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Oleg Ya. Samoilov and the negative hydration in aqueous electrolyte solutions

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Abstract: Is presented information about O.Ya. Samoilov, doctor of chemical sciences, professor, the author of the discovery in 1957 of the phenomenon of negative hydration in electrolyte solutions. The essence of this phenomenon is briefly stated.

Keywords: electrolyte solutions, ion hydration, molecular kinetic approach

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Professor Oleg Ya. Samoilov 1921-1980

The 26th March 2021 marked the 100th anniversary of the birth of the outstanding scientist Oleg Yakovlevich Samoilov, the author of the discovery of the phenomenon of negative hydration - an increase in the mobility of water molecules in the hydration shell of sufficiently large singly charged ions (K⁺, Rb⁺, Cs⁺ at normal temperature). This discovery was later confirmed by the method of NMR relaxation on nuclei of central ions (H.G. Hertz, R.K. Mazitov), the method of cold neutron scattering (A.G. Novikov), and molecular dynamics (computer experiment) (A. Geiger, M.N. Rodnikova, S.A Zasypkin) This is a very important discovery that explained a number of experimental facts



that cannot be understood from the standpoint of thermodynamics. For example, the phenomenon of negative viscosity of aqueous solutions of salts of the indicated singly charged ions or the behavior of Na⁺ and K⁺ ions in biological systems. Here is an example: "The phenomenon of negative and positive hydration is associated with the antagonism of sodium and potassium observed in geological and biological processes. It manifests itself, in particular, in the fact that potassium ions predominate in the cytoplasm of cells, and sodium ions in the intercellular fluid. During the passage of a nerve impulse, sodium ions enter the inside of the axon, and potassium ions go outside. The ratio between

potassium and sodium changes in the nucleus of a developing fertilized egg, when the cleavage process is replaced by differentiation" (G.G. Malenkov).

We point out that, like any mobility, negative hydration depends on temperature. Reviews on negative hydration are listed in the following list:

- 1. Samoilov OYa. The structure of aqueous solutions of electrolytes and hydration of ions. Moscow, Nauka Publ., 1957.
- 2. Geiger A. Molecular dynamics simulation study of the negative hydration effect in aqueous electrolyte solutions. *Ber. Bunsenges. Phys. Chem.*, 1981, 85:52.
- 3. Buslaeva MN, Samoilov OYa. Microdynamics of solvation. In: *The Chemical Physics of Solvation. Part A.* P. 391. Elsevier, 1985.
- 4. Rodnikova MN. Microdynamics of hydration. In: *The method of molecular dynamics in physical chemistry*, p. 235. Moscow, Nauka Publ., 1996.
- 5. Rodnikova MN. Negative hydration of ions. *Elektrokhimiya*, 2003, 39(2):192 (in Russ.).
- 6. Rodnikova MN, Chumaevsky NA. On the spatial network of hydrogen bonds in liquids and solutions. *Zurnal strukt. khimii*, 2006, vol. 47. Application. S. 154 (in Russ.).

The discovery of the phenomenon of negative hydration was made by O.Ya. Samoilov on the basis of his proposed molecular kinetic approach to the study of liquid solutions, based on the peculiarities of the physics of the liquid state of matter - a condensed but mobile phase. It is the mobility of particles that underlies the molecular-kinetic approach to liquid solutions proposed by O.Ya. Samoilov.

In this approach, it was emphasized that the mobility of particles in a liquid does not depend on the total interaction energy of the particles, but on its change at small distances from the particle, i.e. revealed the role of short-range forces in liquid solutions. This approach was of great importance for both the fundamental and applied science of solutions.

A mass of followers appeared, but the first was O.Ya. Samoilov, who proposed a molecular kinetic approach to the study of liquid solutions. He published the main positions of this approach in his outstanding work "The structure of aqueous solutions of electrolytes and hydration of ions" 1957.

I would like to emphasize such an amazing quality of O. Ya. Samoilov as a scientist - this is his scientific intuition. It is based not on the vastness of knowledge, not on the ability to carry out calculations, but on some amazing sense of scientific logic and the ability to think.

After the book was published and translated into Japanese, German and English, the name of O. Ya. Samoilov and his new approach to the study of liquid solutions became known in world science. Scientists were drawn to him. A seminar was needed. The work of the seminar by O.Ya. Samoilov is shown at the end of this issue in RENSIT magazine.

The name of O.Ya. Samoilov is inextricably linked with the SCIENCE of liquids and liquid solutions.