

About the Possibility of Water Purification from Dissolved Organic Admixtures by Means of Freezing

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(Received December 16, 2002; in revised form June 3, 2003)

Abstract

The efficiency of freezing-unfreezing procedure for purification of tap water about 200 ml in volume from soluble organic admixtures at a temperature of $-17\text{ }^{\circ}\text{C}$ is investigated experimentally. It is shown that the extent of removal of the organic admixtures under the indicated conditions is 0.3.

INTRODUCTION

The present investigation is a continuation of the works [1, 2] in which the efficiency of freezing procedure for water purification from insoluble and soluble inorganic admixtures was studied under the conditions recommended for obtaining melted water: volume to be frozen, $\sim 0.5\text{ l}$; temperature, $-17\text{ }^{\circ}\text{C}$. It was demonstrated in these works that under the indicated conditions a single application of the freezing procedure is ineffective for water purification.

The goal of the present work is quantitative investigation of the efficiency of freezing procedure for purification of tap water from the dissolved organic impurities. The essence of experiments (on absorption and fluorescence) was to compare the concentrations of impurities in the initial and melted water. Efficiency of water purification from the soluble organic impurities by means of freezing under the above-indicated conditions was reported only in [3] describing the studies of the efficiency of this procedure for water purification from aldehydes.

The mechanism of water purification from soluble organic admixtures by means of freez-

ing (preparing melted water) is as follows: when freezing water, at first ice is formed in most cool places; the ice displaces admixture molecules into the space occupied by the liquid (non-frozen) phase. Since cooling proceeds from the periphery of the volume to be frozen, an admixture dissolved in the liquid phase gets collected in the centre. Further, two procedures are used to obtain melted water: either complete freezing or incomplete one is carried out. In the latter case, non-frozen water with admixtures which is in the centre of the volume is poured out; when complete freezing is used, the central part of the frozen volume is removed by melting. The remaining ice melts; the resulting water is considered to be purer than the initial one.

One can easily see that the proposed water purification procedure is in fact a version of the directed crystallization procedure [4]. A difference from the generally accepted procedure is the direction of crystallization front movement. For directed crystallization, consolidation occurs only in one direction (for instance, along a lengthy cylinder), while during freezing in usual vessels it occurs simultaneously in

several directions (top-down, bottom-up, from sides to centre). It should be noted that under ideal freezing conditions, when it is possible to grow single crystals of ice, water purification degree can be close to 100 %, since only He and NH_4F molecules can get built into the ice structure without distorting it [5].

EXPERIMENTAL

The samples of tap water were taken from the city waterpipe of the upper region of Akademgorodok (Novosibirsk). The amount of residues of the dissolved organic substances in the samples of the initial and melted tap water was determined on the basis of the intensity of absorption (Specord spectrophotometer) and the intensity of the fluorescence spectrum. The fluorescence spectrum of tap water (to be more exact, of organic impurities which are always present even in twice distilled water [6]) was a broad unstructured band with a maximum at $\lambda = 450$ nm. Luminescence spectra were recorded in standard quartz cells with a volume about 4 cm³. Observation geometry was -90° (Strobe fluorimeter [7]). Degassing of the samples was not carried out.

The efficiency of water purification by freezing was estimated for the purified water with the help of degree (extent) of recovery α and with concentrating coefficient β for non-purified (polluted) water; these values were determined using equations:

$$\alpha_i = 1 - I_i / I_0 \quad (1)$$

$$\beta_i = I_i / I_0 \quad (2)$$

Here I_0 , I_i are the absorption intensities ($\lambda_{\text{obs}} = 240$ nm) or the intensities of fluorescence bands ($\lambda_{\text{obs}} = 450$ nm) for the samples of the initial water and water obtained after melting the ice taken from i place, respectively.

Ice was sampled from different (i) places of the frozen water volume in the experiments with complete freezing by chipping the corresponding parts off the bulk ice lump. The following places of the frozen volume were taken: point I (thickness of chipped layer from the edge up to 1 cm) and point III (chip ± 1 cm from the centre). In experiments

with incomplete freezing, an m place was non-frozen water.

When measuring the kinetics of freezing, water samples with a volume of 150 ml each were placed in 10 polyethylene beakers and cooled in freezer compartment at -17°C for 100 min. After that, the samples were taken out from time to time with an interval of 20 min, and the volume of non-frozen water was measured. The fluorescence spectra of non-frozen water and water melted from ice were recorded after ~ 1 h after unfreezing the last sample.

RESULTS AND DISCUSSION

General observation. Absorption and fluorescence spectra of the initial water and the spectra of water obtained after unfreezing the ice which was prepared from completely frozen volume of the initial water did not differ from each other. This means that: 1) freezing procedure does not distort the structure of absorption centres and fluorophores; 2) concentration of impurities is not changed during freezing – unfreezing the same volume.

Absorption (complete freezing). The absorption spectrum, which was a monotonously decreasing dependence of the intensity on wavelength, did not change for any water sample, independently of the place of the frozen and then melted sample from which it was taken. Only the intensity of absorption changed depending on sample (in proportion for all wavelengths). The absorption intensity of the sample taken from point III was substantially higher than the absorption intensity of the initial sample. In turn, the absorption intensity of the initial sample was higher than the absorption intensity of water sample taken from point I. The results mean that impurity concentration is lower in places where freezing occurs earlier (edge) and higher in places where freezing occurs later (centre). Quantitatively, recovery coefficient is $\alpha_I = 0.3 \pm 0.075$ and concentrating coefficient is $\beta_{\text{III}} = 1.3 \pm 0.05$. This result agrees qualitatively with the generally accepted knowledge about the efficiency of water purification with the help of freezing. However, the effect of water purification from impuri-

ties is not large quantitatively (recovery coefficient is 0.3).

Fluorescence (complete freezing). The shape of contours of fluorescence spectra of the samples of initial and melted tap water from the ice samples taken from different places of the completely frozen volume was unchanged. Only the intensity of these spectra changed. The intensity of luminescence of the organic impurities from the volume frozen at first (point I) is lower than their intensity in the initial sample ($\alpha_I = 0.25 \pm 0.05$). *Vice versa*, the intensity of fluorescence of the samples of melted water obtained from the ice of point III is higher than that in the initial sample ($\beta_{III} = 1.3 \pm 0.05$). One can see in the data presented that the results of luminescence and absorption experiments coincide within experimental error.

Incomplete freezing (~50 %). For point I, the recovery degree is $\alpha_I = 0.30 \pm 0.05$, while for non-frozen volume (point III) concentrating coefficient is $\beta_{III} = 1.25 \pm 0.04$. So, the results of determination of water purification coefficients for complete and incomplete freezing procedures exhibited good agreement, both qualitatively and quantitatively. This was to be expected, since these procedures do not principally differ from each other.

The dependencies of impurity recovery degree α and concentrating coefficient β on freezing time are shown in Fig. 1, a and b. (The presented dependencies depict mean values averaged over the results of 3 series of experiments.) It follows from these data that the amounts of dissolved organic substances in the solid and liquid phases plotted *versus* freezing time have a noticeable scattering. (The dependence of the amount of non-frozen water on time is a linearly decreasing function with an accuracy not worse than 5 %). The presence of scattering is likely to be connected with the random character of adsorption of admixtures in ice, which is in turn due to stochastic spatial shape of water crystallization front [8]. Chance character of the formation of spatial direction of the crystallization front (based on probabilistic processes) provides fluctuations in the surface area of the freezing front for the single crystal of ice being formed, which finally should inevitably affect its adsorption properties. It is the chance character of the formation of the

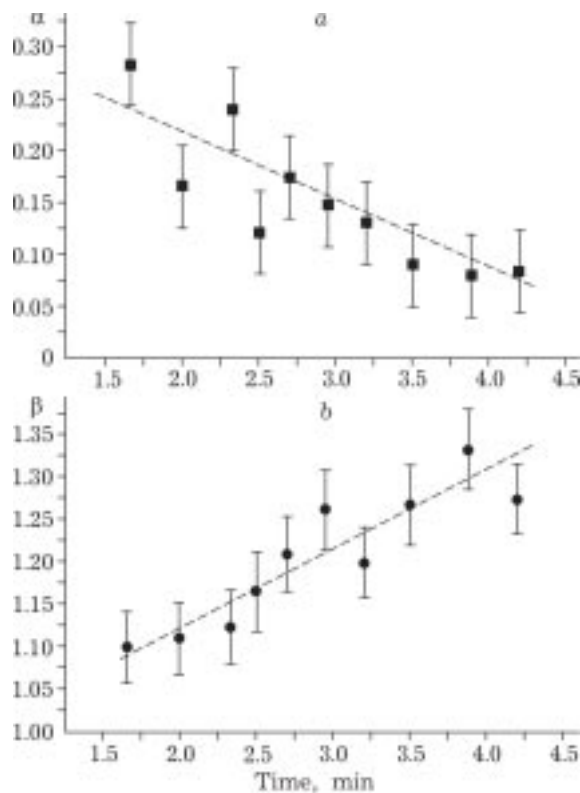


Fig. 1. Dependence of recovery degree α (a) and concentrating coefficient β (b) for tap water on freezing time: a - ice; b - non-frozen water.

spatial shape of crystallization front that provides the presence of cell-dendritic structure [4]. The condition of the formation of dendritic structures (dendrite partitioning) for the case without mixing is as follows:

$$(dT/dx)_{x=0} V^{-0.5} \leq AC_L \quad (3)$$

Here $(dT/dx)_{x=0}$ is the temperature gradient in the liquid to be cooled; V is the rate of movement of crystallization front; C_L is the concentration of impurity near the crystallization front; A is the constant which only slightly depends on the kind of the system. Provided that condition (3) is fulfilled, the molecules of impurities get into the formed cells of inter-dendrite surface and get stuck there, which allows the possibility of random capturing of liquid drops with the admixture. In addition, the impurity can be adsorbed not in the cells of inter-dendrite space but on the surface of solidification front. Thus, the impurity can get frozen into the ice by at least two independent means, so, it is unlikely that the kinetics of changes in the concentration

of admixture in ice and correspondingly in non-frozen water during freezing can be expected to be monotonously smooth.

One can see from the data shown in Fig. 1, *a*, that the recovery degree α decreases with time (while the degree of water freezing increases). In principle, this is right the result to be expected, because purer ice is formed at first during freezing. An increase in coefficient β with time for non-frozen water (see Fig. 1, *b*) means increase of pollution and is explained by an increase in impurity content. This result is also in agreement with the generally accepted opinion that impurities get concentrated in non-frozen part while water freezing proceeds.

Thus, the recovery degree of organic impurities for tap water purification by means of single freezing cycle, according to the results obtained from luminescence and absorption experiments, is 0.25–0.30. We showed previously [1, 2] that the recovery degree is about the same for tap water purification from insoluble and soluble inorganic impurities (CaCO_3). Finally, it was demonstrated in [10] that the recovery degree for NaCl as impurity is also 0.25–0.30. So, independently of the kinds of impurities, the efficiency of water purification is the same. This means that under the conditions recommended in popular and medical publications for obtaining melted water (volume to be frozen: 0.2–0.5 l, temperature: -17°C) the decisive factor is freezing conditions but not a type of intermolecular interaction between the dissolved impurity and ice. This factor is high freezing rate V , which is ~ 0.9 cm/h under the indicated conditions. Indeed, this rate substantially exceeds the rate necessary for obtaining ideal ice: 0.05 cm/h [11]. The latter is likely to correspond to the conditions of equilibrium crystallization under which the diffusion rate of impurity movement V_{dif} (even in the absence of mixing) is higher than V . To the contrary, under the conditions of our experiment, the impurity has no time to get withdrawn diffusively from the crys-

tallization front because the rate of diffusion of the impurity is much lower than the rate of movement of the solidification front ($V_{\text{dif}} \ll V$, diffusion-free region of crystallization).

CONCLUSION

Thus, in order to obtain actually purified water, independently of impurity type, it is necessary to decrease water freezing rate substantially (to increase freezing time). In practice, this means that it is necessary to place volumes over 5 l in freezing chambers at a temperature of about -17°C . Such conditions for obtaining melted water were intuitively used in [12].

Acknowledgements

The author is sincerely grateful to S. I. Shuiskiy for substantial assistance in experiment and to G. G. Malenkov for fruitful discussions.

The investigation was supported by RFBR (Grant No. 01–03–32448) and INTAS (Grant No. 01–0186).

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