EFFECT OF IMPURITIES ON ELASTIC PROPERTIES OF ICE NEAR THE MELTING POINT

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The effect of impurities (Na^+ and Cl^- ions) on the viscoelastic properties of ice is studied in the temperature interval 210–290 K. It is established that the heating of a sample to temperatures by 15–20 K lower than the melting point results in a considerable decrease of its shear modulus. The observed effect is ascribed to premelting processes. It is shown that the presence of Cl^- ions does not change the premelting temperature of ice, whereas the stress field arising around Na^+ ions introduced into ice results in its variation. The dependence of the characteristic premelting temperature T_p on the concentration of Na^+ ions is obtained. The premelting process is related to the appearance of an intermediate structure, whose degree of disorder is lower than that of water, but higher than that of ice. The temperature dependence of the concentration of the intermediate structure for the objects under study is calculated based upon the experimental data.

In our works [1, 2], we studied the temperature dependence of the dynamic shear modulus G' of ice near the melting point and discovered an anomaly in the behavior of G' consisting in the abrupt decrease of its value due to the heating of a sample starting from the temperature $T = 258$ K, which is by 15 K lower than the melting point.

The aim of this study is to investigate the effect of impurities – Na^+ and Cl^- ions on the observed anomaly.

For this purpose, we employed the technique described in detail in [1, 2] for measuring the temperature dependence of the dynamic shear modulus for ice obtained by means of freezing the water solutions of NaCl and HCl. The latter were prepared using distilled water. The freezing was carried out with a rate of $1\ \frac{\mathrm{K}}{\mathrm{min}}$ in the same flexible cylindrical cell with the inner radius $R = 2.5$ mm and the working length $l = 35$ mm which served for measuring the shear modulus in what follows.

Figure 1 shows the experimental temperature dependences of the dynamic modulus $G'(T)$ for ice with impurities obtained by freezing the NaCl and HCl solutions of various concentrations.

According to the literature data, the anomalous behavior of the dynamic shear modulus is observed in the same temperature interval, in which one registers anomalies of other thermodynamic characteristics: heat capacity, coefficient of thermal expansion, and others. All these anomalies are usually ascribed to the premelting process [3], so it is logical to consider that the anomaly of the dynamic shift modulus is caused by the same process.

In [2], it was shown that the premelting process taking place in ice is caused by the formation of some intermediate structure. In the same work, the concentration of this intermediate structure was calculated as a function of the temperature based upon experimental data.

In a similar way, we calculated the temperature dependences of the concentration of the intermediate structure for the NaCl and HCl solutions on the basis of the experimental dependences obtained in this work (Fig. 1). The obtained temperature dependences are presented in Fig. 2.

Since the untimely decrease of the modulus G' under heating is related to the premelting process, it is logical to correlate the beginning of the premelting process with the start of the abrupt decrease of the modulus and to call the temperature T_p, corresponding to the start of this decrease, a premelting temperature.

The premelting temperature of ice versus the concentration of NaCl and HCl impurities in it is given in Fig. 3.

As one can see from Fig. 3, the considered impurities affect the premelting temperature T_p in different ways. The addition of NaCl significantly shifts T_p toward lower

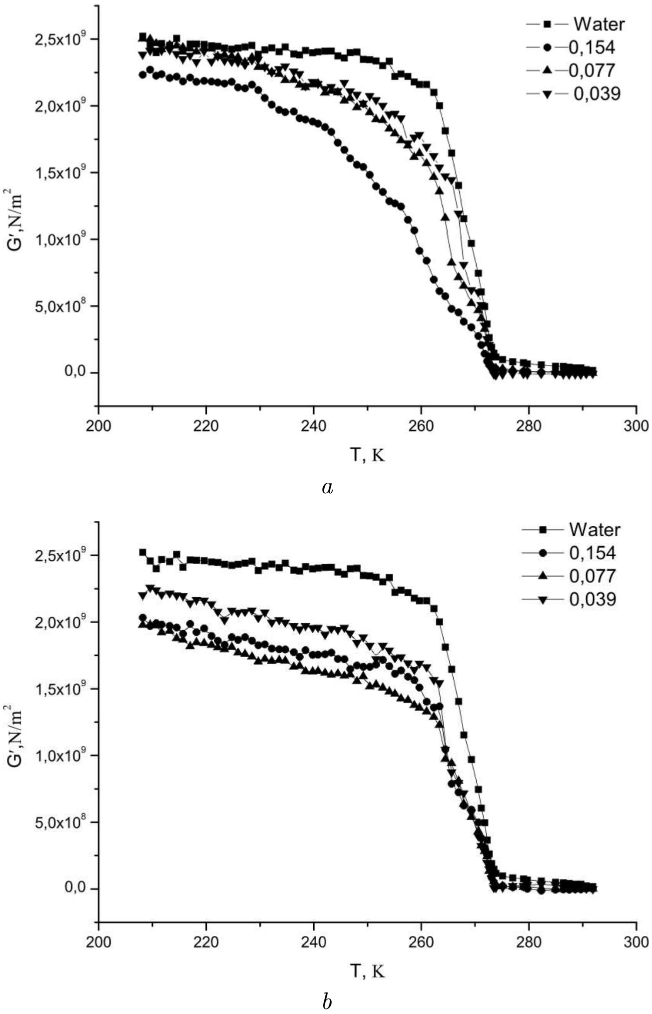

Fig. 1. Temperature dependence of the dynamic shear modulus $G'(T)$ of ice with impurities obtained by freezing NaCl (a) and HCl (b) solutions. (The concentration is measured in units of $m = [\frac{\text{mole}}{\text{kg}}]$)

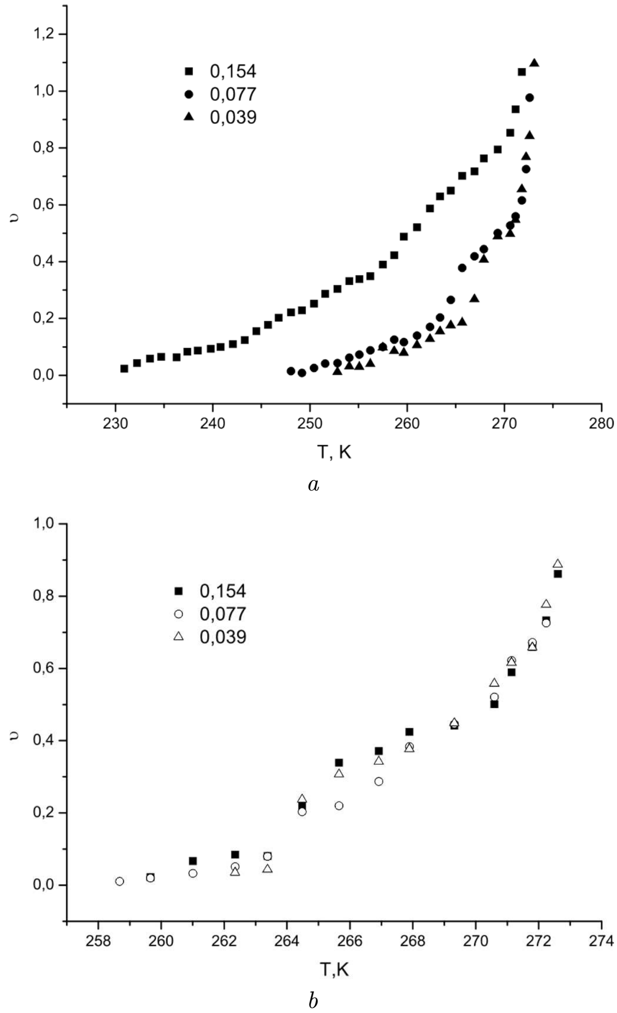

Fig. 2. Temperature dependence of the volume concentration υ of the intermediate structure in ice with NaCl (a) and HCl (b) impurities. (The concentration is measured in units of $m = [\frac{\text{mole}}{\text{kg}}]$)

temperatures, whereas the introduction of HCl practically does not change its position on the temperature scale. Let us analyze this experimental fact.

Strictly speaking, in order to solidly understand the mechanism of the effect of impurities on the premelting process, one needs to know the specific construction of the intermediate structure, whose formation accompanies this process. Unfortunately, there is no unanimous opinion about it in the literature. For today, the only thing one can state with confidence is that the degree of order of this structure is lower than that of ice and higher than that of water.

An increase of the disorder of a crystal is usually related to the appearance of defects in its lattice [5]. That is why one can state that, at $T > T_p$, a lot of some defects arise in ice (without so far specifying their nature). If it is true, then one can conclude, based upon the revealed experimental fact, that NaCl has an influence on the formation of these defects and HCl practically has not.

In [4], it was established that HCl molecules can incorporate into the ice lattice without significantly deforming it. This means that, locating in ice, these molecules practically do not create fields of additional stresses around them, as they do not induce lattice deformations. Thus, on the one hand, HCl molecules create no fields of additional stresses and, on the other hand, the addition of HCl does not influence the formation of defects characteristic of the intermediate structure. These two facts result in the following conclusion: the effect of impurities on the formation of defects inherent in the intermediate structure is realized through the stress field existing around these impurities.

We can state now that there exists a field of additional stresses around a Na^+ ion located in ice. Using the terminology of the continual defect theory [5], this ion can be considered as a deformation center – a set of three normal double forces (double force is two forces of equal magnitudes and opposite signs).

As is known [6, 7], it is impossible to introduce the considered ion into the lattice: it is located in intercrystalline layers of the polycrystal. Thus, after the appearance of Na^+ ions, the crystallite becomes surrounded with deformation centers that create fields of local stresses. The arising field of macroscopic stresses represents a sum of local stress fields from each deformation center.

Let is denote the total macroscopic stress arising in the crystallite due to the presence of deformation centers (Na^+ ions) by p and the minimum stress initiating the formation of defects in the crystallite – by p_c. Since a defect actually represents a region of finite length, we consider the formation of a defect region identifying it with the above-mentioned intermediate structure.

In the neighborhood of the melting temperature, the thermal expansion results in a considerable deformation of the system as compared to its crystalline state. As a result, there arise stresses in the system. Due to this fact, it is logical to consider that the premelting temperature is the temperature, at which these stresses result in the formation of defect regions, i.e. the critical magnitude of the indicated stresses is reached exactly at this temperature.

We will estimate the value of this stress, by using the obtained experimental data.

Let is introduce the notations T_p and T_{p_0} for the premelting temperatures of ice with impurities and without them. Denoting the volume deformation of the thermal expansion corresponding to the premelting temperature by θ, we obtain

$$\theta = \int\limits_0^{T_{p_0}} \alpha(T)dT, \qquad (1)$$

$$\theta_i = \int\limits_0^{T_p} \alpha(T)dT, \qquad (2)$$

where α is the thermal expansion coefficient.

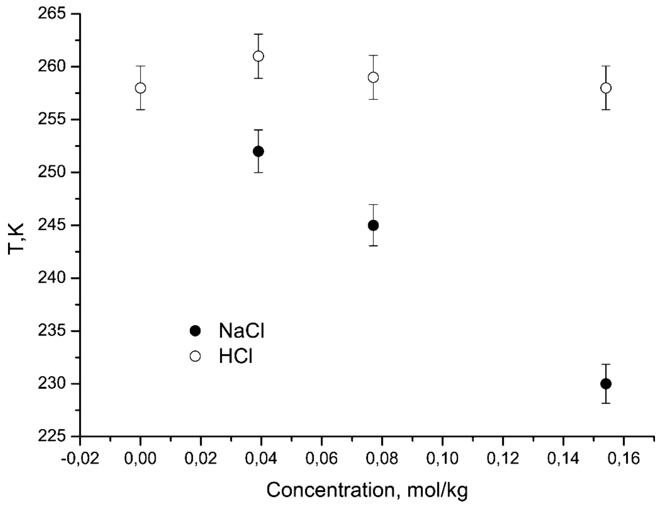

Fig. 3. Premelting temperature T_p versus the NaCl and HCl concentrations. (The concentration is measured in units of $m = [\frac{\text{mole}}{\text{kg}}]$)

We suppose that a decrease of the premelting temperature due to the introduction of impurities is caused by the appearance of additional stresses p. The same way as in the absence of impurities, the deformation initiating the defect formation must be equal to θ. But, in the presence of impurities, only a part of this deformation, namely θ_i, is provided by the thermal expansion. The rest of it $(\theta - \theta_i)$ is created by the additional stress p. So we obtain

$$p = K(\theta - \theta_i), \qquad (3)$$

where K is the volume modulus of elasticity.

Substituting relations (1) and (2) into formula (3), we get

$$p = K\left(\int\limits_0^{T_{p_0}} \alpha(T)dT - \int\limits_0^{T_p} \alpha(T)dT\right). \qquad (4)$$

Expanding the right term of relation (4) into a series in $(T_{p_0} - T_p)$, we obtain the approximate formula

$$p = K\alpha(T_p)(T_{p_0} - T_p). \qquad (5)$$

The volume modulus of elasticity depends on the temperature. That is why there arises the question, which its value should be substituted into formula (5). Generally speaking, expression (3) is a result of the expansion in $(\theta - \theta_i)$. Since expansion (5) is performed with the use of the thermal expansion coefficient $\alpha(T_p)$ for the

Stresses p for various concentrations m

Concentration, $m = [\frac{\text{mole}}{\text{kg}}]$	Stress, $10^7 \frac{\text{N}}{\text{m}^2}$
0.154	2.17
0.077	1.05
0.039	0.5

temperature T_p, it is logical to use the volume modulus for the same temperature $K = K(T_p)$.

Using the well-known (see for example [8]) relation between the volume modulus and the shear modulus

$$K = G\frac{2(1+\mu)}{3(1-2\mu)}, \quad (6)$$

where μ is the Poisson's ratio, we obtain

$$p = G(T_p)\frac{2(1+\mu)}{3(1-2\mu)}\alpha(T_p)(T_{p_0} - T_p). \quad (7)$$

Substituting the values of $G(T_p)$ and $(T_{p_0} - T_p)$ from Fig. 1, the values of $\alpha(T_p)$ taken from the literature [9, 10], and $\mu = 0.34$ into formula (7), we obtain the values of the stress p presented in Table.

The ice melting is preceded by the premelting process taking place in the temperature interval $T_p < T < T_m$. In the course of this process, some intermediate structure that represents an assembly of defect regions is formed. Such regions arise if the deformation exceeds some critical value θ_c.

In the absence of impurities, this deformation is reached due to the thermal expansion at the temperature T_{p_0}. After the introduction of Na^+ ions into ice, a field of additional stresses around them is formed. Due to this fact, the critical deformation is reached at the smaller thermal expansion and, therefore, the lower temperature T_p. Since such a field of additional stresses does not arise around Cl^- ions, their introduction does not influence the premelting temperature T_p.

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ВПЛИВ ДОМІШОК НА ПРУЖНІ ВЛАСТИВОСТІ ЛЬОДУ В ОКОЛІ ТОЧКИ ПЛАВЛЕННЯ

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Р е з ю м е

В інтервалі температур 210–290 К досліджено вплив домішок (іонів Na^+ і Cl^-) на в'язкопружні властивості льоду. Встановлено, що під час нагрівання зразка до температур, на 15–20 К нижчих від точки плавлення, його модуль зсуву зазнає суттєвого зменшення. Спостережений ефект пов'язано з процесами передплавлення. Показано, що вміст іонів Cl^- не змінює температури передплавлення льоду, тоді як поле напружень, що виникає навколо уведених в лід іонів Na^+, приводить до її зміни. Отримано залежність характеристичної температури передплавлення T_p від концентрації іонів Na^+. Процес передплавлення пов'язується із виникненням проміжної структури, ступінь невпорядкованості якої менший, ніж у води, але більший порівняно із льодом. За експериментальними даними розраховано температурну залежність кількості проміжної структури для досліджених об'єктів.