INFLUENCE OF THE CHARGE AND CONCENTRATION OF DISSOLVED IONS ON THE SELF-DIFFUSION OF WATER IN AQUEOUS SOLUTIONS OF ELECTROLYTES. NEUTRON STUDIES

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The researches of water self-diffusion in 1—1 and 1—2 electrolyte solutions of various concentrations have been carried out making use of quasielastic scattering of slow neutrons. It was of interest not only to determine the values of the water self-diffusion coefficients in solutions, but also to obtain an experimental confirmation of the modern theoretical ideas concerning the existence of individual and collective contributions to the self-diffusion coefficient of molecules. The proposed method allowed us not only to describe the scenario of the molecular motion in liquids qualitatively, but also to quantitatively evaluate the relations between the individual and collective modes.

1. Experimental Part

The measurements of the slow neutron scattering in electrolyte solutions were carried out with the use of a multidetector neutron time-of-flight spectrometer on a VVR—M nuclear reactor at the Institute for Nuclear Researches of the NAS of Ukraine. A monochromatic beam of neutrons with the energy $E_0 = 13.26$ meV was used in experiments. The energy resolution of the spectrometer was 0.66 meV. The spectrum of neutrons scattered by a specimen at angles within the range of $9.5 - 101.3°$ was analyzed on an AI–4096 multichannel time analyzer. The researched electrolyte solutions were placed into a plane $140{\times}60$-mm^2 container with windows made of a titanium foil 0.07 mm in thickness for neutrons to pass. The thickness of the electrolyte layer was about 1 mm. The fraction of neutrons scattered by the specimen did not exceed 20% of their total number, which allowed us to neglect the contribution of multiple scattering when interpreting the experimental data.

A block diagram of the experimental setup is shown in Fig. 1. A “white” beam of neutrons generated by reactor *1* and formed by collimator *2* hit a zinc single crystal *3* used as a crystal-monochromator. For the creation of a pulsed flux of monochromatic neutrons, the beam of neutrons with the energy $E_0 = 13.26$ meV reflected from the single crystal was interrupted by mechanical chopper *4* and hit a researched specimen placed in container *5*. Possible variations of the intensity of the monochromatic neutron beam were recorded with the help of monitor *6*. Neutrons scattered by the specimen at various angles were registered by the system composed of eight detectors *7* arranged in a vertical circle with radius $R = 2.82$ m and with the specimen at the center. The energy spectra of scattered neutrons were measured by the time-of-flight method simultaneously at several angles in the range $9 - 117°$. The neutron detectors were disposed at angles of 9.5, 25.1, 40.5, 55.7, 70.9, 86.1, 101.3, and 116.5°. Each detector comprised 15 neutron counters filled with ^{3}He gas.

The simultaneous measurements of neutron spectra were carried out making use of a multidata time analyzer *11* composed of two multichannel time analyzers. One of the latter was used for the measurements of scattered neutron spectra, the other served for the measurements of the background. The memory of the time analyzer of pulses was split according to the number of detectors into 8 groups, with 256 time channels in each. The analyzer was launched with a pulse generated by the magnetic head of the mechanical chopper at the moment

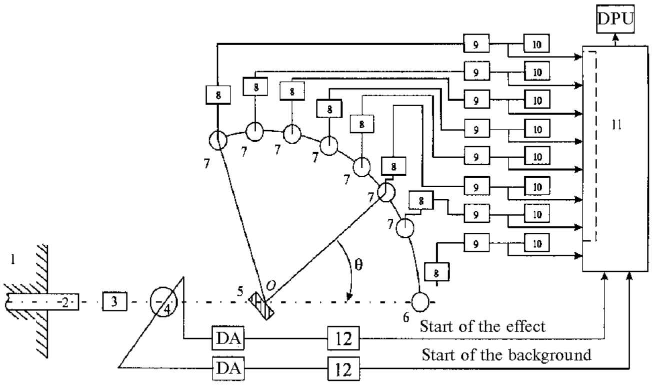

Fig. 1. Block scheme of the experimental setup for studying the dynamics of liquids by the method of quasielastic scattering of slow neutrons

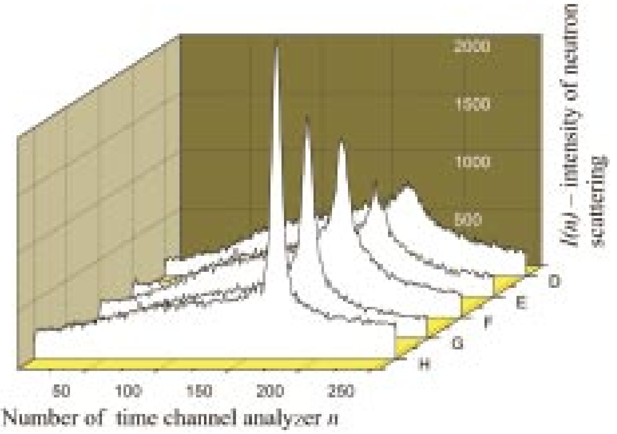

Fig. 2. Spectra of neutron scattering obtained for the LiCl aqueous solution with a concentration of 3 mol/l at the temperature $T = 298$ K. The scattering angles θ are 25.1, 40.5, 55.7, 70.9, and 86.1° (curves H—D, respectively)

when the slit became open for a pulse of the neutron beam to pass.

The reflected beam monitor *6* was used for the supervision over variations of the intensity of the monochromatic neutron beam. It consisted of five counters 20 mm in diameter and 150 mm in length which were placed on the way of monochromatic neutrons at a distance of 2.82 m from the specimen. The filling and thickness of the monitor are equivalent to those of the scattered beam detectors.

The typical shapes of experimental curves obtained for the scattering of slow neutrons by the electrolyte solution at various angles θ are depicted in Fig. 2. In this figure, n is the number of the analyzer's time channel with a resolution of 8 μs, which determined the energy of scattered neutrons, and $I(n)$ is the number of neutrons registered in the n-th channel of the analyzer. The curve $I(n)$ can be divided into two parts, one of which corresponds to inelastic neutron scattering and the other to quasielastic one. It is known that the mechanism of diffusion, which is characteristic of the liquid concerned, manifests itself just in the quasielastic scattering spectra of neutrons, namely, in a broadening of the quasielastic peak in the spectrum of scattered neutrons as compared to that in the spectrum of incident neutrons. The magnitude of the broadening makes it possible to estimate how strongly the excited degrees of freedom in the specific liquid are connected with diffusion, as well as to draw conclusions about the character of this diffusion.

As is seen from Fig. 2, there is no clear distinction between proper inelastic and quasielastic scatterings in the spectrum of neutron scattering. The boundary between those two types of neutron inelastic scattering in a liquid is relative to a great extent, especially at large scattering angles ($Q > 2$), when the intensity of quasielastic scattering decreases. In this connection, we had to apply a special technique to isolate quasielastic scattering from the total scattering of neutrons [1].

A well-fitted Lorentz curve for $Q = 1.71$ Å (the scattering angle $\theta = 40.5°$) was subtracted from the spectrum of neutrons scattered at this angle. The difference, which constituted the contribution of inelastic scattering to the measured spectrum, was subtracted then from the spectrum of neutrons scattered at an angle of 55.7°, taking into account the normalizing factor which was calculated while analyzing the scattering of neutrons by vanadium atoms. The described procedure is illustrated in Fig. 3 step-by-step. The Lorentz curve obtained in such a way for the scattering angle $\theta = 55.7°$ is shown in Fig. 3 by a solid curve. The same procedure was also carried out for other scattering angles.

Every scattering angle corresponds to a certain value of the transferred wave vector $\mathbf{Q} = \mathbf{k}_0 - \mathbf{k}$, where $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors which describe the neutron state before and after scattering, respectively. The experimental dependences of the broadening of quasielastic peaks ΔE on the square of the transferred wave vector Q^2 were analyzed in the framework of

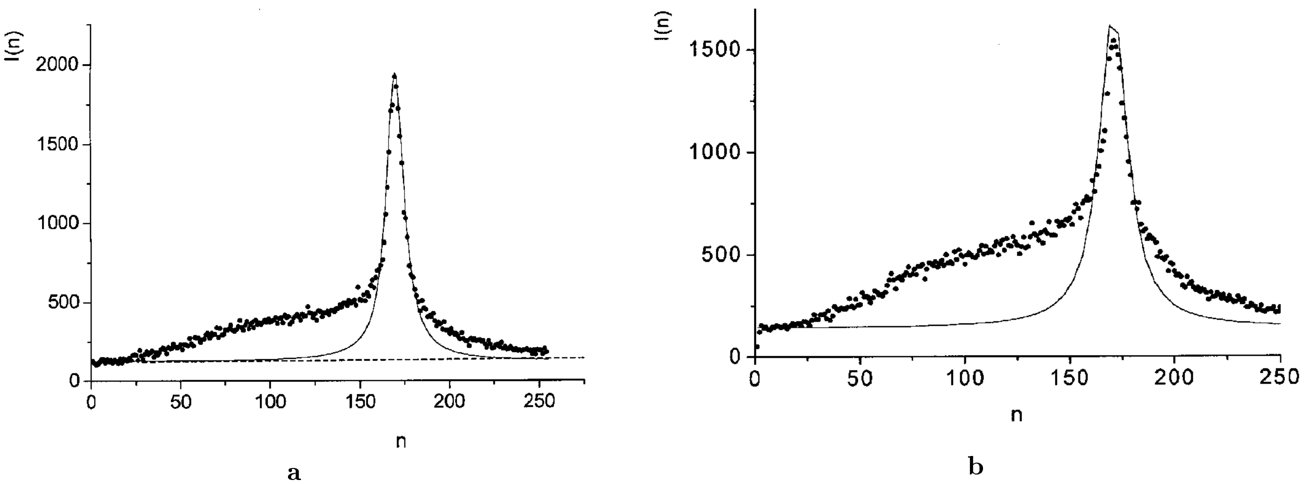

Fig. 3. Spectra of neutrons scattered in the LiCl aqueous solution ($C = 3$ mol/l, $T = 298$ K) at the angles $\theta = 40.5$ (a) and 55.7° (b)

certain models of self-diffusion [2], namely,

$$\Delta E = 2\hbar Q^2 D \tag{1}$$

for the model of continuous diffusion,

$$\Delta E = \frac{2\hbar}{\tau_0}\left[1 - \frac{\exp\{-2W\}}{1 + D Q^2 \tau_0}\right] \tag{2}$$

for the Singwi—Sjölander model of jump diffusion, and

$$\Delta E = \frac{2\hbar}{\tau_0}\left[1 + D_0 Q^2 \tau_0 - \frac{\exp\{-2W\}}{1 + D Q^2 \tau_0}\right] \tag{3}$$

for the Ivanov model, where, in addition to the jumps of molecules from one center of oscillations to another, the continuous diffusion of the very centers of oscillations was also taken into account.

2. Theoretical Basis for Splitting the Self-Diffusion Coefficient into Collective and One-Particle Components

In accordance with modern considerations, the motion of atoms in a liquid comprises a combination of two modes: fast one-particle motions of vibration character and relatively slow collective motions, the latter result in molecular diffusion and the disordering of the molecule arrangement [3]. From this point of view, two contributions to the self-diffusion coefficient are distinguished: collective ("Lagrange") and one-particle ("Frenkel") ones which are connected with the long- and short-time character of behavior, respectively, of diffusing molecules. The total self-diffusion coefficient is a sum of those contributions [4, 5]:

$$D = D^{\mathrm{L}} + D^{\mathrm{F}}. \tag{4}$$

The observation period of a molecule in the neutron experiment is

$$t_{\mathrm{ob}} = \frac{1}{6D\,Q^2}. \tag{5}$$

Therefore, changing the conditions of the neutron experiment, it becomes possible to change the observation period too. For large values of Q, the observation period of a diffusing molecule is short ($t_{\mathrm{ob}} \sim 10^{-13}$ s), so that fast motions are mainly observed. As Q decreases, t_{ob} increases, and neutrons begin to "feel" slower collective motions of molecules ($t_{\mathrm{ob}} < 10^{-11}$ s).

Basing on the time-scale hierarchy, i.e. assuming fast motions of a molecule to be responsible for the one-particle contribution and slower motions for the collective component, the broadening of the quasielastic peak can be written down as

$$\Delta E = \Delta E_K + \Delta E_o, \tag{6}$$

where ΔE_K and ΔE_o are the collective and one-particle components, respectively, of the quasielastic peak broadening.

Then, Eq. (3), which describes the experimentally observed broadening of the quasielastic peak, looks like

$$\Delta E = 2\hbar D_K Q^2 + \frac{2\hbar}{\tau_0}\left[1 - \frac{\exp\{-2W\}}{1 + Q^2(D - D_K)\tau_0}\right], \tag{7}$$

where D_K and D_o are the collective and one-particle components, respectively, of the self-diffusion coefficient $D = D_c + D_o$, and τ_0 is the dwell time of a molecule in the equilibrium position.

For the aqueous solutions of electrolytes, a hydrated ion can be considered as a Lagrange particle. At the same time, water molecules take part in both one-particle (moving within the hydration spheres or jumping from one to another) and collective (together with their hydration spheres) motions.

Analyzing the experimental dependences $\Delta E(Q^2)$ makes it possible to obtain the asymptotics of Eq. (7) for large and small Q^2, which allows the parameters τ_0, D_K, and D_o of this equation to be estimated (Fig. 8). The analysis of formula (7) shows [3] that, at small values of Q^2 ($Q^2 \to 0$) and, correspondingly, at large observation periods t_{op},

$$\Delta E \approx 2\hbar D_K Q^2 + \frac{2\hbar}{\tau_0}\left[1 - 1 + D_o Q^2 \tau_0\right] = 2\hbar D Q^2, \quad (8)$$

which allows the total self-diffusion coefficient of molecules of a liquid to be determined from the slope of the linear, at small Q^2 values, part of the dependence $\Delta E(Q^2)$. For large values of the transferred wave vector ($Q^2 \to \infty$, a short observation period), Eq. (7) reads

$$\Delta E = 2\,\hbar\, D_K\, Q^2 + \frac{2\,\hbar}{\tau_0}. \quad (9)$$

Thus, analyzing the behavior of the dependences $\Delta E(Q^2)$ at large Q^2 values, the collective component of the self-diffusion coefficient and the dwell time τ_0 can be determined. Then, the one-particle component of the self-diffusion coefficient is $D_o = D - D_K$.

For the parameters D, D_c, and τ_0 to be determined, the experimental data were fitted by the theoretical curve (7) in the whole range of variation of the squared transferred wave vector.

Thus, with the help of the method of incoherent quasielastic scattering of slow neutrons and basing on the time-scale hierarchy of molecular motions, the self-diffusion coefficient can be split into the one-particle and collective components, which allows the fractions of water molecules in hydration spheres and in the free state in the solutions under investigation to be estimated.

3. Experimental Objects

To elucidate the role and to evaluate the contribution of the collective motions to the self-diffusion coefficient of solvent molecules, we carried out the researches of slow neutron scattering in the aqueous solutions of electrolytes by varying the charge and concentration of solute ions.

According to the method described above, the separation of the collective and one-particle contributions to the self-diffusion coefficient of water molecules was fulfilled for the LiCl, NaCl, CsCl, KI, and $CoCl_2$ aqueous solutions with various concentrations and for some aqueous solutions of multivalent electrolytes at a constant concentration of 3 mol/l. All researches were carried out at a constant temperature of 298 K. The obtained values of the self-diffusion coefficient D, the collective contribution D_c, and the dwell time τ_0 are quoted in Tables 1, 2, and 3.

4. Results of Researches

First, we carried out the researches dealing with self-diffusion of ions of 1—1 electrolytes in aqueous solutions of a constant concentration (3 mol/l) and temperature (298 K). The results presented in Fig. 4 and Table 1 bring us to the following.

The monovalent ions dissolved in water, owing to their different dimensions and forms, affect the structure and transport characteristics of water differently. Really, the dependences $\Delta E(Q^2)$ for the NaCl, $NaNO_3$, and LiCl aqueous solutions are situated below while those for the CsCl, Cs, and KI ones above the analogous dependence for pure water. This corresponds to lower values of the diffusion coefficient of water molecules in the NaCl, $NaNO_3$, and LiCl aqueous solutions and to its higher values in the CsCl, Cs, and KI ones than the self-diffusion coefficient of pure water molecules. In turn, such a situation corresponds to the cases of positive and negative hydration, respectively.

The appearance of positive or negative hydration depends mainly on the dimensions of dissolved ions. Ions

Table 1

Substance	Cation radius R, Å	D, 10^{-9} m^2/s	D_c, 10^{-9} m^2/s	D_c/D, %	τ_0, 10^{-12} c
LiCl	0.78	1.38 ± 0.15	0.97 ± 0.1	71%	
NaCl	0.98	1.52 ± 0.10	0.39 ± 0.02	25%	2.41 ± 0.07
$NaNO_3$	0.98	1.87 ± 0.10	0.35 ± 0.03	19%	2.15 ± 0.05
H_2O		2.30 ± 0.15	0.26 ± 0.04	11%	1.73 ± 0.1
CsCl	1.65	2.58 ± 0.09	0.20 ± 0.02	8%	1.22 ± 0.04
CsI	1.65	2.73 ± 0.10	0.28 ± 0.02	10%	1.09 ± 0.02
KI	1.33	2.84 ± 0.10	0.32 ± 0.01	11%	0.89 ± 0.02

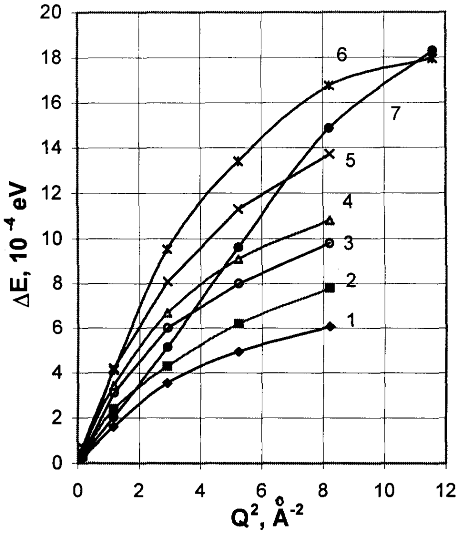

Fig. 4. Dependences $\Delta E(Q^2)$ of the quasielastic peak broadening on the square of the transferred wave vector for water (*3*) and the aqueous solutions of NaCl (*1*), $NaNO_3$ (*2*), CsCl (*4*), CsI (*5*), KI (*6*), and LiCl (*7*). $C = 3$ mol/l, $T = 298$ K

with crystallographic radii $R < 1.3$ Å (e.g., $R_{\mathrm{Na}^+} = 0.98$ Å and $R_{\mathrm{Li}^+} = 0.78$ Å) can penetrate into structural cavities of water without essential variation of the cavity dimensions. Relatively small monovalent ions cause a strengthening of the ordered structure and an expansion of regions where the ordering is observed. On the contrary, big ions, penetrating into the structural cavities of water, deform them in a mere geometrical sense, inducing breaks of hydrogen bonds between water molecules, which results in the growth of the self-diffusion coefficient of water molecules in the solution.

Comparing the self-diffusion coefficients of water in the investigated solutions and pure water (Table 3), a conclusion can be drawn that cations influence the mobility of water molecules in solutions to a greater extent than anions do. For example, considering the solutions of NaCl and CsCl salts (Fig. 4), we see that, although anions Cl^- are the same in both the cases, the availability of Na^+ cations, whose dimensions are smaller than those of water molecules, results in positive hydration and a reduction of the self-diffusion coefficient of water, while Cs^+ cations cause negative hydration and an increase of this coefficient.

For the investigated solutions, provided their identical concentration $C = 3$ mol/l, the collective

Table 2

Substance	Cation radius R, Å	Self-diffusion coefficient D, 10^9 m²/s
$ZnCl_2$—H_2O	0.74	1.43 ± 0.15
$CoCl_2$—H_2O	0.80	1.29 ± 0.10
$NiCl_2$—H_2O	0.74	0.68 ± 0.05
$MgCl_2$—H_2O	0.74	0.63 ± 0.05
$CrCl_3$—H_2O		0.39 ± 0.05
$AlCl_3$—H_2O		0.27 ± 0.05

Table 3

Substance	C, mol/l	D,10^9 m²/s	D_c, 10^9 m²/s	$\frac{D_c}{D} \times 100\%$	Dwell time, τ_0, 10^{-12}
H_2O	—	2.30 ± 0.10	0.26 ± 0.04	11 %	1.73 ± 0.10
NaCl—H_2O	1	2.0 ± 0.10	0.27 ± 0.01	13.5 %	1.91 ± 0.05
	2	1.73 ± 0.09	0.31 ± 0.02	18 %	2.05 ± 0.05
	3	1.52 ± 0.10	0.33 ± 0.03	22 %	2.41 ± 0.04
	4	1.34 ± 0.08	0.35 ± 0.02	26 %	2.80 ± 0.03
LiCl—H_2O	0.5	2.13 ± 0.09	0.36 ± 0.05	17 %	
	1	1.91 ± 0.10	0.63 ± 0.03	33 %	
	3	1.38 ± 0.10	0.97 ± 0.10	71 %	—
	5	1.03 ± 0.05		∼ 100 %	
	10	0.61 ± 0.05		∼ 100 %	
$CoCl_2$—H_2O	1	1.80 ± 0.10	0.74 ± 0.03	41 %	1.98 ± 0.07
	2	1.52 ± 0.09	0.63 ± 0.02	42 %	2.30 ± 0.08
	3	1.23 ± 0.10	0.48 ± 0.02	40 %	2.96 ± 0.06
	4	1.05 ± 0.10	0.42 ± 0.02	41 %	3.6 ± 0.05
CsCl—H_2O	1	2.35 ±0.10	0.21 ± 0.03	10 %	1.20 ± 0.05
	3	2.58 ± 0.15	0.18 ± 0.02	7 %	1.22 ± 0.04
	5	3.12± 0.10	0.25 ± 0.03	8 %	1.33 ± 0.06
	8	2.77 ± 0.15	0.36 ± 0.03	13 %	1.56 ± 0.05
KI—H_2O	1	2.43 ± 0.10	0.24 ± 0.02	10 %	0.83 ± 0.05
	2	2.54 ± 0.10	0.23 ± 0.03	9 %	0.79 ± 0.06
	3	2.84 ± 0.10	0.31 ± 0.03	11 %	0.89 ± 0.05
	4	2.74 ± 0.15	0.38 ± 0.04	14 %	1.02 ± 0.05
	5	2.63 ± 0.15	0.50 ± 0.04	19 %	1.5 ± 0.07

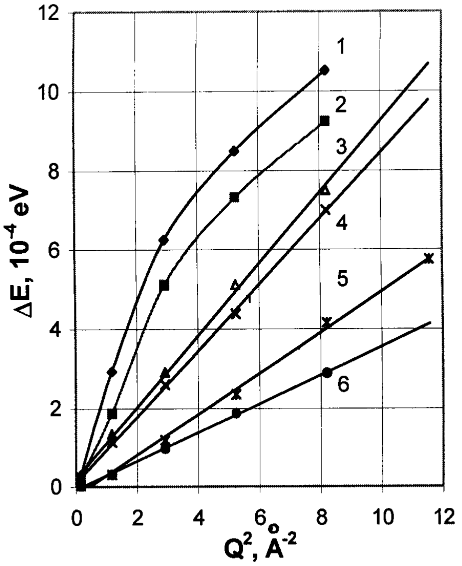

Fig. 5. The same as in Fig. 4 but for the aqueous solutions of $ZnCl_2$ (*1*), $CoCl_2$ (*2*), $NiCl_2$ (*3*), $MgCl_2$ (*4*),$CrCl_3$ (*5*), and $AlCl_3$ (*6*). $C = 3$ mol/l, $T = 298$ K

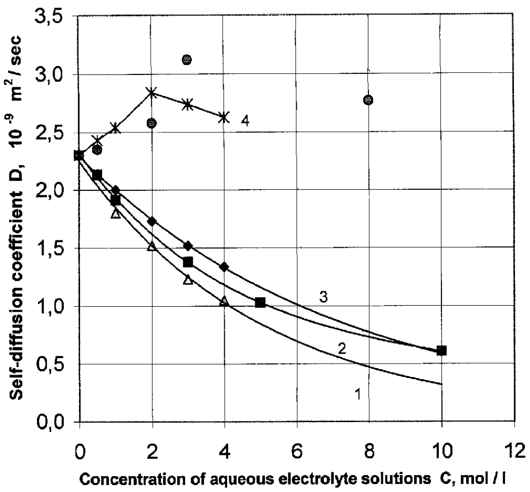

Fig. 6. Concentration dependences of the self-diffusion coefficient of water molecules in the aqueous solutions of $CoCl_2$ (*1*), LiCl (*2*), NaCl (*3*), KI (*4*), and CsCl (circles) electrolytes at the temperature $T = 298$ K

component of the self-diffusion coefficient is larger in the case of positive hydration (the relevant values are 71% for LiCl, 25% for NaCl, and 19% for $NaNO_3$ solutions) and smaller in case of negative hydration (8% for CsCl, 10% for CsI, and 11% for KI solutions) than the corresponding value for a pure solvent (11%). The same is also true for the dwell time τ_0 (see Table 1).

The studies of the self-diffusion processes in aqueous solutions that include ions of different charges are of special interest. To analyze how the charges of dissolved ions influence the mobility of water molecules, the self-diffusion coefficients of water molecules in the $ZnCl_2$, $CoCl_2$, $NiCl_2$, $MgCl_2$, $AlCl_3$, and $CrCl_3$ solutions, with a concentration of 3 mol/l each, were measured. The dependences $\Delta E(Q^2)$ for those solutions are presented in Fig. 5, and the corresponding self-diffusion coefficients are quoted in Table 2.

The tabular data show that there is a significant reduction of the self-diffusion coefficient of water molecules if the charge of dissolved ions increases, which evidences for a strong interaction between multivalent ions and water molecules in solutions. Under the action of multivalent ions, not only the value of the self-diffusion coefficient decreases, but the character of self-diffusion itself also changes. As is seen from Figs. 4 and 5, if monovalent and some, larger by size, divalent ions (e.g., Zn^{2+} and Co^{2+}) are dissolved in water, the process of self-diffusion is described within the frame of the Oskotskii–Ivanov model. For small divalent ions and all the investigated trivalent ions, the linear dependence of ΔE on Q^2 is observed, which corresponds to the model of continuous diffusion.

Since the concentrations of the investigated solutions were identical and they had the same Cl^- anion, the difference in the character of self-diffusion can be caused by different structures of the close environment of cations. When considering the transfer phenomena, it is possible to assume that it is mainly water molecules in the first hydration sphere that move together with monovalent ions, whereas small multivalent ions also interact, rather strongly, with more distant water molecules. It results in the formation of the second hydration sphere around a multivalent ion (secondary hydration). Therefore, solvent molecules bound to those hydration spheres do not almost take part in self-diffusion independently, but move together with an ion, which corresponds to the model of continuous diffusion.

The self-diffusion coefficient of water in electrolyte solutions depends substantially on the concentration of ions in a solution, either increasing or decreasing as the electrolyte concentration grows, which depends on the type of a dissolved ion (Fig. 6). For example, the self-diffusion coefficients of the aqueous solutions of NaCl, LiCl, and $CoCl_2$ salts decrease following an exponential law as the salt concentration increases. At large concentrations, positively hydrated ions bind more and more water molecules in hydration spheres, which results in a significant strengthening of the water

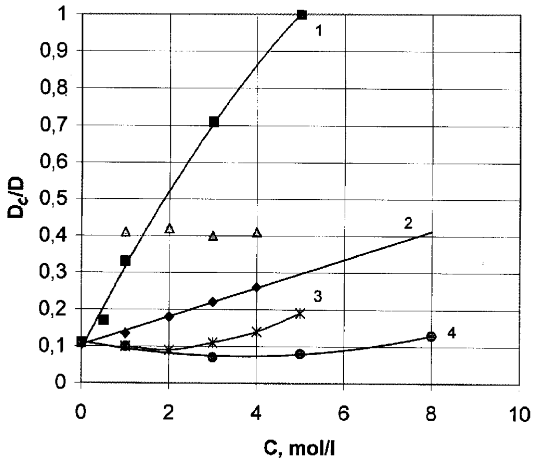

Fig. 7. Concentration dependences of the relative fraction of the collective component in the self-diffusion coefficient of water molecules in the aqueous solutions of LiCl (*1*), $CoCl_2$ (triangles), NaCl (*2*), KI (*3*), and CsCl (*4*) electrolytes at the temperature $T = 298$ K

structure and a reduction of the self-diffusion coefficient of solvent molecules.

For the CsCl—H_2O and KI—H_2O solutions with negatively hydrated cations, the slope of the $D(C)$-curves changes its sign: the self-diffusion coefficient increases along with the salt concentration growth within a certain concentration interval. It is connected with a destructive effect of negatively hydrated ions on the water structure. As is seen from Fig. 6, a distinct maximum is observed on the $D(C)$-curves for the CsCl and KI solutions at a certain concentration ($C = 5$ mol/l for the CsCl and $C = 3$ mol/l for the KI solutions). If the concentration grows further above those characteristic values, the self-diffusion coefficient of water molecules begins to decrease. At large salt concentrations, the interaction between ions may prevail over the interaction between ions and solvent molecules, so that the self-diffusion coefficient of solvent starts to diminish with the growing concentration.

Fig. 7 shows the concentration dependences of the relative contribution of collective motions to the self-diffusion coefficient of the aqueous solutions of the investigated electrolytes. As the concentrations of the NaCl—H_2O and LiCl—H_2O solutions grow (see Table 3), the amplitude of the collective component of the self-diffusion coefficient increases, while the total self-diffusion coefficient diminishes simultaneously. It is hard for water molecules, which form hydration spheres, to take part in the self-diffusion process and in the exchange process between free water molecules and the molecules of the neighboring hydration spheres. Moreover, owing to hydration, the growth of concentration is accompanied by an increase of the number and the dimensions of “Lagrange” particles, which enhances the effect of obstacles and results in the augmentation of the collective component of the self-diffusion coefficient of water molecules.

It is worth noting that the concentration-induced enlargement of the collective contribution to the self-diffusion coefficient is extremely strong for the LiCl—H_2O solution. At the concentrations $C > 5$ mol/l, the one-particle component of the self-diffusion coefficient of water molecules is absent. Owing to a small radius of the Li^+ cation and a large strength of the electric field near its surface, its hydration sphere turns out considerably denser than those of other univalent ions under consideration. Therefore, in the case of large concentrations, all water molecules become bound in the hydration spheres of Li^+ ions and participate in the diffusion process together with the Li^+ hydration spheres only, i.e. following the collective mechanism.

The larger the ion charge, the higher the probability for a water molecule to take part in a collective motion as one of the particles from the ion environment. Therefore, an increase of the ion charge results in a reduction of the one-particle component and a growth of the collective component of the self-diffusion coefficient. Really, the values of D_c for the $CoCl_2$ solution are larger than the corresponding values for the NaCl one in the whole range of concentrations. In addition, notwithstanding the growth of the Co^{2+} ion concentration in the solution, the collective component of the self-diffusion coefficient remains constant within the limits of experimental errors and amounts to approximately 40% of the total self-diffusion coefficient.

For the CsCl and KI aqueous solutions, the concentration dependences of the collective component of the self-diffusion coefficient (Fig. 7) have non-monotonous character. This testifies to that the effect of obstacles may prevails over the destructive effect of negatively hydrated ions in the CsCl and KI concentrated solutions when the amount of ions dissolved in water increases. In addition, direct bonds between dissolved ions become essential at high electrolyte concentrations.

On the basis of the experimental data dealing with quasielastic scattering of slow neutrons and with the help of expression (7), we estimated the dwell time of a water molecule in the hydration spheres of ions (see Table 3).

As should be expected, in the case of positive hydration (the solutions of LiCl, NaCl, and $CoCl_2$ salts),

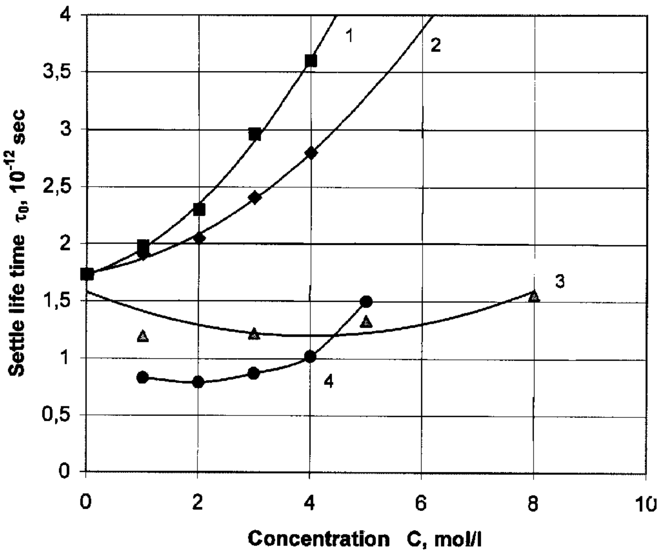

Fig. 8. Concentration dependences of the dwell time of a water molecules in the equilibrium position in the aqueous solutions of NaCl (*1*), $CoCl_2$ (*2*), CsCl (*3*), and KI (*4*) electrolytes at the temperature $T = 298$ K

the dwell time τ_0 increases along with increase in the ion concentration in water. In the case of negative hydration (the solutions of CsCl and KI salts), the dependence $\tau_0(C)$ has a non-monotonous character, passing through a minimum at a certain, specific for each solution, value of concentration (Fig. 8).

For aqueous solutions of multivalent electrolytes, the experimental data correspond to the model of continuous diffusion, so that our method does not allow the dwell time to be determined. Water molecules in the hydration spheres of multivalent ions exchange with molecules of neighbor hydration spheres, the time scale of the process being beyond the scope of the presented method. Therefore, the time interval when the protons of a water molecule are bound with the specified ions is larger than 10^{-10} s.

5. Conclusions

Thus, the results of our researches of the self-diffusion coefficients of water molecules in the aqueous solutions of electrolytes have shown that dissolved substances change the structure of water, with the dissolved ions being capable to strengthen or to loosen it, depending on conditions. It has been revealed that the self-diffusion coefficient of water molecules decreases as the charge of the dissolves ion grows and the ion size diminishes, being exponentially dependent on the concentration of ions in a solution.

The researches have confirmed the validity of the modern theoretical ideas concerning the existence of the one-particle “Frenkel” and collective “Lagrange” contributions to the self-diffusion coefficient of molecules in both pure liquids and solutions, with the relative role of those contributions depending on the solution composition.

Analyzing the neutron experimental data and on the basis of the time-scale hierarchy of molecular motions, we have split the self-diffusion coefficient into the one-particle component and the collective one. The fraction of the collective component in the self-diffusion coefficient increases as the valence of the dissolved ions grows and depends on the solution concentration.

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ВПЛИВ ЗАРЯДУ ТА КОНЦЕНТРАЦІЇ РОЗЧИНЕНИХ ІОНІВ НА ПРОЦЕСИ САМОДИФУЗІЇ ВОДИ У ВОДНИХ РОЗЧИНАХ ЕЛЕКТРОЛІТІВ. НЕЙТРОННІ ДОСЛІДЖЕННЯ

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Резюме

Методом квазіпружного розсіяння повільних нейтронів проведено дослідження самодифузії води у водних розчинах одно-одно- та одно-двозарядних електролітів різної концентрації. Становило інтерес не тільки визначити значення коефіцієнтів самодифузії в розчинах, а також одержати експериментальне підтвердження сучасних теоретичних припущень про існування індивідуальних та колективних внесків у коефіцієнт самодифузії молекул. Запропонована нами методика дозволила не тільки якісно намалювати картину руху молекул, але й кількісно оцінити співвідношення індивідуальних та колективних рухів молекул в рідинах.