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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Distribution of Components in Aqueous Systems of Nonelectrolytes at Oriented Ice Crystallization

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Abstract—Data are presented on the kinetics and distribution of components at the nonequilibrium crystallization of ice in aqueous system of a nonelectrolyte (water–saccharose) in an original installation operating on the semiconductor thermoelements. The obtained information is important for the better understanding of the nature of aqueous solutions of nonelectrolytes at the temperature $T \sim 0$°C and form the practical viewpoint as well for the solving a problem of separation of components in aqueous systems.

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The processes of oriented crystallization can be used for both exploring the aqueous systems of nonelectrolytes at low temperature and for the creation of the methods of separation and purification. In this work the oriented crystallization was carried out using special original installation operating on the basis of the Peltier effect. Cooling of solution in this case is performed by means of a cooling pipe immersed into the bulk solution. The cooling rate iss controlled by changing the current magnitude in the thermoelement that defines the temperature difference between their hot and cold joints and the respective heat flow through the cooling pipe.

Earlier [1] with this procedure has been investigated the processes of crystallization in pure water and in sodium chloride solutions. For the elucidation of general regularities of the process it is necessary to study also the solutions of nonelectrolytes because behavior of the latter at low temperature was not sufficiently studied, in particular near the points of phase transitions. Therefore we used as the object of investigation a typical nonelectrolyte saccharose that is useful owing to its high solubility in water and the possibility of carrying out the study in a wide range of concentration.

The system saccharose–water has been studied earlier by the method of fractional melting [2]. The information obtained concern position of eutectic point in this system. But at the study several problems appeared due to anomalous behavior of the system in the vicinity of the presumed eutectic point. Therefore seems actual further study of this system by the method of oriented crystallization.

EXPERIMENTAL

Elimination of heat from the bulk solvent is advantageous in several aspects over the cooling of solution at its surface from the viewpoint of the efficiency of components separation. The dissolved substance is stepwise replaced by the crystallization front from the bulk center rather than from surface, and capture of the substance by the forming ice is much diminished. The heat elimination is performed via the cooling pipe that, depending on a certain task, can be immersed into the solution at a given point. Direction and value of the heat flow can be defined by the modules direction an electric current magnitude in them. The installation is depicted in Fig. 1.

Between the cold joints of the modules (*1*) connected consecutively into electric chain is mounted the cooling pipe (*2*) made of aluminum. For heat elimination from the hot joints is used a heat exchanger (*3*) to which the cooling liquid (water) is passed from the hose (*4*). The thermoelectric modules take heat away from the cooling pipe immersed to the solution (*5*). At the cooling, on the cooling pipe occurs crystallization of ice (*6*). The saccharose solution 150 ml volume varied by concentration was placed into plastic vessel and 50.0 ml of the solution was crystallized using the

installation. The experiment was carried out at the current magnitude 1.5 and 3.0 A. The environment temperature was 20°C. The time of the experiment beginning, the ice formation beginning and of the solution 50.0 ml freezing duration were registered. After completing the experiment, the liquid was separated from the ice and heated to room temperature, and then concentration of saccharose cliquid was measured by refractometric method. The remaining ice was melted, and the saccharose concentratioin clsolid was measured at room temperature. Calculation of effective distribution coefficient was calculated according to the relation:

$$k_{\text{eff}} = c_{\text{solid}}/c_{\text{liquid}},$$

where csolid is saccharose concentration in the melt and cliquid is saccharose concentration in the not crystallized sulution.

The crystallization kinetics was judged from two parameters: (1) time gap between the switching current on and the beginning of ice crystallization on the cooling pipe and (2) duration of crystallization of a constant volume of the solution. Plots of these parameters against the concentration of the parent solution are depicted in Figs. 2 and 3. The time before the crystallization beginning grows also with increase in the concentration of parent solution, due to decrease in the temperature of ice crystallization. The small jumps on the curve *1* can be obligated to the difference in behavior of the solution in the precrystallization state and different prone to overcooling at different concentrations. At the current

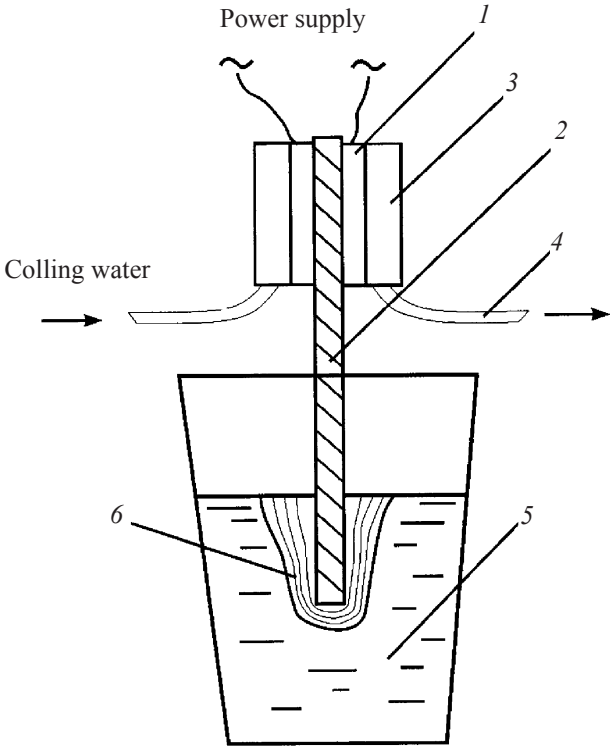

Fig. 1. Laboratory installation for crystallization of solutions.

magnitude 3.0 A (curve *2*) the crystallization begins 2–2.5-fold earlier that at the magnitude 1.5 A (curve *1*), that is explained by the higher rate of heat elimination. In the concentration range 0–40 wt% the time before crystallization beginning varies insignificantly, but near 60 wt% grows sharply. At higher concentrations the registration of the moment of crystallization beginning is

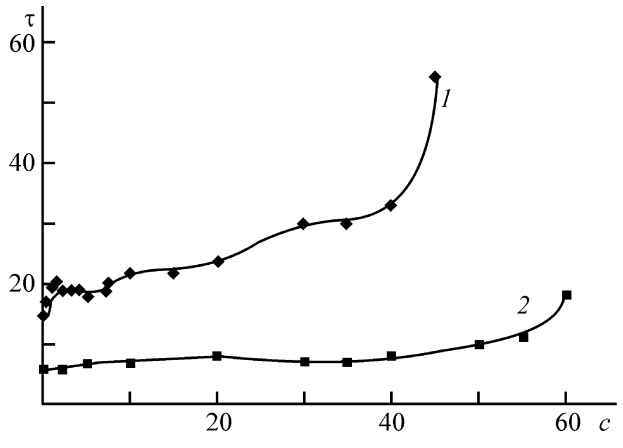

Fig. 2. Dependence of the time τ (min) of the ice crystallization beginning on the saccharose concentration c (wt %) in solution. Current magnitude (A): (*1*) 1.5, (*2*) 3; the same in Figs. 3 and 4.

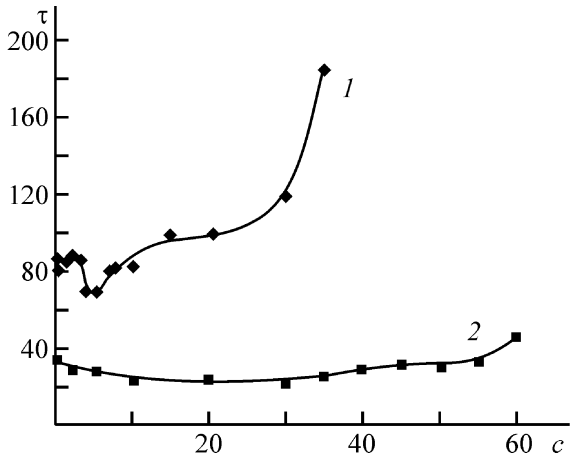

Fig. 3. Dependence of duration τ (min) of crystallization of the solution constant volume on the saccharose concentration *c* (wt %).

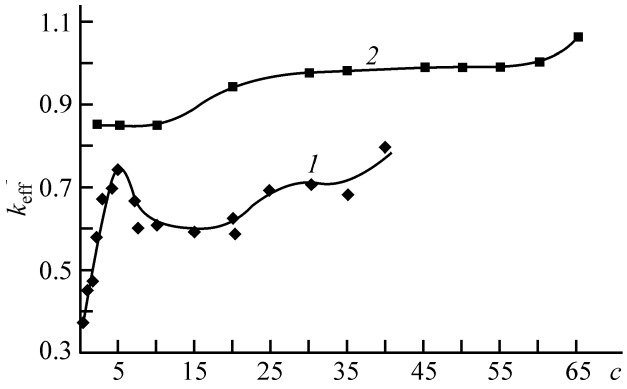

Fig. 4. Plot of effective distribution coefficient k_{eff} on the saccharose concentration c (wt%) in the solution.

fixed difficultly. Increase in the solution viscosity when the concentration grows promotes transformation of the solution into the state close to glass-like one. This fact has been confirmed in [3].

In Fig. 3 is depicted the crystallization time of a constant volume of solution at the different current magnitudes. At the current 1.5 A (curve *1*) in the concentration range 0–5 wt % the crystallization duration is some less. This is explainable by the changes in the structure of the forming ice. At a very low concentration is formed rather a dense ice with low heat conductivity that decelerates the process of crystallization. Increase in the parent solution concentration to 4–5% makes ice more friable and accelerates the process of crystallization and hence decreases its duration. Further increase in the saccharose concentration increases the crystallization duration that is consistent with the preceding results (Fig. 2) and is explained by the same factors. At higher concentration both attaining the crystallization temperature and crystallization of the ice constant volume require more time. At the concentration 35 wt % the crystallization duration achieves 3 h and even more, and in solutions with higher concentration occurs crystallization of the volume less than 50 ml: the current magnitude becomes insufficient for cooling solution to the required temperature. At the current 3.0 A (Fig. 3, curve *2*) the crystallization duration average is 3–4 times less than with the current 1.5 A. This is explained by higher rate of heat elimination. Like the case of 1.5 A, here occurs certain shortening of the crystallization duration at low concentrations. The increase in time at high concentrations in this case is less emphasized.

For the description of the distribution of components between solid and liquid phases we used effective distribution coefficient k_{eff}. Unlike the equilibrium coefficient that for the aqueous systems in the hypoeutectic region has value equal or close to zero, the effective distribution coefficient practically commonly is much higher than zero. (There is no respective reference data for the system of saccharose–water). Several factors can affect the keff value, including character of heat elimination, direction of crystallization, degree of the process nonequilibrium. In Fig. 4 (curve *1*) is depicted a plot of effective distribution coefficient against the parent solution concentration at the current magnitude 1.5 A.

On the curve *1* (Fig. 4) can be isolated three regions. The first one, from 0 to 5 wt%, is characterized by monotonic and fast grow of the effective distribution coefficient; probably the defining factor in this case is the structure of the formed ice. Dense ice at low concentrations replaces dissolved substance to the solution more effectively. At higher concentrations of the solution the ice density falls sharply, it becomes more friable. The maximum on this curve corresponds to the minimum on the curve *1* (Fig. 3). This can be explained by the assumption that at the relatively fast crystallization of ice the time for passing the dissolved substance to the solution is not sufficient. At further increase in the concentration the crystallization duration grows and the effective coefficient falls. The second region, from 5 to 15–20 wt% corresponds to decrease in k_{eff}. The ice structure is not changed substantially and the time becomes to be the main factor. The crystallization proceeds rather slower that results in effective separation and respectively in decrease of the effective distribution coefficient, to 0.6 at the concentration 15–20 wt %. The third region, from 15 to 20 wt%, is characterized by some increase in the effective coefficient. This is connected with the further changes in the ice structure: the crystallized solution initially transforms into a viscous mass coating the cooling pipe, and further it solidifies stepwise. Therewith the separation efficiency falls while the effective distribution coefficient grows.

The values of the coefficients at the current 3 A (curve *2*), are noticeable higher than the obtained with the current magnitude 1.5 A (curve *1*). This is connected with the faster crystallization under these conditions because the time is insufficient for the transfer the dissolved substance to the solution. In the concentration range 10–20 wt % the distribution coefficient grows from approximately 0.85 to 0.95–0.98 and further remains practically unchanged up to the concentration 60 wt %. At the concentration above 60 wt % it grows, and at the saturation the k_{eff} equals to 1.06–1.07.

According to the earlier experiments [2] the eutectic concentration in the system of saccharose–water is near 58.5%. Right near this concentration in the experiments occurred sharp increase in the duration of the ice crystallization (Fig. 2) and some other changes in the behavior of solutions. These changes can be connected with the transfer from the hypoeutectic to the eutectic concentration. But should be noted the somewhat unusual behavior of the saccharose–water system near the eutectic point. At the comparison of the results on the fractional ice melting [2] and the oriented crystallization is seen that in the both cases occurs smooth change in the character of crystallization near the eutectic point. At the fractional melting of the ice crystallized from the aqueous solutions of saccharose its behavior remains approximately constant in the concentration range 54–62 wt % [2]. The concentration in the course of melting varies insignificantly, the same true for the final fractions of the melt. The same picture occurred also in the experiments of oriented crystallization. Content of the dissolved substance (saccharose) remained approximately constant both in ice and in the not crystallized solution.

Moreover, the experiments showed that at the concentration 50–58 wt % the value of k_{eff} can be either higher or lower than unity depending on the volume of the crystallized solution. Such behavior of the solution of saccharose together with its tendency to vitrification points to the restriction of application of the classic consideration of phase equilibrium and eutectic under these conditions. In the real processes when crystallization and melting are nonequilibrium can be more useful to apply the term "eutectic area" assuming the region adjacent to eutectic on the phase diagram where behavior of the system vary insignificantly both at crystallization and at melting.

CONCLUSIONS

1. It is established that in the aqueous system of nonelectrolyte (saccharose–water) the duration of crystallization of constant volume of ice achieves minimum at the concentration of the parent solution near 5 wt % that is explained by difference in the structure of the forming ice.

2. Effective distribution coefficients at the ice crystallization are determined to be equal 0.6–0.7 at the current magnitude 1.5 A and 0.8–1.0 at 3.0 A. The best conditions for the separation is current 1.5 A and concentration 0–5 and 10–20 wt %.

3. The distribution of components at the crystallization of ice is affected by the rate of the crystallization process and the structure of the forming ice.

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