion—base pair are shown in Fig. 5. The energies and corresponding distances are listed in Table 5. The calculated geometric parameters are in good agreement with the experimental data obtained from X-ray studies of crystal hydrates: the carbonyl O atom...Na^+ distance is 2.43 Å (according to the reported data, it lies in the range 2.34 to 2.56 Å)[20—22], the pyridine N atom...Na^+ distance is 2.415 and 2.613 Å,[28] the carbonyl O atom...K^+ lies in the range 2.68—2.84 Å,[25,26] and the pyridine N atom...K^+ distance is 3.15 Å.[24] At the same time, the energies obtained from *ab initio* calculations[29,30] are regularly lower than those we calculated and correspond to shorter distances to the base atoms. Thus, according to Ref. 29, the Na^+...O distance is 2.00—2.15 Å [29] while according to Ref. 30, the Na^+...O distance is 2.26 Å, the Na^+...N distance lies in the range 2.30—2.41 Å, the K^+...O distance is 2.67 Å, and the K^+...N lies in the range 2.79—2.86 Å. This is not surprising, since our PFC were specially elaborated for the simulation of bulk medium where no such short contacts are present. Moreover, several ion—base complexes (with the ion location near the NH_2 group) we studied are nonplanar (see the Z values in Table 5), whereas only planar configurations have been considered

Table 5. Characteristics of ion—nitrogen base interaction *in vacuo*

Base	Position[a]	E		E_1^{ai}	E_2^{ai}		R_{iO}		R_{iN}		Z	
		Na^+	K^+	Na^+	Na^+	K^+	Na^+	K^+	Na^+	K^+	Na^+	K^+
9-Methyl-	1	−18.02	−12.66	−26.4	—[b]	—[b]	—	—	2.46	2.85	0.00	0.12
adenine	2	−15.16	−10.24	−24.0	—[b]	—[b]	—	—	2.47	2.87	0.05	0.01
	3	−14.28	−8.64	−21.3	−26.5[c]	−15.0[c]	—	—	2.46	2.84	0.37	0.69
9-Methyl-	1	−45.30	−35.09	−53.9	−59.7[c]	−42.95[c]	2.42	2.76	2.46	2.81	0.00	0.00
guanine	2	−8.64	−3.51	−14.6	—[b]	—[b]	—	—	2.46	2.89	0.38	1.93
9-Methyl-	1	−46.36	−35.65	−51.7	—[b]	—[b]	2.40	2.71	2.47	2.84	0.00	0.00
cytosine												
9-Methyl-	1	−19.95	−14.78	−32.9	—[b]	—[b]	2.37	2.73	—	—	0.00	0.00
thimine	2	−14.94	−10.49	−28.7	—[b]	—[b]	2.39	2.77	—	—	0.00	0.00

Note. E is the calculated energy of the ion—base interaction (kcal mol^{-1}); E_1^{ai} is the energy of Na^+ interaction with adenine (guanine, cytosine, or uracil) obtained from *ab initio* calculations;[29] E_2^{ai} is the energy of the ion interaction with adenine (or guanine) obtained from *ab initio* calculations;[30] R_{iO} and R_{iN} are the distances (Å) between the ion and the base O or N atoms (see Fig. 5, dotted lines), respectively; Z is the distance (Å) between the ion and the base plane.

[a] The position numbers describing the relative position of the ion, see Fig. 5.

[b] No data are available.

[c] Averaged for two procedures reported in Ref. 30.

in the literature.[29,30] It should also be noted that according to *ab initio* calculations,[30] the base—K^+ distances are fairly close to both our data and the experimental values.

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