Melting of ice near a hydrophilic surface

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Adiabatic calorimetry and nuclear magnetic resonance techniques have been used to study the melting of ice in a disperse hydrophilic medium (quartz glass). Melting occurs in the temperature range 180–273 K. The dependence of the differential heat of melting on the temperature and the thickness of the liquid film is obtained. This dependence has at a film thickness 16 Å, a minimum due to the reduction of the entropy of water near the surface of ice and increase of the entropy near a hydrophilic surface.

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1. INTRODUCTION

At the present time there is increased interest in the study of disperse systems for which the surface energy cannot be neglected.[1] Many physical properties in such objects, such as the nature of phase transitions, differ substantially from those of a homogeneous bulk sample. The melting of any crystal, if we do not consider defects and impurities, starts from its surface.[2] The presence of a film of liquid water on the boundary between ice and water vapor has been demonstrated, in particular, by the NMR method.[3] This film exists in the range of temperatures from 260 to 273 K and with increase of the temperature its thickness increases.

The contact of ice with a hydrophilic surface causes melting to occur over a range of temperatures from about 180 K to 273 K,[4] i. e., the range is extended about one hundred degrees. For experimental study of these effects it is necessary to have a rather extended surface, i. e., the sample must be a disperse system. Water-saturated disperse systems are quite common. Among them are biological objects, sedimentary rocks, and many artificial materials. Kuraev *et al.*[4] showed that the nature of the dependences of the amount of melted ice on the temperature obtained for samples of albumin and water, clay minerals and water, and quartz glass and water is the same within experimental error. The amount of unfrozen water in the samples is determined uniquely by the area of the surface of the hydrophilic particles, by the properties of the surface, and by the temperature of the sample. The water in the samples at temperatures below 273 K is stable, since it is in thermodynamic equilibrium with ice and was formed in melting of ice.

In Ref. 5 it was first shown experimentally that the heat of melting of ice near a hydrophilic surface of quartz glass is less than the heat of melting of bulk ice. In Ref. 6 this qualitative result was confirmed for ice interacting with a surface of aluminum oxide. These two studies have the following deficiencies.

1. The integral heat of melting is investigated. Since melting occurs in a temperature range of the order of 100 K, this quantity is not very informative.

2. In calculation of the heat effect, the change in the ratio of the phases in the sample during the melting process was not taken into account.

These deficiencies are due to objective factors. Interpretation of a specific-heat anomaly that extends over several tens of degrees on the basis of only calorimetric data is impossible. Data are necessary on the temperature dependence of the ratio of the phases in the sample.

In our work we studied the differential (in the mass of melted ice) heat of melting of ice in a hydrophilic disperse system. The differential heat of melting was calculated from comparison of calorimetric data with NMR data on the ratio of phases in the sample. This permitted a more complete description to be obtained of the process of melting of ice in such systems and, at least in its approximate features, explanation of its molecular mechanism.

2. SAMPLES AND EXPERIMENTAL METHOD

In the present work we experimentally investigated the melting of ice near a hydrophilic surface of quartz glass (vitreous silica, aerosil). The particles of aerosil were spheres with an average diameter 194 Å and a specific surface of 140 m²/g. The content of SiO_2 in the aerosil was 99. 97% by weight. The surface of the aerosil consisted of hydroxyl groups,[7] and therefore surface dissociation did not introduce impurities into the water. The investigations were carried out by two methods: NMR was used to obtain the amount of melted ice as a function of the temperature of the sample,[4] and the calorimetric method was used to study the specific heat of the sample under the pressure of saturated water vapor.[1]

Three samples were studied by means of adiabatic calorimetry. Samples No. 1 and 2 differed only in the content of aerosil (see the table). The distilled water had a conductivity pf 3. 2 micromhos/meter, which corresponds to a concentration of electrolyte $1.4 \cdot 10^{-6}$ wt. %. To study the influence of small impurities on the melting of ice in such a system, Sample No. 3 was prepared in a water solution of NaCl of concentration $3 \cdot 10^{-5}$ wt. %. Before preparation of the samples the aerosil was heated for days at 570 K, cooled, wetted with water under vacuum, and outgassed. The prepared sample was introduced into the calorimetric cell by a syringe. The content of water in the sample was determined before and after drying. The sample studied by NMR was prepared in exactly the same way.

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TABLE I.

Sample No.	Concentration, mol H_2O/kg aerosil	Total aerosil surface in sample, m^2	Liquid water content, in wt. % of total water content		
			250 K	266 K	271 K
1	1756	102	0.34	0.78	3.18
2	265	760	2.22	5.19	21.1
3	350	493	1.68	3.92	15.9
4*	370	—	1.59	3.72	15.1

*This sample was studied by the NMR method.[4]

In the calorimetric apparatus the cell was further outgassed by heating to 360 K, cooling, and evacuation to $7 \cdot 10^{-3}$ Pa at 100 K. All of the experimental studies were carried out under the same conditions. Before the measurements the samples were cooled to 78 K, and during the experiment their temperature was only increased. The cooling time of the calorimetric cell was $2.4 \cdot 10^3$ sec, and that for the sample used in the NMR studies $8 \cdot 10^2$ sec.

The technique of determining the amount of melted ice by the NMR method in an autodyne broad-line spectrometer has been described elsewhere.[4] The specific heat was measured in an adiabatic calorimeter of the VNIIFTRI design. A similar apparatus and measurement technique have been described, for example, in Ref. 9. A check of our apparatus on the specific heat of distilled water and ice showed that in the temperature range 90–360 K the average error of the measurements of the specific heat was less than 0.2%. A comparison was made with data obtained in several laboratories (see Ref. 10). The size of the calorimetric step in the melting range of ice was on the average 0.2 K.

The specific heats of water and ice in the samples are shown as functions of the temperature in Fig. 1. These dependences are shown by the continuous lines, since there are more than 500 experimental points and on the scale used they merge. The specific-heat anomaly due to the melting of ice near a hydrophilic surface was smeared out considerably on the low-temperature side. The high-temperature branch of the specific-heat anomaly was smeared by no more than 0.5 K.

In a bulky uniform sample without impurities the heat of transformation is liberated (or absorbed) at a strictly defined temperature. In this case the anomaly in the specific heat has the form of a delta function. In a real sample the δ-function is smeared out. The nature and extent of the smearing are determined by the distribu-

tion and quantity of inhomogeneities in the sample. Thermodynamic (equilibrium) impurities lead to conversion of the δ-function into a trapezoid whose area os equal to the heat of transformation (see for example Ref. 11). Nonequilibrium (frozen) impurities, lattice defects, and other inhomogeneities characteristic of solids lead to a more or less smooth smearing of the δ-function in the direction of low temperatures. In our case the smearing of the low-temperature branch of the c_p anomaly is due almost completely to the presence of the hydrophilic surface. This can be seen from the fact that the contribution to the specific heat of the samples due to the melting of the ice is proportional to the surface area of the vitreous silica glass in the samples. In Fig. 2 we show the temperature dependence of the contribution of the heat of melting of the ice to the specific heat of the samples per unit surface area of aerosil. The points for all three samples lie satisfactorily on the same straight line.

Let us consider the possible causes of the errors which determine the reliability of the observed effect and the confidence intervals of the values obtained.

To determine the effect of the impurities contained in the water on the premelting of the ice in the sample, we prepared sample No. 3 containing $3 \cdot 10^{-5}$ wt. % NaCl. Since an increase in the amount of impurity in the water by 20 times did not influence the premelting of the ice within the experimental error (see Fig. 2), the influence of the impurities on the observed effect can be neglected. In addition we studied the premelting of ice prepared from outgassed distilled water. In our apparatus the contribution to the specific heat due to premelting of bulk ice was observed beginning at 269.5 K. However, in the temperature interval 269.5–270.5 K this contribution was two orders of magnitude less than the contribution due to the melting of ice at the hydrophilic surface. In sample No. 1 the premelting of bulk ice gives an effect comparable with the melting at the surface only at 272 K. In interpretation of the results we considered the region of temperatures below 271.3 K. Therefore the influence of premelting of ice lying beyond the surface layer in the sample on the effect
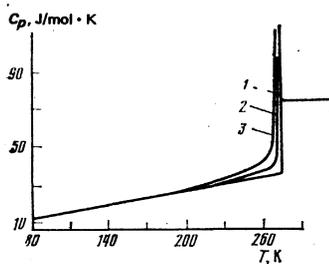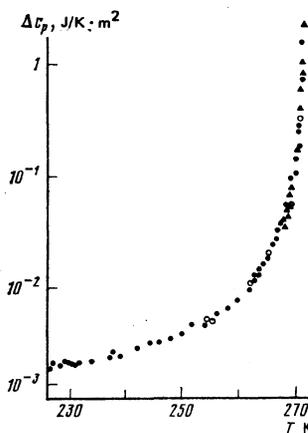

FIG. 1. Specific heat of water and ice in samples as functions of temperature: 1—specific heat of distilled water, 2—specific heat of ice and water in Sample No. 1, 3—the same in Sample No. 2.

FIG. 2. Excess specific heat due to melting the ice on the surface of the aerosil: ▲—Sample No. 1, ●—Sample No. 2, ○—Sample No. 3.

studied can be neglected.

The dependence of the specific heat in temperature was measured three times each for Samples No. 1 and No. 2. The investigation of each sample lasted for five months. Complete reproducibility of the dependences was obtained within experimental error. Consequently we can neglect the following sources of error; the effect of solution of the material of the cell and the aerosil during the experiment, redistribution of the aerosil in the sample, and aggregation of the particles of the aerosil. Since the contribution of the heat of melting to the specific heat of the samples is proportional to the surface area of the aerosil (see Fig. 2), we can also neglect the influence of the aerosil particles on each other.

As was mentioned above, a film of liquid water exists at the ice-vapor boundary.[3] In the spontaneous outgassing of the water during freezing, an extended separation surface can be formed. Therefore we carefully outgassed the samples. The only ice-vapor separation boundary in the samples was due to the parasitic volume of the cell (the unused volume). It amounted to $2 \cdot 10^{-3}\%$ of the aerosil-water separation boundary in Sample No. 1 and $2 \cdot 10^{-4}\%$ in Sample No. 2. Obviously the effect of this surface can be neglected.

The possible contibution to the specific heat of the sample due to sublimation of ice is two orders of magnitude less than the experimental error in the temperature range 80 to 273 K. The error in determination of the excess specific heat of the sample due to melting its greater than the error in measurement of the entire specific heat of the sample. This error is determined by the amount of ice which has melted. For sample No. 2 this error decreases from 15% at 250 K to 0. 2% at 269 K. The error in measurement of the amount of melted ice in the NMR method is practically independent of temperature over the range of interest here.

The results of the experiment are given in Fig. 3. For each temperature we obtained up to ten NMR spectra, and the results were averaged (see Ref. 4). The maximum deviation of the amount of melted ice, obtained from a single measurement, from that calculated with the approximation formula (2) does not exceed 15%. The error in determining the derivative of the amount of melted ice in the sample with respect to the temperature is estimated by us not to exceed 15%.

From analysis of the sources of error it is evident that in the interval 255–271 K the error in the quantities calculated from comparison of NMR and calorimetric data is determined by the error of the NMR method. At temperatures below 255 K this error is determined by the combined error of the calorimetric and NMR data.

3. EXPERIMENTAL RESULTS

Since melting in a disperse hydrophilic medium occurs over a wide range of temperatures, in describing it one must intorduce the differential heat of melting:

$$\frac{dQ}{dm_L} = \frac{\partial Q}{\partial T}\frac{dT}{dm_L} \approx \frac{\Delta c_p \Delta T}{\Delta m_L}, \tag{1}$$

where Q is the heat which goes into melting of the ice in the sample, Δm_L is the change in the amount of melted ice in moles on change of the temperature by ΔT, $\Delta T = T_2 - T_1$ is the calorimetric step (difference in temperatures after and before heating of the sample), and Δc_p is the excess specific heat due to melting. Obviously the quantity dQ/dm_L has meaning when ΔT is much less than the interval of melting. In a massive sample $dQ/dm_L = \lambda$ (λ is the molal heat of melting of ice).

For calculation of the differential heat of melting, the temperature dependences of the specific heat of the calorimetric cell and of the molal heat capacity of the aerosil and the ice were approximated by polynomials

$$c = \sum_{n=0}^{5} a_n T^n. \tag{a}$$

The temperature dependence of the amount of melted ice at the surface of the aerosil was approximated by the sum of two exponentials:

$$m_L = A m_a [\exp(0.336-644/T) + \exp(104-28212/T)], \tag{2}$$

where m_a is the quantity of aerosil in the sample and A is a constant.

The relation for calculation of the differential heat of melting of ice near a hydrophilic surface has the form

$$\frac{dQ}{dm_L} = \frac{[c-c_k-c_{pa}m_a-c_{ps}m_w-(c_{pL}-c_{ps})m_L(T)]\Delta T}{m_L(T_2)-m_L(T_1)}, \tag{3}$$

where c is the experimentally determined value of the specific heat of the cell with the sample and c_k is the specific heat of the cell; c_{pa}, c_{ps}, and c_{pL} are the respective isobaric molal heat capacities of the aerosil, ice, and water in the sample; m_w is the total amount of water in the sample; $T = (T_1 + T_2)/2$.

In calculation of dQ/dm_L by means of Eq. (3) one uses the isobaric specific heat of the water located between the surfaces of the ice and the quartz glass. The dependence of c_{pL} on temperature is not known to us. However, as long as $(c_{pL} - c_{ps})m_L(T) \ll \Delta c_p$, the uncertainty in the value of c_{pL} does not affect the result. For sample No. 2 a change of c_{pL} by $\pm 100\%$ in the temperature interval 265–273 K will lead to a change of dQ/dm_L by $\pm 5\%$ (at 265 K). Therefore in the temperature region 263–273 K the confidence level for dQ/dm_L as a function of T is determined by the error in the
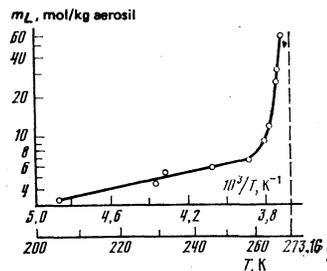

m_L, mol/kg aerosil

FIG. 3. Content of melted ice near aerosil surface as a function of temperature from the data of Ref. 4. The solid line shows the dependence described by Eq. (2).
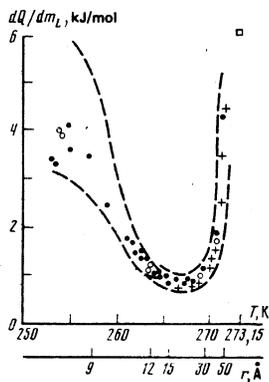
FIG. 4. Differential molal heat of melting of ice in various samples: +—Sample No. 1, ●—Sample No. 2, ○—Sample No. 3, □—heat of melting of pure ice; r is the thickness of the layer.

NMR measurements (see Fig. 4).

In the temperature interval 250–263 K we have $(c_{pL} - c_{pS})m_L(T) \lesssim \Delta c_p$. For interpretation of the result in this temperature range we assumed that c_{pL} at any temperature is less than the specific heat of water at 273.15 K and greater than the specific heat of ice at this temperature. This assumption is based on the fact that for $T > 273$ K the specific heat of the water in sample No. 2 has a small systematic deviation (within the experimental error) in the direction of decrease of the value in comparison with Sample No. 1 and pure water. We calculated the differential heat of melting for three cases:

1) c_{pL} was taken equal to the specific heat of the ice. This corresponds to the upper limit of the confidence interval.

2) c_{pL} over the entire temperature range was taken equal to the specific heat of water at 273.15 K. This corresponds to the lower limit of the confidence interval.

3) c_{pL} rises linearly from the specific heat of ice at 180 K to the specific heat of water at 273.15 K. The experimental points shown were calculated on this assumption.

For $T < 250$ K we have $(c_{pL} - c_{pS})m_L(T) \gtrsim \Delta c_p$ and even a qualitative estimate of dQ/dm_L is impossible if there are no reliable data on the temperature dependence of c_{pL}.

Let us estimate the effective thickness of the layer of melted ice on the surface of a particle of aerosil. The ice content in a monolayer calculated from the adsorption isotherm is $8 \cdot 10^{-6}$ mol/m² of surface. We shall take the thickness of a monolayer equal to the "diameter" of a water molecule (2.8 Å). The density of the unfrozen water outside the monolayer we shall take equal to 1 g/cm³. Then with allowance for the spherical shape of the particles it is easy to calculate from the NMR data some effective layer thickness. With increase of the amount of ice on the surface, this quantity will acquire a clearer geometric meaning. In Fig. 4 below the temperature axis we have shown an axis on which the thickness of the water layer is plotted.
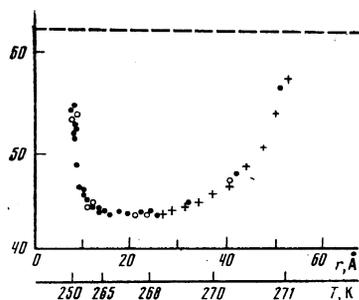

FIG. 5. Variation of differential molal entropy in the layer of unfrozen water: +—Sample No. 1, ●—Sample No. 2, ○—Sample No. 3; the dashed line is the entropy of water at 273.16 K; r is the thickness of the layer. Along the vertical axis we have plotted dS_L/dm_L in J · mol⁻¹ · K⁻¹.

The temperature dependence of dQ/dm_L shown in Fig. 4 has a minimum at 267 K. At the minimum point the differential heat of melting of the ice in the sample is about seven times smaller than the heat of melting of massive ice. On reduction of the melting temperature from 271.3 K to 268 K, dQ/dm_L drops exponentially.

Let is calculate the differential molal entropy of water near an aerosil surface:

$$\frac{dS_L}{dm_L} = \frac{1}{T}\frac{dQ}{dm_L} + \bar{S}_s, \qquad (4)$$

where $\bar{S}_S$ is the molal entropy of ice. We shall assume that the entropy of ice S_S does not change near a hydrophilic surface, i.e., that $dS_S = \bar{S}_S dm_L$. This assumption is based on the experimental data. As a result of the rapid growth of the confidence interval with decrease of the water layer thickness, we consider only ice located less than 8.5 Å from the aerosil surface. Anderson and Hoekstra[12] showed on the basis of x-ray structure studies of ice near a hydrophilic surface that hexagonal Ice-I is formed on freezing already at a distance of more than 6 Å from the surface. Our data show that the specific heat capacity of the ice in the samples in the interval from 80 to 200 K does not differ essentially from that of Ice-Ih. Consequently we can assume also that the entropy of the ice in the samples is close to the entropy of Ice-Ih at the corresponding temperature. The dependence of the entropy of the water on the thickness of the water layer at the aerosil surface, calculated from the relation (4), is shown in Fig. 5.

4. DISCUSSION OF RESULTS

The nonmonotonic dependence obtained by us for the differential heat of melting of ice as a function of temperature, and consequently also the dependence of the differential entropy of water on the thickness of the film on the vitreous silica glass (r), can be explained as follows. The change in the entropy of the film of water located between the two surfaces is due to the competing influences of the two surfaces.

Short-range order in water corresponds approximately to the structure of Ice-Ih.[13] Consequently, interaction of water with the surface of ice leads to a decrease of its entropy. This has the result that, over the entire range of film thicknesses studied, the diffe-

rential entropy is less than the entropy of bulk water. With increase of the thickness of the film of water on the surface of the ice, the entropy of the water in it rises and approaches the entropy of bulk water. The NMR data confirm that in the temperature range 267–273 K the melting of ice in hydrophilic disperse systems is determined by the interaction of the water with the ice surface.[4]

The interaction of water molecules with the hydrophilic surface will lead to an increase in the entropy of the film, since the adsorption centers on the surface of the aerosil are arranged chaotically, and the short-range order is characteristic of water. The correlation radius between the positions of the centers of two molecules of water (r_c), obtained from x-ray diffraction experiments, is ≈ 8 Å.[14,15] The change of the entropy of the water as the result of its interaction with the hydrophilic surface of the aerosil should occur for $r \lesssim 2r_c$. The results of our experiment agree completely with this qualitative description. On increase of the thickness of the water layer from 8 Å to 16 Å the differential entropy drops.

Since the influence of the ice surface on the differential entropy of the water in the film is felt at a larger distance than the influence of the hydrophilic surface, these two factors acting together produce a minimum at $r = 2r_c$ in the dependence of dS_L/dm_L on the film thickness.

It should be noted that the change of entropy of the film can also influence the effective reduction of the dimensionality of the system. In a monolayer, liquid water is two-dimensional. We are considering the case in which the film thickness is several times greater than the thickness of a monolayer and is close to the correlation radius in bulk water. Such a film can be considered to be a system with dimensionality $2 < d < 3$. An effective reduction of the dimensionality evidently should lead to a further lowering of the entropy of the liquid.

It is interesting to note that the principal changes in the differential heat of melting of ice and of the melting temperature occur at a layer thickness less than 55 Å, i.e., the thickness of the water layer with changed properties near the aerosil surface does not exceed a few correlation radii. It must also be pointed out that a reduction of the melting temperature of ice by 5–6 K leads to a decrease of the differential heat of melting by several times.

5. CONCLUSION

Thus, the nature of the melting of ice in a hydrophilic disperse medium is determined by the substantial change in the properties of the water located in a layer, whose thickness is of the order of the correlation radius, between surfaces of different structure.

We have limited ourselves to a qualitative interpretation of the results. The degree of universality of these results in application to hydrophilic surfaces of

different origin remains unclear. The effect of "reduction of the dimensionality" should be universal for thin films, and in principle it can be calculated. The influence of the ice surface can also be evaluated quantitatively if one starts with a definite molecular model of water. In regard to further experimental studies, the most important problem is to investigate the properties of films of water on surfaces whose thickness is close to that of a monolayer.

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[1] The specific heat of water and ice at the pressure of the saturated vapor, in the temperature range studied, does not differ within experimental error from the specific heat at constant pressure c_p.[8] Therefore in what follows the specific heat of the sample is designated as c_p.

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