

# THEORY OF THE HYDRATION OF IONS IN AQUEOUS SOLUTION

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Samoilov has shown<sup>1-3</sup> that the translational motion of particles (atoms, molecules, ions) in liquids, in particular in aqueous electrolyte solutions, is determined not by the total energy of interaction between the particles (the energy required to separate the interacting particles to infinity) but by the corresponding activation energy, which depends on the variation in potential over short distances near the particles. According to this view, the important factor in the properties of solutions is not so much the long-range interaction between particles, as interactions which, though weak, decrease rapidly with distance: it is these interactions which make a considerable contribution to the potential barriers to be overcome by the particles in their motion in solution. These ideas allowed Samoilov to determine, from the temperature dependence of ionic mobilities in solution and of the coefficient of self-diffusion in water, the mean residence time  $\tau_i$  of water molecules in the vicinity of ions in aqueous solution. He has given<sup>1</sup> the value of  $\tau$ , the residence time of a water molecule in the equilibrium position in water at 25°, calculated from data on Raman spectra of water and on self-diffusion in water. Values of the ratio  $\tau_i/\tau$  have been found for several monatomic ions<sup>2</sup>. The accompanying Table gives these values<sup>2</sup> together with  $\tau_i$  calculated on the basis of Samoilov's value of  $\tau$ ,<sup>1</sup> together with the crystallographic radii of the ions  $r_i$ .<sup>5</sup>

At the present time the nuclear magnetic resonance method has provided the only data with which the values of  $\tau_i$  in the Table can be compared. Investigations of the nuclear magnetic relaxation of <sup>17</sup>O in aqueous solution has given<sup>4</sup> exchange rate constants ( $k_I$ , s<sup>-1</sup> at 298°K) of water molecules in the solution immediately adjacent to certain paramagnetic cations. It is obvious that  $k_I = 1/\tau_i$ . According to Swift and Connick<sup>4</sup>, for the Mn<sup>2+</sup> ion  $k_I = 3.1 \times 10^7$ , so that  $\tau_i$  for this ion is about  $3 \times 10^{-8}$  s. Thus their value for the Mn<sup>2+</sup> ion lies between the values for Ca<sup>2+</sup> and Mg<sup>2+</sup> (see Table). Moreover, from its crystallographic radius (0.91 Å)<sup>5</sup> the doubly charged cation Mn<sup>2+</sup> occupies an intermediate position between the doubly charged cations Ca<sup>2+</sup> and Mg<sup>2+</sup>.

Swift and Connick's results for the Cu<sup>2+</sup> cation are of especial interest. In dilute aqueous solution the immediate environment of the copper cation has a bipyramidal structure (six water molecules surrounding this cation form an elongated octahedron). The four water molecules which are located in the same plane are at distances of 1.95–2.05 Å from the copper cation, i. e. at distances which are less than the sum of the crystallographic radius of the copper ion (0.80 Å)<sup>5</sup> and the "radius" of the water molecule (1.40 Å)<sup>6</sup>. Strong covalent interaction occurs between these water molecules and the copper ion. The two water molecules located on the axis perpendicular to the above plane

TABLE. Hydration of some monatomic cations<sup>2</sup>.

| Ion           | Ca <sup>2+</sup>  | K <sup>+</sup>    | Na <sup>+</sup>   | Li <sup>+</sup>   | Co <sup>2+</sup>  | Mg <sup>2+</sup>  |
|---------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| $r_i$ , Å     | 1.65              | 1.33              | 0.98              | 0.88              | 1.04              | 0.74              |
| $\tau_i/\tau$ | 0.57              | 0.65              | 1.46              | 3.48              | 2.16              | 86.30             |
| $\tau_i$ , s  | $1 \cdot 10^{-9}$ | $1 \cdot 10^{-9}$ | $2 \cdot 10^{-9}$ | $6 \cdot 10^{-9}$ | $4 \cdot 10^{-9}$ | $2 \cdot 10^{-7}$ |

are at considerably greater distances from the copper ion (2.20–2.45 Å, which are greater than the above sum). There is no direct contact between them and the copper cation, and therefore covalent interaction cannot be assumed here. These molecules are subject only to the electrostatic field of the doubly charged cation, the potential of which is determined by the distance from the latter. A distance of 2.45 Å corresponds to a cationic radius of 1.05 Å. Swift and Connick obtained values of  $k_I$  separately for the four water molecules closest to the copper ion and for the two more remote water molecules. In the latter case  $k_I$  was  $2 \times 10^8$ , and hence  $\tau_i = 5 \times 10^{-9}$  s. This value of  $\tau_i$ , obtained by Swift and Connick, was extremely close to the value for the Ca<sup>2+</sup> ion in the accompanying Table. Since the radius of the doubly charged cation Ca<sup>2+</sup> is 1.04 Å, this agreement, like the value of  $\tau_i$  obtained for the Mn<sup>2+</sup> cation in Ref 4, confirms the correctness of the estimates of  $\tau_i$  given by Samoilov<sup>2</sup>.

Samoilov has remarked<sup>3</sup> that covalent interaction between an ion and the water molecules nearest to it results in a considerable increase in the steepness of the sides of the potential well within which the water molecule vibrates, and can hence cause a sharp increase in the values of  $\tau_i$ . According to Ref. 4, the values of  $\tau_i$  for the cations Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup> and the four closest water molecules are respectively  $3 \times 10^{-7}$ ,  $10^{-6}$ ,  $4 \times 10^{-5}$ , and  $10^{-5}$  s. Such comparatively large values of  $\tau_i$  are due to covalent interaction between these cations and the nearest water molecules.

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