Reports of the Academy of Sciences of the USSR

O. Ya. SAMOILOV

1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1958. Volume 121, No. 6

PHYSICAL CHEMISTRY

O. Ya. SAMOILOV

ON THE THEORY OF THE TEMPERATURE DEPENDENCE OF COORDINATION NUMBERS OF IONS IN AQUEOUS SOLUTIONS

(Presented by Academician I. I. Chernyaev, 21 IV 1958)

The average coordination number of particles is one of the principal quantitative characteristics of a liquid. The coordination number is of great importance in the study of the structure and many properties of liquid solutions ([1]). The coordination number is of particular importance in the study of liquids because, in the case of liquids, this quantity depends to a large extent on thermal motion, and above all on the translational motion of particles ([2]). This, in particular, accounts for the large fluctuations of coordination numbers in liquids ([3]).

By the coordination number of an ion in a dilute aqueous solution is meant the average number of water molecules constituting the immediate environment of the ion. The coordination number characterizes to a considerable extent the state of the ion in solution. In the present work, using aqueous electrolyte solutions as an example, the question of the temperature dependence of the coordination numbers of particles in liquid solutions is briefly considered.

Particles of a liquid, and in particular water molecules in aqueous electrolyte solutions, are constantly in translational motion—constantly making activated jumps and exchanging nearest neighbors. The observed values of coordination numbers are associated with two opposing processes: on the one hand, with activated jumps of particles leading to their departure from the nearest environment of the selected particle, and, on the other hand, with activated jumps of particles leading to particles entering the nearest environment of the selected particle. The first process leads to a decrease, the second to an increase, in the coordination number. The coordination number of the selected particle is determined by the equilibrium of exchange of the particles constituting its nearest environment*.

One may write the condition of equilibrium for the case of an aqueous electrolyte solution containing, for example, ions of type i. As before ([2]), the question of coordination numbers is considered for the region of dilute solutions, and it is assumed that the nearest environment of the selected particle consists only of water molecules. Let us select some water molecule and an ion. The equilibrium between these particles of the solution, in the sense of their being surrounded by water molecules, is naturally characterized by the fact that the number of molecules constituting the nearest environment of the selected particles does not change with time and, consequently, the constant exchange does not lead to the transfer of water, for example, from the selected ion to the selected water molecule (or in the reverse direction). The condition of equilibrium may be the equality of the average (for example, per 1 second) numbers of activated jumps of water molecules from the nearest environment of the selected particles

$$n_i j_i = nj, \tag{1}$$

where n_i is the coordination number of the ion, j_i is the average, per 1 sec, number of activated jumps of water molecules constituting the nearest environment of the ion, and n and j are, respectively, the coordination number and the average, per 1 sec, number of activated jumps of water molecules in water. For the quantities j and j_i the following relations may be written: $j = j_0 e^{-E/RT}$ and $j_i = j_{0i} e^{-(E+\Delta E)/RT}$, where j_0 and j_{0i} are pre-exponential factors, and E and $E + \Delta E$ are the values of the corresponding potential barriers (2). Substituting the written relations into equality (1), we obtain $n_i j_{0i} e^{-(E+\Delta E)/RT} = n j_0 e^{-E/RT}$, whence

$$\frac{n_i}{n} = \frac{j_0}{j_{0i}} e^{\Delta E/RT}. \tag{2}$$

Relation (2) determines the temperature dependence of $\frac{n_i}{n}$ and, with it, of n_i (the temperature dependence of n is known from the results of X-ray investigations of water (2)). Differentiating (2) with respect to temperature:

$$\frac{d}{dT}\left(\frac{n_i}{n}\right) = -\frac{\Delta E}{RT^2}\,\frac{j_0}{j_{0i}} e^{\Delta E/RT}. \tag{3}$$

Equality (3) indicates the sign of the change in the coordination number of an ion with temperature:

$$\frac{d}{dT}\left(\frac{n_i}{n}\right) > 0, \quad \text{if } \Delta E < 0$$

and

* In considering the question of the temperature dependence of coordination numbers, one may assume that in a liquid only activated jumps of individual particles take place; collective displacements, for the question under consideration, probably have lesser significance.

$$\frac{d}{dT}\left(\frac{n_i}{n}\right) < 0, \quad \text{if } \Delta E > 0.$$

Thus, in accordance with (3), the coordination numbers of ions with negative hydration ($\Delta E < 0$) should increase with increasing temperature, while the coordination numbers of ions with positive hydration ($\Delta E > 0$) should decrease (relative to the coordination number of water molecules). With increasing temperature, water should be displaced toward ions or away from ions (depending on the sign of ΔE).

The dependence considered here of the temperature changes of coordination numbers on the magnitudes of the potential barriers separating neighboring equilibrium positions of particles is general for many liquid solutions. A manifestation of this dependence is the dissociation of compounds in liquids that occurs with increasing temperature. According to the foregoing, in many cases dissociation amounts to the fact that, with increasing temperature, particles of the liquid move into regions with smaller values of the potential barriers (to such groupings of particles as are characterized by smaller values of the potential barriers).

It follows from relation (3) that the coordination numbers of ions change only slightly with temperature (the square of the absolute temperature is in the denominator). Changes in coordination numbers can be large only in the case of comparatively large values of ΔE. However, relation (3) is, of course, only qualitative. In particular, the change of ΔE with temperature is not taken into account. An attempt should be made to determine experimentally the dependence of the coordination numbers of ions in aqueous solutions on temperature. A comparison of the experimental results with the considerations presented here would probably contribute greatly to elucidating the mechanism of thermal motion of particles in aqueous electrolyte solutions.

N. S. Kurnakov Institute of General and Inorganic Chemistry
Academy of Sciences of the USSR

Received
3 IV 1958

CITED LITERATURE

1. V. K. Semenchenko, *Zhurn. neorg. khim.*, **1**, No. 6, 1131 (1956).

2. O. Ya. Samoilov, *Structure of Aqueous Electrolyte Solutions and Hydration of Ions*, Publishing House of the Academy of Sciences of the USSR, 1957.

3. V. K. Prokhorenko, I. Z. Fisher, *ZhFKh*, **31**, No. 9, 1245 (1957).

Note: Figure translations are in progress. See original paper for figures.