

---

doi: 10.15407/ujpe62.09.0769

V.I. BULAVIN,<sup>1</sup> I.M. V'YUNYK,<sup>2</sup> YA.I. LAZAREVA<sup>2</sup>

<sup>1</sup>National Technical University "Kharkiv Polytechnical Institute"

(2, Kyrpychova Str., Kharkiv 61002, Ukraine; e-mail: bulavin@kpi.kharkov.ua)

<sup>2</sup>V.N. Karazin National University of Kharkiv

(4, Svoboda Sq., Kharkiv 61022, Ukraine)

## DIFFUSION AND MICROSCOPIC CHARACTERISTICS OF SINGLY CHARGED ION TRANSFER IN EXTREMELY DILUTED AQUEOUS SOLUTIONS

PACS 66.10.C, 66.10.Ed,  
66.20.Gd

*Diffusion coefficients and microscopic characteristics of the length ( $\bar{d}$ ), time, and rate of ion diffusion displacement have been calculated for 19 singly charged ions ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $CNS^-$ ,  $ClO_4^-$ ,  $NH_4^+$ ,  $Me_4N^+$ ,  $Et_4N^+$ ,  $Pr_4N^+$ ,  $Bu_4N^+$ ,  $Pent_4N^+$ , and  $BPh_4^-$ ) in water at temperatures from 273.15 to 473.15 K. The calculations are based on the literature data concerning the limiting molar electric conductivity of those ions. The analysis of the data obtained shows that the length of the ion diffusion displacement  $\bar{d}$  correlates with the type of ion solvation. If the average value  $\bar{d}$  exceeds the crystallographic (structural) radius  $r_i$  of an ion, the latter is solvated positively. However, if  $\bar{d}$  is less than  $r_i$ , the ion solvation is negative.*

*Keywords:* singly charged ions, diffusion, electric conductivity, Stokes radius, negative solvation.

### 1. Introduction

Diffusion in liquid ion-molecular systems (LIMSs) belongs to processes that are important from the practical viewpoint, but the description of which is difficult. Diffusion plays a large role in the animated and unanimated nature, governs the mechanism and kinetics of chemical reactions, and forms a basis for many processes in chemical engineering.

The motion of an ion in an extremely diluted solution is hindered by a characteristic viscous friction, which is proportional to the ion velocity. This friction counteracts the driving force and restricts the process rate [1]. The modern theory of ionic diffusion in liquids is based on the molecular mechanism. However, it has not been developed as perfectly as the theory

of electric conductivity (EC). This fact is associated with the lack of experimental data, on the one hand, and with a more complicated nature of the diffusion phenomenon, on the other hand. Therefore, it is a challenging task to obtain experimental values for the diffusion coefficients of various ions – as well as their dependences on the solvent, temperature, and pressure – because those data will allow the phenomenon of ionic diffusion in various solutions to be understood more profoundly.

It is of interest to calculate the diffusion coefficient  $D_i^0$  and to estimate the microscopic values of the length, time, and velocity of diffusion displacement (the translational jump), by using the experimental data for the limiting molar electric conductivity (LMEC) of ions and the viscosity of a solvent. There is no doubt that the diffusion is strongly connected with the state of ions in a solvent and, first of all, with

their solvation [2]. The establishment of this relation for various types of ions will allow the mechanism of diffusion in electrolyte solutions to be understood more comprehensively.

Two rather general approaches are used for the interpretation of the ionic solvation: thermodynamic and kinetic ones [3]. They do not exclude but complement each other. The kinetic approach was developed by Samoilov. It describes the short-range solvation resulting from the short-range ion-molecule (I-M) and molecule-molecule (M-M) interactions [4, 5]. A correlation between the solvation degree of ions and the experimentally found value for the diffusion displacement  $\bar{d}$ , which was found by us, allowed the latter quantity to be recommended for a quantitative characterization of the ionic effect on the translational exchange of water molecules, and the concept of "Stokes" radius to be replaced by the diffusion displacement length. Attention is attracted by the fact that, unlike the traditional approach, the recommended one is more convenient. It allows the microdynamic parameter  $\bar{d}$  to be calculated at a certain temperature, irrespective of the diffusion mechanism.

The microscopic parameters of ion transfer ( $\bar{d}$ ,  $\tau$ ,  $V$ ) are characterized on the basis of one of the basic points of the kinetic theory. According to it, the short-range solvation is governed by the energy difference between the ion-molecule and molecule-molecule short-range interactions in a solution.

Samoilov's approach [4] is based on the consideration of the solvent-solvent interaction as the dominating factor. According to Samoilov [4], the kinetic stability of an ionic solvate is determined by the ion-induced change in the activation energy of the exchange process between solvent molecules located near the ion and in the solvent bulk. By applying the Frenkel scenario for the particle thermal motion in a liquid, Samoilov [4] calculated the quantitative characteristics  $\Delta E_i$  and  $\tau_i/\tau_0$  for the short-range solvation. Depending on the signs on those quantities, he divided all ions into two groups:

$$1) \Delta E_i > 0, (\tau_i/\tau_0) > 1,$$

and

$$2) \Delta E_i < 0, (\tau_i/\tau_0) < 1.$$

The former corresponds to the positive solvation, and the latter to the negative one. The presence of positive and negative solvations was confirmed by a lot

of theoretical and experimental methods [3]. By using the model of fused spheres, Collins [6] found that singly charged ions with a small size and a high charge density (kosmotropic ions) strongly bind water molecules, whereas ions with a large size and a low charge density (chaotropic ions) are bound with water molecules more weakly than water molecules with one another. According to this model, water molecules are considered as zwitterions with the radii of cation and anion parts equal to 1.06 and 1.78 Å, respectively.

The issue concerning the mechanism of why the water molecules that are nearest to an ion possess an enhanced mobility remains challenging. During last decades, a number of theoretical researches of this phenomenon have been carried out. They were based on the application of nonequilibrium statistical mechanics [7–11]. In those works, special attention was paid to modern microscopic approaches, which became possible owing to the development of molecular-dynamics simulation (MDS) methods. A combination of theoretical elaborations with MDS methods allows Samoilov's model to be interpreted at the molecular level in terms of pair correlation functions.

In their work [7], Chong and Hirata performed a theoretical research dealing with the hydration of singly charged monatomic ions. The research was carried out in the framework of the extended reference interaction site model (RISM). The analysis of the information obtained allowed the cited authors to establish that partial molar volumes (PMVs) characterize the ion-molecule interaction. The performed theoretical calculation of  $\Delta E_i$  with the use of the mean-force potential (MFP) made it possible to interpret the short-range ionic hydration at the molecular level. It was found that the ion-water interaction is not equivalent to the water-water interaction. The theoretical classification of ions into positively and negatively solvated ones on the basis of  $\Delta E_i$ -sign is in qualitative agreement with the underlying Samoilov's theory.

Kalyuzhnyi *et al.* [8], by using the Collins water model [6] and the Chandler–Silbey–Ladanyi integral equation, determined MFPs for the ion-water and water-water interactions, as well as  $\Delta E_i$  values for eight singly charged ions. The cited authors showed that kosmotropions correspond to positive  $\Delta E_i$  values ( $\Delta E_i > 0$ ), whereas chaotropic ions to negative ones ( $\Delta E_i < 0$ ), which agrees with Samoilov's ideas concerning the positive and negative solvations.

In Syrnikov's model describing the liquid structure as a system of nonlinear interacting oscillators [9, 10], the hardener of a solvent structure is a substance that enhances the vibrational stability of the solvent structure, and a structure destroyer reduces it. Those substances are characterized by the positive and negative solvations, respectively. Syrnikov [10] considered the transfer in liquids to be mainly driven by a non-activation mechanism. To describe the positive and negative solvations, he proposed to use Van Hove functions [9]. The cited author [9, 10] attracted attention to the fact that the self-diffusion of water molecules is different in a solution and in pure water.

In work [11], a structural simulation of hydration spheres was carried out for eight singly charged ions, by using the MDS method in an NVT ensemble. The analysis of the results obtained showed that, for the  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{F}^-$  ions, water molecules are exchanged more rarely than the nearest molecules in water, whereas, for the  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  ions, the situation is inverse. Therefore, the calculated self-diffusion coefficient for water molecules in the hydration spheres of ions and the obtained V-structures testify that the positive solvation is typical of the  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{F}^-$  ions, whereas the negative solvation is characteristic of the  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  ones.

Hence, the results of theoretical researches [7–11] confirm the basic point of Samoilov's theory, which actually reveals the nature of short-range solvation and, therefore, the essence of the phenomena of negative and positive hydrations.

## 2. Calculations

In this work, the diffusion coefficient  $D_i^0$  was calculated for 19 ions (these are  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{CNS}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NH}_4^+$ ,  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$ ,  $\text{Bu}_4\text{N}^+$ ,  $\text{Pent}_4\text{N}^+$ , and  $\text{BPh}_4^-$ ) in water at a temperature of 298.15 K. The same parameter was also calculated for the  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$ , and  $\text{Bu}_4\text{N}^+$  ions in water in a temperature interval of 298.15–473.15 K. The calculations were carried out, by using the known equation for the Nernst–Einstein limiting law [12]

$$D_i^0 = \frac{RT}{|z|F^2} \lambda_i^0, \quad (1)$$

where  $\lambda_i^0$  is the experimental value of LMEC for singly charged ions [13, 14],  $z_i$  the ion charge,  $R$  the gas constant,  $F$  the Faraday number, and  $T$  the temperature (in kelvins).

The values of  $D_i^0$  calculated by Eq. (1) for 19 ions in water at a temperature of 298.15 K are quoted in Table 1. They are in good agreement with literature data [12, 15]. As the temperature increases, the values of  $D_i^0$  grow for the  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  ions in water.

By combining relation (1) with the Stokes equation, we obtain the Stokes–Einstein equation

$$\bar{d} = \frac{kT}{6\pi D_i^0 \eta_0}, \quad (2)$$

which describes a relation between the diffusion coefficient  $D_i^0$ , the solvent viscosity  $\eta_0$ , and the “Stokes” radius  $\bar{d}$ . Here,  $k$  is the Boltzmann constant. This equation is used when calculating  $\bar{d}$  from the viscosity data. In so doing, one should bear in mind that its validity is restricted by the descriptive capabilities of the Stokes law [5]. Nevertheless, Eq. (2) is used quite often [2, 16] for the solution of the inverse problem, i.e. for the estimation of the “Stokes” radius of an ion from the known experimental values for  $D_i^0$  (or  $\lambda_i^0$ ) and  $\eta_0$  under the assumption that the Stokes law describes a characteristic viscous slowing-down and confines the velocity of an ion migrating from the initial position to the nearest neighbor equilibrium one. Although this evaluation of the parameter  $\bar{d}$  is, to some extent, not rigorous, it is rather universal [5], because it allows one to study its dependence on the temperature, solvent, structural radius of ion, and so forth. The establishment of the dependence of  $\bar{d}$  on the indicated factors is useful for understanding the diffusion phenomenon in LIMSs and for finding how the ion solvation affects it.

The results of calculations of the parameter  $\bar{d}$  for singly charged ions in water at a temperature of 298.15 K are quoted in Table 1. In addition, they are depicted in Figs. 1 to 3 (in Figs. 3 to 6, the symbols  $\circ$  correspond to cations, and the symbols  $\blacklozenge$  to anions; the enumeration of ions coincides with that in Table 1). The results obtained agree well with literature data [2, 16]. Table 1 also contains data on the structural radii: radii according to Goldschmidt [3] for monatomic ions, radii according to Krungalz [17] for tetra-alkyl ammonium (TAA) ions, and thermochemical radii [3] for the  $\text{CNS}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  ions. By

Table 1. Parameters of singly charged ions in water at a temperature of 298.15 K

No.	Ion	$r_i \times 10^{10}$ , m	$1/r_i \times 10^{-10}$ , $m^{-1}$	$\lambda_i^0 \times 10^4$ , $S \cdot m^2/mol$	$D_i^0 \times 10^9$ , $m^2 \cdot s^{-1}$	$\bar{d} \times 10^{10}$ , m	$(\bar{d} - r_i) \times 10^{10}$ , m	$\bar{d}/r_i$	$\tau \times 10^{12}$ , s	$V_i$ , $m \cdot s^{-1}$	$B$ , $dm^3/mol$
1	Li <sup>+</sup>	0.78	1.2821	38.68	1.03	2.37	1.59	3.04	9.09	26.0	0.146
2	Na <sup>+</sup>	0.98	1.0204	50.13	1.34	1.83	0.85	1.87	4.17	43.9	0.085
3	K <sup>+</sup>	1.33	0.7519	73.55	1.96	1.25	-0.08	0.94	1.33	94.1	-0.009
4	NH <sub>4</sub> <sup>+</sup>	1.37	0.7299	73.60	1.96	1.25	-0.12	0.74	1.33	94.1	-0.008
5	Rb <sup>+</sup>	1.49	0.6711	77.71	2.07	1.18	-0.31	0.79	1.12	105.3	-0.033
6	Cs <sup>+</sup>	1.65	0.6061	77.08	2.05	1.19	-0.46	0.72	1.15	103.4	-0.047
7	Me <sub>4</sub> N <sup>+</sup>	2.16	0.4630	44.90	1.20	2.04	-0.12	0.95	5.78	35.3	0.123
8	Et <sub>4</sub> N <sup>+</sup>	2.80	0.3571	32.70	0.87	2.81	0.01	1.00	15.1	18.6	0.385
9	Pr <sub>4</sub> N <sup>+</sup>	3.35	0.2985	23.40	0.62	3.92	0.57	1.17	41.3	9.49	0.916
10	Bu <sub>4</sub> N <sup>+</sup>	3.83	0.2611	19.34	0.52	4.75	0.92	1.24	72.3	6.57	1.275
11	Pent <sub>4</sub> N <sup>+</sup>	4.30	0.2326	17.40	0.46	5.28	0.98	1.23	101.0	5.23	-
12	F <sup>-</sup>	1.33	0.7519	55.40	1.48	1.66	0.33	1.25	3.10	53.5	0.107
13	Cl <sup>-</sup>	1.81	0.5525	76.40	2.03	1.20	-0.61	0.66	1.18	101.5	-0.005
14	NO <sub>3</sub> <sup>-</sup>	1.89	0.5291	71.38	1.90	1.29	-0.60	0.68	1.46	88.4	-0.043
15	CNS <sup>-</sup>	1.95	0.5128	66.40	1.77	1.38	-0.57	0.71	1.79	77.0	0.022
16	Br <sup>-</sup>	1.96	0.5102	78.14	2.08	1.17	-0.79	0.60	1.10	106.7	-0.033
17	I <sup>-</sup>	2.20	0.4545	76.80	2.05	1.20	-1.01	0.54	1.17	102.5	-0.073
18	ClO <sub>4</sub> <sup>-</sup>	2.36	0.4237	67.60	1.80	1.36	-1.00	0.58	1.71	79.4	-0.058
19	BPh <sub>4</sub> <sup>-</sup>	4.08	0.2451	19.90	0.56	4.36	0.28	1.07	56.6	7.71	1.114

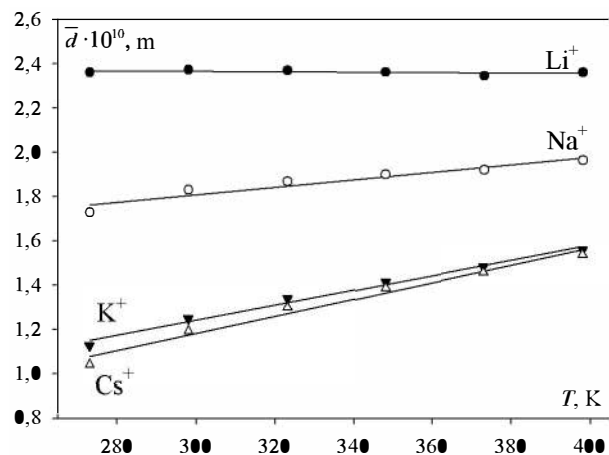


Fig. 1. Polyterms of the parameter  $\bar{d}$  for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup> ions in water

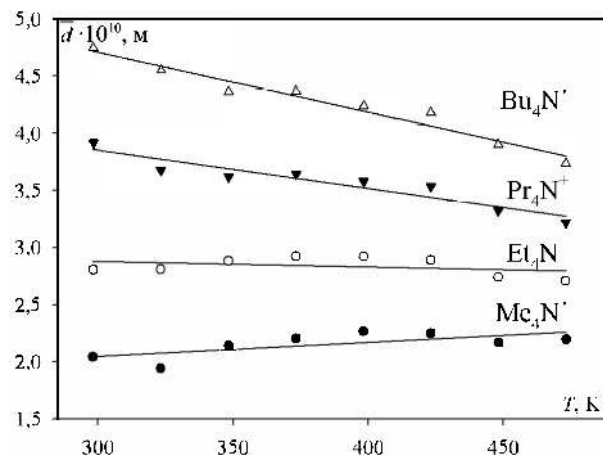


Fig. 2. Polyterms of the parameter  $\bar{d}$  for tetra-alkyl ammonium ions in water

analyzing the results of calculations obtained for the quantity  $\bar{d}$ , the following regularities were revealed.

1. The value of  $\bar{d}$  for singly charged ions in water depends on the temperature (Figs. 1 and 2) and the structural radius of ion (Fig. 3) and correlates with the solvation degree of ions according to Samoilov [4]. In the case of a negatively solvated ion,  $\bar{d}$  is

smaller than the structural radius of this ion; whereas, for a positively solvated ion, it is larger than the radius of the latter (Table 1).

2. The dependence of  $\bar{d}$  on the reciprocal structural radius of the ion,  $1/r_i$ , is nonmonotonic, and, in general, it is described by asymmetric curves with a minimum for both cations and anions (Fig. 3). It is of interest that the location of the minimum corresponds

to the negatively solvated isoelectronic ions  $\text{Rb}^+$  and  $\text{Br}^-$ , which are characterized by almost identical values of the parameter  $\bar{d}$  and, hence,  $D_i^0$ . In the case of anions, the minimum is observed at larger  $r_i$ -values (smaller  $1/r_i$ -values) than for cations.

3. Attention is attracted by the fact that the values of  $\bar{d}$  for negatively hydrated monatomic ions ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ), in spite of some difference between them (due to the charge sign, the magnitude of structural radius, and the solvation mechanism), increase with the temperature, but remain almost constant at a constant temperature,  $\bar{d}_{298.15} \approx 1.2 \times 10^{-10}$  m (Table 1).

4. The sign of the temperature coefficient (TC) for  $\bar{d}$  was found to be positive ( $\partial\bar{d}/\partial T > 0$ ) for negatively hydrated ions and negative ( $\partial\bar{d}/\partial T < 0$ ) for positively hydrated ones, except for the  $\text{Na}^+$  and  $\text{Et}_4\text{N}^+$  ions.

5. The parameter  $\bar{d}$  also turned out sensitive as a characteristic of short-range solvation in the case of ions with a low charge density (the TAA and  $\text{BPh}_4^-$  ions in Table 1).

The characteristic time  $\tau$  of a single translational displacement (a jump) of the ion was evaluated, by using the known equation [18]

$$\tau = \frac{(\bar{d})^2}{6D_i^0}. \quad (3)$$

In so doing, the quantity  $\bar{d}$  was identified with the length of the root-mean-square displacement of the ion. The results of calculations obtained for 19 singly charged ions in water at a temperature of 298.15 K are quoted in Table 1. In Fig. 4, the dependences  $\tau(1/r_i)$  for anions and cations at this temperature are depicted. Table 2 demonstrates the results of calculation of the parameter  $\tau$  for singly charged cations and anions in water in a wide temperature interval. One can see that, as the temperature increases, the value of  $\tau$  for examined ions decreases.

The quantities  $\bar{d}$  and  $\tau$  were used to calculate the velocities of translational displacement of ions in water by the formula

$$V = \frac{\bar{d}}{\tau}. \quad (4)$$

The results of corresponding calculations for a temperature of 298.15 K are quoted in Table 1. The dependences of  $V$  on  $1/r_i$  for cations and anions are described by curves with a maximum (Fig. 5). Only

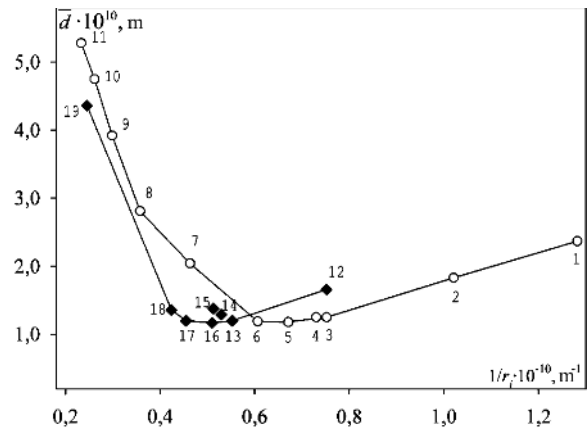


Fig. 3. Isotherms  $\bar{d}$  versus  $1/r_i$  for singly charged ions in water at a temperature of 298.15 K

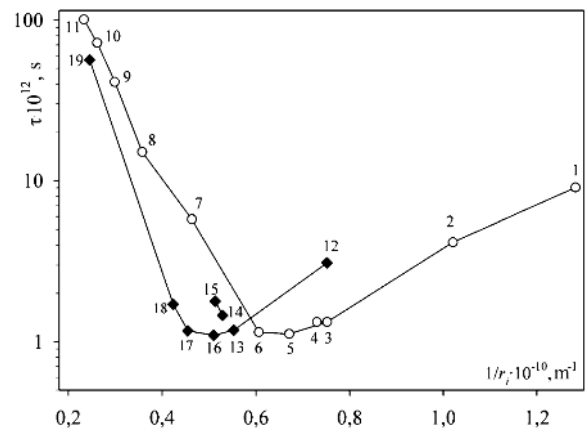


Fig. 4. Dependence of the time of diffusion displacement of singly charged ions in water on  $1/r_i$  at a temperature of 298.15 K

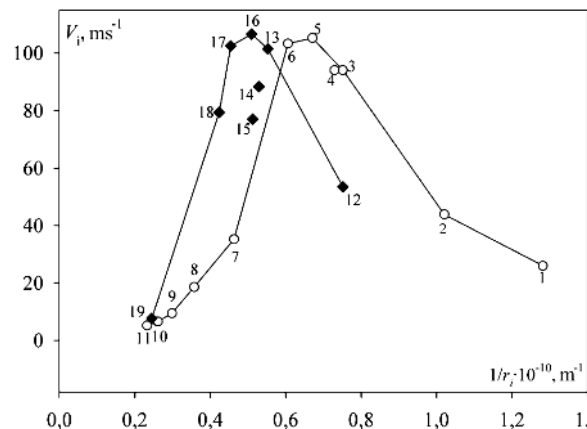


Fig. 5. Dependence of the velocity of diffusion displacement of singly charged ions in water on  $1/r_i$  at a temperature of 298.15 K

Table 2. Time of average diffusion displacement of singly charged ions in water at temperatures of 273.15–473.15 K

Ion	$\tau \times 10^{12}$ , s								
	273.15 K	298.15 K	323.15 K	348.15 K	373.15 K	398.15 K	423.15 K	448.15 K	473.15 K
Li <sup>+</sup>	19.6	9.09	5.15	3.27	2.23	1.65	1.20	0.87	0.72
Na <sup>+</sup>	7.70	4.17	2.52	1.70	1.22	0.95	0.73	0.54	0.47
K <sup>+</sup>	2.12	1.33	0.92	0.70	0.56	0.47	0.39	0.31	0.29
Rb <sup>+</sup>	1.69	1.12	0.82	0.65	0.52	0.45	0.37	0.30	0.27
Cs <sup>+</sup>	1.68	1.15	0.84	0.66	0.53	0.45	0.38	0.29	0.27
Me <sub>4</sub> N <sup>+</sup>	10.2	5.78	2.83	2.44	1.86	1.47	1.13	0.85	0.71
Et <sub>4</sub> N <sup>+</sup>	35.0	15.1	8.58	5.94	4.34	3.14	2.40	1.72	1.33
Pr <sub>4</sub> N <sup>+</sup>	82.6	41.3	19.2	11.8	8.37	5.77	4.38	3.04	2.24
Bu <sub>4</sub> N <sup>+</sup>	162.1	72.3	36.4	20.6	14.4	9.56	7.23	4.92	3.48
Cl <sup>-</sup>	2.08	1.18	0.79	0.58	0.45	0.38	0.31	0.24	0.22
Br <sup>-</sup>	1.85	1.10	0.76	0.57	0.44	0.37	0.31	0.23	0.21
I <sup>-</sup>	2.01	1.17	0.78	0.58	0.45	–	–	–	–

the CNS<sup>-</sup> and NO<sub>3</sub><sup>-</sup> anions do not lie on the isotherm  $V - 1/r_i$ , which may probably be associated with the spatial structure of those ions. The velocity is maximum for the Br<sup>-</sup> anion and the Rb<sup>+</sup> cation. As the temperature grows, the velocity of ionic diffusion in water substantially increases.

### 3. Discussion of the Results

Before proceeding to the discussion of established regularities and obtained dependences, let us dwell on the physical sense of the quantity  $\bar{d}$  calculated from the data on  $D_i^0$  and  $\eta_0$ . When describing the transport processes in electrolyte solutions, hydrodynamic equations based on the Stokes law have been often used for a long time. This law is considered [2, 5] to be qualitatively correct only for ions with large radii. The introduction of the hydrodynamic “Stokes” radii extended the capabilities of hydrodynamics. The Stokes law became applicable to positively solvated ions with a high charge density. In this case, the size increase of such ions in comparison with the structural radii was explained by the formation of stable hydration shells around them, which are characterized by the thickness  $\bar{d} - r_i$ . However, ions with medium dimensions and low charge densities (classified as negatively solvated ones) did not fit the concept of “Stokes” radii. Those ions caused a lot of inconveniences and stimulated the disappointment of researchers [2, 16, 19]. Quite often, such cases re-

mained without attention. Only those ions were considered, for which there existed a substantiated explanation. Actually, for ions classified as negatively solvated, the “Stokes” radii have nothing in common with their actual radii. Furthermore, as the temperature grows, the “Stokes” increase for those ions and, at rather low temperatures, can reach the value of corresponding structural radii (see Figs. 1 and 2 and the K<sup>+</sup> and Et<sub>4</sub>N<sup>+</sup> cations in Table 1).

Taking a relationship between the parameter  $\bar{d}$  and the structural radius of an ion into account, its variation under the temperature influence, and the drift (jump-like) mechanism of ion diffusion, we made some modifications to the concept of the parameter  $\bar{d}$ . We assume that, in the case of negative solvation, the radius of an ion inserted into a structured solvent remains equal to the structural one, and the ion shifts in the diffusion mode by the distance  $\bar{d} < r_i$  during the characteristic time  $\tau$ . In other words, the parameter  $\bar{d}$  should be regarded as a microdynamic length of a certain discrete displacement passed by the ion between two equilibrium positions. If the ion has been subjected to the action of only a drag force resulting only from the solvent viscosity, then we would have had that  $\bar{d} = r_i$ . In the case of negatively solvated ions, an additional drag force is induced by a network of H-bonds in the solvent. It hinders the exchange of molecules between associates composed of pure water molecules and the solvate shell and is responsible for the length of ion displacement  $\bar{d}$ .

This concept, clear and simple, can be extended onto positively solvated ions ( $\bar{d} > r_i$ ). In this case, the difference  $\bar{d} - r_i$  should be considered as a deviation from the Stokes law [5] rather than the solvate shell thickness. In other words, the concept of the discrete displacement length is not deprived of physical sense. The difference  $\bar{d} - r_i$  (or the ratio  $\bar{d}/r_i$ ) describes a real behavior of an ion in the solution and identically characterizes the short-range solvation in the cases of both positively and negatively hydrated ions. Evidently, by its order of magnitude, the parameter  $\bar{d}$  can be compared with the distances between ions and molecules. Generally speaking, the diffusion displacement length can be equal to the structural radius of the ion, larger or smaller than it.

The correlation revealed between  $\bar{d}$  and the solvation degree of ions according to Samoilov testifies that the diffusion is associated with the short-range solvation, and the displacement length is a measure of the latter. The short-range solvation of ions in extremely diluted electrolyte solutions with structured solvents is a result of the short-range ion-molecule (I-M) and molecule-molecule (M-M) interactions [4, 5]. Therefore, the decrease or increase of  $\bar{d}$  in comparison with the structural radius of an ion can be explained in the framework of Samoilov's kinetic theory of solvation [4]. According to this theory, the essence of negative solvation consists in that I-M bonds are weaker than M-M ones. The weak holding of water molecules by negatively solvated ions ( $\bar{d} - r_i < 0$ ,  $\bar{d}/r_i < 1$ ) creates favorable conditions for the free motion of the former in the solution. On the other hand, we have a hindering action of the H-bond network. Until the ion remains negatively solvated, the second process, which is associated with the structure ordering of a solvent, prevails. In other words, the length of a diffusion displacement of negatively solvated ions is shorter than  $r_i$ . Then, according to Eq. (2), the value of  $D_i^0$  is larger.

On the contrary, in the case of ions with positive solvation in water ( $\bar{d} - r_i > 0$ ,  $\bar{d}/r_i > 1$ ), the I-M interaction prevails over the M-M one. In other words, the time of the water molecule holding in the primary solvate shell (PSS) of an ion is longer than that in associates composed of pure water molecules. Under the influence of thermal motion, the decomposition of molecular water associates favors the diffusion of more stable I-M solvates. The latter, owing to their higher stability, have the longer path of a diffusion

displacement  $\bar{d}$ . According to Eq. (2), the reduction of  $D_i^0$  and  $\eta_0$  promotes an increase in  $\bar{d}$ . In the framework of the Stokes law, the growth of  $\bar{d}$  in comparison with  $r_i$  can be reasonably explained [16, 20] by the formation of a kinetically stable solvate complex, which gradually moves as a whole.

For negatively hydrated ions, the difference  $\bar{d} - r_i < 0$  increases by absolute value, as the temperature grows, i.e. it becomes more and more negative. This corresponds to the weakening of the drag influence of the H-bond network, i.e. to a weakening of the negative solvation and, accordingly, a strengthening of the positive one.

At the physical level, the fulfilment of the equation  $\bar{d} - r_i = 0$  (or  $\bar{d} = r_i$ ) corresponds to the total absence of ion hydration, i.e. we have a hard sphere in a liquid solvent characterized by a macroscopic viscosity. The fulfilment of those equations under real conditions can be explained by the mutual compensation of the opposite short-range I-M and M-M interactions.

An absolutely different mechanism governing the translational exchange of water molecules takes place in the case of ions with a low charge density and non-polar hydrophobic groups. It is known [21] that the own size rather than the charge plays a key role in the influence of those ions on the exchange. The excess charge – positive ( $R_4N^+$ ) or negative ( $BPh_4^-$ ) – is screened by hydrophobic groups, which react with polar water molecules very weakly. As one can see from Table 1 and Fig. 2, the parameter  $\bar{d}$  calculated for hydrophobically solvated ions depends, in general, on the structural radius; it is sensitive to the size of hydrophobic groups and the temperature. Attention is attracted by the fact that the parameter  $\bar{d}$  has large positive values that exceed their counterparts for ions positively solvated following the donor-acceptor mechanism ( $Li^+$ ,  $Na^+$ ). Furthermore, with the growth of structural radii in the cation series  $Me_4N^+ - Pent_4N^+$ , both the  $\bar{d}$ -value and the deviation  $\bar{d} - r_i$  from the Stokes law increase, which testifies to the growth of the hydrophobic solvation degree of TAA ions.

According to the clathrate-hydration (iceberg) model [22], the ions with nonpolar groups promote [23] (induce [22]) the clusterization of water molecules that are bound with one another by means of H-bonds and are more stable than in pure water at the same temperature. The cluster structures formed near hydrophobic groups of ions have a drag effect on the dif-

fusion of ions. Therefore, the hydrophobic hydration (HH) is not a consequence of the strong interaction between water molecules and hydrophobic ions. It is a result of the promotion (induction) of an interaction between water molecules by hydrophobic groups and its enhancement.

The determined sign of the temperature coefficient (TK) for the diffusion displacement length in the series of TAA ions is also of interest:  $\partial\bar{d}/\partial T > 0$  for the  $\text{Me}_4\text{N}^+$  cation,  $\partial\bar{d}/\partial T \approx 0$  for the  $\text{Et}_4\text{N}^+$  ion, and  $\partial\bar{d}/\partial T < 0$  for the  $\text{Pr}_4\text{N}^+$  and  $\text{Bu}_4\text{N}^+$  ions.

In the case of  $\text{Et}_4\text{N}^+$  cation, the transition from the negative to positive hydration ( $\bar{d}/r_i = 1$ ) takes place at a temperature of 298.15 K. The Stokes–Einstein law is obeyed for this ion in the examined temperature interval (273.15–473.15 K). At the same time, the  $\text{Pr}_4\text{N}^+$  and  $\text{Bu}_4\text{N}^+$  cations are solvated hydrophobically. Those regularities agree with the data of work [22]. Such a variation character of the TC of the parameter  $\bar{d}$  is a confirmation [23] of a gradual change in the properties at the transition from substances with prevailing hydrophilic properties ( $\text{Me}_4\text{N}^+$ , Table 1) to substances, in which only hydrophobic properties reveal themselves ( $\text{Bu}_4\text{N}^+$ ). This is an evidence that HH is not an exception, but represents one of the manifestations of the same phenomenon known as solvation.

A comparison between the values of the parameter  $\bar{d}$  for the  $\text{Bu}_4\text{N}^+$  and  $\text{BPh}_4^-$  ions demonstrates that the characteristics of the hydrophobic hydration are affected not only by the own size of ions, but also by other factors such as the charge sign, the nature of nonpolar hydrophobic groups ( $\text{Bu}^+$ ,  $\text{Ph}^-$ ), and so forth.

The closeness of the values of the parameter  $\bar{d}$  that was revealed for negatively hydrated ions ( $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) under isothermal conditions may probably be associated with the closeness of the solvent molecule sizes and the translational displacement lengths for those ions. Those close values also testify to the identical drag effect of a solvent with hydrogen bonds on a moving ion. The Walden–Pisarzhevsky rule is obeyed for the indicated ions in water.

The established different signs of TC for the parameter  $\bar{d}$  of singly charged ions can be explained on the basis of Eq. (2) and making use of Samoilov's theory [4]. After differentiating this equation with respect to the temperature and making simple transformations,

we obtain the following equation for the relative temperature coefficient (RTC) of the diffusion displacement length  $\beta_{\bar{d}}$ :

$$\beta_{\bar{d}} = \frac{1}{T} - \beta_{\eta_0} - \beta_{D_i^0}, \quad (5)$$

where  $\beta_{\eta_0}$  and  $\beta_{D_i^0}$  are the RTCs for the pure solvent viscosity and the ion diffusion coefficient, respectively. Since the conditions  $\frac{1}{T} > 0$ ,  $\beta_{\eta_0} < 0$ , and  $\beta_{D_i^0} > 0$  are always satisfied, the sign in the case of constant temperature is actually determined by the opposite signs of  $\beta_{\eta_0}$  and  $\beta_{D_i^0}$ .

As one can see from Eq. (5), the positive value of RTC for the diffusion displacement length ( $\beta_{\bar{d}} > 0$ ) gives rise to the inequality

$$\left(\frac{1}{T} - \beta_{\eta_0}\right) > \beta_{D_i^0}, \quad (6)$$

and the negative RTC ( $\beta_{\bar{d}} < 0$ ) to the inverse inequality

$$\left(\frac{1}{T} - \beta_{\eta_0}\right) < \beta_{D_i^0}. \quad (7)$$

Hence, the parameter  $\bar{d}$  is a good sensitive criterion for the influence of ions on the translational exchange of water molecules, which makes it possible to classify ions into positively, hydrophobically, or negatively hydrated ones. Negatively solvated ions behave as if they have critical dimensions [24]. Namely, ions with smaller dimensions create a stable hydration shell, and their sizes become larger in water as a result of the solvophilic hydration. At the same time, for the dimensions larger than critical, the ions are solvofobically solvated. The larger the hydrophobic hydration, the larger are their dimensions.

The influence of the size of singly charged ions on the translational motion of water molecules in a solution manifests itself, both for cations and anions, in isotherms plotted in the coordinates  $\bar{d} - r_i$  versus  $1/r_i$  (Fig. 6), which characterize the short-range hydration. It is well known that those isotherms have a minimum [16, 21]. The existence of the latter was explained by Samoilov for aqueous solutions [21] as the transition from the mainly solvophilic to mainly solvofobic solvation of ions. In general, the order of ion arrangement at isotherms follows from their different influences on the solvent structure. Cations and anions are placed at different isotherms [16] due to the asymmetric distribution of charges at the solvent atoms, which is responsible for the asymmetry



of the structure and the dynamics of the cation and anion solvations.

The isotherm  $\bar{d} - r_i$  versus  $1/r_i$  qualitatively reproduces the isotherm  $\Delta E_a$  versus  $1/r_i$  for cations, which was presented in works [4, 20]. Below the axis  $1/r_i$ , there is a region of negative hydration. Surely, the determined character of ion arrangement at the isotherm  $\bar{d} - r_i$  versus  $1/r_i$  depends on the solvent structuring, as well as on the charge, own size, structure, and electron-donor properties of ions.

The time of the average diffusion displacement,  $\tau$ , depends on the solvation degree of ions and is described in the coordinates  $\tau$  versus  $1/r_i$  by curves with wide minima (Fig. 4), in which negatively solvated cations and anions with  $\tau \leq 2$  ps are located. Hence, the environment of negatively solvated ions remains “long-term” during short time intervals, because the exchange of water molecules between the nearest-to-ion environment and the molecules in the bulk is limited by the strength of the H-bond network. Therefore, the diffusion displacement of negatively solvated ions should take place together with water molecules in the environment that are weakly held by ions. In this case, the local diffusion coefficient of water molecules should be close to the ion diffusion coefficient. The close values of the displacement lengths of negatively solvated monatomic singly charged ions with and without water molecules confirm this hypothesis.

The diffusion displacement of the  $K^+$  and  $NH_4^+$  ions is isotropic on the picosecond time scale. The slowing-down of the motion of water molecules in clathrate structures promoted by the  $R_4N^+$  ions is a result of the short-range non-Coulomb interactions and testifies to the strengthening of H-bonds, which grows together with  $R$ . During long time intervals ( $\tau > 41$  ps for the  $Pr_4N^+$ ,  $Bu_4N^+$ ,  $Pent_4N^+$ , and  $BPh_4^+$  ions), the environment near an ion has enough time to change. Owing to cooperative character of the formation and the breaking of H-bonds, the cluster-clathrate structures promoted by TAA ions should not be rigid and “long-term” [22]. Under the influence of thermal motion, small oscillations of the latter become interrupted due to a jump-like change in the equilibrium position.

Not less interesting microscopic characteristic of singly charged ions is the velocity  $V$  of the average diffusion displacement. This parameter, as well as other microscopic characteristics, is sensitive to the ion size

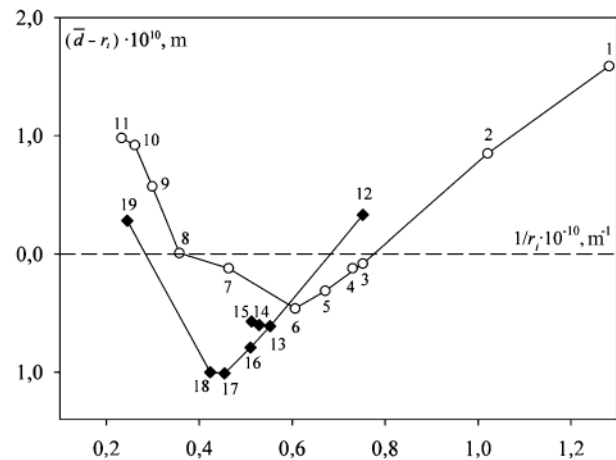


Fig. 6. Isotherms  $\bar{d} - r_i$  versus  $1/r_i$  for singly charged ions in water at a temperature of 298.15 K

and the temperature and correlates with the solvation degree of ions. The isotherms for cations and anions in the coordinates  $V$  versus  $1/r_i$  (Fig. 5) are characterized by curves with a maximum. The  $CNS^-$  and  $NO_3^-$  ions lie somewhat aside from the curve for anions.

By classifying ions in water on the basis of the velocity of their average diffusion displacement, we come back to conclusions concerning three groups of ions, which were presented above.

1. The most mobile are negatively solvated ions with a velocity of 77–106.7 m/s.

2. The least mobile are the so-called “frozen” ions with a velocity of 5.23–9.49 m/s.

3. There is an intermediate group containing hydrophilically (positively) hydrated ions ( $Li^+$ ,  $Na^+$ , and  $F^-$ ), and the  $Me_4N^+$  and  $Et_4N^+$  ions. Probably, the latter have a certain contribution from the hydrophobic hydration component, but the hydrophilic one prevails all the same, especially for the  $Me_4N^+$  ion, which agrees with the results of work [22]. For negatively solvated ions, the velocity of a diffusion displacement, as well as  $\bar{d}$ , grows together with the temperature.

#### 4. Conclusions

The most important result of our research is the establishment, for the first time, a correlation between the microscopic parameter of a discrete diffusion displacement  $\bar{d}$  and the solvation degree of ions according to Samoilov. This correlation allows the param-

eter  $\bar{d}$  to be used for a quantitative characteristic of the short-range hydration of ions, and the concept of "Stokes" radius to be replaced by the diffusion displacement length. In this approach, the hydrodynamic model of ionic transfer in LIMSs, which is based on the Stokes equation, is capable to qualitatively explain the features of the dynamics of ions in the solutions and to make predictions concerning the influence of various factors on the short-range hydration of ions in terms of the kinetic theory of solvation. The thickness of a solvate shell,  $\bar{d} - r_i$ , obtains a new meaning at that (now, this is a deviation from the Stokes law) and, like  $\bar{d}$ , has a physical meaning for singly charged ions of various nature.

Unlike the traditional approach to the calculation of quantitative parameters of the kinetic hydration with the use of the data on the temperature dependence of the LMEC of ions, the parameter  $\bar{d}$  can be calculated at a certain temperature. The value of diffusion displacement  $\bar{d}$  is determined by the properties of both the ion and the solvent and can be found irrespective of the diffusion scenario (a drift or a jump).

1. D. Evans, M. Matesich. The measurement and interpretation of electrolytic conductance. In *Techniques of Electrochemistry*, edited by A.J. Yeager, E. Salkind (Wiley, 1973), Vol. 2, p. 10.
2. K.M. Elkind, I.G. Trunova. Connection of hydration with transport phenomena in aqueous electrolyte solutions. *Trudy Nizhegor. Gos. Tekh. Univ.* N 4 (97), 272 (2012) (in Russian).
3. G.A. Krestov. *Thermodynamics of Ionic Processes in Solutions* (Khimiya, 1984) (in Russian).
4. O.Ya. Samoilov. *Structure of Aqueous Electrolyte Solutions and the Hydration of Ions* (Consultants Bureau, 1965).
5. T. Erdei-Gruz. *Transfer Phenomena in Water Solutions* (Wiley, 1974).
6. K. Collins. Charge density-dependent strength of hydration and biological structure. *Biophys. J.* **72**, 65 (1997).
7. S. Chong, F. Hirata. Ion hydration: Thermodynamic and structural analysis with an integral equation theory of liquids. *J. Phys. Chem. B* **101**, 3209 (1997).
8. Y. Kalyuzhnyi, V. Vlady, K. Dill. Hydration of simple ions. Effects of the charge density. *Acta Chim. Slov.* **48**, 309 (2001).
9. Yu.P. Syrnikov. Modern ideas of the thermal motion in fluids and the notions of positive and negative hydrotrons. *Zh. Strukt. Khim.* **25**, 51 (1984) (in Russian).
10. Yu. Syrnikov. *Thermodynamic Properties of Solutions under Extreme Conditions* (Ivanovo Khim.-Tekhnol. Inst., 1986) (in Russian).
11. I.B. Shirobokov, N.A. Velma. Modelling the structure of hydrate shells of alkali metal and halogenide ions by statis-

- tic methods. *Vestn. Udmurtsk. Univ. Fiz. Khim.* No. 4-2, 37 (2008) (in Russian).
12. P. Atkins, J. de Paula, *Physical Chemistry* (W.H. Freeman and Co., 2006) [ISBN: 978-1429218122].
13. B.S. Smolyakov. Limiting equivalent electroconductivity of ions in water at temperatures up to 200 °C. *Vestn. Kharkov. Univ. Vopr. Elektrokhim.* **139**, 37 (1976) (in Russian).
14. E.G. Larionov. To the calculation of the limiting electroconductivity of individual ions at high temperatures and pressures. *Izv. Sibirsk. Otdelen. AN SSSR. Ser. Khim.* **6**, 3 (1976) (in Russian).
15. J. Koryta, J. Dvorak, V. Bogachkova. *Electrochemistry* (Mir, 1977) (in Russian).
16. O.N. Kalugin. Dynamics of solvated ion in infinitely dilute solution: from phenomenology to microscopic description. *Vestn. Kharkov. Univ. Khim.* No. 9 (32), 13 (2002) (in Russian).
17. Yu.A. Karapetyan, V.N. Eichis, *Physico-Chemical Properties of Nonaqueous Electrolyte Solutions* (Khimiya, 1989) (in Russian).
18. J. Frenkel. *Kinetic Theory of Liquids* (Dover, 1955).
19. Y. Marcus. Are ionic Stokes radii of any use? *J. Solut. Chem.* **41**, 2082 (2012).
20. M.N. Rodnikova. Negative hydration of ions. *Elektrokimiya* **39**, 214 (2003) (in Russian).
21. O.Ya. Samoilov. To the fundamentals of the kinetic theory of hydrophobic hydration in dilute aqueous solutions. *Zh. Fiz. Khim.* No. 8, 1857 (1978) (in Russian).
22. J.E. Gordon. *Organic Chemistry of Electrolyte Solutions* (Wiley, 1975).
23. Yu.M. Kessler, A.L. Zaitsev. *Solvophobic Effects: Theory, Experiment, Practice* (Khimiya, 1989) (in Russian).
24. B. Damaskin, O. Petrii, G. Tsirlina. *Fundamentals of Theoretical Electrochemistry* (Khimiya, 2006) (in Russian).

Received 15.09.16.  
Translated from Ukrainian by O.I. Voitenko

V.I. Булавін, І.М. В'юнук, Я.І. Лазарева

#### ДИФУЗІЯ І МІКРОСКОПІЧНІ ХАРАКТЕРИСТИКИ ДОВЖИНИ, ЧАСУ ТА ШВИДКОСТІ ПЕРЕНОСУ ОДНОЗАРЯДНИХ ІОНІВ У ГРАНИЧНО РОЗБАВЛЕНИХ ВОДНИХ РОЗЧИНАХ

Резюме

Коефіцієнти дифузії і мікроскопічні характеристики довжини ( $\bar{d}$ ), часу і швидкості дифузійного зміщення 19 однозарядних іонів ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{CNS}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NH}_4^+$ ,  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ ,  $\text{Pr}_4\text{N}^+$ ,  $\text{Bu}_4\text{N}^+$ ,  $\text{Pent}_4\text{N}^+$ ,  $\text{VPh}_4^-$ ) в воді при температурах від 273,15 К до 473,15 К розраховано з літературних даних щодо граничної молярної електричної провідності цих іонів. Аналіз отриманих даних показав, що довжина дифузійного зміщення іона корелює з його типом сольватованості. При середніх значеннях  $\bar{d}$ , що перевищують кристалографічний (структурний) радіус іона ( $r_i$ ), останній сольватований позитивно. Якщо ж величина  $\bar{d}$  менша  $r_i$ , то спостерігається негативна сольватація.