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Abstract

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ON METASTABLE STRUCTURES IN AQUEOUS SOLUTIONS

(Presented by Academician A. V. Shubnikov, 17 XI 1966)

In the last 20 years, in many countries, magnetic treatment of water for boilers has found wide application; as a result of it, certain metastable formations arise that can serve as crystallization centers. The centers are formed throughout the entire volume, as a result of which, instead of a scale layer, an easily removable loose precipitate is formed. Magnetic treatment is used in all cases where the formation of many crystallization centers in an aqueous solution is desirable (for improving concrete, in sugar refining, and in other processes), and also, in a number of cases, makes it possible to increase the efficiency of flotation processes; here the effect is associated with a change in the surface tension of the solution. Many authors have investigated changes in the physicochemical properties of aqueous solutions as a result of treatment by a magnetic field ([1]). A large and, at first glance, contradictory body of material has accumulated. However, no molecular model of the phenomenon has yet been proposed ([2]). Below is a brief description of the model of the phenomenon that we propose, based on the indisputable facts of the appearance of crystallization centers and of the change in the surface tension of an aqueous solution as a result of magnetic treatment. The model explains many of the contradictory results of special investigations by different authors.

First of all, it is natural to suppose that the appearance of crystallization centers and the change in surface tension are two consequences of one and the same phenomenon, namely, the appearance in the solution, as a result of magnetic treatment, of certain structures that play the role of large ions. These ions serve as crystallization centers, and their appearance leads to a change in the surface tension of the solution.

Developing O. Ya. Samoilov' s ideas on the structure of aqueous electrolyte solutions, V. I. Yashkichev analyzed the question of the concentration dependence of the surface tension of a solution containing ions possessing "negative" hydration. It was shown that the change in surface tension as a result of the introduction of such ions at a certain small concentration must be equal to zero, and at an even lower concentration must pass through a minimum ([3]). Such a minimum was observed in the work of Jones and co-workers ([4], [5]).

Authors who studied the change in the surface tension of aqueous solutions as a result of magnetic treatment also found that in the region of small concentrations of calcium ions (distilled water), as a result of treatment the surface tension decreases ([6]), whereas as a result of treatment of river water it increases, and the more so, the greater the initial carbonate hardness ([7]). It should be noted that the crystallization centers must be sufficiently large ions, and they always possess negative hydration according to O. Ya. Samoilov.

With the aid of the concepts we are developing regarding the appearance and role of large ions, the dependence of the effectiveness of magnetic treatment on the initial carbonate hardness and the difference, known from practice, in the stability of the special properties of magnetically treated river and distilled water are explained. River water retains its special properties for many days, while distilled water loses its special features after 24 hours ([1]).

Indeed, a high concentration of the large ions that form leads to an increase in surface tension and thereby to a decrease in the solubility of gases, in particular CO_2. In this case equilibrium (1) shifts to the right, CO_2 escapes into the atmosphere, and $CaCO_3$ precipitates on crystallization centers

$$Ca^{2+} + 2HCO_3^- \rightleftarrows CO_2 + H_2O + CaCO_3. \qquad (1)$$

Thus, even before heating, the large ions—crystallization centers—become overgrown with aragonite. Upon heating, the large metastable ions are destroyed and the solubility of CO_2 decreases. The number of crystallization centers that have not had time to become overgrown with aragonite decreases, while those that have continue to grow. The effectiveness of the treatment is the lower, the smaller the number of centers that have had time to become overgrown.

It is noteworthy that the effectiveness of magnetic treatment, which depends linearly on the initial carbonate hardness, falls to zero at a calcium-salt concentration of the order of $1 \cdot 10^{-4}$ mol/l ([8]). This is precisely the concentration at which, as a result of treatment, the surface tension changes so little that even concentration fluctuations do not create conditions for the overgrowth of nuclei by aragonite. When distilled water is treated, the surface tension decreases, the solubility of gases increases, and the nuclei do not become overgrown. Centers that have become overgrown with aragonite are, naturally, preserved much longer than unprotected ones, which are more subject to the vicissitudes of thermal motion.

In connection with the above, it cannot be considered accidental that 10^{-4} mol/l is also the critical concentration above which, when an electrolyte solution is frozen, the Workman-Reynolds potential does not arise ([9]), and that the special properties of meltwater are also retained for 24 hours ([10]). Apparently, the isomorphic capacity of ice and the appearance of a critical concentration at which the change in surface tension as a result of magnetic treatment changes sign are two phenomena very close in mechanism.

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The spatial separation of ions of different sign, which upon freezing of a solution leads to the appearance of a potential difference, is apparently a necessary condition for the emergence of metastable structures in aqueous solutions. Indeed, such separation during magnetic treatment is ensured by the Lorentz forces acting on ions in water flowing between poles. The trajectories of ions of different sign are twisted in different directions. Other physical methods of water treatment are also associated with the spatial separation of ions. Such are the ultrasonic method, treatment by an electric field, and others (^{11}).

From the above one may conclude that large metastable ions are apparently structures formed by a single ion bound in some way with a sufficiently large number of water molecules. What kind of structures might these be?

In 1959 L. Pauling suggested the possibility of the existence in water of clathrate structures known for gas hydrates. Such structures can exist in water the longer, the better the molecular formations sitting in them correspond to the sizes of the cavities of these structures. Thus, if sufficiently symmetrical formations with sizes close to the cavities of clathrate structures appeared in solution, they could stabilize the clathrate structure forming around them; and if these formations carried a charge, then in this way the metastable large ions sought by us could arise.

Under certain conditions, the calcium ion can form the calcium hexaaqua complex $[Ca(H_2O)_6]^{2+}$ (^{12}). This octahedral complex is formed by a donor-acceptor bond: each of the water molecules gives one electron to calcium, as a result of which the latter forms an octahedral hybrid orbital $3d^2 \cdot 4s \cdot 4p^3$ (^{13}, ^{14}). At the same time there exist—

···orbitals of the water molecule undergo substantial changes. The angle HO—H increases strongly, and the O—H distance decreases. As a result, as was shown by K. B. Yatsimirskii by another, indirect method, the radius of the hexaaqua complex increases in comparison with the radius of the initial ion by only 1.57 Å (^{15}), which for $[Ca(H_2O)_6]^{2+}$ gives a diameter of 5.16 Å. This diameter agrees well with the diameter of one of the cavities of the clathrate structure (5.2 Å) (^{16}).

Thus, clathrate water structures stabilized by calcium hexaaqua complexes are apparently large metastable ions that impart special properties to water treated with a magnetic field. The need for spatial separation of the ions is also understandable. External ion pairs (cation $-H_2O$ $-$anion), encountered even in very dilute solutions (^{16}), hinder both the formation of hexaaqua complexes and the construction of clathrate structures.

Biological effects of a magnetic field testify in favor of the idea that calcium ions are incorporated into the large ions formed during magnetic treatment. The effects of magnetic action are identical to the effects of a sharp decrease in the concentration of free calcium ions in the intercellular fluid.

The scope of the present communication does not allow us to dwell in greater detail on discussion of the results of individual works and on the numerous consequences confirming the validity of the model adopted by us.

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

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