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Studies on the Efficiency of Water Purification from Metal Sulphates by Incomplete Freezing Method

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Abstract

Using a freezing-unfreezing procedure, an efficiency parameter k_{pur} for water purification from metal sulphates ($MnSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ и $VSO_4 \cdot 5H_2O$) has been investigated depending on the fraction of frozen aqueous solution *(g)* and on the temperature of freezing (*T*). The following kinds of relationships have been revealed: 1) a monotone k_{pur} decrease; 2) a monotone k_{pur} increase 3) k_{pur} growth with the increase in the fraction of frozen aqueous solution up to $g > 0.3–0.4$ and the subsequent decrease at $g > 0.4$ (non-monotone dependence). The influence of the factors those prevent obtaining high values of k_{pur} is under discussion. They include the impossibility to separate ice from liquid solution drops with impurities located on the ice surface due to the sampling technique (adhesion-caused factor) and freezing-in the impurities within interdendritic cavities at the solid-melt interface (dendrite-caused factor).

Key words: water purification, freezing–unfreezing procedure, absorption spectra, aqueous solutions of metal sulphates

INTRODUCTION

The efficiency of employing the method of incomplete freezing and the subsequent water unfreezing in order to obtain purified potable water, as well as the problems connected with its use, were reported in [1–3]. Earlier we have demonstrated that the efficiency of water purification with the use of the incomplete freezing method is negatively influenced to a considerable extent by the two factors such as an adhesion-caused ("distorting") and a dendrite-caused ("polluting") one [2]. In order to obtain water purified to a maximum extent one should know optimum conditions which will determine the character of relationship between the water purification level, the freezing rate and the fraction of ice under forming. However, such information, as a rule, is not available from the literature. So, the efficiency of water purification from inorganic impurities was only sporadically reported in the literature [4, 5]. The authors of these works have established that at the freezing temperature equal to −17 °C and at the volume of aqueous solutions samples ranging within 0.3–0.5 L the efficiency of purifying aqueous solutions from such salts as NaCl, $CaCO_3$ and from trace inorganic impurities in industrial water under performing one freezing–unfreezing cycle amounts to 30–40 %. However, there are no data concerning the relationship between the efficiency of water purification and the values of freezing temperature and freezing level presented in the mentioned papers.

The present work is devoted to the studies on the efficiency of water purification from a number of model pollutants (vanadium, cop-

per, manganese and iron sulphates) employing the freezing–unfreezing method depending on ice fraction and temperature. The choice of metal sulphates as a subject of inquiry is caused by the fact that metal sulphates represent one kind of widely known inorganic pollutants occurring in natural and potable water. So, the sanitary-and-epidemiologic regulations and specifications [6] indicates a wide spread occurrence of these compounds, their hazardous properties as well as the necessity for taking into account the regulations concerning their concentration in potable water.

EXPERIMENTAL

For the experiments we used chemically pure grade metal sulphates such as $MnSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ и $VSO_4 \cdot 5H_2O$ with no additional purification. Aqueous solutions were prepared using distilled water. The concentration of metal salts amounted to $(1–2) \cdot 10^{-4}$ mol/L.

As a freezer we used Biryusa refrigerating chamber additionally equipped with an electronic processor that allowed controlling the temperature of freezing in the chamber compartments within the range from −2 to −30 °C to an accuracy within ±0.5 °C. The initial temperature of solutions under freezing was varied within the range of 8–24 °C. The freezing of samples was carried out using polyethylene beakers of cylindrical shape; the volume of solutions under investigation was 130–135 mL, sample height in the glass being approximately equal to 7 cm. Six samples of one metal sulphate aqueous solutions were simultaneously placed into the refrigerating chamber (the beginning of solutions freezing) at each temperature value. In order to determine the 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 volume of the liquid was determined to an accuracy of ±0.5 mL. The difference between the volumes of initial and non-frozen solution (V_{ini} 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

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

The value of freezing rate v (expressed in mL/min) was determined from the kinetics of ice formation for each temperature. The velocity of freezing front movement V (expressed in cm/h) was estimated basing on the assumption that the initial bulk under freezing represents a ball with the volume W_0 = 135 mL and radius r_0 = 3.23 cm, which being frozen up to g = 0.5 after passing the freezing time $t_{g = 0.5}$ is transformed into the ball of 67.5 mL in volume with the radius $r_{g = 0.5}$ = 2.56 cm. Thus, the velocity of freezing front movement was determined as

$$V = (3.23 - 2.56)/t_{g = 0.5} = 0.67/t_{g = 0.5} \quad (2)$$

Absorption spectra for the aqueous solutions of sulphates were registered using a Hewlett-Packard spectrophotometer; they demonstrated the absorption intensity which monotonously decreases within the range of 200–800 nm. A standard 1 cm thick optical cell was used. The concentration of the salt was determined from the optical density (absorbance) value at the wavelength λ = 210 nm. The choice of λ = 210 nm was caused by the fact that this wavelength provides the range of measured absorbance values to vary within 0.05–1, which at an especially measured spectrometer accuracy level equal to $\pm 5 \cdot 10^{-4}$ allows one to register reliably the changes in metal salt concentration. The temperature of spectra registration amounted to (22±2) °C.

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

$$k_{pur} = OD_{ini}/OD_{ice} = C_{ini}/C_{ice} \quad (3)$$

where OD_{ini} are OD_{ice} are optical density (absorbance) values at the wavelength of 210 nm for the initial aqueous solution of metal sulphates and for the solution after unfreezing the ice, respectively; C_{ini} and C_{ice} are the concentrations of the initial sulphate solution and of the solution after unfreezing the ice, respectively.

It should be emphasized that in the case of such a way to determine water purification efficiency (the integral over time) the increase in k_{pur} with an increase in fraction of non-frozen water implies the reduction of impurity concentration in the ice formed, and *vice versa.*

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

RESULTS AND DISCUSSION

In all the experiments the temperature of the solution under freezing prior to the beginning of crystallization (the formation of ice) amounted to −1.5...−2 °C and then (at the moment of crystallization beginning) increased abruptly up to 0.5−1 °C.

At the freezing temperature values of −3.5 and −6.5 °C the aqueous solutions of $MnSO_4 \cdot 5H_2O$ and $FeSO_4 \cdot 7H_2O$ demonstrated a distinct formation of ice not only at the walls of a beaker, but also in the bulk of the solution. The ice formed after pouring water off represented a loose stuff with a great amount of non-frozen solution which could not be separated from ice (being visually similar to cotton wool staying within water). Further such a state of water-ice stuff will be referred to as "wet ice". This effect is especially pronounced at T =−3.5 °C (at −6.5 °C there is a lower amount of wet ice observed). The presence of ice all over the sample under freezing indicates that there are crystallization centres present not only at the walls of a beaker, but also in the bulk.

Figure 1 demonstrates kinetic curves of ice formation in aqueous solutions of metal sulphates for different temperature values. One can see that quite satisfactory linear functional dependences are inherent in all the solutions.

Figure 2 displays OD values experimentally observed for unfrozen and non-frozen metal sulphate solutions depending on the fraction of ice at different temperatures. It should be noted that with the procedure of freezing-

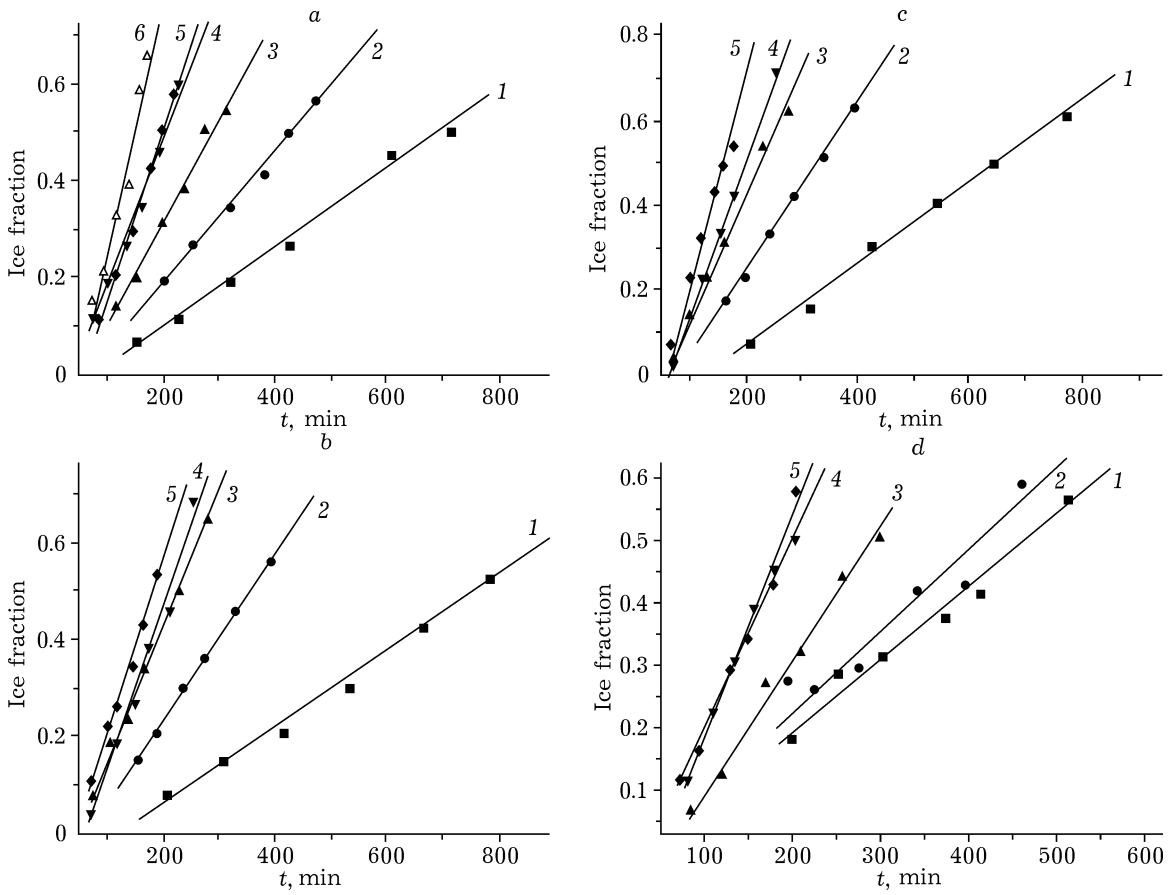

Fig. 1. Ice fraction (g) depending on freezing time for the solutions of metal sulphates $MnSO_4 \cdot 5H_2O$ (a), $CuSO_4 \cdot 5H_2O$ (b), $VSO_4 \cdot 5H_2O$ (c), $FeSO_4 \cdot 7H_2O$ (d) at different temperature values, °C: a: −3.5 (*1*), −6.5 (*2*), −10 (*3*), −15 (*4*), −20 (*5*), −25 (*6*); b–d: −3.5 (*1*), −10 (*2*), −15 (*3*), −20 (*4*), −25 (*5*).

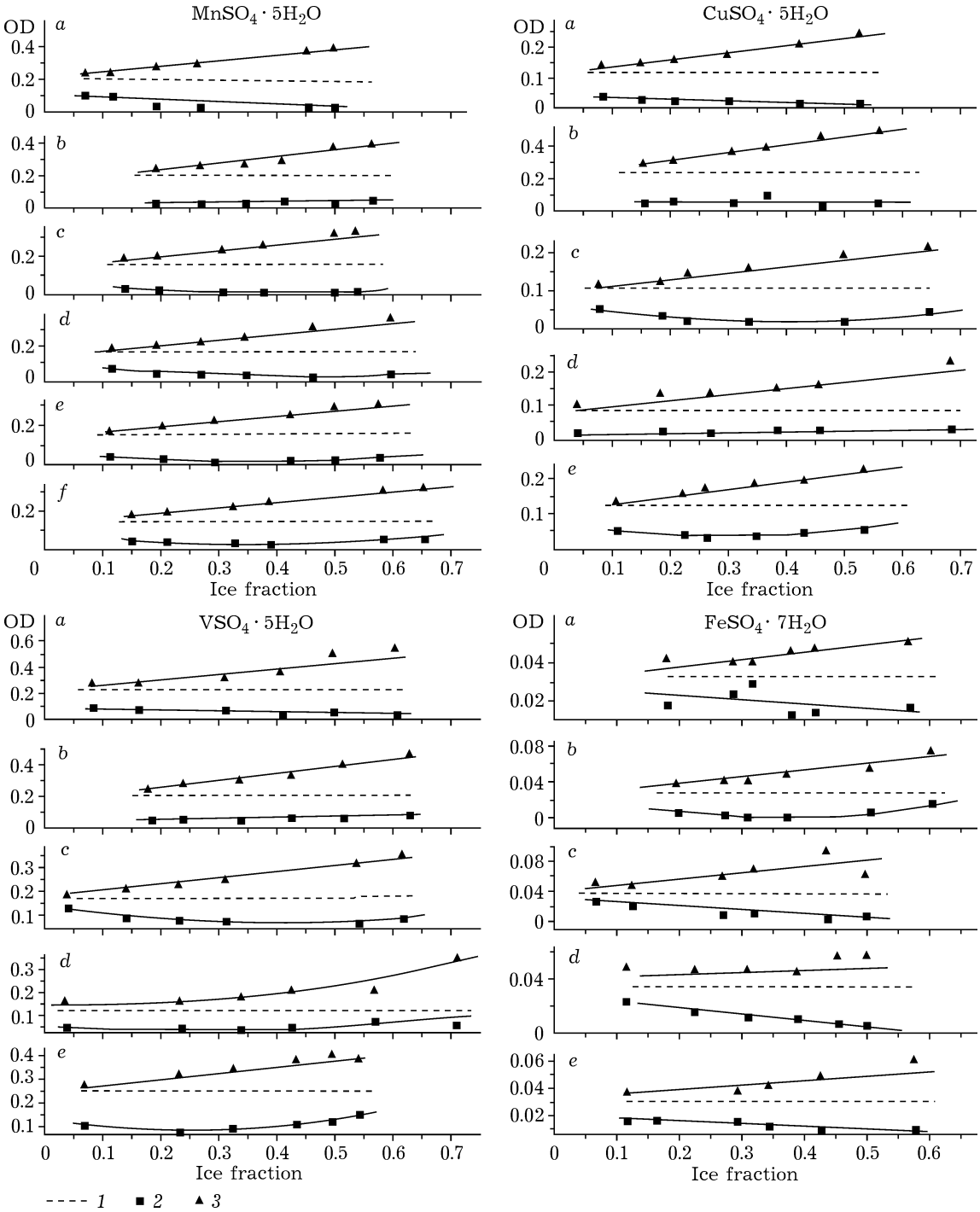

Fig. 2. Values of optical density (OD) for aqueous solutions of metal sulphates depending on the ice fraction (*g*) for different temperature values: *1* – initial solutions, *2* – after ice thawing, *3* – non-frozen solutions. Here and in Fig. 3:

Curves	*T*, °C			
	$MnSO_4 \cdot 5H_2O$	$CuSO_4 \cdot 5H_2O$	$VSO_4 \cdot 5H_2O$	$FeSO_4 \cdot 7H_2O$
a	−3.5	−3.5	−3.5	−3.5
b	−6.5	−10	−10	−10
c	−10	−15	−15	−15
d	−15	−20	−20	−20
e	−20	−25	−25	−25
f	−25	–	–	–

unfreezing carrying out the shape of absorption spectra did not change. It is seen that for all the temperature values at $g = 0.5$ there is an equality of changes in OD values within ±10 % error observed for non-frozen and frozen solutions ($OD_{n/f}$ and $OD_{ice,}$ respectively), *i. e.* $OD_{n/f} - OD_{ini} \approx OD_{ini} - OD_{ice}$. This fact means that the reduction of the salt concentration in the ingot of ice against the salt concentration in the initial solution corresponds to an increase in the salt concentration in the frozen solution against its concentration in the initial solution. Thus, the balance of conservation of matter is obeyed by the process of freez-

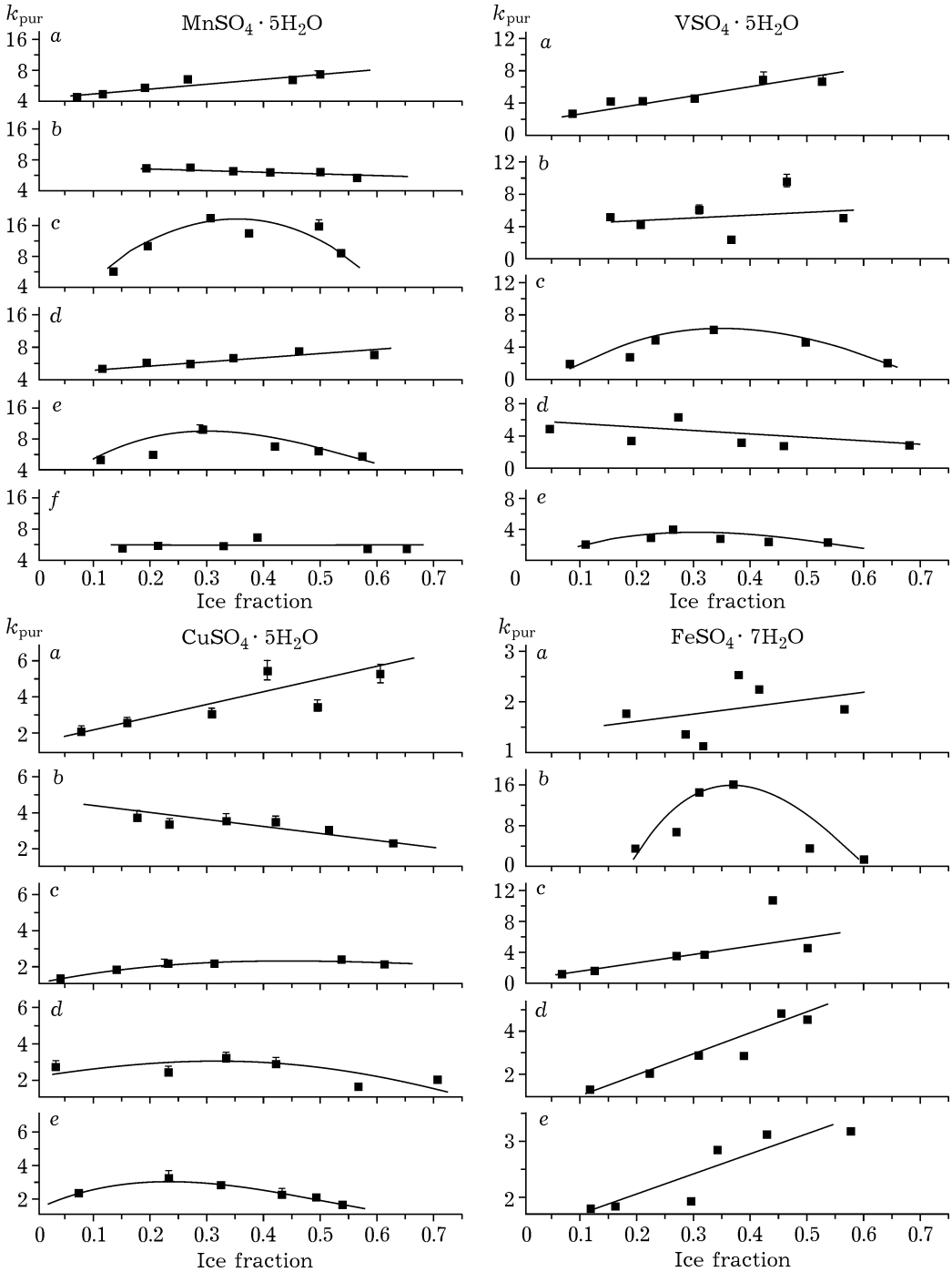

Fig. 3. Purification factor (k_{pur}) values for aqueous solutions of metal sulphates depending on the ice fraction (g). For designations see Fig. 2.

ing. Also for all the sulphates at any temperatures there is an $OD_{n/f}$ growth observed with the increase in the fraction g of frozen water, which means that there is enrichment of the non-frozen phase by metal sulphates.

Figure 3 displays the value of k_{pur} depending on g for different temperature values. One can see that the entire data set could be conditionally divided into three groups. The first group typically exhibits k_{pur} reduction at all the values g: $VSO_4 \cdot 5H_2O$ (−3.5 °C), $CuSO_4 \cdot 5H_2O$ (−3.5, −10 °C), $MnSO_4 \cdot 5H_2O$ (−3.5 °C), $FeSO_4 \cdot 7H_2O$ (−6.5, −15, −20, −25 °C); the second group differs in the k_{pur} increasing at all the values of g: $VSO_4 \cdot 5H_2O$ (−10 °C), $CuSO_4 \cdot 5H_2O$ (−20 °C), $MnSO_4 \cdot 5H_2O$ (−6.5 °C); the third group at first demonstrates an increase in the k_{pur} with growing the fraction of frozen water up to $g \approx 0.3-0.4$, and then there is a subsequent reduction of k_{pur} observed: $VSO_4 \cdot 5H_2O$ (T = = −15, −20, −25 °C), $CuSO_4 \cdot 5H_2O$ (−15, −25 °C), $MnSO_4 \cdot 5H_2O$ (−10, −20, −15, −25 °C), $FeSO_4 \cdot 7H_2O$ (−10 °C). Thus, a non-monotone relationship between k_{pur} and g is inherent in a considerable part of the samples under investigation. In addition, the majority of samples demonstrate (9 relationships from 12 ones) at $g > 0.4$ and $T > -5$ °C the reduction of k_{pur}; with the increase in g at $T = -3.5$ °C the value of k_{pur} exhibits an increase (three relationships from three ones). The data obtained allow us to conclude that at the freezing temperatures $T = -15$ °C the concentration of salts in frozen water increases with growing the ice fraction, *i. e.* the ice becomes more polluted. On the contrary, at $T = -3.5$ °C the increase in the ice fraction results in a decrease in the concentration all the salts, *i. e.* the ice becomes more pure.

The conditions of carrying out our experiments (freezing without stirring) were those that even the most minimal velocity of freezing front movement (V ~ 0.1 cm/h at −3.5 °C) was higher than the freezing front movement velocity (V = 0.05 cm/h [7, 8]) corresponding to the value for ideal ice formed with no impurities and no dendrites. Under the conditions of our experiment the formation of dendrites took place, therefore the effect of growing the impurities concentration in ice with growing g would be always observed, since the concentration of impurities at the solid-melt interface increases with the increase in g and, accordingly, the probability of entering the impurities into interdendritic cavities grows. From the physical standpoint, the hitting of impurities into dendritic cavities could be connected with the fact that the diffusion rate for an impurity molecule at the freezing front of an overcooled liquid is low as compared to the velocity of freezing front movement [3, 9]. As a result, the solution with a higher impurity concentration in comparison with ice would enter into interdendritic space, in which connection the concentration of salts in the thaw water after freezing and unfreezing would be high (the dendrite-caused, or, in other words, the polluting factor in the procedure of water purification through recrystallization). Earlier this effect was experimentally observed for the processes of directional crystallization [3]. Under the conditions of our experiment (at least, during the freezing front movement from the wall to the centre) similar processes of ice dendrite formation could take place, too, which would result in entering an impurity into the interdendritic space at the solid-melt interface. Nevertheless, the extrusion of an impurity from the structure of ice (the recrystallization factor in the procedure of water recrystallyzing) is always inevitable, since only the molecules of Ar and NH_4F could be isomorphically incorporated into ice under water freezing [10]. Thus, a true functional dependence between k_{pur} and g, representing a joint influence of the recrystallization and dendrite-caused factors, should be presented by a monotone decreasing function: there should be a maximal k_{pur} value at low values of g and the subsequent k_{pur} reduction with the increase in g.

However, as it was already mentioned earlier, the feature of ice sampling with employing the method of incomplete freezing to measure the concentration of impurities in thaw water does not allow one to obtain true relationship between k_{pur} and g. It is connected with the fact that the amount of impurities is determined analyzing ice with an additional amount of impurities rather than pure ice. These additional impurities are contained in the drops of non-frozen solution located surface on the surface of ice, and it is rather problematic to separate them or to determine the concentration. The concentration of impurities in

the drops of non-frozen solution is higher than the concentration of impurities in the ice formed, and finally this fact would result in a somewhat higher experimentally observed concentration of impurities as compared to a true impurity concentration in ice. Thus, the true concentration of impurities is veiled by the effect of adhesion of non-frozen solution drops due to the way of sampling chosen (the adhesion-caused factor). The effects connected with the adhesion-caused factor, i.e. with the adhesion of the drops of an impurity at the surface of ice and microcracks therein (not within interdendritic space!) under incomplete freezing, are well-known and could be considered among basic disadvantages of both estimation, and proper the efficiency of purifying substances with this method. Thus, the adhesion-caused factor always takes place under the conditions of our experiments concerning the measurement of concentration of impurities in ice, whereas the influence of this factor upon the k_{pur} value would decay with the reduction of the solid-melt interface (the freezing front surface), *i. e.* with the increase in the ice fraction.

Thus, the observable efficiency of impurity capturing within ice is determined by joint influence of adhesion-caused, recrystallization and dendrite-caused factors. At low g values the value of k_{pur} could be low due to a prevailing contribution of the adhesion-caused factor, whereas at high g values this fact could be connected with the prevailing contribution of the dendrite-caused factor to the purification process, *i. e.* the k_{pur} dependence on g might be of non-monotone nature. In the case of prevailing influence of the dendrite-caused or adhesion-caused factors the type of k_{pur} dependence on g can be either monotone increasing or monotone decreasing function, respectively. Both factors are of the stochastic nature: concentration and temperature fluctuations are inherent in dendrite-caused factor, whereas the adhesion-caused factor is connected with the fluctuations of the amount of microcracks formed and, accordingly, of ice surface area whereon the solution drops with impurities [11] could be located.

It follows from the results of our work that the maximal values of k_{pur} for aqueous solutions of different metal sulphates are different (Fig. 4). It should be noted that with the

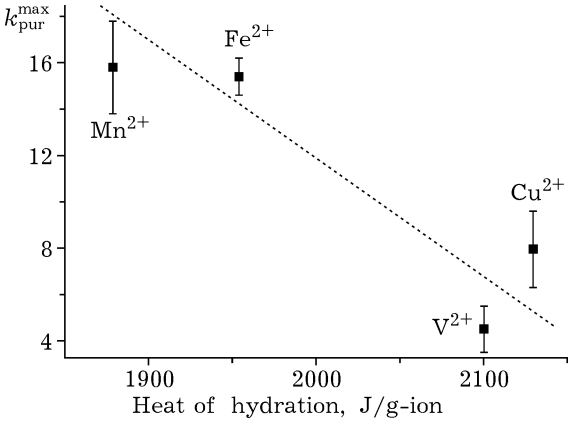

Fig. 4. Maximal values of k_{pur} depending on the heat of hydration for ions.

increase in the heat of hydration for metal ions (ΔH) [11] the efficiency of water purification exhibits a decrease (the values of k_{pur} are reduced). At present time this functional dependence is difficult to explain due to the fact that there are no data available concerning heat of hydration, entropy and free energy of adsorption for metal ions on the surface of ice.

CONCLUSION

Within the framework of the concepts presented the data concerning the k_{pur} value dependence on g could be interpreted as it follows. When non-monotone k_{pur} dependences on g are observed, at low values of g the value of k_{pur} is moderate due to prevailing the contribution of the adhesion-caused factor to the concentration of impurities in thawed ice, whereas at high g values the value of k_{pur} decreases owing to prevailing the contribution of the dendrite-caused factor to the concentration of impurities in ice. The monotone increase or monotone decrease in the k_{pur} value with the increase in the ice fraction reflects various parts of non-monotone function. In the case of increasing k_{pur} with growing g the physical conditions are corresponding to the initial part of a non-monotone k_{pur} dependence on g (the main influence of the adhesion-caused factor only), whereas in the case of k_{pur} reduction with the growth of g the physical conditions are corresponding to the part a non-monotone dependence at high g values (the main influence of the dendrite-caused factor only).

The data obtained allow us to conclude that the type of the relationships observed between the efficiency of water purification, the ice fraction and the freezing temperature value is determined by stochastic processes accompanying the process of freezing. Hence, the k_{pur} value could be to a considerable extent determined by the entry conditions of freezing. Nevertheless, all the set of k_{pur} relationships with respect to g and T parameters could be consistently explained within the framework of a unified concept of the occurrence of the three factors taking place during water purification by the method of incomplete freezing.

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