

THE COORDINATION NUMBERS OF ALKALI METAL CATIONS IN DILUTE AQUEOUS SOLUTIONS AND IN THE GASEOUS PHASE

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The problem of the interaction of ions with the nearest water molecules and the coordination numbers (CN) of ions in solution is fundamental in the theory of aqueous solutions. At the same time, different approaches lead to different and sometimes directly contradictory conclusions. For example, it has been stated that with increase in temperature, the hydration of ions in solution increases [1], remains unchanged [2], and decreases [3]. The coordination number of ions in aqueous solution is the average number of water molecules in the first coordination sphere of the ion. Study of the coordination numbers of ions in solution is particularly important in connection with the fact that short-range forces play a unique role in determining the properties of solutions [4, 5], and many processes involve particularly the first coordination sphere.

Judging from the results of a number of papers, the coordination numbers of the alkali metal cations in dilute aqueous solutions are close to 4.* Thus the calculation carried out by Bernal and Fowler [6] shows that the maximum values of the hydration energy for singly charged cations in dilute aqueous solutions are achieved for CN = 4. X-ray diffraction [7-9] and thermochemical [4, 10] data for the corresponding solutions give $CN \approx 4$. For the sodium ion, the value CN = 4 was also found by the NMR method [11]. Borina and Samoilov [12] established a relationship between the coordination numbers of ions in solutions and values for the boundaries between ions with positive and negative hydration ($r_1^0 \approx 1.2$ Å); it was found that the experimental data on the density of aqueous solutions can be reconciled with the experimental value of the boundary only for values of the coordination numbers of the alkali metal cations close to 4. These coordination numbers are related to the tetrahedral structure of water and the decisive role of the short-range forces.

Tikhomirov [13] examined the problem of the relationship between the short-range hydration and the coordination numbers of ions and the state of the free solvent, and showed that the intensification of the translational motion of the molecules of free water should lead to an increase in the average coordination number and to further hydration of the ion. The conclusion that there is a relationship between the short-range hydration of ions and the structural state of the solvent was reached by Yastremskii and Samoilov [14], who studied the dielectric constant of aqueous solutions of electrolytes at a frequency of 9400 MHz. In this work it was shown that stabilization of the structure of water by molecules of methyl alcohol leads to a decrease in the short-range hydration of ions; on the other hand, with increase in temperature, as a result of the breakdown of the structure of water itself, the short-range hydration of the ions in solution increases. An increase in the short-range hydration of ions with increase in temperature has been observed by a number of authors [1, 15, 16]. The increase in hydration with increase in temperature takes place because the intensification of the rotational oscillations of the particles causes the directed hydrogen bonds in the structure of water itself to be broken more rapidly than the less directed bonds between the ion and the water molecules. The change in the relationship between the energy of interaction of the water molecules with the ion and the energy of the interaction between the water molecules leads to an increase in the short-range hydration of the ion

*In solutions with medium and high concentrations, the short-range hydration of the ions changes under the influence of the fields of the other ions present in the solution, and the values of the coordination numbers should differ from the values for dilute solutions. The structures of the crystal hydrates may be produced in these solutions.

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with temperature and transfer of water molecules from the free solvent to the ion. This transfer is responsible for the simultaneous increase in the coordination number. The increase in the coordination number of the ions in solution with increase in temperature was established experimentally in [10]. In [17] a study was made of the pressure dependence of the short-range hydration of the sodium and potassium cations. It was established that with increase in pressure (to 1000 bar), the short-range hydration of these cations is increased as a result of the breakdown of the structure of water itself.

In aqueous solutions, the structure of water is the factor responsible for the decrease in the short-range hydration of ions. It is natural that at this level of thermal motion of the particles, the hydration of ions in the gaseous phase, where the structure of the solvent is not present, should be greater than the short-range hydration of the ions in dilute aqueous solutions. Munson and Tyndall [18] studied the mobility of ion clusters of the type $M^+ \cdot nH_2O$ (where $M^+ = Li^+, Na^+, K^+, Rb^+, Cs^+$) in a medium of inert gases. The addition of different quantities of water vapor to the inert gas in which the mobilities of the emitted alkali metal ions were determined altered the rate of ion transfer, and the upper limit of the value of n in the cluster was found from the nature of the relationships obtained. It was found that under the conditions of thermal motion of the molecules equivalent to room temperatures, equilibrium in the clusters for all the alkali metal ions is observed for $n \approx 6$. With increase in the atomic number of alkali metal, the value of n decreases slightly, due in the author's opinion to the decrease in the surface density of the charge of the ion. With increase in temperature and increase in the thermal motion, dissociation of the clusters begins, leading to a decrease in n . The coordination number of the ion in the cluster is equal to the hydration number if all the water molecules are arranged in the first coordination sphere, and less than the hydration number if some of the water molecules are situated at a greater distance. In any case, the coordination numbers of the alkali metal cations in the clusters, judging from the results of this work, do not exceed six.

Thus from a comparison of the short-range hydration of ions in dilute aqueous solution and in the gaseous phase it may be concluded that the relationship between solvation and the structure of the solvent determines the lower values of the coordination numbers of ions in solution. Over a wide range of temperatures, the coordination numbers of the alkali metal cations in dilute aqueous solutions can apparently vary from ~ 4 , when the structure of the water is not broken down (is stabilized), to 6, when the water structure is not present. It may be noted that the temperature dependence of the coordination numbers in the gaseous phase, according to the data of Munson and Tyndall, is the opposite of that observed in dilute aqueous solutions at temperatures which are not too high. This emphasizes the influence of the structure of the solvent as a factor decreasing the short-range hydration of ions.

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