

## Studies on the Efficiency of Water Purification from Phenol by Incomplete Freezing Method

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### Abstract

Using a freezing-unfreezing procedure, an efficiency of water purification from phenol  $k_{\text{pur}}$  has been investigated depending on the fraction of frozen aqueous solution ( $g$ ) and on the temperature of freezing  $T$  (freezing rate). The following kinds of dependences have been revealed: 1) a monotonous  $k_{\text{pur}}$  increase with  $g$  increasing at  $-3.5$ ,  $-6.5$ ,  $-10$ ,  $-15$  °C; 2)  $k_{\text{pur}}$  increase with the increase in the fraction of frozen aqueous solution up to  $g \approx 0.2$  and the subsequent  $k_{\text{pur}}$  decrease at freezing temperature values of  $-20$  and  $-25$  °C (nonmonotonic dependence). Influence of the causes those prevent obtaining high values of  $k_{\text{pur}}$  (veiling of the “purifying” factor) is discussed. They include the impossibility to separate the solution stuck onto the surface of ice from ice itself due to the sampling technique (the “distorting” factor) and freezing-in impurities into interdendritic cavities at the solid-melt interface (the “polluting” factor). A conclusion is drawn that the optimal technological conditions in the use of the water freezing method for water purification consist in the freezing when the solid-melt interface velocity is about 0.2 cm/h up to gaining the value of  $g \sim 0.5$ .

**Key words:** freezing-unfreezing procedures, water purification efficiency, phenol, distorting factor, polluting factor, purifying factor

### INTRODUCTION

The demands for pure potable water and, accordingly, the urgency of its obtaining for contemporary society is proceeding with increase. This fact is indicated by a continuously growing market of various potable water grades as well as an increase in the sales volume of pure water all over the world. As a rule, the technology for obtaining pure potable water is based on the filtration method that includes many stages thus being rather expensive. In this connection the development and application of alternative methods for obtaining pure water is of special interest. One of them is presented by a well-known method of partial (incomplete) freezing with subsequent unfreezing the frozen initial water. This method was known for a

long time, but it had not found wide practical application [1, 2].

For the application of this water purification method, besides obligatory economic advantages (for example, the opportunities in using cheap cooling sources), one should determine optimum conditions not only with respect to energy consumption, but also regarding the physicochemical parameters those provide obtaining the maximum values of water purification coefficients ( $k_{\text{pur}}$ ). The need for determining optimum conditions to obtain the most purified water is *a priori* “caused by the following circumstances.

From the standpoint of the directional crystallization theory, in order to obtain well-purified water with the use of the full freezing method an aqueous solution should be frozen

in such a way as to prevent the formation of dendrites at the freezing front (solid-liquid interface) [3]. Further, after full freezing it is necessary to remove the fraction of ice (for example, 5 %) formed last, obtaining then the purified water from the residuary ice via thawing. However, this method of pure water obtaining is useless for practical needs in view of a long duration of freezing (the process is carried out at low freezing rate) and due to the inconveniences connected with separating the fraction of ice containing impurities.

In this connection a more plausible application could likely be found by partial freezing rather than by full one, since a non-frozen part of the initial solution can be removed simply and quickly enough. However, with the use of such a method for ice obtaining, there are solution drops with impurities stuck onto the surface of ice due to its wetting with water, which can result in decreasing the purification level. Another effect inherent both in the method of full and of incomplete freezing consists in "lodging" and subsequent freezing-in the molecules of impurities into interdendritic space at the solid-melt interface. The two mentioned factors result in decreasing the purification level.

It is obvious that as the fraction of ice increased the influence of the first factor decreases due to the reduction of the surface/volume ratio for the frozen ice, whereas the influence of the second factor increases owing to the growth of the concentration of impurities at the solid-melt interface. Thus, in order to obtain water purified as much as possible one should choose the optimum conditions those determine the character of purification level dependence on the rate of freezing and the fraction of ice formed. There are scarcely such data concerning water purifying from organic impurities by the method of freezing available in the literature. There is only a paper [4] where an effect is described for technical water 30 % additional cleaning from organic impurities at the temperature of  $-17^{\circ}\text{C}$ . In addition, the authors of [5] demonstrated that the efficiency of water purification from aldehydes at  $-17^{\circ}\text{C}$  depends on the size of a hydrophobic part of the molecule and can be as much as 90 %. The freezing level of water in [4, 5] amounted to about 50 %.

The present work is devoted to the studies on the efficiency of water purification from phenol using the freezing-unfreezing method depending on the fraction of ice and on the temperature (the freezing rate). The purpose of the work consisted in determining the freezing conditions required for obtaining water purified as much as possible. The choice of phenol as a subject of inquiry is caused by the fact that phenol is one of widely known organic pollutants occurring in natural and potable water, and at the same time as certifying water quality by sanitary inspection services just the phenol concentration has to be first of all determined. The analysis of water purification efficiency of was carried out using an absorption spectroscopy technique, which allowed us to easily and reliably determine the variation of phenol concentration in aqueous solutions during the procedure of freezing-unfreezing.

## EXPERIMENTAL

Phenol of analytical grade was used in the experiments with no additional purification. Double distilled water was used for preparing solutions. The concentration of phenol amounted to  $7.5 \cdot 10^{-4}$  mol/L.

A "Biryusa" refrigerating chamber was used as a freezer; it was additionally equipped with an electronic processor that allowed controlling the temperature of freezing in the chamber compartments within the range from  $-2$  to  $-30^{\circ}\text{C}$  to accuracy within  $\pm 0.5^{\circ}\text{C}$ . The initial temperature of solutions under freezing amounted to  $(22 \pm 2)^{\circ}\text{C}$ . The freezing of samples was carried out using polyethylene beakers of cylindrical shape; the volume of solutions under investigation was 130 mL.

Seven samples of aqueous solutions were simultaneously placed into the refrigerating chamber (the beginning of solutions freezing) at a certain temperature. For the determination of water freezing kinetics the beakers were in an orderly sequence took out of the refrigerating chamber and a non-frozen solution was then poured into a graduated cylinder. The difference between the volumes of initial and non-frozen solution ( $V_i$  and  $V_{n/f}$ , respectively) was taken as the volume of ice  $V_{ice}$ . The fraction

of frozen water  $g$  was determined according to the formula

$$g = V_{\text{ice}}/V_i \quad (1)$$

Absorption spectra were registered using a Hewlett-Packard spectrophotometer. Optical cells were used with the thickness of 1 cm. The optical density (absorbance) value was determined at the wavelength  $\lambda = 270$  nm being in direct proportion to the concentration of phenol. The temperature of spectra registration amounted to  $(22 \pm 2)$  °C.

The value of water purification efficiency  $k_{\text{pur}}$  was determined from the ratio

$$k_{\text{pur}} = A_i/A_{\text{ice}} = C_i/C_{\text{ice}} \quad (2)$$

where  $A_i$  are  $A_{\text{ice}}$  are optical density (absorbance) values at the wavelength of 270 nm for the initial aqueous solution of phenol and for the solution after unfreezing ice, respectively;  $C_i/C_{\text{ice}}$  are the concentrations of the initial phenol solution and of the solution after unfreezing ice, respectively. It should be noted that with such a way to determine water purification efficiency (integral over time) the increase in  $k_{\text{pur}}$  as the fraction on non-frozen water increased implies the reduction of impurity concentration in the ice formed.

The value of freezing rate  $v$  (in mL/min) was determined from the kinetics of ice formation for each temperature. The velocity of freezing front movement  $V$  (in cm/h) was estimated basing on the assumption, that the initial bulk under freezing represents a ball with the volume  $W_0 = 300$  mL and radius  $r_0 = 4.21$  cm, which being frozen up to  $g = 0.5$  during the freezing time  $t_{g=0.5}$  is transformed to the ball of 150 mL in volume with the radius  $r_{g=0.5} = 3.34$  cm. Thus, the velocity of freezing front movement was determined as

$$V = (4.21 - 3.34)/t_{g=0.5} = 0.87/t_{g=0.5} \quad (3)$$

The rate of molecular diffusion  $V_D$  (in cm/h) was calculated according to the formula  $R^2 = 6Dt$  (4)

where  $R^2$  is a squared root-mean-square displacement of a particle in a time  $t = 1$  h;  $D$  is the diffusion coefficient for molecules in an aqueous solution at the temperature of 0 °C, approximately equal to  $10^{-5}$  cm<sup>2</sup>/s [6]. The root-mean-square displacement of a particle in a time  $t = 1$  h, determined from the equation (4), amounted to 0.46 cm.

The temperature of solutions under freezing was measured with the use of a copper-constantan thermocouple and a mercury thermometer.

## RESULTS AND DISCUSSION

For the freezing temperature values amounting to  $-3.5$  and  $-6.5$  °C and  $g < 0.2$ , as a sample taken out of the freezing chamber in 3–5 s, the formation of ice in the bulk was distinctly observed. The ice formed after water separation (pouring off) represented a loose mass (being visually similar to cotton wool staying within water). Further such a state of water-ice mass will be mentioned as “wet ice”. The formation of the loose mass occurred after taking the beaker out of the freezer rather than inside the refrigerating chamber.

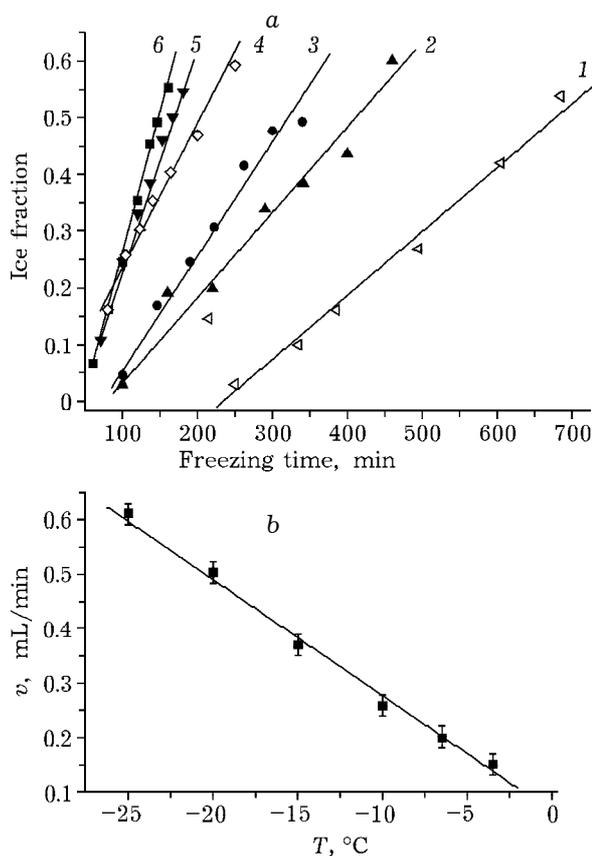


Fig. 1. Kinetics of ice formation in aqueous solutions of phenol at the freezing temperature values of  $-3.5$  °C (1),  $-6.5$  (2),  $-10$  (3),  $-15$  (4),  $-20$  (5),  $-25$  °C (6) (a) and the dependence of phenol solution freezing rate  $v$  on freezing temperature  $T$  (b).

Till the moment when a sample was taken out of the freezer, the aqueous solution, to all appearance, represented overcooled water with crystallization nuclei distributed all over the volume. Hence, upon taking a beaker out and unavoidable vibration influence the formation of ice occurred all over the volume of the sample under freezing. In this case the temperature within the sample grew from  $-1.5 \dots -2$  °C to  $0.5-1.5$  °C. At  $g > 0.2$  the formation of ice occurred from walls, bottom as well as from the surface of a solution. By this it is meant that at  $g > 0.2$  and corresponding time of freezing the crystallization nuclei were finally generated at the walls of the beaker and on the surface as at the most cold points. The formation of ice directed from the walls, bottom and solution surface was observed, as a rule, at the freezing temperature below  $-10$  °C and all  $g$  values. However, at  $T < -10$  °C for  $g \leq 0.1$  in some cases, liquid ice formation was observed, too.

Figure 1, *a* demonstrates kinetic curves of ice formation in phenol aqueous solutions for various values of temperature. It is obvious that satisfactorily linear dependences are characteristic of all the solutions. The slope ratio values for corresponding plots those characterize the freezing rate  $v$ , are presented in Fig. 1, *b*. One can see that the freezing rate increases linearly with the temperature reduction.

Figure 2 demonstrates absorption spectra of phenol at the freezing temperature of  $-10$  °C for different  $g$  values. It is apparent that the shape of the initial absorption spectrum of phenol during the freezing-unfreezing procedure remains unchanged, variations being observed only for absorption intensity. With other temperature values similar changes were observed in the absorption spectra of phenol depending on the freezing level. Thus, one can conclude that for the samples of unfrozen ice the concentration of phenol is always lower as com-

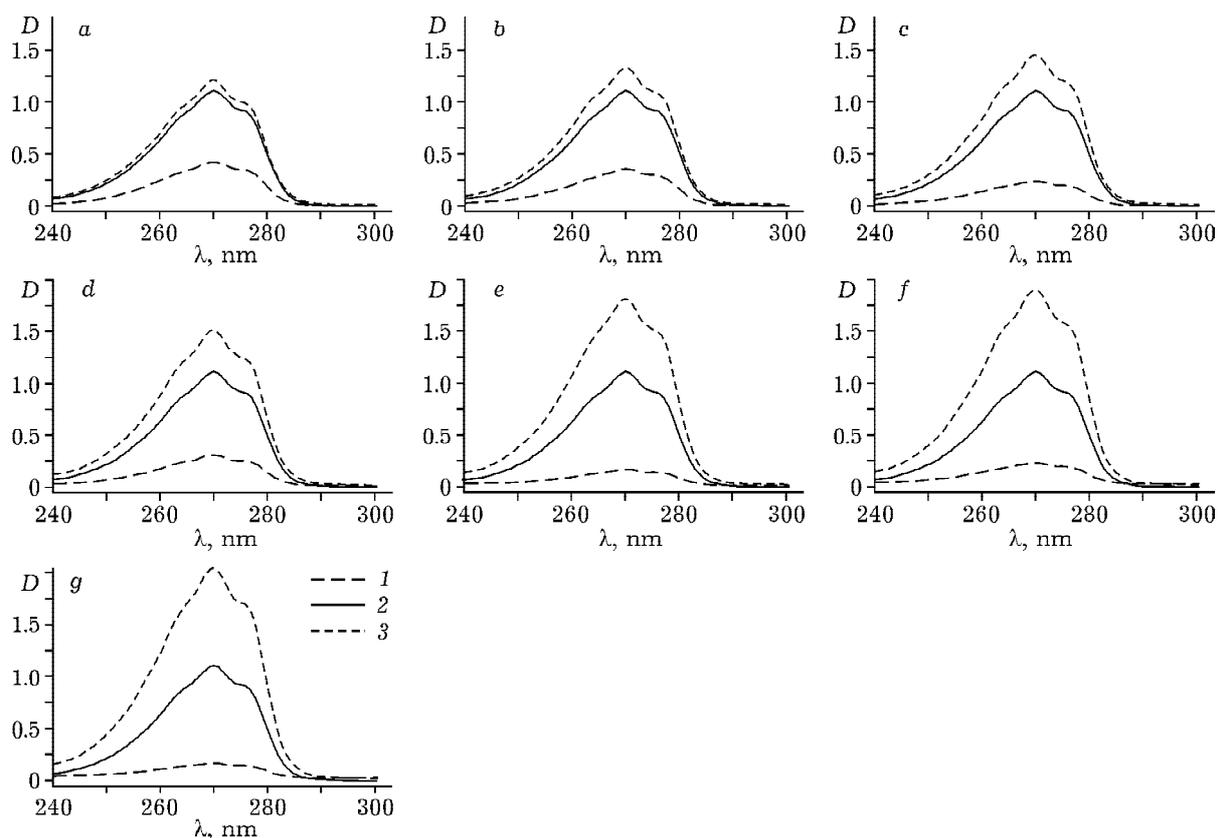


Fig. 2. Absorption spectra for phenol aqueous solutions for different values of freezing level  $g$  ( $T = -10$  °C): 0.05 (*a*), 0.17 (*b*), 0.27 (*c*), 0.31 (*d*), 0.41 (*e*), 0.48 (*f*), 0.50 (*g*); 1 - absorption spectrum of the phenol solution after unfreezing ice, 2 - absorption spectrum of the initial solution of phenol, 3 - absorption spectrum of non-frozen phenol solution.

pared to phenol concentration for the initial sample, whereas for the samples of non-frozen water it is always higher in comparison with phenol concentration for the initial sample. These data unequivocally indicate that the application of the procedure of freezing-unfreezing really promotes water purification from impurities.

Figure 3 displays the dependences of the optical density (absorbance) values for unfrozen and frozen aqueous phenol solutions on the fraction of ice for various temperatures. One can see that for all the temperature values at  $g = 0.5$  within  $\pm 10\%$  there is an equality observed for changing the absorbance values for non-frozen and frozen solutions ( $A_{n/f}$  and  $A_{ice}$ , respectively) with respect to optical density of initial solutions ( $A_i$ ), *i.e.*  $A_{n/f} - A_i \approx A_i - A_{ice}$ . The occurrence of such equality represents the simplest condition in order to control the conservation of the substance, from which substance the aqueous solution has to be purified. So, for example, the attempts to estimate the efficiency of water purifying from toluene impurities appeared unsuccessful due to the lack of such equality. Fulfilling the condition of balance such as  $A_{n/f} - A_i \approx A_i - A_{ice}$  implies that the reduction of phenol concentration in the ingot of ice with respect to the concentration

of phenol in the initial solution corresponds to the increase in phenol concentration in the non-frozen solution with respect to the concentration of phenol in the initial solution.

Figure 4 demonstrates the dependences of  $k_{pur}$  value on  $g$  parameter for different temperatures. It is seen that all the data set can be conditionally divided into three groups. For the first group a monotonous increase of  $k_{pur}$  is typically observed at  $T > -10^\circ\text{C}$ ; the second group of the data is distinguished by almost constant  $k_{pur}$  values at  $T = -15^\circ\text{C}$ ; for the third group one can observe an increase in  $k_{pur}$  value with the growth of the fraction of frozen water up to  $g \approx 0.2$  with the subsequent  $k_{pur}$  reduction at  $T < -15^\circ\text{C}$  (nonmonotonic dependence). The analysis of the dependences obtained allows one to conclude that at the freezing temperature  $T < -15^\circ\text{C}$  the concentration of phenol within the frozen solution increases with the growth of ice fraction, *i.e.* ice becomes more polluted ( $k_{pur}$  values decrease). On the contrary, at  $T < -15^\circ\text{C}$  the concentration of phenol decreases with the growth of ice fraction, *i.e.* ice becoming more pure. In addition, it should be noted that for all the temperature values at  $g < 0.1$  the value of  $k_{pur}$  is less than 3.

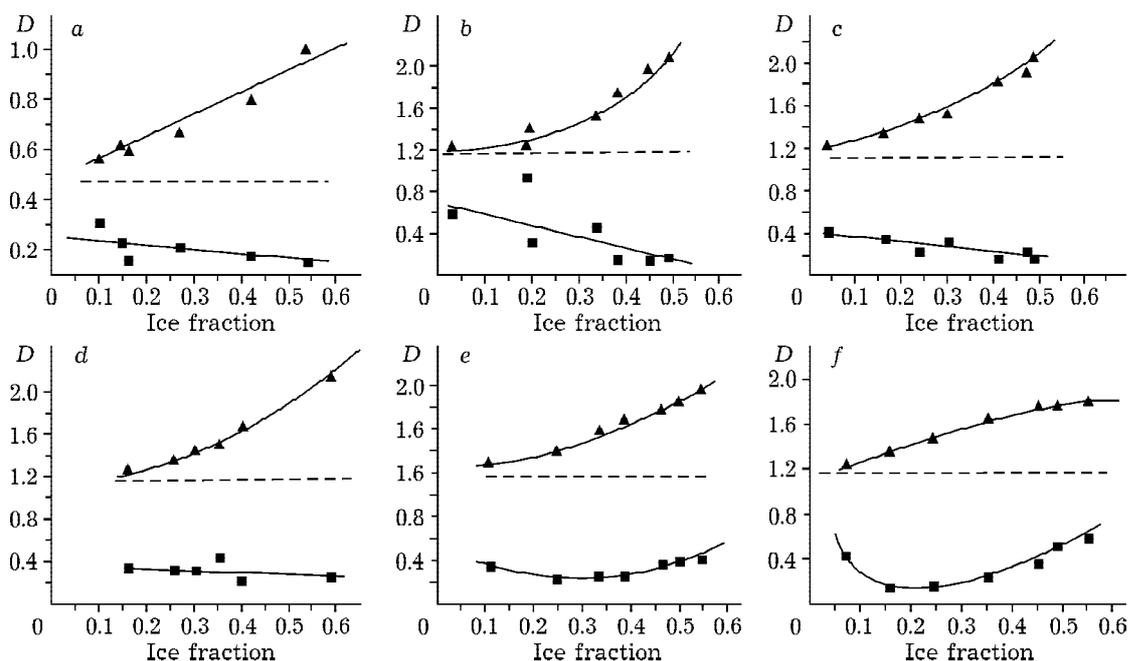


Fig. 3. Dependence of phenol solution optical density (absorbance) on the ice fraction for different values of freezing temperature,  $^\circ\text{C}$ : -3.5 (a), -6.5 (b), -10 (c), -15 (d), -20 (e), -25 (f); 1 - initial solution, 2 - unfrozen solution, 3 - non-frozen solution.

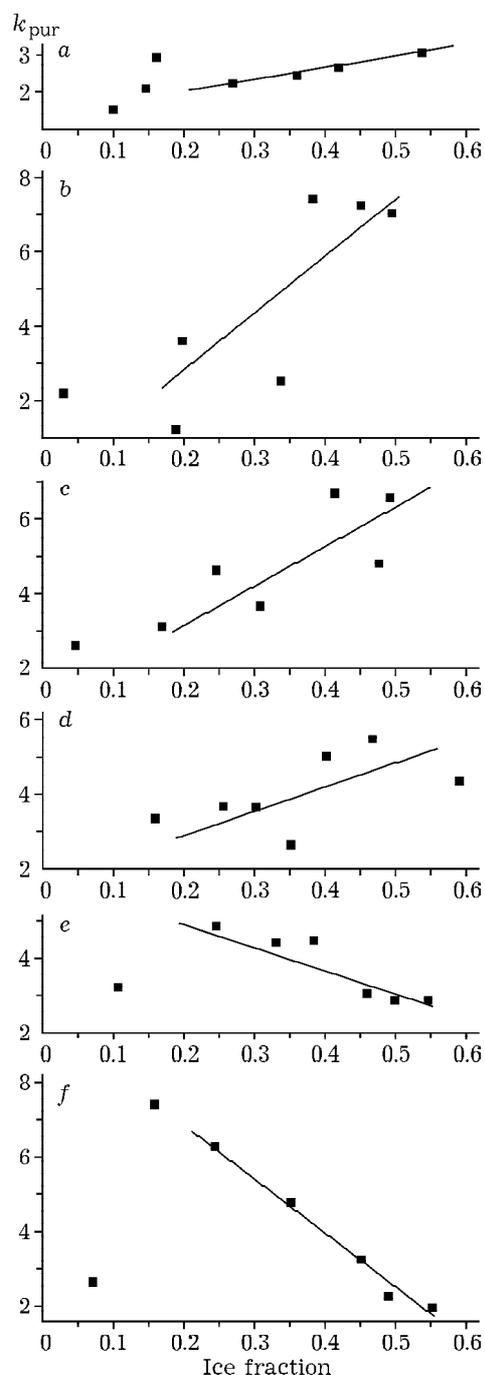


Fig. 4. Dependence of phenol solution purification coefficient  $k_{\text{pur}}$  on the ice fraction for different values of freezing temperature, °C:  $-3.5$  (a),  $-6.5$  (b),  $-10$  (c),  $-15$  (d),  $-20$  (e),  $-25$  (f).

Data presented in Fig. 4 allow one to determine optimum conditions for the maximal level of water purification with the use of the freezing-unfreezing method as it follows: the freezing temperature values for the solution ranging within  $-6.5 \dots -10$  °C,  $g = 0.5$ . Indeed, under

these freezing conditions the efficiency of purification is observed to be maximal ( $k_{\text{pur}} \sim 8$ ). It is evident that a practically significant parameter of freezing is not the temperature, but the freezing rate determined by the features of a freezer. In our case the freezing rate amounted to 25 and 37 mL/h at the temperature of  $-6.5$  and  $-10$  °C, respectively. The mentioned values of freezing rate are inherent in the volume under freezing equal to 300 mL.

From this standpoint a more universal value to describe the process of freezing is presented by the velocity of freezing front movement ( $V$ ). For the temperature of  $-6.5$  and  $-10$  °C this value amounted to 0.16 and 0.25 cm/h, respectively, which is lower than the diffusion rate ( $V_D \sim 0.46$  cm/h). By this it is meant that there is almost no impurity concentration gradient at the solid-melt interface in unfrozen solutions at these temperatures, since the diffusion movement provides the elimination of this gradient and represents a natural stirring means.

From the results obtained it follows that at  $T = -25$  °C the efficiency of water purification is comparable with the purification efficiency obtained at the temperatures of  $-6.5$  and  $-10$  °C, however high purification coefficients are observed at  $g \sim 0.15$ . In this connection, from the practical point of view, since there is an insignificant fraction of ice formed the obtaining of purified water at  $T = -25$  °C is much less favourable than at the temperatures of  $-6.5$  and  $-10$  °C. Thus, water purification from phenol seems to be most efficient at the freezing level less than 50 % of initial water volume at the freezing front movement velocity of  $\sim 0.2$  cm/h.

From Fig. 4, a–g it follows also that within the range of  $g = 0.15$ – $0.55$  the slope ratio values for the plots of  $k_{\text{pur}}$  against  $g$  are to a considerable extent dependent on temperature (freezing rate). As it follows from the data presented in Fig. 5, the slope ratio values for the plots of  $k_{\text{pur}}$  against  $g$  vary over a wide range (up to the change of sign) depending on freezing rate.

The basis for water purification using a recrystallization method is formed by the property of water to form under freezing the ice with a lower impurity concentration as compared to that of initial water. When the conditions are chosen well this “purifying” factor, as a matter of principle, should promote ob-

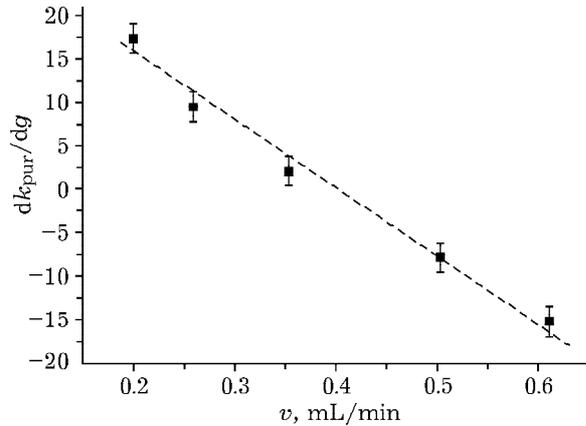


Fig. 5. Dependence of  $dk_{\text{pur}}/dg$  on the freezing rate  $v$ .

taining a high purification coefficient ( $\sim 100$ ). However, the conditions of our experiments (freezing without stirring) are such that even the lowest freezing front movement velocity ( $V \sim 0.12$  cm/h at  $-3.5$  °C) was higher than the freezing front movement velocity ( $V = 0.05$  cm/h) that provides almost ideal ice formation under the conditions of the directional crystallization ( $k_{\text{pur}} \sim 100$ ) [7, 8].

It is known that when the velocity of freezing front movement  $V = 0.05$  cm/h, the formation of dendrites does not occur. Under the conditions of our experiment the formation of dendrites took place, hence, the effect of increasing the impurity concentration in ice with growing  $g$  will be always observed, since the concentration of impurity at the solid-melt interface increases with the increase in  $g$  and, correspondingly, the probability of impurity entering the interdendritic cavities grows. As a result, the solution with a higher impurity concentration will enter the interdendritic space to remain there after freezing. This effect of “lodging” within the interdendritic space should result in the growth of salts concentration in the ingot of ice (the “polluting” factor of the recrystallization water purification procedure). Earlier this fact was observed experimentally for the processes of directional crystallization [3, 9].

Under the conditions of our experiment (at least, when the freezing front movement from a wall to the centre occurs) similar processes of ice dendrite formation could also take place; this should give rise to the increase in the concentration of an impurity at the solid-melt interface and, consequently, to the increase in

the probability of an impurity entering the interdendritic space with growing  $g$ . As a result, a decrease in the purification coefficient should be observed. Thus, a true dependence  $k_{\text{pur}}(g)$ , representing a combined influence of the “purifying” and “polluting” factors, must be a monotone decreasing function: the maximum  $k_{\text{pur}}$  value being observed at low  $g$  values with the subsequent  $k_{\text{pur}}$  reduction with the increase in  $g$ .

However, the features of ice sampling of at application of a method of incomplete freezing for the measurement of impurity concentration in thawed ice does not allow one to obtain a real  $k_{\text{pur}}$  dependence on  $g$  value. As mentioned earlier, this is connected with the fact that there is no pure ice formation observed. On the contrary, the formation of ice with the drops of the liquid solution stuck to the ice surface occurs. Avoiding this effect seems to be not possible yet. The concentration of impurities in the solution stuck onto the surface of ice is higher than the concentration of impurities in the ice formed. In the final analysis, this fact can result and results in a higher experimentally observed concentration of impurities with respect to the real concentration in ice determined by the “purifying” and “polluting” factors.

Thus, real concentration of impurities is veiled owing to the sampling method chosen (the “distorting” factor). The effects connected with the “distorting” factor (the sticking of solution drops onto the surface of ice) are well-known, belonging to main shortcomings of both estimations, and efficiency values for purifying the substances with the use of incomplete freezing method. Thus, the “distorting” factor always takes place under the conditions of our experiment concerning the measurement of impurity concentration in ice. The effect of this factor on the  $k_{\text{pur}}$  value will decay with the decrease in the area of the solid-melt interface, *i.e.* with the increase in the fraction of ice. Hence, the maximal influence of this factor resulting in  $k_{\text{pur}}$  value reduction should be observed at low  $g$  values.

So, the efficiency of purification is determined by a joint contribution of the “purifying”, “polluting” and “distorting” factors. As mentioned above, at low  $g$  values the value of  $k_{\text{pur}}$  may be low due to a prevailing contribution of the “distorting” factor to impurity con-

centration, whereas at high  $g$  values such a behaviour could be connected with a prevailing contribution of the “polluting” factor to impurity concentration, *i.e.*  $k_{\text{pur}}$  dependence on  $g$  is nonmonotonic. Such dependences are observed for freezing temperature values of  $-20$  and  $-25$  °C. In the case of the prevailing influence of the “polluting” or “distorting” factors within a wide range of  $g$  values the type of  $k_{\text{pur}}$  dependence on  $g$  can represent either a monotonously increasing function, or a monotonously decreasing one, respectively. In particular, one of the variants of such a function presented by a monotonous  $k_{\text{pur}}$  increase with growing  $g$  can be observed at  $T > -15$  °C ( $T = -10, -6.5$  and  $-3.5$  °C). This result might be explained by decreasing the contribution of the “distorting” factor into the value of  $k_{\text{pur}}$ .

The dependence of  $k_{\text{pur}}$  on the freezing rate  $v$  for certain values of  $g$  (0.5, 0.31, 0.2) may be considered as an additional argument for the concepts concerning the presence of the two factors, those in an opposite manner influence the  $k_{\text{pur}}$  dependence on  $g$  (Fig. 6). The values of  $k_{\text{pur}}$  for  $g = 0.5, 0.31$  and  $0.2$  were obtained *via* the interpolation of  $k_{\text{pur}}(g)$  dependences at different temperatures (see Fig. 4, *b-g*). (It should be noted that when plotting the dependences presented in Fig. 6, the  $k_{\text{pur}}$  dependence on  $g$  for  $T = -3.5$  °C was not taken into account (see Fig. 4, *a*). This dependence will be separately considered later.) One can see that the character of  $k_{\text{pur}}$  dependences on  $v$  for different  $g$  values is considerably different (see Fig. 6, *a-c*). So, for  $g = 0.5$  one can observe a decrease in  $k_{\text{pur}}$  as  $v$  value increased; for  $g = 0.2$  only growth is observed, whereas for  $g = 0.31$  the value of  $k_{\text{pur}}$  almost does not depend on  $g$ .

The reduction of  $k_{\text{pur}}$  value for  $g = 0.5$  with the growth of the freezing rate can be explained in a simple manner: for this fraction of ice the increase in the freezing rate is accompanied by an increase in the concentration of phenol molecules “lodged” within dendritic cavities at the solid-melt interface, which results in the reduction of the purification coefficient. The increase in  $k_{\text{pur}}$  with the growth freezing rate at  $g = 0.2$  represents an unexpected, at first sight, result. Nevertheless, within the framework of the concept on the presence of two factors determining  $k_{\text{pur}}$  this fact is also easily explained:

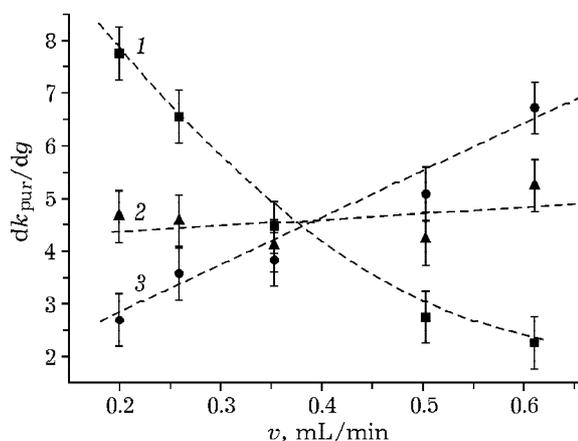


Fig. 6. Dependence of phenol solution purification coefficient  $k_{\text{pur}}$  on the freezing rate  $v$  for different values of the ice fraction  $g$ : 0.5 (1), 0.31 (2), 0.2 (3).

at low solution freezing rates the formation of ice occurs mainly in the bulk and, hence, the efficiency of sticking the solution onto the surface of ice formed will be high. Accordingly, a prevailing effect on the purification efficiency will be exerted by a “distorting” factor that promotes decreasing the efficiency ( $k_{\text{pur}} \sim 2.5$ ).

With the increase in the freezing rate the probability of ice formation in the bulk decreases, which results in the reduction of the “distorting” factor, thus the efficiency of purification will grow ( $\sim 7.5$ ). Therefore, the  $k_{\text{pur}}$  growth at  $g = 0.2$  with the increase in  $v$  implies that the contribution of the “distorting” factor decreases, whereas the “polluting” factor still does not begin influencing, which allows one to observe an increase in  $k_{\text{pur}}$ . The absence of the  $k_{\text{pur}}$  dependence on  $v$  at  $g = 0.31$ , to all appearance, could be connected with the fact that at this value of  $g$  the total effect of the “distorting” factor decreasing contribution and of the “polluting” factor increasing contribution is equal and does not depend on the freezing rate. The value of  $k_{\text{pur}}$  observed under these conditions is lower than the maximum one since there are both influencing factors those results in the  $k_{\text{pur}}$  value reduction.

It is interesting to note that the dependence of  $k_{\text{pur}}$  on  $v$  (see Fig. 6) within the limits of an experimental error demonstrates an “isobestic” point at  $k_{\text{pur}} \sim 4.2$  and  $v \sim 0.38$  mL/min. The occurrence of an isobestic point can also serve as an argument for the validity of the concept on the presence of two processes influencing in

an opposite manner, those determine both the  $k_{pur}$  on  $v$ , and the  $k_{pur}$  value itself.

Let us consider the dependence of  $k_{pur}$  on  $g$  at  $T = -3.5$  °C (see Fig. 4, a). Contrary to the expectations the maximum value of  $k_{pur}$  for this temperature appeared lower as compared to that for lower temperature values. Indeed, according to the directional crystallization data and theory, the  $k_{pur}$  should grow with the reduction of the freezing rate. Within the framework of the concept on the occurrence of several factors determining the value of  $k_{pur}$ , the following explanation may be proposed for low  $k_{pur}$  values observed.

For  $T = -3.5$  °C and low  $g$  values a significant level of ice formation in the bulk is observed, which results in the reduction of  $k_{pur}$  due to the influence of the “distorting” factor. Thus, under the conditions much more close to “ideal” ones corresponding to the formation of ice without impurities [7, 8], the formation of “dirtier” ice occurs. With the increase in  $g$  the contribution of the “distorting” factor decays (the area of ice interface decreasing), therefore the efficiency of ice purification grows. The value of  $k_{pur}$  is still determined by the “distorting” factor preventing the  $k_{pur}$  from an increase and, hence, preventing ice from exhibiting the properties excluding an isomorphic embedding of impurities into the ice crystal structure [9]. In this connection the use of water recrystallization and incomplete freezing procedure for water purification at  $T = -3.5$  °C (the freezing at freezing front velocity of  $\sim 0.2$  cm/h) at any freezing level is unpractical.

Within the framework of the concept on the presence of three factors determining  $k_{pur}$  value, the maximum of  $k_{pur}$  within the temperature range of  $-6.5 \dots -10$  °C may be explained in such a way: at  $T < -10$  °C the probability for penetrating an impurity into intradendritic space is high because of a high velocity of freezing front movement (the “polluting” factor), whereas at  $T > -10$  °C under the conditions of loose ice formation a high degree of sticking onto ice is observed for the liquid solution with high concentration of impurities (the “distorting” factor). Thus, at the temperature at about  $-10$  °C the total effect of both factors on  $k_{pur}$  value is minimal, which represents an explanation of the maximum  $k_{pur}$  value for

aqueous solutions of phenol. The temperature, at which the maximum  $k_{pur}$  values are observed, to all appearance, could depend on the volume of a sample under freezing (at the same freezing rate values).

The maximum value of  $k_{pur}$  for the temperature of  $-20$  and  $-25$  °C at  $g \sim 0.2$  within the framework of the concept on a number of factors determining  $k_{pur}$  value might be explained as it follows. At  $g < 0.1$ , as mentioned above (see Fig. 4, e, g), the formation of wet ice occurs, which results in a high level of sticking and, correspondingly, in low  $k_{pur}$  values (a considerable influence of the “distorting” factor). At  $g > 0.15$  the contribution of the “distorting” factor for these temperature values rapidly decreases, and at  $g \sim 0.2$  a situation arises when the contribution of the “distorting” factor is already low, whereas the contribution of the “polluting” factor is still low, *i.e.* a minimal contribution of both pollution mechanisms takes place, which allows obtaining rather high  $k_{pur}$  values.

## CONCLUSION

Thus, in order to obtain water purified as much as possible from aqueous solutions of phenol using the method of freezing and subsequent non-frozen phase separation it is necessary to carry out freezing at the crystallizing front velocity amounting to  $\sim 0.2$  cm/h up to obtaining the ice fraction  $g \sim 0.5$ .

We have also carried out the experiments on purifying aqueous solutions by the freezing method from some organic substances (humic acids, pyrene derivative molecules, eosin), as well as the experiments on additional purification of tap water from organic substances. For all the mentioned solutions the results obtained have confirmed the conclusion concerning optimum conditions determined for water treatment drawn with respect to water purification from phenol ( $T \sim -10$  °C,  $g \sim 0.5$ ).

So, the obtained dependences of water purification efficiency on the freezing fraction and rate are consistently explained within the framework of the concept concerning the presence of “polluting” and “distorting” factors. These factors always take place in the process of wa-

ter recrystallization when the incomplete freezing method is applied under “non-ideal” conditions, and prevent obtaining the  $k_{\text{pur}}$  values expected in the case of the only “purifying” factor taking place.

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