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KINETIC SOLVATION OF SINGLY CHARGED IONS IN THE SERIES OF THE HYDROXYL GROUP- SOLVENTS

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The results of study of kinetic solvation in the systems: single-charged ion - hydroxyl group-solvents: light H_2O and heavy D_2O water, ethylene glycol (EG), methanol, ethanol, n-propanol at 298,15 K are presented. In the series of single-charged ions Li^+- Na^+- K^+- Cs^+- Cl^- -Br^- - I- their radii consistently increase, and in the transition from light water to n-propanol dielectric permittivity gradually decreases. Therefore, we have possible to analyze the behavior of a single ion in the series of hydroxyl group-solvents depending on their structure, dielectric permittivity, viscosity (η_0), isotopic composition, and the number of OH-groups in the molecule. Type of ion solvation was determined by the friction attractive coefficient $\zeta_{at}=6\pi(\overline{d} - \boldsymbol{r}_i)\eta_0$. Here $\overline{d}$ are the ion translational displacement length, $\boldsymbol{r}_i$ is ion structural radius. The sign of ζ_{at} correlates with the type of ion solvation: when $\zeta_{at} >0$ is positive solvation, the ion strengthens the solvent structure and is kosmotrope. When $\zeta_{at} <0$, the solvent structure is destoyed, ion solvates negatively, is a chaotrope. The parameter ζat sequentially decreases as the ion structural radius increases and with the transition from water to n-propanol in the series of hydroxyl group-solvents i.e., with a decrease of the solvent's dielectric permittivity. Li^+ and Na^+ ions are kosmotropes in each of hydroxyl group-solvents. K^+, Cs^+, Cl^-, Br^- and I- ions in light and heavy water, in ethylene glycol are chaotropes, but in methanol, ethanol and n-propanol are cosmotropes. This reveals the individuality of the solvent structure.

In the series of solvents with a spatial network of H-bonds (light and heavy water, ethylene glycol), the negative solvation of ions increases due to the increasing strength of the H-bond network and successive increase in solvent viscosity in this series. The presence of two OH-groups in ethylene glycol molecule and the substitution of H atom for D atom in heavy water D_2O molecule also facilitate this. The structure of primary alcohols lacks a strong network of H-bonds. The latter are quite easily destroyed, allowing the ions to penetrate into solvents structure and thus positively solvate.

Our conclusions on type of ionic solvation are based on the ratio between the ionic-molecular $\zeta_{ат}^{IM}$ and intermolecular $\zeta_{ат}^{MM}$ components of the friction attractive coefficient ζ_{at} for each of the ions in each solvent. At $\zeta_{ат} >0$, when solvation is positive, then $\zeta_{ат}^{IM} > |\zeta_{ат}^{MM}|$. In other words, the ion-molecular interaction exceeds the intermolecular. On the contrary, at $\zeta_{ат} <0$ solvation is negative and $|\zeta_{ат}^{MM}| > \zeta_{ат}^{IM}$. In this case, the intermolecular interaction is stronger than the ionic-molecular one.