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COMPENSATION OF ISOTOPE EFFECTS AT The NEAR SOLVATION OF SINGLY CHARGED IONS IN LIGHT AND HEAVY WATERS

The diffusion coefficients D_i^0 and the microscopic characteristics of the diffusional displacement length $\overline{d}$, time τ, and velocity V of 18 singly charged ions (Li^+, Na^+, K^+, Cs^+, Me_4N^+, Et_4N^+, Pr_4N^+, Bu_4N^+, F^-, Cl^-, Br^-, I^-, ClO_3^-, ClO_4^-, BrO_3^- IO_3^-, IO_4^-, and OBz^-) in heavy and light waters at temperatures of 283.15 and 298.15 K have been calculated on the basis of literature data concerning the limiting molar electric conductivity of those ions. Using the proposed parameter $(\overline{d} - r_i)$, where r_i is the structural radius of an ion, the type of the solvation of those ions is determined: it is positive, if $(\overline{d} - r_i) > 0$, and negative, if $(\overline{d} - r_i) < 0$. The solvent isotope effects (SIEs) – namely, the variations of the ion diffusion coefficient, $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$, the length, $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$, time, $\tau_\mathrm{H}/\tau_\mathrm{D}$, and velocity, $V_\mathrm{H}/V_\mathrm{D}$, of the translational ion displacement, and the solvent viscosity, η_0^D/η_0^H, as a result of the substitution $H \rightarrow D$ in H_2O – are calculated and analyzed. It is found that, in the case of SIE, the deviation of $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$ or $V_\mathrm{H}/V_\mathrm{D}$ from 1 can be up to 25.0–25.9%, whereas, for the near solvation SIE, the deviation of $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$ from 1 is an order of magnitude lower. These facts are explained on the basis of a derived equation, where the SIE $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$ is the product of the inverse SIEs $\eta_0^\mathrm{D}/\eta_0^\mathrm{H}$ and $D_{i\mathrm{D}}^0/D_{i\mathrm{H}}^0$. The low $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$-values are obtained due to the opposite effect of the indicated factors, which points to the compensation of the intermolecular and ion-molecular interactions. Hence, since those interactions govern the near solvation of singly charged ions in H_2O and D_2O, the results obtained testify to a significant solvent effect on this process.

Keywords: solvent isotope effect, singly charged ions, diffusion, electrical conductivity, short-range solvation, negative solvation.

1. Introduction

In work [1] devoted to the study of the influence of ions on the mobility of neighbor solvent molecules, we established a correlation between the sign of the deviation $(\overline{d} - r_i)$ of the translational displacement $\overline{d}$ from the structural radius r_i and the ion solvation according to Samoilov [2]. The established correlation formed a basis of the approach developed in work [1] for determining the near solvation of ions in structured solvents. In order to find criteria for positive and negative solvations, the following inequalities were proposed: for the positive solvation,

$$(\overline{d} - r_i) > 0; \tag{1}$$

for the negative solvation,

$$(\overline{d} - r_i) < 0. \tag{2}$$

Later, the existence of such a correlation was confirmed for singly charged ions in monoethanolamine [3] and ethylene glycol [4] (in solvents with a spatial network of H-bonds), which testifies to the sensitivity of the proposed approach and its applicability to determining the solvation of ions according to Samoilov. Following Samoilov [2], the solvation was considered not as the binding of any number of solvent molecules by an ion, but as the influence of the latter on the translational motion of the neighbor molecules.

Considering the relationship between the parameter $\overline{d}$ and the structural radius, as well as the tem-

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perature dependence of $\overline{d}$, the interaction of an ion with the closest solvent molecules was characterized by the difference $(\overline{d} - r_i)$, which was called the deviation from the Stokes–Einstein law in work [1]. This law is strictly obeyed only for the model of a rigid spherical ion moving in a continuous medium (continuum) characterized by the macroscopic viscosity η_0. A criterion for the applicability of the Stokes–Einstein law is the condition $(\overline{d} - r_i) = 0$, i.e., the equality $\overline{d} = r_i$, which is a geometric limit of switching from negative to positive solvation [5] and, from the physical viewpoint, corresponds to the absence of ion solvation. If the condition $\overline{d} = r_i$ is satisfied, only the slowing-down force induced by the solvent viscosity η_0 acts on the ion.

The validity of the choice of the difference $(\overline{d} - r_i)$ as a measure of the ionic influence on the mobility of the closest solvent molecules (the measure of near solvation) was demonstrated in work [6], where we used a friction coefficient independent of the nature of the force acting on the particle. In work [6], it was also shown that the difference $(\overline{d} - r_i)$ follows from the difference between the total, ζ, and viscous, ζ_ν, friction coefficients, which are characterized by the quantities $\overline{d}$ and r_i, respectively. The parameter $\overline{d}$ is considered by us [1, 3, 4, 6] as a characteristic microscopic length of some discrete displacement between two equilibrium positions that an ion passes during a characteristic time τ. The structural radius of the ion r_i was considered as its inherent and constant [7] characteristic, which quantitatively takes into account its behavior in the continuum approximation. Since the values of the radii of tetraalkylammonium (TAA) ions are ambiguous, we used the specific scale of Marcus radii [8] and the hydrodynamic condition of "slipping" when using the Stokes–Einstein law.

It was interesting to apply the approach developed in works [1, 3, 4, 6] to determine the microscopic characteristics of translational displacement (MCTDs) – $\overline{d}$, τ, V, and $(\overline{d}-r_i)$ – for singly charged ions in heavy water, which is an isotopically substituted liquid solvent with respect to light water. The phenomenon of isotopic substitution of a certain element in a compound by its isotope, which is known as the isotope effect [5, 9], is quite interesting and examined for various properties. Isotope effects are typical of a good many chemical elements, especially light ones. The essence of the isotope effect consists in the substitution of a chemical element by its isotope; as a result, the properties of simple substances or chemical compounds that are different in their isotopic compositions and molecular masses become also different.

Among isotopically substituted solvents, studies of the structured ones are of great interest. Water is the most researched of them. A characteristic feature of structured solvents is the formation of a spatial network of H-bonds [10], which is responsible for the specificity of their molecular structure. The latter governs numerous, including anomalous, properties of solvents and affects various processes running in electrolyte solutions.

Among other processes taking place in electrolyte solutions, solvation plays a very important role. This phenomenon is explained in the framework of two approaches [11]: thermodynamic and kinetic ones. The results obtained while studying the isotope effects in electrolyte and non-electrolyte solutions in the framework of the thermodynamic approach were summarized in book [5]. The kinetic approach [2] analyzes the near solvation phenomenon resulting from short-range ion-molecule (I-M) and molecule-molecule (M-M) interactions and is based on the study of the kinetic properties of ions in solutions.

A considerable number of studies were devoted to the study of the influence of singly charged ions on the translational mobility of heavy-water molecules [12–17]. As a result, the important information was obtained. By analyzing the data obtained for the near solvation of 1-1-electrolytes in heavy water [12–17], the following facts were established:

1. In most cases, the conclusion made by Rabinovich [18] that heavy water is a more structured solvent than light one is confirmed. According to Rabinovich, this is a consequence of a higher strength of the deuterium bond and a more regular tetrahedral coordination of D_2O molecules. According to one of the main statements of Samoilov's kinetic theory of near solvation [2], the strengthening of the solvent structure leads to the solvation weakening, and its destruction to the solvation enhancement. However, there are a lot of issues concerning this complicated process that remain unanswered.

2. Information obtained via various experimental methods has mostly a qualitative character. It is restricted with respect to ions and temperature, sometimes being contradictory. The application of the approach developed in works [1, 6] to study the influence of singly charged ions of various nature on the mobil-

Table 1. **Characteristics of singly charged ions in heavy water at $T = 283.15$ and 298.15 K**

Ion	$r_i \times 10^{10}$, m	$m_i^{\text{gen}} \times 10^9$, C/m	$\lambda_i^0 \times 10^4$, $\text{Sm} \cdot \text{m}^2/\text{mol}$		D_i^0, $\text{m}^2 \cdot \text{s}^{-1}$		$\overline{d} \times 10^{10}$, m		$(\overline{d} - r_i) \times 10^{10}$, m		$\tau_i \times 10^{12}$, s		V_i, $\text{m} \cdot \text{s}^{-1}$	
			283	298	283	298	283	298	283	298	283	298	283	298
Li^+	0.78	2.05	20.27	31.36	0.513	0.835	2.41	2.39	1.63	1.61	18.9	11.4	12.8	21.0
Na^+	0.98	1.63	27.78	41.62	0.703	1.108	1.76	1.80	0.78	0.82	7.34	4.87	24.0	37.0
K^+	1.33	1.20	42.85	61.40	1.08	1.635	1.14	1.22	−0.19	−0.11	2.01	1.52	56.7	80.3
Cs^+	1.65	0.97	45.47	64.44	1.15	1.716	1.07	1.16	−0.58	−0.49	1.66	1.31	64.5	88.6
Me_4N^+	2.80	0.57	24.25	36.61	0.613	0.975	3.03	3.07	0.23	0.27	37.4	24.2	8.1	12.7
Et_4N^+	3.37	0.48	17.07	26.44	0.432	0.704	4.29	4.25	0.92	0.88	107	64.1	4.0	6.6
Pr_4N^+	3.79	0.42	11.91	18.84	0.301	0.502	6.15	5.97	2.36	2.18	314	178	2.0	3.4
Bu_4N^+	4.13	0.39	9.71	15.62	0.246	0.416	7.55	7.19	3.42	3.06	579	311	1.3	2.3
F^-	1.33	1.20	–	44.79	–	1.193	–	1.67	–	0.34	–	3.91	–	42.8
Cl^-	1.81	0.89	43.69	62.83	1.10	1.67	1.12	1.19	−0.69	−0.62	1.90	1.41	59.0	84.4
Br^-	1.96	0.82	45.10	64.67	1.14	1.72	1.08	1.16	−0.88	−0.80	1.71	1.30	63.2	89.2
I^-	2.20	0.73	44.89	63.79	1.14	1.70	1.09	1.17	−1.11	−1.03	1.74	1.34	62.6	87.3
ClO_3^-	2.00	0.80	36.85	53.23	0.932	1.42	1.33	1.41	−0.67	−0.59	3.16	2.33	42.1	60.5
BrO_3^-	1.91	0.84	32.32	46.14	0.817	1.23	1.51	1.62	−0.40	−0.29	4.65	3.56	32.5	45.5
IO_3^-	1.82	0.88	22.63	33.64	0.572	0.896	2.16	2.23	0.34	0.41	13.6	9.25	15.9	24.1
ClO_4^-	2.36	0.68	39.19	55.94	0.991	1.490	1.25	1.34	−1.11	−1.02	2.63	2.01	47.5	66.7
IO_4^-	2.49	0.64	31.16	45.42	0.788	1.21	1.57	1.65	−0.92	−0.84	5.21	3.75	30.1	44.0
OBz^-	3.26	0.49	–	26.19	–	0.697	–	2.86	–	−0.40	–	19.5	–	14.6

ity of D_2O molecules made it possible to explain the weak solvent isotope effect (SIE) at the near solvation and its variability owing to the compensation of the I-M and M-M interactions in the solutions of singly charged ions, when changing from light to heavy water. The ratios between the calculated parameters in the H_2O and D_2O cases were used as the corresponding SIE magnitudes.

2. Calculation Technique

Using the data on the limiting molar electrical conductivity λ_0 for the singly charged Li^+, Na^+, K^+, Cs^+, Me_4N^+, Et_4N^+, Pr_4N^+, Bu_4N^+, F^-, Cl^-, Br^-, I^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, IO_4^-, and OBz^- ions presented in works [15–17, 19], we calculated, in this work, their diffusion coefficients D_i^0 in heavy water at the temperatures $T = 283.15$ and 298.15 K. For this purpose, we used the Nernst–Einstein equation

$$D_i^0 = \frac{RT}{|z_i| F^2} \lambda_i^0, \tag{3}$$

where z_i is the ion charge, R the gas constant, and F the Faraday number. Then, using the results obtained for D_i^0 of ions and the data for the viscosity η_0 of pure solvent [20], we calculated the translational displacement length of ion, $\overline{d}$, in D_2O at the indicated temperatures with the help of Stokes–Einstein equation

$$\overline{d} = \frac{kT}{f D_i^0 \eta_0}, \tag{4}$$

where k is the Boltzmann constant, and $f = 4\pi$ or 6π, depending on the specific ion. Namely, the Stokes–Einstein law was presented under the "sliding" condition ($f = 4\pi$) for the tetraalkylammonium (TAA) ions Me_4N^+, Et_4N^+, Pr_4N^+, and Bu_4N^+, and under the "sticking" condition ($f = 6\pi$) for other ions.

The characteristic time τ of translational ion displacement was evaluated according to the well-known formula

$$\tau = \frac{\overline{d}^{\,2}}{6 D_i^0}. \tag{5}$$

The velocity V of translational ion displacement was calculated as the ratio

$$V = \frac{\overline{d}}{\tau}. \tag{6}$$

The values of the parameters D_i^0, $\overline{d}$, τ, and V calculated according to Eqs. (3)–(6) for singly charged

Table 2. **Solvent isotope effects for the diffusion coefficient ($D^0_{i\mathrm{H}}/D^0_{i\mathrm{D}}$), the parameters $\overline{d}_i$ ($\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$) and ($\overline{d}_i - r_i$) (($\overline{d}_\mathrm{H} - r_i$)/($\overline{d}_\mathrm{D} - r_i$)), and the time ($\tau_\mathrm{H}/\tau_\mathrm{D}$) and velocity ($V_\mathrm{H}/V_\mathrm{D}$) of diffusional displacement of singly charged ions at T = 283.15 and 298.15 K**

Ion	$D^0_{i\mathrm{H}}/D^0_{i\mathrm{D}}$		$\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$		$(\overline{d}_\mathrm{H} - r_i)/(\overline{d}_\mathrm{D} - r_i)$		$\tau_\mathrm{H}/\tau_\mathrm{D}$		$V_\mathrm{H}/V_\mathrm{D}$	
	283.15 K	298.15 K	283.15 K	298.15 K	283.15 K	298.15 K	283.15 K	298.15 K	283.15 K	298.15 K
Li^+	1.359	1.234	0.979	0.992	0.969	0.988	0.741	0.799	1.328	1.238
Na^+	1.253	1.200	1.023	1.017	1.051	1.037	0.834	0.858	1.225	1.184
K^+	1.241	1.199	1.035	1.025	0.790	0.727	0.865	0.868	1.200	1.172
Cs^+	1.235	1.195	1.047	1.026	0.914	0.939	0.880	0.878	1.185	1.163
$\mathrm{Me_4N}^+$	1.277	1.231	1.003	1.000	1.044	1.000	0.794	0.814	1.270	1.225
$\mathrm{Et_4N}^+$	1.280	1.236	1.002	0.991	1.011	0.955	0.783	0.794	1.279	1.246
$\mathrm{Pr_4N}^+$	1.286	1.235	0.997	0.987	0.992	0.963	0.771	0.785	1.294	1.259
$\mathrm{Bu_4N}^+$	1.297	1.250	0.992	0.990	0.983	0.977	0.752	0.793	1.313	1.251
F^-	–	1.241	–	0.994	–	0.971	–	0.793	–	1.248
Cl^-	1.245	1.216	1.027	1.008	0.957	0.984	0.862	0.831	1.199	1.211
Br^-	1.246	1.209	1.037	1.009	0.955	0.983	0.849	0.846	1.212	1.188
I^-	1.239	1.206	1.036	1.017	0.964	0.981	0.868	0.859	1.193	1.187
$\mathrm{ClO_3^-}$	1.255	1.210	1.023	1.007	0.955	0.983	0.838	0.841	1.227	1.204
$\mathrm{BrO_3^-}$	1.236	1.211	1.040	1.012	0.850	0.931	0.869	0.849	1.194	1.192
$\mathrm{IO_3^-}$	1.243	1.217	1.032	1.005	1.206	1.024	0.860	0.830	1.201	1.216
$\mathrm{ClO_4^-}$	1.241	1.208	1.032	1.015	0.964	0.980	0.863	0.851	1.193	1.192
$\mathrm{IO_4^-}$	1.242	1.198	1.031	1.018	0.946	0.964	0.858	0.869	1.206	1.175
OBz^-	–	1.234	–	0.993	–	1.050	–	0.800	–	1.247

ions in heavy water are quoted in Table 1. Table 1 also contains values for the structural radii of ions: the Goldschmidt radii for monoatomic ions [1], the van der Waals radii for TAA ions [21], the Marcus radius for the benzoate ion OBz^- [8], and the thermochemical radii for other ions [11]. Here, we also present the magnitudes of the generalized moment m_i^gen [22], which characterizes the electrostatic interaction forces in ion-molecular systems. This parameter was calculated according to the formula

$$m_i^\mathrm{gen} = \frac{|z|\overline{e}}{r_i}, \tag{7}$$

where $\overline{e}$ is the elementary charge.

When calculating the SIE values, the required parameters of ions in light water were taken from works [1, 6].

3. Analysis of Calculation Results

The values of the parameter D_i^0 calculated for the examined ions in heavy water, similarly to their behavior in light water, increase with the temperature. If the temperature is constant, D_i^0 increases with the structural radius for monoatomic ions; but this parameter decreases for TAA cations. The reduction of D_i^0 is also observed along the series $\mathrm{ClO_3^-}$, $\mathrm{BrO_3^-}$, $\mathrm{IO_3^-}$, and $\mathrm{ClO_4^-}$, $\mathrm{IO_4^-}$. The substitution H → D in water at 298.15 K leads to the decrease of D_i^0 for singly charged ions by the factor $D^0_{i\mathrm{H}}/D^0_{i\mathrm{D}} = 1.192 \div 1.250$, i.e., by 19.2–25.0% (Table 2). The reduction of the ratio $D^0_{i\mathrm{H}}/D^0_{i\mathrm{D}}$ (the measure of the isotope effect) with the growing temperature testifies to a destruction in the more structured solvent $\mathrm{D_2O}$, which creates more favorable conditions for the ionic solvation, which is responsible for the diffusion.

As it occurs in the case of light water, the parameter $\overline{d}$ for singly charged ions in heavy water also depends on the temperature and the structural ionic radius (Table 1). It also correlates with the Samoilov solvation of ions [2]. In the case of ions that are negatively solvated in $\mathrm{D_2O}$, we have $\overline{d} < r_i$, so that $\left(\overline{d} - r_i\right) < 0$, whereas, for positively solvated ions, $\overline{d} > r_i$ and $\left(\overline{d} - r_i\right) > 0$ (Table 1).

The dependence of $\left(\overline{d} - r_i\right)$ on m_i^gen has the opposite character for the cations of alkali metals and TAA in both heavy and light waters (Fig. 1), which points to different slowing-down mechanisms for D_2O (H_2O) molecules in the solvate shells of ions. It is of interest that the minimum values of the near solvation parameter $\left(\overline{d} - r_i\right)$ for the Cs^+ cation are negative and almost identical in light (-0.46×10^{-10} m) and heavy (-0.49×10^{-10} m) waters.

The value of the parameter $\overline{d}$ for negatively solvated monoatomic ions in heavy water at a constant temperature of 298.15 K (Table 1) remains approximately constant $[(1.16 \div 1.22) \times 10^{-10}$ m], as it occurs in light water $[(1.17 \div 1.25) \times 10^{-10}$ m].

Unlike the H_2O case, the temperature effect in D_2O was studied in a narrow temperature interval of 283.15–298.15 K. However, the temperature coefficient of the parameter $\overline{d}$, TC $= \partial\overline{d}/\partial T$, demonstrates the same tendency. Namely, both in H_2O and D_2O, it has opposite signs for negatively and positively solvated ions [1]. In particular,

- $\partial\overline{d}/\partial T > 0$ for negatively solvated ions,
- $\partial\overline{d}/\partial T < 0$ for positively solvated ones.

The ions Na^+, IO_3^-, and Me_4N^+, for which $\partial\overline{d}/\partial T > 0$, are exceptions from this regularity (Table 1).

Also interesting is the dependence of $\left(\overline{d} - r_i\right)$ on m_i^{gen} for anions (Fig. 2). It is characterized by the availability of three branches that converge in a somewhat stretched minimum formed by the ions I^- and ClO_4^-. The left branch is formed by the ions ClO_4^-, IO_4^-, and OBz^-; the right one by the ions I^-, Br^-, Cl^-, and F^-; and the middle one by the ions ClO_4^-, ClO_3^-, BrO_3^-, and IO_3^-.

Rather unexpected is the behavior of the quantity $\overline{d}$ and, accordingly, its deviation $\left(\overline{d} - r_i\right)$ from the Stokes–Einstein law, which, taking the deviation sign into account, constitutes the criterion for ionic solvation. The values of the parameter $\overline{d}$ calculated in the D_2O case turned out close to those found in the H_2O case. In contrast to the ratios $D^0_{i\text{H}}/D^0_{i\text{D}}$, $\lambda^0_{i\text{H}}/\lambda^0_{i\text{D}}$, and V_H/V_D, the values of the ratios $\overline{d}_\text{H}/\overline{d}_\text{D}$ and $\left(\overline{d}_\text{H} - r_i\right) / \left(\overline{d}_\text{D} - r_i\right)$ regarded as the measures of SIE turned out close to 1 (Table 2). The deviation of two latter SIE from 1 is at the level of experimental data error. The maximum deviation for the Cs^+ cation amounts to 2.6%. At the same time, the maximum deviation of the same effect from 1 for the SIEs $D^0_{i\text{H}}/D^0_{i\text{D}}$, $\lambda^0_{i\text{H}}/\lambda^0_{i\text{D}}$, and V_H/V_D is an order of magnitude higher and equals 25.8% at a temperature of 298.15 K (Table 2). Furthermore, the deviation sign is also different: $\overline{d}_\text{H}/\overline{d}_\text{D} > 1$ for negatively solvated ions except for IO_3^-, and $\overline{d}_\text{H}/\overline{d}_\text{D} < 1$ for positively solvated ones except for Na^+. By the way, the magnitude of deviation from 1 depends on the temperature. A temperature decrease by 15 K makes the maximum deviation from 1 almost twice as large (for the Cs^+ cation, its value amounts to 4.7%) (Table 2).

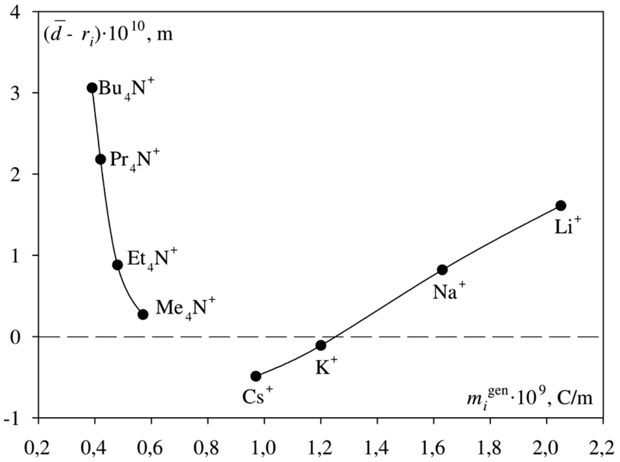

Fig. 1. Dependence of the parameter $(\overline{d} - r_i)$ on m_i^{gen} for cations in heavy water at a temperature of 298.15 K

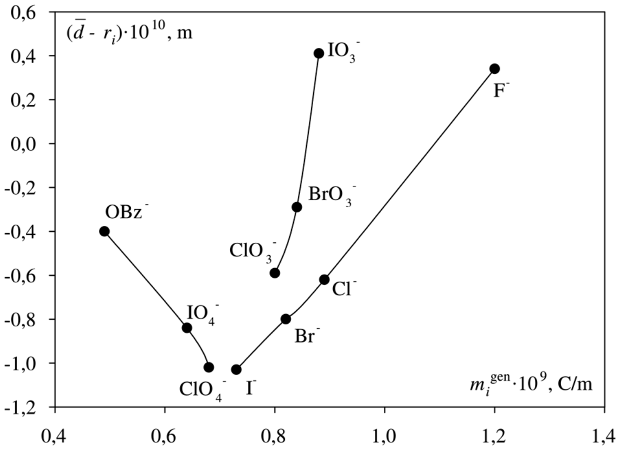

Fig. 2. Dependence of the parameter $(\overline{d} - r_i)$ on m_i^{gen} for anions in heavy water at a temperature of 298.15 K

The substitution H → D in H_2O increases the characteristic time of translational displacement for singly charged ions. The ratio $\tau_\text{H}/\tau_\text{D} < 1$ testifies that under the same conditions, the slowing-down effect of the ion in D_2O is larger than in H_2O (Table 2). Attention should be paid to the fact that the values of τ_D and τ_H are close to each other for monoatomic negatively solvated ions: $\tau_\text{D} = 1.30 \div 1.52$ ps and $\tau_\text{H} = 1.10 \div 1.33$ ps [1].

The highest velocity V of translational displacement in the diffusion mode, both in D_2O and H_2O, is inherent to negatively solvated monatomic ions: 80.4–89.2 m/s in D_2O (see Table 1) and 94.1–106.7 m/s in H_2O [1]. As the temperature grows, the velocity of singly charged ions in D_2O and H_2O increases (Table 1). The substitution of protium by deuterium, H → D, in H_2O at 298.15 K leads to a reduction of the translational displacement velocity by a factor of $V_\mathrm{H}/V_\mathrm{D} = 1.163\div1.259$ (Table 2).

4. Discussion

The following discussion of the calculation results obtained for the diffusion coefficients D_i^0 and the microscopic characteristics of translational displacement of 18 singly charged ions in light and heavy water, as well as the established regularities, is based on the assumption that owing to the presence of H- and D-bonds, H_2O and D_2O are highly structured solvents. Their molecules have similar geometric parameters and electronic structures, but they differ in their masses. The substitution of the protium atom by the deuterium one, H → D, makes the reduced mass of the whole D_2O molecule approximately twice as large as that of the H_2O molecule [23], which brings about the frequency variation of all vibrations, including zero ones, and, as a result, affects the energy of dispersion intermolecular interactions [23].

When considering the near solvation of ions, we adopt that the key role belongs to the H(D)-bound solvent. The decrease in the self-diffusion coefficient D_s at the substitution H → D [24] evidences a higher structuring in D_2O: the SIE for the self-diffusion coefficient $D_{s\mathrm{H}}/D_{s\mathrm{D}} > 1$ and, as a result, the viscosity increases, $\eta_0^\mathrm{D}/\eta_0^\mathrm{H} > 1$ [15]. At the same time, the both ratios, which characterize the solvents, are close by magnitude and, being the SIEs, are equal to 1.23 at a temperature of 298.15 K [15, 24]. As the temperature increases, the both SIEs decrease: $D_{s\mathrm{H}}/D_{s\mathrm{D}}$ from 1.23 at 303.15 K to 1.00 at about 673.15 K [24], and $\eta_0^\mathrm{D}/\eta_0^\mathrm{H}$ from 1.283 at 283.15 K to 1.225 at 298.15 K [15].

The higher structuring of D_2O is also evidenced by the SIE value for the ion diffusion coefficient, $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0 > 1$ (Table 2), which can be explained by the growth of the slowing-down action of the more structured D_2O solvent on the examined ions. If the temperature increases from 283.15 to 298.15 K, the SIE $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$ for them decreases but remains larger than 1 (Table 2), which is a result of the destruction, first of all, of the more structured solvent. The destruction of stronger D-bonds creates conditions for the growth of near ionic solvation and manifests itself in the diffusion coefficients. Their values for the studied ions in heavy water are lower than in light water if $T = \mathrm{const}$.

However, destructuring in H_2O and D_2O can take place under the influence of ions as well. The SIE $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0 > 1$ (Table 2) and either decreases along the series of the same-type ions $\mathrm{Li^+}$–$\mathrm{Na^+}$–$\mathrm{K^+}$–$\mathrm{Cs^+}$, $\mathrm{F^-}$–$\mathrm{Cl^-}$–$\mathrm{Br^-}$–$\mathrm{I^-}$, and $\mathrm{ClO_4^-}$–$\mathrm{IO_4^-}$, or increases along the series $\mathrm{Me_4N^+}$–$\mathrm{Et_4N^+}$–$\mathrm{Pr_4N^+}$–$\mathrm{Bu_4N^+}$ and $\mathrm{IO_3^-}$–$\mathrm{BrO_3^-}$–$\mathrm{ClO_3^-}$ as the ionic radius grows.

Of course, the mobility of solvent molecules depends not only on ions, but also on the strength of H- and D-bonds. The SIE can be considered as a measure of the ionic effect on the solvent. It is interesting that, most often, the magnitudes of SIEs calculated using the properties (η_0, D_s) of pure solvents (H_2O, D_2O) and their ionic solutions do not match. According to the deviation of the SIE $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$ for the ion diffusion coefficient from the SIE $\eta_0^\mathrm{D}/\eta_0^\mathrm{H}$ for the viscosity, the researched ions can be divided into two groups (see Table 2):

- the ions for which the SIE for the viscosity prevails over the SIE for the ion diffusion coefficient, $\eta_0^\mathrm{D}/\eta_0^\mathrm{H} > D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$ (these are negatively solvated ions);
- the ions for which the SIE for the ion diffusion coefficient prevails over the SIE for the viscosity, $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0 > \eta_0^\mathrm{D}/\eta_0^\mathrm{H}$ (these are positively solvated ions).

At a constant temperature, the SIE $\eta_0^\mathrm{D}/\eta_0^\mathrm{H} = \mathrm{const}$, whereas the SIE $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$ varies in such a way that it remains smaller than the viscosity ratio $\eta_0^\mathrm{D}/\eta_0^\mathrm{H}$ for the negatively solvated ions, but larger than $\eta_0^\mathrm{D}/\eta_0^\mathrm{H}$ for the positively solvated ones.

The parameter $\overline{d}$, which was proposed in work [1] as a sensitive quantitative characteristic of the near ionic hydration, also manifests itself well in D_2O. According to the results of our research, the substitution H → D gives rise to almost identical ionic solvations of ions in H_2O and D_2O, which is associated with the close values of the relevant molecular parameters [23]: the bond lengths ($l_\mathrm{OH} \approx l_\mathrm{OD}$), the valence angles ($\angle\mathrm{HOH} \approx \angle\mathrm{DOD}$), the tetrahedral structure, the same electronic structure. Hence, those molecules have almost identical properties, except for their masses [23]. In the opinion of the author of work [25], the non-equivalence of H and D arises owing to the simultaneous action of local and dispersion forces of intermolecular interaction, whose energies depend differently on the temperature and pressure in light and heavy waters. It is noteworthy that the deviation of the ratio $\overline{d}_{\rm H}/\overline{d}_{\rm D}$ from 1 can be used to classify the examined ions as negatively ($\overline{d}_{\rm H}/\overline{d}_{\rm D} > 1$) or positively ($\overline{d}_{\rm H}/\overline{d}_{\rm D} < 1$) solvated ones. Furthermore, for the SIEs $D^0_{i{\rm H}}/D^0_{i{\rm D}}$, $\lambda^0_{i{\rm H}}/\lambda^0_{i{\rm D}}$, and $V_{\rm H}/V_{\rm D}$, the deviation from 1 can reach 26% at a temperature of 298.15 K.

Considering the ratio $\overline{d}_{\rm H}/\overline{d}_{\rm D}$ as the SIE that characterizes the near solvation of studied ions in light and heavy waters, the interesting and somewhat unexpected relationship $\overline{d}_{\rm H}/\overline{d}_{\rm D} \approx 1$ can be explained on the basis of the Stokes–Einstein law (4). Substituting the right-hand side of Eq. (4) into the ratio $\overline{d}_{\rm H}/\overline{d}_{\rm D}$, we obtain the expression:

$$\frac{\overline{d}_{\rm H}}{\overline{d}_{\rm D}} = \frac{\eta_0^{\rm D} D^0_{i{\rm D}}}{\eta_0^{\rm H} D^0_{i{\rm H}}}, \tag{8}$$

where the indices H and D refer to light and heavy waters, respectively. From this expression, it follows that this ratio is the inverse to the Pisarzhevsky–Walden product [15] for D_2O and H_2O. It can be written as the product of factors characterizing the degree of contributions made by the viscosity and ion-diffusion-coefficient isotope effects in heavy and light waters:

$$\frac{\overline{d}_{\rm H}}{\overline{d}_{\rm D}} = \left(\frac{\eta_0^{\rm D}}{\eta_0^{\rm H}}\right)\left(\frac{D^0_{i{\rm D}}}{D^0_{i{\rm H}}}\right). \tag{8a}$$

According to this equation, the isotope effect of the near solvation, $\overline{d}_{\rm H}/\overline{d}_{\rm D}$, is equal to the product of the inverse ratios between the viscosities of the solvents and between the diffusion coefficients of ions in them, i.e., the product of the inverse SIEs for the viscosity and the ion diffusion coefficient.

The first multiplier on the right-hand side of Eq. (8a) is constant at $T = \text{const}$ and does not depend on the nature and properties of the ion. It characterizes the solvents (H_2O and D_2O) at the macroscopic level. On the contrary, the multiplier $D^0_{i{\rm D}}/D^0_{i{\rm H}}$ depends on the size and charge of the ion and characterizes both the ion and the solvent. The both multipliers on the right-hand side of Eq. (8a) change, if the temperature changes: the ratio $\eta_0^{\rm D}/\eta_0^{\rm H}$ decreases, and the ratio $D^0_{i{\rm D}}/D^0_{i{\rm H}}$ increases as the temperature grows. Hence, those multipliers affect oppositely the deviation of the ratio $\overline{d}_{\rm H}/\overline{d}_{\rm D}$ from 1. The values of the ratio $\left(\overline{d}_{\rm H} - r_i\right) / \left(\overline{d}_{\rm D} - r_i\right)$ also remains close to 1.

The underestimated values of the SIE $\overline{d}_{\rm H}/\overline{d}_{\rm D}$ and the ratio $\left(\overline{d}_{\rm H} - r_i\right) / \left(\overline{d}_{\rm D} - r_i\right)$ are a result of the compensation of the I-M and M-M interactions governing the near ionic solvation. Such values testify to a substantial effect of the solvent on this phenomenon. The complete compensation of the M-M and I-M interactions in the solutions of singly charged ions in light and heavy waters is satisfied under the condition $\overline{d}_{\rm H}/\overline{d}_{\rm D} = 1$ or the equality $\eta_0^{\rm D}/\eta_0^{\rm H} = \left(D^0_{i{\rm D}}/D^0_{i{\rm H}}\right)^{-1}$ between the components of Eq. (8a), which is confirmed experimentally (Table 2): $\overline{d}_{\rm H}/\overline{d}_{\rm D} = 1.00$ for the Me_4N^+ ion at $T = 298.15$ K.

In the case of negatively solvated ions, $\overline{d}_{\rm H}/\overline{d}_{\rm D} > 1.00$ (i.e., the I-M bonds are weaker than the M-M ones), and the inequality $\eta_0^{\rm D}/\eta_0^{\rm H} > D^0_{i{\rm D}}/D^0_{i{\rm H}}$ is satisfied (see Table 2). This conclusion is consistent with Rabinovich's concept [18], according to which D_2O is a more structured solvent than H_2O. The reason for the higher structuring of D_2O is the fact that D-bonds are stronger than H-bonds [18]. The enhancement of the D_2O structuring at the H → D substitution in water leads to the viscosity growth by $\eta_0^{\rm D}/\eta_0^{\rm H} = 1.225$ times (at 298.15 K). Under the predominance of the ion-molecular interaction over the intermolecular one in the case of positive ionic solvation, the inequality $\eta_0^{\rm D}/\eta_0^{\rm H} < D^0_{i{\rm D}}/D^0_{i{\rm H}}$ holds. This condition is confirmed by the results obtained for positively solvated ions, except Na^+ and IO_3^-.

5. Conclusions

The most important result of our research concerning the influence of singly charged ions on the mobility of their nearest molecules of light or heavy water consists in the registration and explanation of the low values obtained for the solvent isotope effect (SIE) for the near solvation, $\overline{d}_{\rm H}/\overline{d}_{\rm D}$. The substitution H → D showed that the solvation of ions in H_2O and D_2O is almost identical, because the $\overline{d}_{\rm H}/\overline{d}_{\rm D}$ parameter was close to 1. Its maximum deviation from 1 reached 2.5÷2.6% for the K^+ and Cs^+ ions at a temperature of 298.15 K (Table 2), being at the level of the experimental data error. It is of interest that, in the cases of the SIE for the ionic diffusion, $D^0_{i{\rm H}}/D^0_{i{\rm D}}$, or the velocity of translational displacement of ions, $V_{\rm H}/V_{\rm D}$, the deviation of this parameter from 1 increases up to 25.0÷25.9% (Table 2). On the other hand, according to the deviation of the parameter deviation rfom 1, the examined ions, except for Na^+ and IO_3^-, distinctly demonstrate either negative ($\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D} > 1$) or positive ($\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D} < 1$) solvation (Table 2).

To explain those somewhat unexpected results on the basis of the Stokes–Einstein law, Eq. (8a) was derived. According to the latter, the SIE $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$ is the product of the inverse SIEs for viscosity, $\eta_0^\mathrm{D}/\eta_0^\mathrm{H}$, and the ionic diffusion coefficient, $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$. Considering the opposite actions of those coefficients on the SIE, it was found that the low SIE values (i.e., some non-equivalence between H and D [25]) are a result of the compensation of the M-M and I-M interactions, which govern the near solvation of singly charged ions in H_2O and D_2O, So the low SIE values testify to a significant influence of the solvent on this parameter.

In the case of negatively solvated ions, we have $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D} > 1$, and the intermolecular interaction prevails over the ion-molecular one: $\eta_0^\mathrm{D}/\eta_0^\mathrm{H} > D_{i\mathrm{D}}^0/D_{i\mathrm{H}}^0$; whereas, for positively solvated ions, $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D} < 1$, and the ion-molecular interaction prevails over the intermolecular one: $\eta_0^\mathrm{D}/\eta_0^\mathrm{H} < D_{i\mathrm{D}}^0/D_{i\mathrm{H}}^0$.

The complete compensation of the M-M and I-M interactions takes place, if the condition $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D} = 1$ holds so that $\eta_0^\mathrm{D}/\eta_0^\mathrm{H} = D_{i\mathrm{D}}^0/D_{i\mathrm{H}}^0$ (see Table 2, the Me_4N^+ cation at 298.15 K). Those conditions are confirmed experimentally (Table 2) and are in agreement with Samoilov's [2] and Rabinovich's [18] viewpoints on the near solvation.

No less significant results were obtained, while studying the influence of ions on the SIE $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$ for the ion diffusion coefficients in light and heavy waters. It is found that the value of $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$ changes not only, if the temperature increases, but also under the influence of ions. The ions affect the solvent via various mechanisms and substantially change its structure, which can be observed in the experiment (Table 2). As one can see from Table 2, the value of the ratio $D_{i\mathrm{H}}^0/D_{i\mathrm{D}}^0$ decreases along the series of similarly solvophilically solvated ions Li^+–Na^+–K^+–Cs^+, F^-–Cl^-–Br^-–I^-, ClO_4^-–IO_4^-, and IO_3^-–BrO_3^-–ClO_3^- with the reduction of the generalized moment m_i^gen that characterizes the forces of electrostatic interaction in ion-molecular systems. At the same time, in the case of the solvophobically of solvated ions, the ratio $D_{i\mathrm{D}}^0/D_{i\mathrm{H}}^0$ increases, as the parameter m_i^gen decreases along the series Me_4N^+–Et_4N^+–Pr_4N^+–Bu_4N^+, which testifies to the non-electrostatic character of the solvate shell formation in this group of ions.

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КОМПЕНСАЦІЯ ІЗОТОПНИХ ЕФЕКТІВ ПРИ БЛИЖНІЙ СОЛЬВАТАЦІЇ ОДНОЗАРЯДНИХ ІОНІВ У ЛЕГКІЙ ТА ВАЖКІЙ ВОДІ

Коефіцієнт дифузії (D_i^0) і мікроскопічні характеристики довжини $(\overline{d})$, часу (τ) і швидкості (V) дифузійного зміщення 18 однозарядних іонів (Li^+, Na^+, K^+, Cs^+, Me_4N^+, Et_4N^+, Pr_4N^+, Bu_4N^+, F^-, Cl^-, Br^-, I^-, ClO_3^-, ClO_4^-, BrO_3^- IO_3^-, IO_4^-, OBz^-) у важкій та легкій воді при 283,15 K і 298,15 K розраховано з літературних даних щодо граничної молярної електричної провідності цих іонів. Із застосуванням запропонованого нами параметра $(\overline{d} - r_i)$, (r_i – структурний радіус іона), визначено тип сольватації цих іонів: позитивна, якщо параметр $(\overline{d} - r_i) > 0$; негативна – при значеннях $(\overline{d} - r_i) < 0$. Розраховано та проаналізовано ізотопні ефекти розчинника (ІЕР) при заміні $H \to D$ у H_2O: коефіцієнта дифузії іонів $D^0_{i\mathrm{H}}/D^0_{i\mathrm{D}}$, довжини $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$, часу $\tau_\mathrm{H}/\tau_\mathrm{D}$ і швидкості $V_\mathrm{H}/V_\mathrm{D}$ трансляційного їх зміщення та ІЕР в'язкості розчинника η_0^D/η_0^H. Встановлено, що у випадку ІЕР $D^0_{i\mathrm{H}}/D^0_{i\mathrm{D}}$ або $V_\mathrm{H}/V_\mathrm{D}$ відхилення від 1 становить до 25,0–25,9%, а для ІЕР ближньої сольватації $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$ – на порядок нижче. Пояснення цих фактів проведене на підставі одержаного нами рівняння, у якому ІЕР $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$ є добутком зворотних ІЕР η_0^D/η_0^H і $D^0_{i\mathrm{D}}/D^0_{i\mathrm{H}}$. Низькі значення $\overline{d}_\mathrm{H}/\overline{d}_\mathrm{D}$ зумовлені протилежним характером впливу цих співмножників, що вказує на компенсацію міжмолекулярних та іон-молекулярних взаємодій, які визначають ближню сольватацію однозарядних іонів у H_2O та D_2O і свідчать про значний вплив на останню розчинника.

Ключові слова: ізотопний ефект розчинника, однозарядні іони, дифузія, електрична провідність, ближня сольватація, негативна сольватація.