SPECIFIC FEATURES OF MOTION OF CATIONS AND ANIONS IN ELECTROLYTE SOLUTIONS

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The nature of mobility of ions and water molecules in dilute aqueous solutions of electrolytes (at most fifteen water molecules per ion) is investigated. It is shown that the behavior of the mobility coefficients of water molecules and ions, as well as the self-diffusion coefficients of water molecules, are determined by the radii of their hard shells rather than by the effect of the hydrogen bond network. It is established that the influence of hydration effects on the density of the system and the self-diffusion coefficients of water molecules does not exceed several per cent. Based on microscopic concepts, it is shown that the different behaviors of a K^+ cation and an F^- anion with equal rigid radii are in good agreement with specific features of the intermolecular interaction described by the generalized Stillinger–David potential [1, 2].

1. Introduction

For today, a substantial body of information is accumulated on the thermal motion of water molecules and ions in water electrolyte solutions (see [3–13]). Now, of interest is the experimental study of the kinetic and electrophysical properties of electrolytes. The specific features of motion of water molecules and ions have a certain effect on the thermodynamic properties of liquids and liquid systems [14]. The study of a structure and a character of thermal molecular motion in electrolytes with the help of the quasielastic scattering of slow neutrons [5–10] and molecular dynamics methods [11–13] acquires still larger importance.

There also exists a large number of substantial theoretical works [15, 16] devoted to the description of properties of electrolytes. The main efforts in them are concentrated on the adequate allowance for hydration effects and the correct reflection of the role of hydrogen bonds. However, a lot of questions (very simple, at first sight) remain practically unanswered. A typical example is peculiarities of the manifestation of hydration effects depending on the radii of ions and the signs of their charges.

Let us illustrate this fact by the example concerning the behavior of the self-diffusion coefficients of water molecules as functions of the cation and anion sizes. The corresponding values of the self-diffusion coefficients $D_s^{(w)}$ of water molecules in several dilute solutions of electrolytes at the temperature $T = 296$ K are given in Table 1 presenting the dependence of $D_s^{(w)}$ on the anion size. The solution concentration in the table is specified by the number z_w of water molecules per one ion (the value of z_w is given in parentheses near the chemical formula of an electrolyte, for example NaCl(15.9)). The minimal value $z_w = 15$ thus corresponds to the electrolyte concentration equal to 3.3 mole mutual effect of cations and anions can be neglected to a satisfactory accuracy. It is also worth adding to the table the self-diffusion coefficient of water molecules in the CsI(17.4) solution: $D_s^{(w)}$=2.71×10^{5} cm²/s.

We note that, according to [17, 18], the self-diffusion coefficient of molecules in water at the same temperature $T = 296$ K is equal to

$$D_s^{(w)} = 2.35 \times 10^{-5} \text{cm}^2/\text{s}. \qquad (1)$$

The number of hydrogen bonds formed by one molecule in water at the same temperature is approx-

T a b l e 1. Self-diffusion coefficients of water molecules in water solutions of singly charged electrolytes [5]

			LiBr(30)	LiI(24.8)
$D_s^{(w)} \times 10^5$, cm²/s			2.3	2.18
	NaCl(15.9)	NaBr(16.5)	NaI(16.1)
$D_s^{(w)} \times 10^5$, cm²/s		2.14	2.26	2.38
	KF(15)	KCl(16.1)	KBr(16.1)	KI(16.4)
$D_s^{(w)} \times 10^5$, cm²/s	1.99	2.44	2.68	2.8

imately equal to $n_{\rm H} \approx 2.5$ [19–22]. In this case, the average distance between water molecules is close to the hydrogen bond length $l_{\rm H} \approx 2.8$ Å. Comparing (1) with the values of the self-diffusion coefficients given in Table 1, one can conclude that the self-diffusion coefficients of water molecules considerably depend on the combinations of cations and anions even in dilute solutions of electrolytes.

In this work, we analyze the mobility coefficients of water molecules as functions of the cation and anion sizes in the close connection with the behavior of the solution density. In this way, we try to make certain conclusions concerning the role of hydration effects in solutions of electrolytes. In addition, to discover the nature of asymmetry effects in the interaction of anions and cations with water molecules, the microscopic ideas about the character of their interaction are involved. This aspect of the problem is solved on the basis of the generalized potential of interparticle interaction proposed in [1,2,23].

2. Dependence of the Self-Diffusion and Mobility Coefficients of Water Molecules and the Mobility Coefficients of Ions on Their Size

To analyze the results presented in Table 1, let us consider how the self-diffusion coefficients of water molecules in solutions of electrolytes correlate with the radii of dissolved ions. The latter are not determined unambiguously, but considerably depend on the method of their determination. In this connection, we consider the following ionic radii: 1) those found from crystallographic conceptions; 2) those chosen to favor the correct reproduction of the molecular dynamics in solutions of electrolytes by means of computer simulation, and 3) those estimated from the ion polarization. To make the picture complete, we consider also the ionic radii determined from hydrodynamic considerations. The corresponding results are gathered in Table 2.

In the first row of Table 2, one can see the crystallographic radii $r_{\rm c}$ [24]. The second row contains the ionic radii r_σ found from computer experiments [25] for the

T a b l e 2. Rigid (three upper rows) and Stokes radii of cations and anions

	Li$^+$	Na$^+$	K$^+$	Cs$^+$	F$^-$	Cl$^-$	Br$^-$	I$^-$
$r_{\rm c}$, Å	0.6	0.95	1.33	1.69	1.36	1.81	1.95	2.16
r_σ, Å	0.76	1.3	1.67	1.94	1.56	2.2	2.27	2.59
r_α, Å	0.45	1.12	1.41	2.02	1.51	2.33	2.55	2.93
$r_s^{(\mu)}$, Å	2.38	1.84	1.25	1.19	1.66	1.21	1.18	1.19
$r_{\rm c}^{(D)}$, Å	1.91	1.88	1.14	1.15	1.77	1.33	1.22	1.35

description of the dispersion (van der Waals) interaction between ions and water molecules. The ionic radii r_α determined from the ion polarizations α (see Table 3) according to the formula

$$r_\alpha = 1.5\alpha^{1/3} \qquad (2)$$

are presented in the third row. It is worth noting that, in the simplest model of an ion presenting it as a conducting sphere, the polarization is equal to $\alpha = r_{\rm sph}^3$, where $r_{\rm sph}$ is the sphere radius. With regard for the fact that a conducting sphere reflects ion properties only approximately, the coefficient 1.5 in (2) is chosen to provide the minimum deviation of the ionic radii r_α from $r_{\rm c}$. The radii $r_{\rm c}$, r_σ, and r_α will be called rigid ionic radii.

For the sake of comparison, the fourth and fifth rows of Table 2 present the Stokes ionic radii determined from the formulas

$$r_s^{(\mu)} = \frac{1}{6\pi\eta\mu^{(I)}} \qquad (3)$$

and

$$r_s^{(D)} = \frac{k_{\rm B}T}{6\pi\eta D_s^{(I)}},$$

where $\mu^{(I)}$ and $D_s^{(I)}$ stand for the mobility and the self-diffusion coefficient of ions determined by computer modeling in [25–27], whereas η is the shear dynamic viscosity of electrolyte solutions [28].

An important supplement to these data can be the Stokes radii of water molecules in electrolyte solutions gathered in Table 1. They are determined by the formula

$$r_s^{(w)} = \frac{k_{\rm B}T}{6\pi\eta D_s^{(w)}} \qquad (4)$$

and form Table 4 as well. In contrast to $r_s^{(\mu)}$ and $r_s^{(D)}$, the values of $r_s^{(w)}$ practically do not depend on the type of a dissolved electrolyte, as is worth expecting. At the same time, the obtained radii $r_s^{(w)}$ are noticeably smaller than the hard-sphere radius of water molecules, if identifying the latter with a half of the hydrogen bond length [29, 30]. Here, it is worth noting that hydrodynamic concepts can be used only on the scales significantly exceeding the corresponding molecular ones. That is why we make conclusion that the application of hydrodynamic conceptions to the self-diffusion process of water molecules is inconsistent.

T a b l e 3. Ion polarizations, Å^3 [26]

Li$^+$	Na$^+$	K$^+$	Cs$^+$	F$^-$	Cl$^-$	Br$^-$	I$^-$
0.029	0.179	0.83	2.42	1.04	3.66	4.77	7.1

One can see that the ionic radii used in the computer experiment somewhat exceed their crystallographic values. In the both cases, one observes, however, a monotonous growth of the cation and anion radii with increase in masses. The same dependence is registered for the ionic radii obtained from the ion polarizations.

On the contrary, the Stokes radii of water ions and molecules demonstrate the opposite behavior. The largest Stokes radius corresponds to a small Li$^+$ cation, whereas the least one is observed for an I$^-$ anion. There also exists a certain asymmetry in the behavior of cations and anions of the same radius. Indeed, the differences in the Stokes radii of K$^+$ and F$^-$ ions, as well as in their mobilities (see Table 5), significantly exceed the differences in the values of their rigid radii r_c, r_σ, and r_α. This fact is to a certain extent unexpected. It should be related to the noticeably different character of the interaction of water molecules with K$^+$ and F$^-$ ions, as well as with all other cations and anions. This important fact is thoroughly analyzed in Section 4 by the example of K$^+$ and F$^-$.

As follows from Tables 1 and 2, the self-diffusion coefficients of water molecules as functions of their rigid radii satisfy the following regularities:

1) for dilute lithium and sodium solutions of electrolytes, in which $r_c < \frac{1}{2} l_H$, the following inequality is met: $D_s^{(w)}(el) < D_s^{(w)}$. The condition $r_c < \frac{1}{2} l_H$ is evidently violated only for Cs$^+$. In solutions of potassium electrolytes, where $r_c(K^+) \sim \frac{1}{2} l_H$, one observes a transition from the previous relation between the self-diffusion coefficients of water molecules to the inequality $D_s^{(w)}(el) > D_s^{(w)}$;

2) in solutions of electrolytes with a fixed cation, except for lithium ones, the self-diffusion coefficients of water molecules grow with the anion radius;

3) in lithium electrolytes, the character of the dependence of $D_s^{(w)}(el)$ on the anion radius is opposite to the second conclusion.

With regard for the fact that the concentrations of different singly charged cations and anions are close to each other, the differences in the behavior of $D_s^{(w)}(el)$ can be caused by the following reasons: 1) geometrical factors and 2) their different effect on the structure of the local environment (hydration effects). The first

possibility should be discarded, as the geometrical obstacles must decrease with the cation radius, which conflicts with experimental data. But a reconfiguration of the local structure of water in the direct environment of cations and anions appears more noticeable, as their rigid radii increase.

Indeed, comparing the values of $r_s^{(\mu)}$, $r_s^{(D)}$, and $r_s^{(w)}$, one can see that, as the rigid radii of cations and anions increase, their Stokes radii approach the Stokes radius of water molecules. It is natural to interpret this fact as the joint drift of large ions together with water molecules that enter hydrated shells formed around them. It is worth noting that the effect of a local reconfiguration of the solution structure is insignificant, because the rise or fall of the self-diffusion coefficient of water molecules usually does not exceed ten per cent and is proportional to the mole concentration of electrolyte impurities.

3. Analysis of the Hydration Energy of Ions and the Density of Electrolyte Solutions

The dependence of the Stokes ionic radii on the rigid sizes of cations and anions is closely related to the phenomenon of the so-called positive or negative ion hydration [14, 31, 32]. Indeed, according to [33], the sign of the ion hydration energy is determined by the quantity $\Delta W = W - W_I$, where W is the average binding energy of two neighboring water molecules, and W_I is the average value of their interaction energy in the presence of ions. An ion close to the neighboring water molecules results in their additional polarization and an increase of the attractive forces acting between them. In the absence of hydrogen bonds, the difference $W - W_I$ must be positive, as the both terms W and W_I are negative. If a cation or an anion partially destroys hydrogen bonds, then the absolute value of W_I can become lower than that of W, i.e. the negative sign of ΔW will testify to the local breakage of the hydrogen bond network. Table 6 presents the dimensionless combination $\Delta \tilde{W} = \Delta W / 3 k_B T_m$ (where $3 k_B T_m$ is the energy of translational thermal motion of two water molecules

T a b l e 4. Stokes radii of water molecules in solutions of electrolytes gathered in Table 1

	LiBr	LiI	NaCl	NaI	KF	KCl	KBr	KI
η	1.009	0.97	0.997	0.957	1.053	0.936	0.917	0.912
$r_s^{(w)}$	0.934	1.025	1.015	0.951	1.034	0.949	0.881	0.85

T a b l e 5. Mobility coefficients of ions determined from the conductivity of electrolytes ($\mu_c = \tilde{\mu}_c \times 10^8$) [27] and by computer simulation of the mean-square shift of an ion ($\mu_\Gamma = \tilde{\mu}_\Gamma \times 10^8$) and its autocorrelation velocity function ($\mu_v = \tilde{\mu}_v \times 10^8$) [25]

	Li$^+$	Na$^+$	K$^+$	Cs$^+$	F$^-$	Cl$^-$	Br$^-$	I$^-$
$\tilde{\mu}_c$	4.01	5.19	7.62		5.7	7.91	8.13	7.96
$\tilde{\mu}_\Gamma$	4.75	4.98	7.12	7.32	4.04	6.88	7.2	6.23
$\tilde{\mu}_v$	4.59	5.02	7.20	7.36	3.85	6.42	6.85	6.27

at the crystallization temperature $T_m = 273$ K) as a function of the type of ions. Analyzing Table 6, one can see that Li$^+$ and Na$^+$ cations, whose rigid radii are less than a half of the hydrogen bond length (i.e. a half of the average intermolecular distance between water molecules), conserve a rather intact structure of the local hydrogen bond network and intensify the interaction between neighboring molecules. A relatively small value of $\Delta W(\mathrm{Na}^+)$ can be interpreted as a consequence of the more significant bending of hydrogen bonds as compared to that as a reaction to the introduction of a small-sized Li$^+$ cation. A K$^+$ cation, whose rigid radius is close to a half of the hydrogen bond length, causes a damage of the local hydrogen bond network, which results in the negative sign of ΔW. In the same way, one can explain the negative sign of ΔW for a Cl$^-$ anion.

At the same time, it is worth noting a significant asymmetry in the behavior of ΔW for K$^+$ and F$^-$ ions having almost identical rigid radii (see Table 2). The positive sign of $\Delta W(\mathrm{F}^-)$ testifies to the fact that an F$^-$ anion does not completely break the local configuration of hydrogen bonds, though significantly deforms it. It is clearly proved by a relatively small value of $\Delta \tilde{W}$. To our opinion, the appearance of this asymmetry is caused by the polarization component of the interaction between ions and water molecules. The existence of the asymmetry in the behavior of cations and anions was first noted in [34, 35].

On the other hand, the role of hydration effects can be estimated, by analyzing the density of weak solutions of electrolytes (see Table 7). We must actually estimate a deviation of the density of the real solution from that of the ideal one. By definition, an electrolyte solution can be considered as ideal if the volumes occupied in it by water molecules and dissolved ions acquire the same values as in water and electrolyte melts. For such an electrolyte solution, the following relation must be met:

$$v_{\mathrm{w}}^{(0)} n_{\mathrm{w}} + (v_{\mathrm{c}}^{(0)} + v_{\mathrm{a}}^{(0)}) n_{\mathrm{el}} = 1. \qquad (5)$$

Here, n_{w} and n_{el} denote the number densities of water and electrolyte molecules in the real solution, while $v_{\mathrm{w}}^{(0)}$, $v_{\mathrm{c}}^{(0)}$, and $v_{\mathrm{a}}^{(0)}$ are the volumes occupied by water molecules and ions in water and in melted or solid electrolytes. The values of n_{w} and n_{el} can be obtained from the definition of the mass density of an electrolyte solu-

tion:

$$\rho = m_{\mathrm{w}} n_{\mathrm{w}} + (m_{\mathrm{c}} + m_{\mathrm{a}}) n_{\mathrm{el}}$$

and its weight concentration

$$x = \frac{(m_{\mathrm{c}} + m_{\mathrm{a}}) n_{\mathrm{el}}}{m_{\mathrm{w}} n_{\mathrm{w}} + (m_{\mathrm{c}} + m_{\mathrm{a}}) n_{\mathrm{el}}}.$$

Hence,

$$n_{\mathrm{w}} = (1 - x) \frac{\rho}{m_{\mathrm{w}}}, \quad n_{\mathrm{el}} = x \frac{\rho}{m_{\mathrm{c}} + m_{\mathrm{a}}}. \qquad (6)$$

A real electrolyte solution is described by the relation similar to (5):

$$v_{\mathrm{w}} n_{\mathrm{w}} + (v_{\mathrm{c}} + v_{\mathrm{a}}) n_{\mathrm{el}} = 1, \qquad (7)$$

though it contains the real volumes occupied by a water molecule, cation, and anion. That is why a deviation of the dimensionless combination

$$\delta = v_{\mathrm{w}}^{(0)} n_{\mathrm{w}} + (v_{\mathrm{c}}^{(0)} + v_{\mathrm{a}}^{(0)}) n_{\mathrm{el}} - 1 \qquad (8)$$

from zero serves as the measure of adeviation of a water electrolyte solution from the ideal one. Moreover, positive values of the non-ideality parameter ($\delta > 0$) will correspond to the formation of hydrated shells around ions, in which the water density will be larger as compared to the density of bulk water. Indeed, the formation of a hydrated shell is accompanied by a decrease of the volume occupied by a water molecule ($v_{\mathrm{w}} < v_{\mathrm{w}}^{(0)}$). The variation of the volumes occupied by cations and anions in weak electrolyte solutions can be neglected.

Let us substitute the following values of the parameters $v_{\mathrm{w}}^{(0)}$, $v_{\mathrm{c}}^{(0)}$, and $v_{\mathrm{a}}^{(0)}$ in (8): $v_{\mathrm{w}}^{(0)} = \frac{m_{\mathrm{w}}}{\rho_{\mathrm{w}}^{(0)}}$, $v_{\mathrm{c}}^{(0)} + v_{\mathrm{a}}^{(0)} = \frac{m_{\mathrm{c}} + m_{\mathrm{a}}}{\rho_{el}^{(0)}}$, where $\rho_{\mathrm{w}}^{(0)}$ and $\rho_{\mathrm{el}}^{(0)}$ are the water and electrolyte densities in the liquid and amorphous states. With regard for the number densities of water and electrolyte impurities determined by relations (6), Eq. (8) takes the form

$$\delta = \frac{\rho}{\rho_{\mathrm{w}}^{(0)}} \left[1 + x \left(\frac{\rho_{\mathrm{w}}^{(0)}}{\rho_{\mathrm{el}}^{(0)}} - 1 \right) \right]. \qquad (9)$$

T a b l e 7. Densities of water electrolyte solutions at the fixed concentration $x_{\mathrm{el}} = 4$ wt.

	F$^-$	Cl$^-$	Br$^-$	I$^-$
Li$^+$		−0.001		
Na$^+$		0.003		
K$^+$			0.003	0.004
Cs$^+$		0.005		

T a b l e 6. Dependence of $\Delta \tilde{W}$ on the type of ions [33]

	Li$^+$	Na$^+$	K$^+$	F$^-$	Cl$^-$
$\Delta \tilde{W}$	3.4	0.06	-4.6	0.52	-2.0

The non-ideality parameter of a dilute solution can be interpreted in somewhat another way. Taking into account that the dominant contribution to δ is given by a variation of the volume occupied by one water molecule, Eqs. (8) and (7) yield: $\delta \approx n_{\mathrm{w}} \delta v_{\mathrm{w}}$. So, to an acceptable accuracy, the non-ideality parameter for a dilute solution is

$$\delta \approx \frac{\delta v_{\mathrm{w}}}{v_{\mathrm{w}}^{(0)}}. \tag{10}$$

The densities of some electrolyte solutions, as well as the parameters of their non-ideality δ, are given in Tables 7 and 8. It is worth noting that the non-ideality parameters obtained according to formula (9) are averaged over the number of water molecules surrounding a certain ion. The change of the relative volume of water molecules in the first hydrated layer of an ion is larger by a factor of z_{w}/z_1, where z_1 is the number of water molecules getting to the first hydrated layer.

In particular, the non-ideality parameter for a NaCl solution at $x_{\mathrm{el}} = 4$ wt. reaches $\delta \approx 0.003$. One can see that the relatively small values of mobility of lithium cations and self-diffusion coefficients of water molecules in lithium electrolytes correspond to negative non-ideality parameters. This testifies to the fact that lithium cations do not favor the formation of hydrated shells around them with densities exceeding that of water. In other cases, such hydrated shells are formed. At the same time, the smallness of δ is an evidence of the fact that hydration effects in dilute electrolyte solutions have a weak effect on their densities.

At relatively small concentrations of electrolytes, the deviation of a solution from ideality is proportional to its mole concentration $c = \frac{m_{\mathrm{w}}}{m_{\mathrm{c}} + m_{\mathrm{a}}} x$:

$$\delta \approx \varepsilon\, c.$$

The quantity ε also can be interpreted as a measure of non-ideality of a solution. For the above-considered solutions, it lies in the range $0.1 < \varepsilon < 0.5$.

The result described in two previous sections allow one to conclude that lithium cations do not radically change the local structure of surrounding water formed

T a b l e 8. Non-ideality parameters of the solutions at the fixed concentration $x_{\mathrm{el}} = 4$ wt.

	F^-	Cl^-	Br^-	I^-
Li^+		−0.001		
Na^+		0.003		
K^+			0.003	0.004
Cs^+		0.005		

with the help of hydrogen bonds. As a result, their thermal motion can be considered as a drift in temporary "cavities", whose generation is favored by the local hydrogen bond network. As the characteristic time of such drift, one can consider the time of existence of hexagonal rings in water, which should be identified, according to [30], with the duration of the settled life of water molecules τ_0. The characteristic shift of a lithium cation can be estimated by the formula $|\Delta \mathbf{r}(\mathrm{Li}^+)| \sim \sqrt{6 D_s(\mathrm{Li}^+)\tau_0}$, or $|\Delta \mathbf{r}(\mathrm{Li}^+)| \approx v_T(\mathrm{Li}^+)\tau_0$. The value of τ_0 at the temperature $T = 295$ K is approximately equal to $(0.8 \div 1) \times 10^{-12}$ s [18]. The self-diffusion coefficient of a Li^+ cation is estimated with the use of the formula $D_s(\mathrm{Li}^+) = k_{\mathrm{B}} T \tilde{\mu}_{\mathrm{c}} \times 10^8$. As a result, the characteristic shift $|\Delta \mathbf{r}(\mathrm{Li}^+)|$ of a lithium cation during an elementary diffusion act is equal to $|\Delta \mathbf{r}(\mathrm{Li}^+)| \approx 2.8 \times 10^{-8}$ cm. The same order of magnitude is characteristic of the combination $v_T(\mathrm{Li}^+)\tau_0$. This allows one to conclude that $|\Delta \mathbf{r}(\mathrm{Li}^+)|$ practically coincides with the average distance between neighboring water molecules or the size of a hexagonal ring. A similar conclusion can be also valid as regards the thermal motion of a Na^+ cation. Indeed, $|\Delta \mathbf{r}(\mathrm{Na}^+)| / |\Delta \mathbf{r}(\mathrm{Li}^+)| \sim \sqrt{\tilde{\mu}_{\mathrm{c}}(\mathrm{Na}^+)/\tilde{\mu}_{\mathrm{c}}(\mathrm{Li}^+)} \sim 1.1$.

On the other hand, cations and anions, whose rigid radii exceed a half of the hydrogen bond length ($r_{\mathrm{I}} > \frac{1}{2} l_{\mathrm{H}}$), destroy the hydrogen bond network around themselves and thus move freer. The rigid radii of K^+ and F^- ions are approximately equal to a half of the hydrogen bond length ($r_{\mathrm{I}} \approx \frac{1}{2} l_{\mathrm{H}}$). That is why the features of their thermal motion considerably depend on the peculiarities of ion-molecule interaction.

4. Interpretation of the Obtained Results Based on Microscopic Concepts

To provide a clearer interpretation of the obtained results, let us apply the microscopic approach, in which the interaction of water molecules and ions is described on the basis of the generalized Stillinger–David polarization potential [2, 23] having the structure

$$\Phi_{\mathrm{wI}} = \Phi_{\mathrm{I}} + \Phi_{\mathrm{II}} + \Phi_{\mathrm{III}} + \Phi_{\mathrm{IV}}, \tag{11}$$

where Φ_i, $i = \mathrm{I, II, III, IV}$ are the components of the potential that describe: Φ_{I} – direct Coulomb interaction with oxygen and hydrogens of a water molecule; Φ_{II} – the charge-dipole interaction between 1) the ion and oxygen and 2) the ion and hydrogens of a water molecule (it is assumed that oxygen and the ion acquire a dipole moment due to their polarization); Φ_{III} – interaction of the dipole moments of oxygen and the ion, and Φ_{IV} –

$R_{K^+O^{2-}} = 4{,}0$ Å
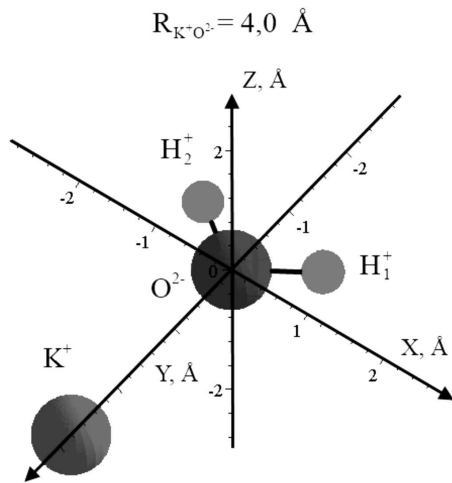

Fig. 1. Molecular system of coordinates

repulsion between electron shells of oxygen and the ion. The explicit form of the contributions $\Phi_{\mathrm{I}} - \Phi_{\mathrm{IV}}$ is given in Appendix.

The positions of ions on equidistant surfaces is determined by the polar (θ) and azimuth (ϕ) angles specified in the molecular system of coordinates (MSC) (Fig. 1). It is assumed that oxygen and hydrogens are located in the plane (x, y) of the MSC so that the axis y coincides with the bisector of the angle formed by O^{2-} and H_1^+, H_2^+ and is directed opposite to hydrogens.

The angular dependence of the energy $\widetilde{\Phi}_{\mathrm{wI}}$ ($\widetilde{\Phi}_{\mathrm{wI}} = \Phi_{\mathrm{wI}}/k_{\mathrm{B}}T_m$, where $T_m = 273$ K is the melting temperature) of interaction between a water molecule and K^+, F^- ions with almost coinciding rigid radii ($r_{\mathrm{c}}(K^+) = 1.33$ Å, $r_{\mathrm{a}}(F^-) = 1.36$ Å), is calculated with the help of formula (11) and depicted in Fig. 2. Considerably different anisotropy characters of the equidistant surfaces of the interaction of K^+ and F^- ions with a water molecule are determined by the different structures of their electron shells: for K^+, the shell is argon-like, whereas it is neon-like for F^-. This is the reason for the noticeably different polarizations of K^+ and F^- ions (see Table 3).

At the same time, the situation somewhat simplifies if ions get to water. This is related to the fact that the interaction of an ion with surrounding water molecules is not accompanied by significant changes of the local arrangement of water molecules. Indeed, the average distance between molecules of water in a vicinity of its crystallization point is close to 3 Å, whereas the sum of the rigid radii of water molecules is approximately equal to the hydrogen bond length, $l_{\mathrm{H}} \approx 2.8$ Å. So, the volume of "empty space" in water is insignificant. The introduction of K^+ and F^- ions is actually possible if

they substitute one of the water molecules in local configurations formed, first of all, by hard cores of the latter. It is worth noting that such cores are close to spheres to an acceptable accuracy [29, 30]. Hydrogen bonds give rise to considerable dipole correlations, as well as multipole correlations of higher order. Moreover, structural violations in water surroundings will grow with increasing deviations of the cation and anion radii from those of K^+ and F^-. Such structural perturbations of water cannot be interpreted, if one is based only on concepts of the dominant role of the hydrogen bond network. However, the analysis based on the averaged intermolecular interaction between an ion and water molecules is quite sound. The interaction is naturally averaged due to the thermal rotation of water molecules. By definition, the averaged interaction potential $G_{\mathrm{wI}}(r)$ is described by the formula

$$G_{\mathrm{wI}}(r) = \frac{\int\int \Phi_{\mathrm{wI}}(r, \theta, \phi) e^{-\beta\Phi_{\mathrm{wI}}} \sin\theta \, d\theta \, d\phi}{\int\int e^{-\beta\Phi_{\mathrm{wI}}} \sin\theta \, d\theta \, d\phi}, \qquad (12)$$

where $\beta = 1/k_{\mathrm{B}}T$. The averaged interaction energy as a function of the distance between K^+ and F^- ions and water oxygen is presented in Fig. 3, where we also show the asymptotic behavior of the averaged potential of interaction between an ion and a water molecule (dotted line) that can be calculated in the explicit form.

Indeed, at large distances between an ion and oxygen, the energy of their interaction is determined by the main terms of the multipole expansion

$$\Phi_{\mathrm{wI}}(r) = \frac{q_{\mathrm{I}}(\mathbf{d}_{\mathrm{w}} \cdot \mathbf{r})}{r^3} +$$

$$+ \frac{1}{r^3}\left[\mathbf{d}_{\mathrm{w}} \cdot \mathbf{d}_{\mathrm{I}} - 3\frac{(\mathbf{d}_{\mathrm{w}} \cdot \mathbf{r})(\mathbf{d}_{\mathrm{I}} \cdot \mathbf{r})}{r^2}\right] + \cdots \qquad (13)$$

which includes the charge-dipole and dipole-dipole interactions. Let the dipole moment of a water molecule be fixed and change only in direction, while let the ion dipole moment arise due to its polarization by the electric field of the water dipole:

$$\mathbf{d}_{\mathrm{I}} = \frac{\alpha_{\mathrm{I}}}{r^3}\left[\mathbf{d}_{\mathrm{w}} - 3\frac{(\mathbf{d}_{\mathrm{w}} \cdot \mathbf{r})\mathbf{r}}{r^2}\right]. \qquad (14)$$

Thus, the main contributions to the energy of dipole-ion interaction take the form:

$$\Phi_{\mathrm{wI}}(r) = \frac{q_{\mathrm{I}}(\mathbf{d}_{\mathrm{w}} \cdot \mathbf{r})}{r^3} + \frac{\alpha_{\mathrm{I}}}{r^6}\left[\mathbf{d}_{\mathrm{w}}^2 + 3\frac{(\mathbf{d}_{\mathrm{w}} \cdot \mathbf{r})^2}{r^2}\right] + \cdots . \quad (15)$$

At sufficiently large distances between a water molecule and an ion,

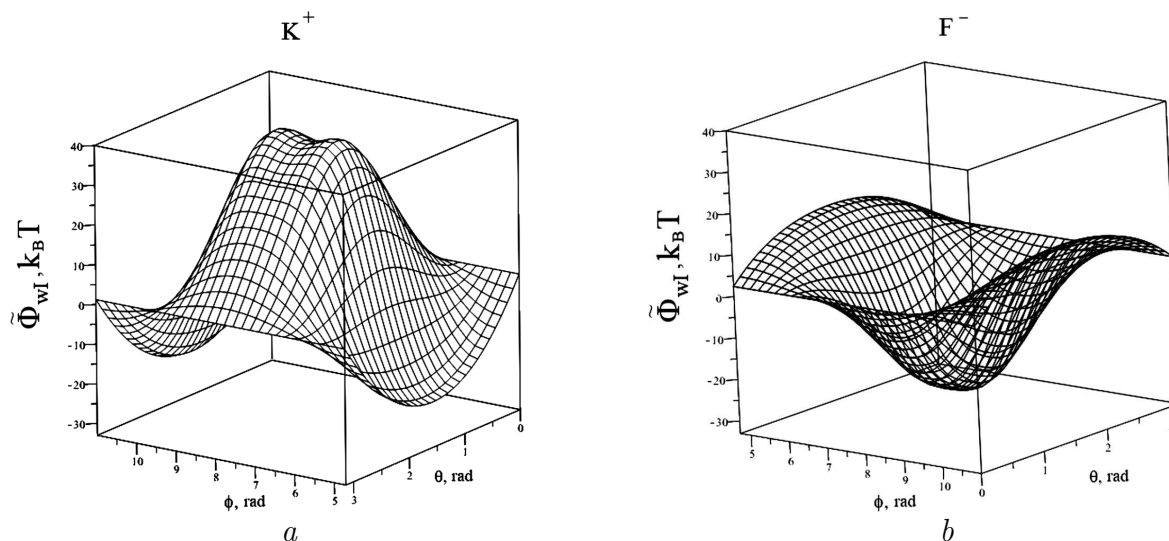$$\exp\left(-\beta\Phi_{\mathrm{wI}}\right) = 1 - \beta\Phi_{\mathrm{wI}} + \cdots .$$

Fig. 2. Equidistant surfaces ($r_{\mathrm{OI}} = 4.0$ Å) of the dimensionless energy of interaction $\widetilde{\Phi}_{\mathrm{wI}}$ between a water molecule and K^+ (a), F^- (b)

That is why the asymptotic behavior of $G_{\mathrm{wI}}(r)$ will be determined by the contributions

$$G_{\mathrm{wI}}(r) = \langle \Phi_{\mathrm{wI}} \rangle_0 - \beta \langle \Phi_{\mathrm{wI}}^2 \rangle_0 + \cdots , \qquad (16)$$

where the index "0" denotes the averaging over the isotropic orientation distribution of water molecules.

Combining (14), (15), and (16), it is easy to make sure that the main contributions to the averaged potential are determined by the following terms:

$$G_{\mathrm{wI}}(r) = -\beta \frac{q_{\mathrm{I}}^2 \mathbf{d}_{\mathrm{w}}^2}{r^4} + 2\frac{\alpha_{\mathrm{I}} \mathbf{d}_{\mathrm{w}}^2}{r^6} + \cdots . \qquad (17)$$

One can see that, regardless of the sign of the ion charge, the averaged interaction between ions and a water molecule at large distances is of attractive character. For singly charged ions, the main asymptotic contribution (from the charge-dipole interaction) does not depend on the type of ion. At the same time, the second contribution is not universal: it directly depends on the polarization of ions.

Particularly, Eq. (17) together with the analysis of Table 3 make one expecting that, at rather large distances ($r > 10$ Å) between an ion and a water molecule, $G_{\mathrm{wF}^-}(r) > G_{\mathrm{wK}^+}(r)$. This conclusion agrees with the calculation results. At the same time, in the case of relatively small distances ($r < 10$ Å), the averaged potential of interaction between an F^- anion and a water molecule appears deeper than $G_{\mathrm{wK}^+}(r)$ (see Fig. 3), owing to which an F^- anion is less mobile than a K^+ cation, which also completely agrees with the data in Table 5.
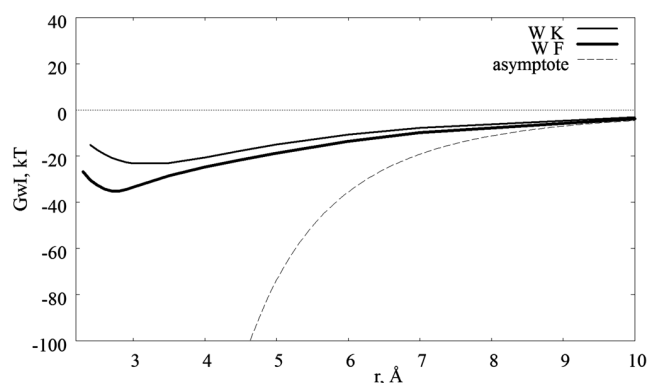

Fig. 3. Distance dependence of the averaged potential $G_{\mathrm{wI}}(r)$ of interaction of a water molecule with K^+ ($\alpha = 0.83$ Å^3) and F^- ($\alpha = 1.04$ Å^3)

5. Discussion of the Results

The study of the transfer processes in dilute solutions of electrolytes performed in this work allows us to make the following conclusions: 1) the key role in the formation of kinetic properties of water electrolyte solutions (first of all, in the behavior of the mobility coefficients of ions and water molecules) is played by their hard-core radii; 2) the standard understanding of the ion motion in "cavities" formed by the hydrogen bond network is, to our mind, inconsistent; 3) the hydrogen bond network in water is not determinative for the character of the ion drift motion, as the sizes of all cations and anions exceed those of "cavities" of the local water structure. In addition, it should be taken into account that a certain local configuration of water molecules exists only during

the time coinciding with the duration of the settled life of molecules τ_0 by order of magnitude. Speaking about the role of hydrogen bonds in the self-diffusion problem, we actually mean the manifestation of strong orientation correlations between the dipole moments of water molecules and multipole moments of higher orders; 4) the behavior of the mobility coefficients of cations and anions in water agrees with that of the averaged potentials of interaction between ions and water molecules. Though this fact is established only for one cation and one anion, it still can be generalized to all other ions based on the similarity principle.

Analyzing the density of dilute solutions of electrolytes, one can see that, if one ion is added per approximately 15 water molecules, the change of the relative volume occupied by one water molecule does not exceed a half of one per cent. This testifies to the fact that hydration effects are related, first of all, to the variation of the local orientation ordering of water molecules rather than to a local change of the density of the system.

The established connection between the behavior of cations and anions and the behavior of the averaged potential is a result of the existence of thermal rotational motion of water molecules. This fact is most obviously manifested in the temperature dependences of the dielectric relaxation time and the shear viscosity of water.

APPENDIX

Let us consider, in brief, the structure of each contribution to the energy of interaction between an ion and a water molecule (Eq. (11)). The first term Φ_{I} [1, 2, 23] determines the direct Coulomb interaction between an ion (hereinafter denoted by character I) and oxygen and hydrogens of a water molecule:

$$\Phi_{\mathrm{I}} = \sum_{j=0}^{j=2} \frac{q_{\mathrm{I}}\, q_j}{r_{ij}}, \tag{D1}$$

where q_{I} is the charge of ion I, $j = 0, 1, 2$, the index j numbers the charges of oxygen and hydrogen of the water molecule ($j = 0$ corresponds to the charge of oxygen, $j = 1, 2$ – to those of hydrogens). It is assumed that the charges are measured in units of the electron charge and $q_{\mathrm{I}} = \pm n$ (n is the ion charge), $q_0 = -2$, and $q_1 = q_2 = 1$.

The second contribution Φ_{II} determines the potential of interaction between the point ion charge and the polarized oxygen of the water molecule. Oxygen is polarized under the action of the

T a b l e 9. Parameters of the potential [2, 32] of interaction between a water molecule and an ion

	b_3	ρ_3, Å^{-1}	b_4	ρ_4, Å^{-1}
K$^+$	64.54	2.569	4282.4	2.569
	b_3	ρ_3, Å^{-1}	b_4	ρ_4, Å^{-1}
F$^-$	–11.45	0.4304	63.95	1.042

field of charges of hydrogens in the molecule itself and the charge of the polarized ion I. The polarization of oxygen results in the appearance of the dipole moment $\mathbf{d}_{\mathrm{O}}$ that characterizes the degree of deformation of the oxygen electron shells. The ion is polarized under the action of the hydrogen field of charges and the charge of oxygen in the water molecule. The polarization of the ion results in the appearance of the dipole moment $\mathbf{d}_{\mathrm{I}}$ characterizing the degree of deformation of the ion electron shells. With regard for the polarization contribution, one obtains

$$\Phi_{\mathrm{II}} = \frac{(\mathbf{d}_{\mathrm{O}} \cdot \mathbf{r}_{\mathrm{OI}}) q_{\mathrm{I}}}{r_{\mathrm{OI}}^3}[1 - L(r_{\mathrm{OI}})] + \frac{(\mathbf{d}_{\mathrm{I}} \cdot \mathbf{r}_{\mathrm{IO}}) q_{\mathrm{O}}}{r_{\mathrm{IO}}^3}[1 - L(r_{\mathrm{IO}})] +$$

$$+ \sum_{j=1,2} \frac{(\mathbf{d}_{\mathrm{I}} \cdot \mathbf{r}_{\mathrm{I}j}) q_j}{r_{\mathrm{I}j}^3}[1 - K(r_{\mathrm{I}j})], \tag{D2}$$

where $\mathbf{d}_{\mathrm{O}}$ and $\mathbf{d}_{\mathrm{I}}$ are the dipole moments of oxygen of the water molecule and the polarized ion I, respectively, whereas $1 - L(r)$ and $1 - K(r)$ are screening functions (see [1, 2, 23]). The dipole moment $\mathbf{d}_{\mathrm{O}}$ is determined in the molecular system of coordinates, whose origin coincides with the center of mass of oxygen of the water molecule. The dipole moment $\mathbf{d}_{\mathrm{I}}$ is determined in the molecular system of coordinates, whose origin coincides with the center of mass of the ion. At large distances, the polarization contribution Φ_{III} is reduced to the interaction between the polarized oxygen of the water molecule and the ion charge, as well as between the polarized ion and the charges of the water molecule.

The component Φ_{III} describing the dipole-dipole interaction of the ion and oxygen has the form

$$\Phi_{\mathrm{III}} = \Phi_{\mathrm{d}}(\mathbf{d}_{\mathrm{O}}, \mathbf{d}_{\mathrm{I}})[1 - K(r_{\mathrm{OI}}/a)], \tag{D3}$$

where

$$\Phi_{\mathrm{d}}(\mathbf{d}_1, \mathbf{d}_2) = \frac{1}{r_{12}^3}\left[\mathbf{d}_1 \cdot \mathbf{d}_2 - \frac{3(\mathbf{d}_1 \cdot \mathbf{r}_{12})(\mathbf{d}_2 \cdot \mathbf{r}_{21})}{r_{12}^2}\right],$$

and $[1 - K(r_{\mathrm{OI}}/a)]$ is the screening function [2, 23].

The repulsion between the electron shells of the ion and oxygen of the water molecule is modeled by the exponential functions [2, 23]:

$$\Phi_{\mathrm{IV}} = \frac{b_3 e^{-\rho_3 r_{\mathrm{IO}}}}{r_{\mathrm{IO}}} + \sum_{j=1,2} \frac{b_4 e^{-\rho_4 r_{\mathrm{I}j}}}{r_{\mathrm{I}j}}, \tag{D4}$$

where b_3 stands for the amplitude of the "ion–oxygen" repulsion energy, ρ_3 is the inverse radius of action of the repulsion forces between the shells of the ion and oxygen, b_4 is the amplitude of the "hydrogen–ion" repulsion energy, and ρ_4 is the inverse radius of action of the repulsion forces between hydrogens and ion electron shells. Their values are gathered in Table 9.

At distances significantly exceeding the sizes of a water molecule and the ion, the interaction potential takes the asymptote

$$\Phi \to \Phi_{\mathrm{d}}(\mathbf{d}_{\mathrm{w}}, \mathbf{d}_{\mathrm{I}}), \tag{D5}$$

where $\mathbf{d}_{\mathrm{w}} = \mathbf{d}_{\mathrm{H}} + \mathbf{d}_{\mathrm{O}}$ is the dipole moment of the water molecule and $\mathbf{d}_{\mathrm{H}}$ is the contribution made to this moment by hydrogens.

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ОСОБЛИВОСТІ РУХУ КАТІОНІВ І АНІОНІВ
В РОЗЧИНАХ ЕЛЕКТРОЛІТІВ

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Р е з ю м е

Досліджено фізичну природу рухливості іонів і молекул води у розбавлених водних розчинах електролітів, коли на один іон припадає не більше п'ятнадцяти молекул води. Показано, що поведінка коефіцієнтів рухливості молекул води і іонів, а також коефіцієнтів самодифузії молекул води вирішальним чином визначається радіусами їх твердих оболонок, а не впливом сітки водневих зв'язків у системі. Встановлено, що вплив гідратаційних ефектів на значення густини системи і коефіцієнтів самодифузії молекул води не перевищує кількох відсотків. На основі мікроскопічних уявлень показано, що відмінна поведінка катіона K^+ та аніона F^-, що мають однакові жорсткі радіуси, добре узгоджується з особливостями міжмолекулярної взаємодії, яка описується узагальненим потенціалом Стілінджера–Девіда [1, 2].