

THE EFFECT OF TEMPERATURE AND PRESSURE ON NEAR HYDRATION OF SINGLY CHARGED MONOATOMIC IONS

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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.

The most modern methods are involved nowadays (including MD modeling) to study the short-range solvation in water. Significant progress has been achieved as a result, new models and mechanisms have been proposed. However, many questions are still not sufficiently developed. One of the most important reasons is the lack of fundamental information on the properties of ions in aqueous solutions over a wide range of temperatures and pressures. This does not allow one to predict (even qualitatively) the effect of pressure on the short-range hydration of ions.

It seems interesting to use the developed in [1] and well-proven approach to determining the criteria for positive $(\bar{d} - r_i) > 0$ and negative $(\bar{d} - r_i) < 0$ ion solvation at different pressures and temperatures.

The diffusion coefficient D_i^0 and the distance of translational displacement of Li^+ , Na^+ , K^+ , Cs^+ , Cl^- and Br^- 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 according to the author's procedure [1]. 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 .

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_{lim}) parameter $(\bar{d} - r_i) = 0$. It corresponds to the transition from negative to positive solvation. Above T_{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.

References

1. Bulavin V.I., V'yunyk I.M., Lazareva Ya.I. Diffusion and microscopic characteristics of singly charged ion transfer in extremely diluted aqueous solutions. *Ukrainian Journal of Physics*. 2017. Vol. 62, № 9. P. 769–778.