NEAR HYDRATION OF SINGLELY CHARGED MONOATOMIC IONS IN EXTREMELY DILUTED SOLUTIONS: THE EFFECT OF TEMPERATURE AND PRESSURE

The diffusion coefficient $D_i^0$ and the distance of translational displacement of Li+, Na+, K+, Cs+, Cl− ions $\bar{d}$ in water at 298.15 K – 423.15 K (25 K step) and pressure from 0.0981 to 784.5 MPa (98.1 MPa step) were calculated from the literature data on limiting molar electrical conductivity. The $D_i^0$ values for these ions increase with pressure growth from 0.0981 to 98.1 MPa at 298.15 K. Further pressure increase (up to 785 MPa) leads to decrease in $D_i^0$. Temperature growth under isobaric conditions leads to an increase in $D_i^0$. Parameter $(\bar{d} - r_i)$ (deviation from the Stokes–Einstein law, $r_i$ is ion structural radius) was used as a criterion for the type of ion solvation. It is shown that Li+ and Na+ ions behave as cosmotropes, or positively solvated structure-forming ions having $(\bar{d} - r_i) > 0$. The Cs+, Cl−, Br− ions behave as chaotropes, or negatively solvated structure-breaking ions having $(\bar{d} - r_i) < 0$. For the K+ ion, the $(\bar{d} - r_i)$ deviation is alternating. At 0.0981 MPa and 298.15 K, the K+ ion is a chaotrope. But at 320 K ($T_{	ext{lim}}$) parameter $(\bar{d} - r_i) = 0$. It corresponds to the transition from negative to positive solvation. Above $T_{	ext{lim}}$ at $P = \text{const}$, the K+ ion is a cosmotrope. At 298.15 K and up to 98.1 MPa, the pressure causes the same change in the $(\bar{d} - r_i)$ deviation as the temperature. On the contrary, at 320 K and higher, the pressure affects the near hydration in the direction opposite to the temperature.

Keywords: monatomic ions, diffusion, diffusion displacement length, positive and negative solvation

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БЛИЖНЯ ГІДРАТАЦІЯ ОДНОЗАРЯДНИХ ОДНОАТОМНИХ ІОНІВ У ГРАНИЧНО РОЗБАВЛЕННИХ РОЗЧИНАХ: ВПИВ ТЕМПЕРАТУРИ ТА ТИСКУ

Коэффициент диффузии $D_i^0$ та довжина диффузійного зміщення $\bar{d}$ іонів Li+, Na+, K+, Cs+, Cl−, Br− у воді при 298,15 К – 423,15 К (шаг 25 К) і тиску від 0,0981 до 784,5 МПа (шаг 98,1 МПа) розрахований на підставі літературних даних щодо їх граничної молярної електричної провідності. Величини $D_i^0$ цих іонів зростають при 298,15 К зі збільшенням тиску від 0,0981 до 98,1 МПа. Подальше підвищення тиску до 785 МПа призводить до зменшення $D_i^0$. Зростання температури в гібаратичних умовах призводить до збільшення $D_i^0$. Параметр $(\bar{d} - r_i)$ (відхилення від закону Стокса–Ейнштейна, $r_i$ – структурний радіус іона) використований як критерій типу сольватації іонів. Показано, що іони Li+ і Na+ ведуть себе як космотропи, або позитивно сольватаціонні структуроутворюючі іони, для яких $(\bar{d} - r_i) > 0$. Іони Cs+, Cl− і Br− – хаотропи, або негативно сольватаціонні структуро-руйніючі іони для яких $(\bar{d} - r_i) < 0$. Для іона K+ параметр $(\bar{d} - r_i)$ є знакоміним. При 0,0981 МПа та 298,15 К іон K+ – хаотроп, але при 320 К ($T_{lim}$) величина $(\bar{d} - r_i) = 0$. Це відповідає переходу від негативної до позитивної сольватації. Вище $T_{lim}$ при $P = \text{const}$ іон K+ є космотропом. При 298,15 K і до 98,1 МПа тиск спричиняє таку ж зміну $(\bar{d} - r_i)$, як і температура. При 320 K і вище тиск впливає на близьку гідратацию у напрямку протилежному дій температури.

Ключові слова: одноатомні іони, дифузія, довжина диффузійного зміщення, негативна сольватація

B.I. BULAVIN, I.N. VYUNNIK, A.V. KRAMARENKO, A.I. RUSINO

БЛИЖНЯ ГІДРАТАЦІЯ ОДНОЗАРЯДНИХ ОДНОАТОМНИХ ІОНІВ В ПРЕДЕЛЬНО РОЗБАВЛЕННИХ РОЗЧИНАХ: ВПИВ ТЕМПЕРАТУРИ І ДАВЛЕННЯ

Коэффициент диффузии $D_i^0$ и длина трансляционного смещения $\bar{d}$ ионов Li+, Na+, K+, Cs+, Cl−, Br− в воде при 298,15 K – 423,15 K (шаг 25 K) и давлении (P) 0,0981 – 784,5 MPa (шаг 98,1 MPa) рассчитаны из литературных данных по предельной молярной электрической проводимости этих ионов. Значения $D_i^0$ при 298,15 K с повышением P от 0,0981 до 98,1 MPa увеличиваются, при возрастании давления от 98,1 до 785 MPa уменьшаются. При T > 298,15 K с увеличением давления $D_i^0$ этих ионов уменьшается. Повышение температуры в изобарических условиях приводит к возрастанию $D_i^0$. Критерием типа сольватаціонного знак отклонений от закона Стокса–
Introduction. The study of ion solvation is one of the most important problems in the chemistry of electrolyte solutions. Both the near and far surroundings of the ion changes in the process of ionic solvation. Many properties of ions and their effect on the solvent can be explained using the concept of solvation. In studying the effect of ions on the dynamics of the closest solvent molecules, the greatest success was achieved in the study of aqueous solutions. According to the work on the water structure, Samoilov [1] divided the ions into two groups:

1) ions solvated positively (ΔE = E₁ – E₂ > 0, τ/τ > 1);
2) ions solvated negatively (ΔE = E₁ – E₂ < 0, τ/τ < 1).

Samoilov [1] includes structure–making ions in the first group, and structure–breaking ions in the second group. In the development of Samoilov’s views, Collins [2] (in the model of soldered spheres) proposed later the “cosmotropes” term for structure–makers. They are singly charged ions of small size (having a high charge density that firmly binds water molecules). Correspondingly, the “chaotropes” are the structure–breakers, or singly charged ions of large size having a low charge density. They bind water molecules weaker than the latter bind each other.

Today highly structured water and aqueous solutions have been studied most fully [3–6]. To study short–range solvation [3] in water, the most modern methods are involved, including molecular dynamics modeling (MDM). As a result, significant progress has been achieved, new models and mechanisms have been proposed [4–6]. At the same time, many questions are still not sufficiently developed.

Modern technologies and theories determine the conduct of research in a wide range of state parameters. However, the lack of fundamental information on the properties of water and ions in aqueous solutions in a wide range of temperatures and pressures does not allow one to predict even qualitatively the effect of pressure on the short–range hydration of ions. Known experimental data [7–11] in terms of the effect of pressure on the dynamics of water molecules closest to the ion are limited both by the range of pressures and temperatures, and by the set of electrolytes. The conclusions of these works are contradictory [7,8,10,12]. Samoilov and co–workers [7, 8], based on the data on the density of dilute aqueous solutions of NaCl, KCl and NH₄Cl, came to the conclusion that with an increase in pressure from 0.1014 to 101.4 MPa the near hydration of Na⁺ and K⁺ ions increases due to the destruction of the water structure. For the NH₄⁺ ion, the close–range solvation characteristic passes through a minimum. Nakahara [11], calculating the number of hydration of ions in an infinitely dilute solution of KCl at 288.15, 298.15 and 313.15 K and pressures from 0.1014 to 507 MPa, showed that they practically do not change with increasing pressure for K⁺ and Cl⁻ ions.

According to Horn [10], an increase in pressure leads not only to the destruction of the intrinsic structure of water in solution, but also to a weakening of near hydration. Toryanik [12] came to the conclusion that ions, as well as temperature and pressure, have a destructive effect on water. He based on the results of a study of the water molecules diffusion coefficient in solutions of lithium, sodium, potassium and cesium chlorides over the temperature range 263–343 K and pressures up to 0.7 GPa.

It seems interesting to use the developed in [13, 14] and well–proven approach to determining the criteria for positive (d – r) > 0 and negative (d – r) < 0 ion solvation. It based on the deviation from the Stokes–Einstein law in the form of a difference (d – r) and reflects the effect of temperature and pressure on the short–range hydration of monatomic ions.

The choice of the difference (d – r) between the distance d of the translational displacement of an ion and its structural radius r, as a measure of the effect on the mobility of the closest solvent molecules was substantiated in [14].

Results. In this work, the diffusion coefficient and the translational displacement distance for Li⁺, Na⁺, K⁺, Cs⁺, Cl⁻ and Br⁻ ions in water at 298.15 K–423.15 K (step 25 K) are calculated from the data on the limiting molar electrical conductivity of ions (λ ′) and pressures from 0.0981 to 784.5 MPa (step 98.1 MPa). The values and were calculated using the Nernst–Einstein (1) and Stokes–
Einstein (2) equations, respectively:

\[ D_i^0 = \frac{RT}{z_iF^2\lambda_i} \]

(1)

\[ \bar{d} = \frac{kT}{6\pi D_i^0\eta_0} \]

(2)

In equations (1) and (2) \( T \) is the temperature, \( K \); \( R \) is the molar gas constant; \( k \) is the Boltzmann constant; \( z_i \) is the charge of the ion; \( F \) is the Faraday number, \( \eta_0 \) is the dynamic viscosity of the solvent. The quantities and \( \eta_0 \) necessary for the calculation by equations (1) and (2) are taken from [15, 16].

The calculated values of the diffusion coefficient and \((\bar{d} - r_i)\) parameter for six singly charged ions in water (at the temperatures and pressures indicated above) are presented in Tables 1 and 2. When calculating the \((\bar{d} - r_i)\) difference, we used the structural radii of ions according to Goldschmidt (in Å): \( Li^+ = 0.78; Na^+ = 0.98; K^+ = 1.33; Cs^+ = 1.65; Cl^- = 1.81; Br^- = 1.96 \) [17].

Table 1 data analysis show that at 298.15 K the value of the diffusion coefficient of the studied ions in water increases while the pressure growing from 0.0981 to 98.1 MPa. Further increase in pressure up to 785 MPa leads to the diffusion coefficient diminishing (Fig. 1). At temperatures above 298.15 K, it also decreases with an increase in the pressure (Table 1). An increase in temperature under isobaric conditions \((P = \text{const})\) leads to an increase in \( D_i^0 \) values.

This pressure influence on the diffusion coefficient at 298.15 K can be explained by water viscosity change [15] (Table 3). In the range of 0.0981–98.1 MPa, the viscosity of water decreases with increasing pressure, but it increases with further pressure growth. With an increase in temperature at \( P = \text{const} \), the viscosity of water decreases (Table 3).

From the analysis of polybaric and polythermal \((\bar{d} - r_i)\) dependences (Table 2; Fig. 2–4), the following conclusions can be drawn:

1. \( Li^+ \) and \( Na^+ \) ions over the investigated temperature range 298.15–423.15 K and pressures 0.0981–784.5 MPa behave like kosmotropes \((\bar{d} - r_i) > 0 \). It indicates the positive hydration. It weakens with pressure growth \((\partial(\bar{d} - r_i) / \partial P < 0)\) at the temperatures studied. Under isobaric conditions, as the temperature rises, the positive hydration of the \( Li^+ \) cation weakens \((\partial(\bar{d} - r_i) / \partial P < 0)\), while that of the \( Na^+ \) cation slightly increases \((\partial(\bar{d} - r_i) / \partial P > 0)\).

2. \( Cs^+ \), \( Cl^- \), \( Br^- \) ions in the investigated temperature and pressure range behave as chaotropes \((\bar{d} - r_i) < 0 \), which indicates negative solvation, which under isothermal conditions increases with increasing pressure, while in isobaric \((P = \text{const})\) decreases with increasing temperature \((\partial(\bar{d} - r_i) / \partial P > 0)\).

3. The most interesting turned out to be the behavior of the \( K^+ \) ion with a change in \( T \) and \( P \). At a saturated vapor pressure \((P_{\text{sat}})\) and \( T = 298.15 \) K, this cation behaves like a chaotrope \((\bar{d} - r_i) < 0 \). As the temperature rises, the value \((\bar{d} - r_i)\) increases and at 320 K it reaches zero. This temperature corresponds to the transition from negative to positive solvation \((T_{\text{lim}} = 320 \) K). Above \( T_{\text{lim}} \) at \( P = \text{const} \), the \( K^+ \) ion behaves like a kosmotrope (Fig. 2). At \( T = 298.15 \) K, an increase in pressure leads to a decrease in \((\bar{d} - r_i)\) parameter, which corresponds to an increase in negative solvation (Fig. 3). Polytherms \((\bar{d} - r_i) - T\) (shown in fig. 2,3) and polybars \((\bar{d} - r_i) - P\) indicate the opposite influence of \( T \) and \( P \) on the short-range solvation of the \( K^+ \) cation in water. The intersection of polytherms and polybars with a zero line allows us to determine the limiting temperatures \((T_{\text{lim}})\) and limiting pressures \((P_{\text{lim}})\) of the transition from negative to positive hydration. They are given in Table. 4.5. The transition from negative to positive hydration is also observed for the \( Rb^+ \) cation (Fig. 4), for which \( T_{\text{lim}} \) is 387 K at saturated vapour pressure.

4. From the analysis of polytherms and polybar of \((\bar{d} - r_i)\) parameter it follows that the \( K^+ \) cation behaves like a chaotrope at 298.15 K regardless of \( P \) in the pressure range 0.0981–784.5 MPa (Fig. 3). At temperatures from 298.15 K to 423.15 K, the chaotropic properties of the \( K^+ \) ion are retained at pressures above 588.6 MPa. At a temperature of 320 K and higher, the pressure acts on the near hydration in the direction opposite to the temperature. At 298.15 K and pressures up to 98.1 MPa, the pressure causes the same change \((\bar{d} - r_i)\) as the temperature. Thus, the opinion existing in the literature [18, 19] that pressure and temperature act on the structure of water in the same direction is valid in the pressure range up to 98.1 MPa at \( T \leq 320 \) K. At higher parameters of state, \( T \) and \( P \) have the opposite effect on near solvation.
Table 1. – Ions diffusion coefficient $D_i^0$ values at different temperatures and pressures

<table>
<thead>
<tr>
<th>P, MPa</th>
<th>$D_i^0$ $10^6$, m$^2$s$^{-1}$</th>
<th>298,15 K</th>
<th>323,15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$^+$ Na$^+$ K$^+$ Cs$^+$ Cl$^-$ Br$^-$</td>
<td>Li$^+$ Na$^+$ K$^+$ Cs$^+$ Cl$^-$ Br$^-$</td>
<td>Li$^+$ Na$^+$ K$^+$ Cs$^+$ Cl$^-$ Br$^-$</td>
</tr>
<tr>
<td>588,4</td>
<td>0.831 1.076 1.598 1.710 1.686 1.710 1.432 1.813 2.563 2.704 2.742 2.771</td>
<td>0.778 1.007 1.499 1.614 1.584 1.603 1.354 1.712 2.430 2.574 2.603 2.624</td>
<td>0.727 0.937 1.401 1.523 1.489 1.502 1.276 1.611 2.295 2.448 2.465 2.479</td>
</tr>
<tr>
<td>686,5</td>
<td>0.778 1.007 1.499 1.614 1.584 1.603 1.354 1.712 2.430 2.574 2.603 2.624</td>
<td>0.727 0.937 1.401 1.523 1.489 1.502 1.276 1.611 2.295 2.448 2.465 2.479</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. – Parameter $(\ddot{d} - r)$ $10^6$ values for ions at different temperatures and pressures

<table>
<thead>
<tr>
<th>P, MPa</th>
<th>$(\ddot{d} - r)$ $10^6$, m</th>
<th>298,15 K</th>
<th>323,15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$^+$ Na$^+$ K$^+$ Cs$^+$ Cl$^-$ Br$^-$</td>
<td>Li$^+$ Na$^+$ K$^+$ Cs$^+$ Cl$^-$ Br$^-$</td>
<td>Li$^+$ Na$^+$ K$^+$ Cs$^+$ Cl$^-$ Br$^-$</td>
</tr>
<tr>
<td>0.0981</td>
<td>1.59 0.85 -0.08 -0.46 -0.61 -0.79</td>
<td>1.60 0.90 0.01 -0.35 -0.53 -0.70</td>
<td>1.60 0.90 0.01 -0.35 -0.53 -0.70</td>
</tr>
<tr>
<td>0.985</td>
<td>1.58 0.84 -0.09 -0.46 -0.62 -0.80</td>
<td>1.56 0.86 -0.02 -0.37 -0.56 -0.73</td>
<td>1.56 0.86 -0.02 -0.37 -0.56 -0.73</td>
</tr>
<tr>
<td>588,4</td>
<td>1.54 0.80 -0.12 -0.49 -0.65 -0.82</td>
<td>1.51 0.83 -0.04 -0.41 -0.59 -0.76</td>
<td>1.51 0.83 -0.04 -0.41 -0.59 -0.76</td>
</tr>
<tr>
<td>686,5</td>
<td>1.45 0.74 -0.17 -0.55 -0.70 -0.87</td>
<td>1.43 0.76 -0.10 -0.47 -0.65 -0.82</td>
<td>1.43 0.76 -0.10 -0.47 -0.65 -0.82</td>
</tr>
<tr>
<td>784,5</td>
<td>1.41 0.71 -0.19 -0.58 -0.73 -0.89</td>
<td>1.38 0.73 -0.12 -0.50 -0.67 -0.84</td>
<td>1.38 0.73 -0.12 -0.50 -0.67 -0.84</td>
</tr>
<tr>
<td>0,985</td>
<td>1.36 0.67 -0.22 -0.61 -0.75 -0.92</td>
<td>1.34 0.70 -0.14 -0.53 -0.70 -0.86</td>
<td>1.34 0.70 -0.14 -0.53 -0.70 -0.86</td>
</tr>
<tr>
<td>686,5</td>
<td>1.32 0.64 -0.24 -0.64 -0.78 -0.94</td>
<td>1.30 0.67 -0.17 -0.55 -0.73 -0.89</td>
<td>1.30 0.67 -0.17 -0.55 -0.73 -0.89</td>
</tr>
<tr>
<td>784,5</td>
<td>1.27 0.61 -0.26 -0.67 -0.81 -0.97</td>
<td>1.26 0.64 -0.19 -0.59 -0.75 -0.91</td>
<td>1.26 0.64 -0.19 -0.59 -0.75 -0.91</td>
</tr>
</tbody>
</table>
Table 3. - Water viscosity at different T and P [15]

<table>
<thead>
<tr>
<th>P, MPa</th>
<th>( \eta ), mPa·s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298,15 K</td>
</tr>
<tr>
<td>0,0981</td>
<td>0,8903</td>
</tr>
<tr>
<td>98,1</td>
<td>0,8780</td>
</tr>
<tr>
<td>196,1</td>
<td>0,9198</td>
</tr>
<tr>
<td>294,2</td>
<td>0,9731</td>
</tr>
<tr>
<td>392,3</td>
<td>1,0440</td>
</tr>
<tr>
<td>490,3</td>
<td>1,1270</td>
</tr>
<tr>
<td>588,4</td>
<td>1,2270</td>
</tr>
<tr>
<td>686,5</td>
<td>1,3370</td>
</tr>
<tr>
<td>784,5</td>
<td>1,4620</td>
</tr>
</tbody>
</table>

Fig. 1 Dependence of ions diffusion coefficient \( D_i^0 \) on pressure at 298.15 K

Fig. 2 Polytherms \( \bar{d} - r_i \) for K⁺ cation in water at different pressures

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Discussion. When discussing the results of the effect of pressure and temperature on the short–range hydration of monatomic singly charged ions, the latter was considered, following [1], not as the binding of a number of solvent molecules by ions, but the effect on the mobility of water molecules in their immediate surroundings. Since we know little about the mechanism of the effect of ions on the solvent, for clarity of the model, we postulate that when a negatively solvated ion (chaotrope) is placed in water, its radius remains equal to its structural radius (Table 2, K+ ion at 348.15 K). In this case, the value can reach the value of the additional inhibition.

Consequently, a decrease in comparison with the value determined by the viscosity of the solvent, then in the case of kosmotrope ions, the ion–molecule (IM) bonds are weaker than the molecule–molecule (MM) bonds [1]. In this case, the mobility of water molecules in the PSS ion is accelerated. The acceleration of water molecules by chaotropes, on the one hand, creates favorable conditions for their free movement in solution, and, on the other hand, the inhibitory effect of the network of H–bonds in the solvent. As long as the condition \((\bar{d} - r_i) < 0\) is observed for the ion, destruction of the structure will prevail near the latter, and the process of ordering of its molecules will prevail in the volume of the solvent.

In the case of kosmotrope ions \((\bar{d} - r_i) > 0\), the IM bonds are stronger than the MM bonds [2], while the mobility of water molecules in the PSS ion slows down, and the \(\bar{d}\) value increases due to the effect of the H–bond network on the exchange of water molecules. It is interesting to note the opposite effect of chaotropes and kosmotropes on the translational motion of water molecules near ions and in its volume. Acceleration of the mobility of water molecules near chaotropic ions leads to their additional deceleration by the H–bond network, and its deceleration under the influence of kosmotrope ions is accompanied, on the contrary, by a weakening of the inhibitory effect on the ion of the H–bond network.

Table 4. – Temperature of transition \(T_{trans}\) from negative to positive hydration for K+ cation

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Li+</th>
<th>Na+</th>
<th>K+</th>
<th>Rb+</th>
<th>Cs+</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>392.3</td>
<td>490.3</td>
<td>588.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5. – Pressure of transition \(P_{trans}\) from negative to positive hydration for K+ cation

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Li+</th>
<th>Na+</th>
<th>K+</th>
<th>Rb+</th>
<th>Cs+</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>33</td>
<td>33</td>
<td>523</td>
<td>523</td>
<td>588</td>
</tr>
</tbody>
</table>
The opposite nature of the influence of temperature and pressure on the \((\bar{d} - r_1)\) parameter as the measure of the influence of ion on the solvent is apparently associated with their different effect on short–range hydration, determined by the IM and MM interactions. In the region of low temperatures, an increase in pressure, like in temperature, has a destructive effect on the structure of water in solution, which is consistent with a change in the properties of water and aqueous solutions [10].

Our results and conclusions regarding the nature of short–range hydration of singly charged ions are consistent with the data of [20], in which a structural and dynamic study of aqueous clusters of Na+, K+, and Cs+ ions was carried out by molecular dynamics modeling. The authors of [20] come to the conclusion that near the K+ and Cs+ ions there is a significant increase in the mobility of water molecules in comparison with the Na+ ion. The increase in mobility is associated with a larger number of “bifurcate” bonds in the first hydration sphere and in the intermediate region between the hydration shells of K+ and Cs+ ions. In this case, according to [20], there is, as it were, a transfer of “bifurcate” bonds from the first hydration sphere to the intermediate region when moving to clusters containing a larger number of water molecules. The very presence of “bifurcate” bonds is considered in this case as defects in the network of H–bonds, which create sufficiently large singly charged ions.

Summary. Chaotropes affect the water structure like temperature growth does, while the kosmotropes influence is similar to the pressure rising effect. In contrast to the temperature growing impact, an increase in pressure leads to a weakening of short–range solvation at \(T > 320 \, \text{K}\).

References


References (transliterated)

Відомості про авторів/Сведения об авторах/ About the Authors

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