SOFT MATTER

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INFLUENCE OF RADIATION ON THE LOCAL STRUCTURE IN A NaCl AQUEOUS SOLUTION

Using the method of molecular dynamics, the influence of radiation within the energy interval $E_r = 0 \div 12$ MeV on the local structure in a 0.14-mol.% NaCl aqueous solution at the temperature $T = 300$ K is studied. No substantial changes in the local structure of the solution were found at energies E_r higher or lower than 9 MeV. At $E_r = 9$ MeV, the local structure changes drastically. This radiation effect can be considered as a maximum one and taking place due to the increase of the probability for cations and anions of the solute to interact with one another and with water molecules.

K e y w o r d s: molecular dynamics method, irradiation, radial distribution function.

1. Introduction

The establishment of quantitative relations between the macroscopic properties of aqueous solutions subjected to various external factors, on the one hand, and the intermolecular interaction, on the other hand, favors the solution of many fundamental and applied problems, in particular, medicobiological ones. While studying changes in the physical properties of solutions invoked by external factors, the methods of researches, which provide a direct information concerning the molecular-kinetic motions of molecules – neutron, optical, dielectric, and others – are used most often. This information forms a basis for the creation of models describing the structure of water and aqueous solutions [1].

Irradiation is one of the least studied external factors that considerably affect the properties of the aqueous solutions of electrolyte salts. Note that researches of the influence of relatively small doses of radiation–namely, β-, γ- , and x-ray radiation–in the energy interval of 5–12 MeV on aqueous electrolyte solutions have become urgent in recent years owing to the extensive use of those solutions in radiation oncology [2,3]. It should also be noted that the corresponding experimental researches meet considerable difficulties. This is so, first of all, because such researches allow the averaged macrocharacteristics of a thermodynamic system (density, viscosity, dielectric permittivity, and so forth) to be analyzed, as a rule. Moreover, the interpretation of the results obtained becomes complicated owing to the integrated influence of anions of various origins, which stimulates changes in the arrangement of water molecules under irradiation. In other words, the results of experimental researches do not allow one to analyze the influence of radiation on the structural, energy, and dynamic properties of examined systems in detail at the microscopic level. Therefore, in order to study the microstructure of ionic solutions in the framework of such problems, the method of molecular simulation (molecular dynamics, MD) is used, as a rule. In this work, this method was used to analyze the microstructure of a model system – a solution "water-NaCl" with the salt concentration $x = 0.14$ mol.%, which is widely used in medicine [4] – subjected to irradiation.

2. Model

The interaction between the molecules in the examined model liquid system was described with the help of an interatomic potential, which is a sum of the van der Waals and Coulomb components [5],

$$U = U_{\mathrm{LJ}} + U_{\mathrm{C}} = \sum_{ij} 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] +$$
$$+ \sum_{ij} \frac{q_i q_j}{r_{ij}}, \qquad (1)$$

where σ_{ij} and ϵ_{ij} are the parameters of the Lennard-Jones potential, r_{ij} is the distance between interacting particles, and q_i is the charge of the i-th particle. The parameter values selected for atoms in a water molecule and ions in the solution are quoted in Table 1.

In the course of calculations, water molecules and ions were considered as Lennard-Jones particles, and the interaction between them was simulated by means of OPLS-potentials [6]. The interaction between water molecules is described in the framework of the SPC/E model [7]. The parameters of interaction between non-identical particles are defined with the help of the combination rule [5]

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2, \quad \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}, \qquad (2)$$

where the subscripts i and j mark the particles of the i-th and j-th kinds, respectively, and the subscript ij is related to non-identical particles.

The influence of radiation on the local structure and the energy properties of the liquid system "water-NaCl" is studied, by using the MD method (the software package DL POLY 4.05 [8]) with a time step of 2 fs. The simulation was carried out for an NVT-ensemble of a cubic cell with periodic boundary conditions and including 256 interacting particles at $T = 300$ K. The volume of an elementary cell was calculated according to the experimental values obtained for the solution density at the same temperature. The long-range electrostatic interaction was taken into account, by summing with the use of the Ewald method [9]. The stabilization of the researched system in NVT was performed with the help of the Berendsen thermostat [10]. In calculations, ions and water molecules were simulated as hard charged model particles with a fixed geometry. The intermolecular parameters were obtained on

a basis of the atom-atom representation for the interaction between the atoms of different kinds.

The simulation algorithm was as follows. The stabilization of the system was attained, by making 8×10^5 calculation steps. Afterward, one of the ions in the system was subjected to the irradiation with an energy in the interval of 0–12 MeV; the energy was equally distributed along all coordinate axes. The system was again allowed to come to the equilibrium state for 10^6 calculation steps. Then, several series of independent calculations with time steps of 200, 160, and 80 fs were carried out to obtain the energy characteristics of the researched system. All radial distribution functions (RDFs) were determined with a step of 200 fs.

The simulation procedure provided us with the data concerning the local structure of the liquid system and its energy and dynamic properties for their further analysis. Note that the information on the local structure of the examined system can be obtained both experimentally (the x-ray diffraction and neutron scattering methods) and theoretically. In the latter case, we calculated the radial distribution functions $G_{XY}(R)$, which characterize the probability to find particles of sort y near particles of sort x:

$$G_{XY}(R) = \frac{\langle N_y(R, R + dR)\rangle}{\rho_y 4\pi R^2 dR}. \qquad (3)$$

In this equation, the numerator equals the average number of particles Y in a spherical layer $(R, R+dR)$, and the denominator normalizes the distribution in such a way [5] that $G_{XY}(R) = 1$ at $N_y = \rho_y$, where ρ_y is the density. The first hydration sphere is defined as a space within a sphere, whose radius is numerically equal to the position of the first RDF minimum. The second hydration shell is defined as the space of a spherical layer between the first and the second RDF minimum.

Table 1. **Charges, parameters of the Lennard-Jones potential, and masses for atoms in water molecules and Na$^+$ and Cl$^-$ ions [6]**

Atom	$q(e)$	σ, Å	ϵ, kJ/mol	M, g/mol
H	0.4238	0	0	1
O	−0.8436	3.169	0.6502	15.99
Na$^+$	+1	2.35	0.1	22.9898
Cl$^-$	−1	4.4	0.1	35.453

The detailed information about the local structure and the properties of aqueous electrolyte solutions can be obtained by analyzing the energy properties of systems, RDF, and number of nearest neighbors, Nz. The latter is proportional to the area under the first peak in the density distribution function and is determined by the expression

$$Nz = \int\limits_{0}^{Z_{\min}} 4\pi\rho_0 \, g_2(r) r^2 dr, \qquad (4)$$

where ρ_0 is the density of the system.

The network of hydrogen bonds between interacting particles is analyzed on the basis of the following criterion: the hydrogen bond is possible if the distance between the oxygen atoms in water molecules is at most 3.5 Å. The hydrogen bond between the nearest neighbors is selected so that the distance between the O and H atoms should be minimum of all possible intermolecular distances. The hydrogen bond angle, which was determined as an angle between the vectors of O–H bonds in neighbor water molecules, accepted values from 130 to 180° [11].

3. Analysis of the Results

3.1. Energy of interaction between molecules

The dependences of the total average energy of interaction between atoms, $\langle E_\Sigma \rangle$, and its Coulomb component, $\langle E_C \rangle$, on the irradiation energy E_r obtained for the solution concerned are presented in Table 2. On the basis of these data, one can see that the growth of the irradiation energy stimulates insignificant changes of the total interaction energy between the molecules in the solution owing to a reduction of the Lennard-Jones contribution and the increase of the Coulomb one. The Lennard-Jones component undergoes the largest variations, which testifies to a reduction of the role of short-range interactions in the system as the irradiation energy increases. In turn, this can indicate

Table 2. **Dependences of $\langle E_\Sigma \rangle$ and $\langle E_C \rangle$ on the irradiation energy E_r**

Average values	Irradiation energy E_r, MeV			
	0	6	9	12
$\langle E_\Sigma \rangle$, kcal/mol	−7.71	−7.81	−7.82	−7.91
$\langle E_C \rangle$, kcal/mol	−9.10	−9.03	−9.06	−8.91

that an increase of the irradiation energy gives rise to local transformations in the liquid structure and changes of the component mobilities. The obtained dependences of the energy parameters in the studied NaCl aqueous solution on the irradiation energy also allow us to suppose that, owing to a reduction of the role of short-range van der Waals interactions and an increase of the role of the Coulomb interaction in the system "water–NaCl", the clusters formed by ions and water molecules change their parameters, which in turn affects the dynamic properties of the system.

3.2. Local structure of the NaCl aqueous solution

To verify our assumptions concerning modifications in the local structure of the examined NaCl aqueous solution under the influence of the irradiation, we determined and analyzed the RDFs, which characterize the probability distribution density for various classes of interactions between particles and make it possible to discern interactions that are the most sensitive to the influence of radiation. In so doing, we paid special attention to the atom-to-atom interactions that considerably affect the processes of local structure formation in water near anions and cations, namely, the interactions $Na^+ ... O^W$, $Na^+ ... H^W$, $Cl^- ... O^W$, $Cl^- ... H^W$, and interactions between water molecules.

First of all, let us consider and analyze the RDFs that describe the probability density for water molecules to be at a certain distance from one another (Fig. 1). The position of the first maximum in the RDF $G^{O^W - O^W}(R)$ corresponds to the distance between the water molecules. From the figure, one can see that the distance between the interacting water molecules does not change under irradiation. The length of the hydrogen bonds between water molecules also is not changed, which is evidenced by the invariable positions of the first and second maxima in the RDF $G^{O^W - H^W}(R)$. The stability of the positions of the first and second minima in the functions $G^{O^W - O^W}(R)$ and $G^{O^W - H^W}(R)$ testifies to the independence of the dimensions of the first and second hydration shells of the irradiation energy. The data obtained allow us to assert that the irradiation does not change the parameters of associates formed by water molecules.

To analyze the influence of radiation on the interaction between Na^+ ions and water molecules, let us

consider the behavior of the RDFs $G^{\mathrm{Na^+-O^W}}(R)$ and $G^{\mathrm{Na^+-H^W}}(R)$. Their first maxima are located at distances of 3.3 and 3.1 Å, respectively (Fig. 2). One can see that the RDF values decrease with the growth of the irradiation energy. In both cases, the positions and the magnitudes of the first and second RDF minima remain constant, which testifies to the independence of the sizes of the first and second hydration shells of the irradiation energy.

When analyzing the interactions $\mathrm{Cl^-...O^W}$ and $\mathrm{Cl^-...H^W}$, of special interest is the RDF $G^{\mathrm{Cl^--H^W}}(R)$, the first maximum of which is located at a distance of 2.2 Å (see Fig. 3). The RDF values also decrease as the irradiation energy grows up to 9 MeV. The irradiation with an energy of 9 MeV gives rise to a substantial anomalous increase of RDF maxima, which exceeds their determination error and testifies to an increase of the probability for this class of interactions.

The analysis of the RDF $G^{\mathrm{Na^+-Cl^-}}(R)$ (see Fig. 4) shows that the increase of irradiation energy stimulates a reduction of RDF values and does not affect the position of the first maximum, which determines the distance between interacting particles. An anomalous behavior of the RDF $G^{\mathrm{Na^+-Cl^-}}(R)$ values is observed at an irradiation energy of 9 MeV. According to the behavior of the $G^{\mathrm{Cl^--Cl^-}}(R)$ dependence plotted in the same figure, it follows that an increase of the irradiation energy to 9 MeV results in an anomalous increase of the RDF maximum position and a reduction of the first minimum magnitude, which testifies to a higher local ordering in the structure of the examined system at the given irradiation energy. For the interaction of $\mathrm{Na^+}$ ions with one another, the RDF $G^{\mathrm{Na^+-Na^+}}(R)$ also grows at an energy of 9 MeV. At this energy, unlike other ones, the first hydration shell can be determined most accurately, which testifies to a higher ordering in the local structure of the researched system. This means that 9 MeV is an energy, at which the probability of the interaction between ions increases, and the anomalous behavior of the magnitudes of corresponding RDFs testifies to that.

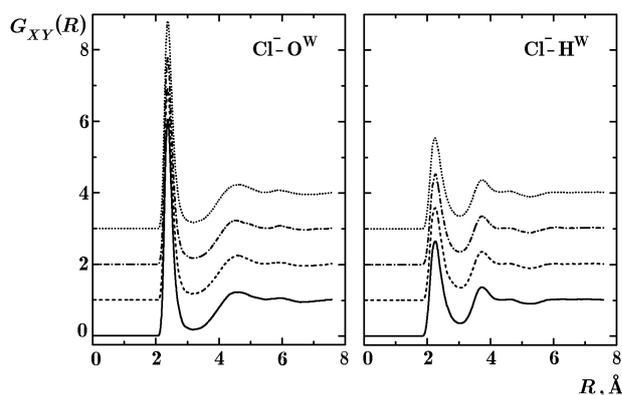### 3.3. The number of nearest neighbors

The analysis of the influence of radiation on the formation of a local structure in the NaCl aqueous solution cannot be complete, if the average number of
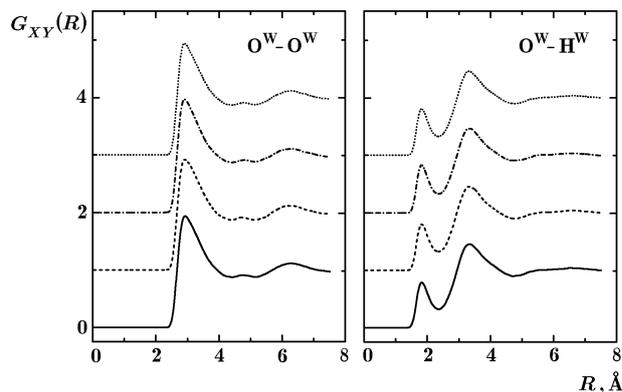
Fig. 1. Radial distribution functions $G^{\mathrm{O^W-O^W}}(R)$ and $G^{\mathrm{O^W-H^W}}(R)$ for the liquid system "water-NaCl" ($x = 0.14$ mol%, $T = 300$ K) at irradiation energies of 0 (solid curves), 4 (dashed curves), 9 (dash-dotted curves), and 12 MeV (dotted curves)
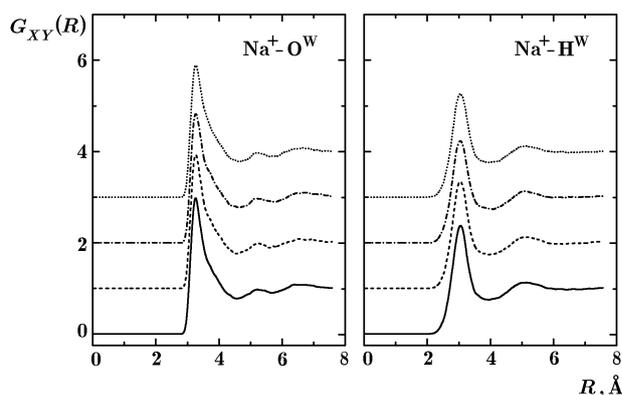
Fig. 2. The same as in Fig. 1, but for the density of probability to find the atoms of water molecules near $\mathrm{Na^+}$ ions

Fig. 3. The same as in Fig. 1, but for the density of probability to find the atoms of water molecules near $\mathrm{Cl^-}$ ions
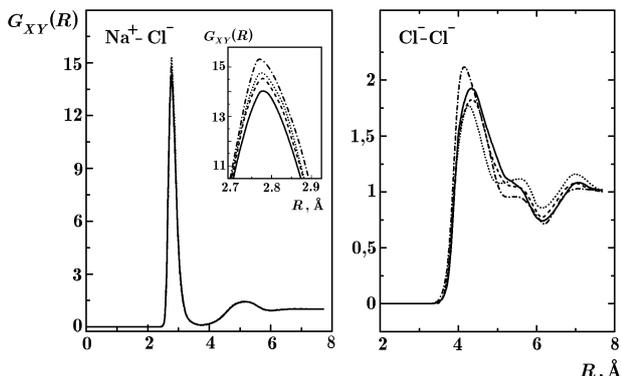
Fig. 4. The same as in Fig. 1, but for the density of probability to find Na^+ and Cl^- ions near Cl^- ions
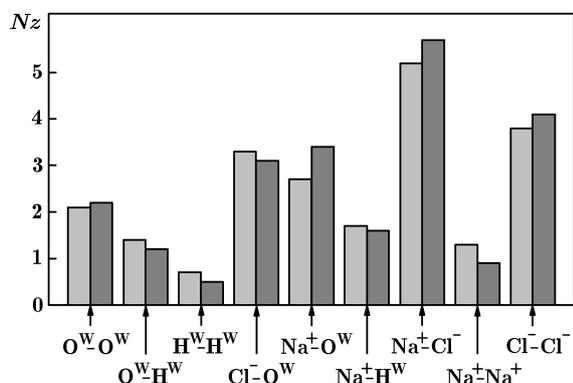

Fig. 5. Dependence of the number of nearest neighbors, Nz, in the examined solution on the irradiation energy: 0, 6, and 12 MeV (gray color), and 9 MeV (dark gray color)

Table 3. **Self-diffusion coefficients**
D **($\times 10^9$ m²/s) for water molecules and Na^+**
and Cl^- ions in the studied solution
at various irradiation energies

Object	Irradiation energy E_r, MeV			
	0	6	9	12
H_2O	2.11	2.22	2.20	2.07
Na^+	0.66	0.52	0.35	0.42
Cl^-	0.58	0.51	0.55	0.56

nearest neighbors Nz is omitted from the consideration. The dependence of this characteristic on the irradiation energy is depicted in Fig. 5.

The analysis of the RDFs $G^{O^W-H^W}(R)$, $G^{H^W-H^W}(R)$, and $G^{O^W-O^W}(R)$ within the first hydration sphere revealed that, if the irradiation energy is lower than 9 MeV, the water molecules are assembled into associates with $Nz = 4.1 \pm 0.3$ molecules. If the irradiation energy exceeds 9 MeV, the increment in the number of nearest neighbors does not exceed the error of the determination of Nz. This result testifies that no changes in the structure of water associates occur under the irradiation in the considered energy interval. The analysis of the values of Nz, which characterize the processes of interaction both between ions themselves and between ions and water molecules, shows that the growth in the number of nearest neighbors at an irradiation energy of 9 MeV exceeds the determination error for this parameter.

The further analysis of the results obtained (Fig. 5) shows that if the irradiation energies are lower or higher than 9 MeV, the interaction between water molecules gives rise to the formation of associates of four molecules, with $Nz = 4.2 \pm 0.3$ water molecules in the vicinity of a Na^+ ion and $Nz = 4.1 \pm 0.3$ water molecules in the vicinity of a Cl^- one. In this case, there emerge the associates of interacting ions and cations consisting of $Nz = 5.1 \pm 0.3$ ionic pairs. If the irradiation energy equals 9 MeV, the number of ionic pairs increases to $Nz = 5.7 \pm 0.3$, and the number of water molecules surrounding a Na^+ ion decreases to $Nz = 3.4 \pm 0.3$. All other changes in the number of nearest neighbors fall within the calculation error limits.

3.4. Self-diffusion coefficient

The self-diffusion coefficients for ions and water molecules are calculated by integrating the temporal autocorrelation function,

$$D = \frac{1}{3} \int \langle V(t)V(0) \rangle \, dt. \qquad (5)$$

The values obtained for the self-diffusion coefficients of water molecules and ions in the examined solution at various irradiation energies are quoted in Table 3.

The results calculated for D^{H_2O} correlate with the data for water obtained experimentally with the use of the method of quasielastic scattering of slow neutrons [12]. From the analysis of the data presented in Table 3, it follows that, as the irradiation energy increases from 0 to 6 MeV, the self-diffusion coefficient for water molecules, D^{H_2O}, slightly grows, for Cl^- ions, D^{Cl^-}, remain almost constant, and for Na^+ ions, D^{Na^+}, decreases.

At irradiation energies lower than 9 MeV, the reconfiguration of the local structure of the solution in vicinities of anions runs more slowly than in vicinities of cations, which is related to substantial differences between the masses and the Stokes radii of those anions and cations (in particular, the Stokes radius equals 1.88 Å for a Na^+ cation and 1.33 Å for a Cl^- anion). As the irradiation energy increases from 6 to 9 MeV, an insignificant reduction of the self-diffusion coefficient for water molecules takes place. The mobility of ions increases at that, whereas the mobility of cations substantially decreases. The reduction of D^{Na^+} values testifies that almost all cations participate in the formation of associates with other solution components at this irradiation energy.

A further increase of the irradiation energy to 12 MeV stimulates the growth of D^{Na^+}, which remains, nevertheless, much lower than D^{Cl^-}. In other words, at energies lower than 9 MeV, the mobility of water molecules in the system does not change. The further increase of the irradiation energy gives rise to a reduction of D^{H_2O} values, which indicates that the free motion of water molecules becomes more complicated. The data obtained confirm our assumption that the mechanisms of interaction between water molecules and between ions are different at studied irradiation energies.

4. Conclusions

Molecular dynamics researches of the influence of radiation on the local structure in the 0.14-mol.% NaCl aqueous solution at $T = 300$ K showed that the structure of clusters formed by water molecules does not depend on the irradiation energy. At the irradiation energies lower or higher than 9 MeV, no substantial changes in the local structure of the examined system take place. At an irradiation energy of 9 MeV, the local structure of the NaCl aqueous solution changes, because the probability for cations and anions to interact with one another and with water molecules increases, which results in a higher ordering of the local structure of the solution. The variation of the irradiation energy affects the dynamic characteristics of the system, and this influence is the most substantial at

an irradiation energy of 9 MeV. Therefore, the radiation effect at the indicated irradiation energy can be considered as maximum for the researched system.

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ВПЛИВ РАДІАЦІЙНОГО
ОПРОМІНЕННЯ НА ЛОКАЛЬНУ
СТРУКТУРУ ВОДНОГО РОЗЧИНУ NaCl

Р е з ю м е

З використанням методу молекулярної динаміки досліджено вплив радіаційного опромінення на локальну структуру водного розчину NaCl із концентрацією 0,14 м.д. при $T = 300$ K в інтервалі енергій опромінення $E_r = 0$–12 МеВ. Встановлено, що при величинах E_r, менших або більших за 9 МеВ, не відбувається кардинальної зміни локальної структури дослідженої системи. При $E_r = 9$ МеВ відбувається суттєва зміна локальної структури розчину і дія радіаційного опромінення може вважатись максимальною, що пояснюється збільшенням ймовірності взаємодії катіонів та аніонів розчиненої речовини між собою та їх взаємодією з молекулами води.