DETERMINATION OF THE MELTING POINT OF ICE IN POROUS GLASS IN RELATION TO THE SIZE OF THE PORES

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The method of proton magnetic resonance is used to determine the melting point of ice particles in the pores of monodisperse porous glasses ranging from 10 to 1000 Å in radius.

The phenomenon of a reduction in the melting point of substances when they are in the form of small particles has long been known and studied theoretically and experimentally. The results of these studies are of theoretical interest because they can be used to check several premises of the theories of melting and capillary condensation [1, 2]. Study of phase transitions of small particles of water is also of practical value for investigating the effect of low temperatures on porous bodies saturated with water – particularly, in solving problems connected with the frost resistance of construction machinery.

However, the empirical data on the dependence of the melting point on the dimensions of ice particles obtained in different studies (see [2-4], for example) differs appreciably in a quantitative sense. The main reason for these deviations, in our opinion, is the fact that porous bodies having a broad distribution of pore sizes were used for the water vessels, and the melting point found in the experiments corresponded to some mean pore radius.

The study [3] represented a definite advance, since it attempted to take into account the actual pore distribution in the specimens used.

It should be noted, however, that the empirical error will be smallest when the specimens used are characterized by minimal dispersion of the pore size. Here, the set of specimens should cover the range of pore radii from about 10 to 1000 Å. This range is dictated by the fact that at a pore radius of more than 1000 Å the melting point T_m differs little from the melting point for the bulk liquid. At pore sizes smaller than 10 Å, the surface of the solid exerts a significant effect. In pores of 3-5 Å radius, the state of the sorbed water molecules corresponds to the "solid" state, even at temperatures in excess of 273°K; the molecules acquire the mobility characteristic of the liquid at temperatures of about 400°K [5].

The authors of [4] attempted to create the above experimental conditions by using as specimens a set of water-saturated porous glasses, which currently are the most monodisperse porous sorbents. However, in three of the six specimens used in the experiment the pore-size dispersion was large. Although the form of the pores in porous glass can be approximated by the model of partially intersecting spherical cavities [6], the authors performed their cal-

TABLE 1. Structural Characteristics of the Porous Glasses Investigated

Number of specimen	Pore radius r, Å	Bulk porosity, %	Specific surface, m^2/g
1	12	26	270
2	66	57	220
3	126	65	155
4	315	74	100
5	1260	69	20

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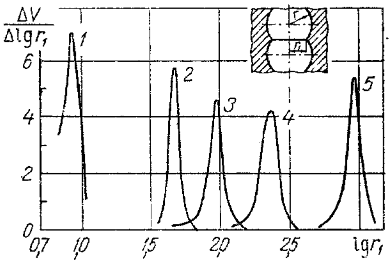

Fig. 1

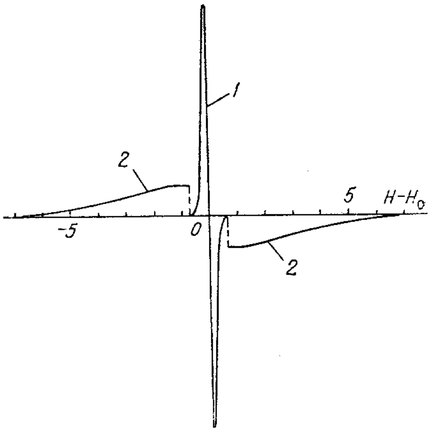

Fig. 2

Fig. 1. Curves of the distribution of the volumes of the pores according to their radii, obtained by the adsorption method (1) and the method of mercury porometry (2-5).

Fig. 2. PMR absorption spectrum (first derivative) for specimen 5 at a temperature of −1.5°C. The central part (1) was obtained with an amplification one-tenth as great as for the rest of the spectrum (2). The amplitude of modulation of the magnetic field was 0.1 Oe. $H - H_0$, Oe.

lations in accordance with the model of cylindrical pores. It was for this reason that they did not account for the fact that the adsorption method and the method of mercury porometry measure the sizes of the mouths of pores, which are smaller than the cavities containing most of the volume of water. Thus, the pore-radius values used in [4] turned out to be biased toward lower values.

The present study attempts to empirically determine the melting point of ice in pores in a solid with allowance for the actual size and shape of the pores. The objects of our study were water-saturated macro- and microporous glasses, and the temperature corresponding to the melting of ice was determined by the method of proton magnetic resonance (PMR).

The porous glasses were obtained from liquidying sodium-borosilicate glasses by treating them with acid (specimen 1) and subsequent treatment with acid and alkali in accordance with [7] (specimens 2-5).

Table 1 shows structural characteristics, while Fig. 1 shows curves of the distribution of the pore volumes in the glasses according to the radii obtained by the adsorption method (specimen 1) and the method of mercury porometery (specimens 2-5). As noted above, both methods give information on the radii r_1 of the narrowest openings, the latter leading to broader cavities with a radius r which determines the size of the ice particles (see the diagram in Fig. 1). The relationship between r and r_1 can be found for specimens 2-5 by means of the equations presented in [6]. Calculations we performed showed that, on the average, $r = 1.4r_1$ for the specimens investigated. The values of r shown in Table 1 were obtained from this formula. As r_1 we took the radii corresponding to the maximums on the distribution curves 2-5 in Fig. 1. In contrast to specimens 2-5, specimen 1 had a spongy-corpuscular structure rather than a spongy structure, so the model of partially intersecting spherical cavities cannot be applied to it. The pore radius in this specimen was determined from the maximum on distribution curve 1 and, with a correction for the thickness of the adsorbed film, proved to be equal to 12 Å.

All of the specimens were saturated with water at a relative vapor pressure $p/p_s = 1$ and were sealed in glass ampoules 4.5 mm in diameter and 50 mm in length.

The melting point of the ice T_m was determined from the PMR absorption spectra, which were obtained with a PMR spectrometer with an autodyne generator made by the Physicotechnical Institute of the Soviet Academy of Sciences. Proton resonance was seen at a frequency of 30 MHz with low modulation of the magnetic field. The amplitude of the modulation was 0.05-0.5 Oe. The sensitivity of the spectrometer for liquid water near 0°C was no worse than $2 \cdot 10^{18}$ molecules of water in the volume of the specimen. The concentration of water in the pores of

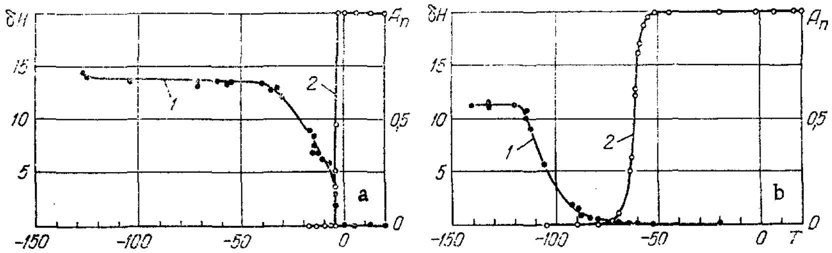

Fig. 3. Dependence of the width of the line (1) and the height of the narrow component (2) of the PMR spectrum on temperature for water-saturated porous glasses: *a*—*r*=315 Å; b—*r*=12 Å. A_n, rel. units; δH Oe; *T*, °C .

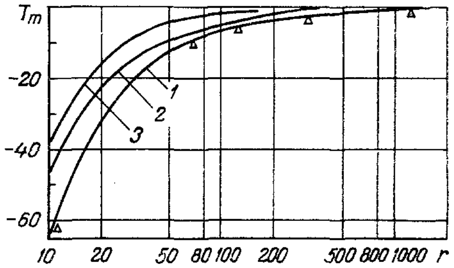

Fig. 4. Dependence of the melting point of ice on the pore gradius: 1) calculation [4]; 2) calculation [2]; 3) experimental data [3]; points show results of our experiment. r, Å; T_m, °C.

specimens was no less than 10^{21} molecules per specimen, i.e., three orders greater than the maximum sensitivity of the PMR spectrometer. The spectra of water in the liquid phase were very narrow, their width amounting to small fractions of an oersted. Transition of the water to the solid state led to an increase in the width of the spectrum by a factor of one hundred.

If the specimen simultaneously contains water in the liquid and solid phases, then the PMR spectrum will consist of two components. The areas of these components will be proportional to the mass fraction of water in the corresponding phases. In the present study, we took the height of the narrow component A_h rather than its area as a measure of the amount of liquid water. The height is proportional to the area. The error is significantly reduced in the present case by measuring the height rather than the ratio of the area of the narrow component to the total area of the spectrum, since in the transition region the broad component is one-hundredth as large as the narrow component at the maximum point (Fig. 2) and in some cases only slightly exceeds the noise level, which makes determination of the total area of the spectrum difficult.

When the height of the narrow component is used in place of the ratio of the areas, it is necessary to introduce a correction for the increase in the total area of the spectrum with a decrease in temperature. The latter is connected with an increase in the populations of the Zeeman energy levels of the resonating nuclei and with an increase in the Q factor of the autodyne circuit. To find the temperature dependence of the area of the PMR spectrum we used a standard specimen (a 4.5-mm-diameter polyethylene rod 50 mm long) containing a large number of protons ($6 \cdot 10^{22}$ in a specimen). For each temperature T we obtained a correction factor K equal to the ratio of the total areas of the spectra of the standard specimen at 0°C to the temperature T. The height of the narrow component A_h, adjusted for the same spectrum area, we found by multiplying the experimentally recorded height by the correction factor K.

The second characteristic of the state of the water was the width of the spectrum δH, measured as the distance between the extremums of the derivative of the absorption line; it conveys information on the mobility of the water molecules. During freezing of the water, the width of the PMR spectrum increases to 12-16 Oe [8].

The specimens, placed in the transducer of the PMR spectrometer, were thermostatted by automatic regulation of the flow of liquid nitrogen. The accuracy of the specimen temperature regulation was ±0.5°C.

Specimen temperature was changed gradually. The PMR spectra were recorded at a constant temperature both during the stage of its reduction and during the stage of its increase. Here, as might be expected, hysteresis was observed: the freezing point was below the melting point in all of the specimens except specimen 1.

Since no metastable states occur during melting, the solid—liquid transition is characterized by the melting point of ice rather than by the freezing point of water.

The temperature at which the experiment was begun was chosen so that the PMR spectrum consisted only of the broad component characteristic of frozen water.

Figure 3 shows examples of the change in the width of the spectrum and the height of the narrow component in relation to temperature (with an increase in temperature). It is apparent that the ice melts within a certain temperature interval. This invertal is 1-2° for specimens 2-5 (Fig. 3a) and about 20° for specimen 1 (Fig. 3b).

There is currently no unanimous agreement on the reasons for the extended solid—liquid transition in pores in solids [9]. Some authors attribute it to the temperature dependence of the thickness of interlayers of unfrozen water, while others think that it is due to the scatter of the dimensions of the melting ice particles. In our opinion, the diffuseness of the transition is due to the dispersion of the pore sizes (see Fig. 1). Thus, as the temperature of completion of melting of ice in pores of the calculated radius we took the temperature corresponding to half the maximum value of the narrow component of the PMR spectrum.

For specimens 2-5 the width of the spectra and their form prior to the beginning of melting (the appearance of the narrow component) are similar to the characteristics of PMR absorption signals obtained for polycrystalline ice [8] and seen earlier for other systems [9]. The available data on the heat of fusion and activation energy of the transition for water in the mobile state in pores in a solid roughly coincides with and is close to the data for ordinary ice [9, 10]. All of this is indirect confirmation of the fact that water crystallizes in pores of radius 60-1000 Å.

The increase in the narrow component occurs more smoothly for specimen 1. This may be connected with scatter of the pore sizes, which as the temperature decreases leads to greater blurring of the transition region. However, it can be assumed that in very small pores the water undergoes vitrification rather than crystallization. This is indirectly confirmed by the results of theoretical [11] and experimental [12] studies, as well as by the absence of hysteresis in the freezing and thawing of water recorded in our tests. The final answer to this question might be obtained by means of x-ray diffraction analysis.

The results of the measurements made are shown in Fig. 4. Since there is presently no theory making it possible to calculate the decrease in the melting point of ice with allowance for its interaction with the surface of a solid, we compared the data obtained with data calculated from formulas derived from thermodynamic representations [2, 4]. We also compared our data with the empirical data most often referred to in the Soviet literature [3]. It is apparent from Fig. 4 that the measurement results agree satisfactorily with the calculated results obtained from the three-phase fusion model in [4] but they deviate markedly from the theoretical and empirical data in [2, 3]. It should be noted that if vitrification of water is seen in specimen 1, then the agreement with the theoretical result for this specimen is random in character.

In conclusion, let us touch briefly on the possibility of extending the results obtained here to other materials. It was shown in [3] that the melting point of ice in pores in hydrophilic substances is independent of their chemical composition. This is not so from a theoretical point of view, since the interaction between an adsorbent and an adsorbate depends on the structure of the surface of the adsorbent. Since the effect of the surface extends only several layers of water molecules adjacent to it [9], it should be expected that the effect of the properties of the surface on the melting point of water will be significant only for very small pores, of a radius less than 30 Å [4]. For coarser pores, a difference in the structure and properties of the hydrophilic surface should not appreciably affect the melting point of ice.

NOTATION

T_m, melting point of water; r, pore radius; r_1, radius of openings leading to pores; p/p_s, relative vapor pressure; A_h, height of narrow component of PMR signal; δH, width of PMR spectrum; V, volume of pores.

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