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GLASS TRANSITION IN SODIUM THIOSULFATE PENTAHYDRATE*)

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Abstract: Recent kinetic approaches to the glass formation may be applied to the examination of the large undercoolings characterizing certain materials. Thus the stable undercooling of sodium thiosulfate pentahydrate (STP), as large as seventy Kelvins, is attributed first to the extremely steep dependence of its nucleation frequency upon temperature, and second to the very small value of the fraction of sites in the crystal-melt interface where molecules may preferentially be added and removed. It was found that characteristic parameter a of STP is equal to 0.17—0.19, that crytical cooling rate is about 100 K/s and that glass transition occurs around 215 K.

1. Introduction

Although the field of amorphous and glassy materials is developing and diversifying very fast, one aspect of it retains the permanent importance. It is the problem of preparation. Among many papers on this problem the paper of D. Turnbull1) is of outstanding value. Turnbull was the first to formulate the empirical rules of transition into glassy state and to count up its essential parameters. According to his findings the glassforming tendency will be greater the larger are: the cooling rate $Q = \mathrm{d}T/\mathrm{d}t$, the liquid-crystal interfacial tension S and glass temperature T_g, and also the smaller are: the volume V of the liquid sample, the density d_s of heterogeneous nuclei and the fraction f of sites in the crystal surface to which molecules can be attached. Some of these can be controlled in the laboratory while the others are simply material constants. The later, though few in number, enable materials to behave with fascinating variety.

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For the purpose of this work it is useful to divide the substances into three groups. The first comprises all materials which crystallize during very slow cooling near to their melting points T_m. Consequently, these cannot be undercooled to any remarkable extent $\Delta T = T_m - T$. Such behaviour is found in monoatomic metals, noble gases, germanium, tellurium etc. Generally, they cannot at present be prepared as bulk glasses.

The members of the second group are the materials that do not crystallize at T_m and allow to be undercooled to very high values of ΔT including the glass temperature T_g. Phosphorus pentoxide P_2O_5, boron trioxide B_2O_3 and arsenic trisulfide As_2S_3 behave just in this manner. It is almost impossible to prepare these compounds as crystals and they appear only in the form of glass.

Finally, the third group comprises all other materials, i. e. those with limited undercoolings $\Delta T < \Delta T_g = T_m - T_g$. The characteristic examples are sodium thiosulfate pentahydrate $Na_2S_2O_3 \cdot 5H_2O$, calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4H_2O$, selenic acid H_2SeO_4, its mono- and tetrahydrate etc. All these substances can be undercooled to relatively large Δ *Ts*, but after that they nevertheless crystallize.

Certainly, treating the undercooling of a liquid system, one has to take into account the dependence of ΔT on the length of time in which the system existed as a liquid at all. As it is known, undercooled liquids and glasses are thermodynamically unstable. In time (a part of a second, or thousands of years) they will transform into their stable state — crystal. To make a distinction we introduce a new quantity, the waiting time $t_w = t_w(\Delta T)$ together with a convention that the undercooling will be considered stable only if a substance in question crystalizes in a waiting time $t_w > 1$ day $\approx 10^5$ s.

In the following we intend to show that the modern approaches to the glass formation problem (D. Turnbull[1]), D. R. Uhlmann[2]), J. C. A. Vreeswijk et al.[3]) may give at least a qualitative insight into the origin of the large stable undercoolings characteristic for the third group of materials. For a detailed analysis we have chosen STP which is commonly employed for the demonstration of large underccolings but for which so far there was unfortunately no adequate explanation.

2. *Glass-formation parameters*

Whether a certain molten substance will crystallize or transform into a glassy state depends on the number of crystal nuclei in the liquid at the undercooling ΔT and also on the rate at which a nucleus (if formed) increases its dimensions at the same ΔT. The equations defining these quantities will progressively introduce all the six Turnbull's parameters mentioned in Introduction. The first equation gives the number of nuclei formed isothermally in a unit volume in a second (nucleation frequency I_0)

$$I_0 = \frac{\mathrm{d}^2 NRT}{3\pi M^2 \eta} \exp\left[- \frac{16\pi \alpha^3 \Delta H_m T_m{}^4}{3R(\Delta T)^2 T^3}\right]. \tag{1}$$

Here d is density of the material, N Avogadro's number, R gas constant, η viscosity and ΔH_m enthalpy of melting. The constant a introduces the liquid-crystal interfacial tension S since a is, according to Turnbull, defined as

$$a = \left(\frac{NM^2}{\mathrm{d}^2}\right)^{\frac{1}{3}} \frac{S}{\Delta H_m}. \tag{2}$$

The physical meaning of this important constant is quite simple. This is the number of monolayers per crystal surface area which would be melted at T_m by an enthalpy ΔH_m equivalent in magnitude to tension S.

Equation (1) also contains the viscosity η of the liquid in question, which itself depends on temperature. We shall use the most general form of this dependence

$$\eta = AT^{\frac{1}{2}} \exp\left[B/(T - T_0)\right], \tag{3}$$

in which A, B and T_0 are the material constants$^{4)}$. Let us have in mind that this equation introduces into consideration the glass temperature T_g through the generally accepted convention $\eta(T_g) = 10^{15}$ P (poise).

It is evident that nucleation frequency (1) is not time-dependent. It depicts the formation of nuclei only at a constant temperature or in conditions where the temperature changes are very slow. However, when the cooling is very fast, or if the melt is highly viscous, the transient effects must be taken into account. According to Hillig$^{5)}$ this is done by the relation $I = I_0 \exp(-\tau/t)$ in which the relaxation time τ is equal to $3\pi M\eta/\mathrm{d}RT$. Thus

$$I = I_0 \exp\left(-\frac{3\pi^2 M\eta}{\mathrm{d}RTt}\right). \tag{4}$$

This way we obtained the nucleation frequency which may be inserted directly into the fundamental equation for the glass preparation

$$n = V\int_0^t I\,\mathrm{d}t, \tag{5}$$

where n is the number of generated nuclei in the volume V of the melt and t is the cooling time. This equation puts a demarcation line between the crystallization and the glass formation. For if the cooling was done in such a way that the integral gives $n < 1$, there should be no nuclei whatsoever in the melt and it should transform into glass. Conversely, if the integral gives $n > 1$ there will be at least one nucleus and the melt will crystallize.

In a few cases equation (5) has been used as the first step in development of a concept of the critical cooling rate. As assuming for a moment $d_s = 0$ and $f = 1$ we have put into consideration five of Turnbull's parameters so far, it remains to determine only Q — the cooling rate. In the approach of Vreeswijk et al.[3]) Q is defined as

$$Q = \frac{\mathrm{d}T}{\mathrm{d}t} = \frac{T_m - T}{t} = \frac{\Delta T}{t}. \tag{6}$$

This formula together with (5) gives

$$n = V \int \frac{I}{Q}\,\mathrm{d}T, \tag{7}$$

which equation (4) transforms into

$$I = I_0 \exp\left(-\frac{3\pi^2 M \eta Q}{dRT\Delta T}\right). \tag{8}$$

If we take the critical value $n = 1$ for the number of nuclei, the cooling rate Q turns to critical cooling rate Q_c. It may be found from the integral

$$\int \frac{I_0}{Q_c} \exp\left(-\frac{3\pi^2 M \eta Q_c}{dRT\Delta T}\right) \mathrm{d}T = \frac{1}{V}. \tag{9}$$

The value of Q_c can therefore be obtained by a consecutive procedure involving the estimation of Q_c, integration, and comparison of the result with $1/V$. All data calculated in the Vreeswijk's paper are related to $V = 1$ cm^3.

Another approach to Q_c has been presented in the work of Uhlmann[2]). He introduced the concept of just-detectable volume fraction x of crystals randomly distributed in a glassy matrix. If $x < 10^{-6}$, the solid has to be treated as glassy. Conversely, if $x > 10^{-6}$ the concentration of crystalline matter is detectable and the solid cannot be treated as glassy. Assuming that nucleation frequency I_0 and the rate of crystal growth u do not depend on time, x may be expressed as

$$x = \frac{\pi}{3} I_0 u^3 t^4. \tag{10}$$

Here t is the time necessary for the formation of crystals up to the volume fraction x. For the crystal growth rate Uhlmann has used the classical expression

$$u = \frac{f\,RT}{3\pi\eta}\left(\frac{d^2}{M^2 N}\right)^{\frac{1}{3}}\left[1 - \exp\left(-\frac{\Delta H_m \Delta T}{RTT_m}\right)\right], \tag{11}$$

in which the last Turnbull's parameter appears. It is f, the fraction of sites in the crystal surface able to accept the molecules from the melt. Let us consider briefly two extreme cases that describe the values of this factor. In one of them crystals grow keeping their surface smooth on the molecular scale. The interface can advance only by the lateral movement of »steps« originating from either two-dimensional nuclei or the screw dislocations. Thus $f \ll 1$. In the other case crystal surface is rough or diffuse. The sources of »steps« are not necessary and crystals can grow perpendicularly to the interface. Factor f is then near to 1. Besides, f must be in some way dependent on the undercooling ΔT. Uhlmann has suggested the simple approximative formula

$$f = 0.2 \frac{\Delta T}{T_m} \tag{12}$$

The critical cooling rate in Uhlmann's approach is defined by the equation (10) which in the $T-t$ coordination system represents the so called TTT curve with a minimum in t-axis. If the coordinates of this minimum are T_n and t_n, the critical cooling rate is given by the formula

$$Q_c = \frac{T_m - T_n}{t_n} . \tag{13}$$

As expected Uhlmann's data for various substances differ from Vreeswijk's, in a few cases even drastically.

3. *Undercooling, crystallization and preparation of glassy STP*

Sodium thiosulfate pentahydrate is a white, crystalline substance melting at $T_m = 49°C = 322$ K. Crystallographic data[6)] show that the crystals are monoclinic and of complicated structure. Some authors have established that STP may have two modifications in the same temperature range. One of them has been called stable modification. It can be prepared from the solution but not by cooling the melt. Crystallization of the molten salt always gives the unstable modification which transforms into the stable one only if undercooled to a great extent. This is, allegedly, an irreversible process: once transformed into the stable phase the samples, if heated, do not revert into the unstable phase anymore. Our experiment did not reproduce such behaviour. This is evident from DTA curves in Fig. 1. obtained on the very pure STP of Riedel de Haen A. G. Upper curve represents the cooling of the molten substance. At about 0°C the crystallization into unstable, and at −30°C into stable form occurs. Since the cooling rate was very small, i. e. 1K/s, The undercooling was stable and equal to 50K.

Lower DTA curve in Fig. 1. represents the heating of the sample, this time transformed into glassy state (see later). On this curve one can see a descent at −58°C. Overlooking for a moment the following peak, the descent may be seen as a shift of the zero line, and may be ascribed to the change of thermal capacity or to the glass transition. The temperature T_g should therefore have the value of 215K. The sharp peak with a maximum at about −35°C is, of course, caused by the crystallization of the glass. Apparently the crystallization gives crystals in their stable phase since the following endothermic signal may be explained as transi-

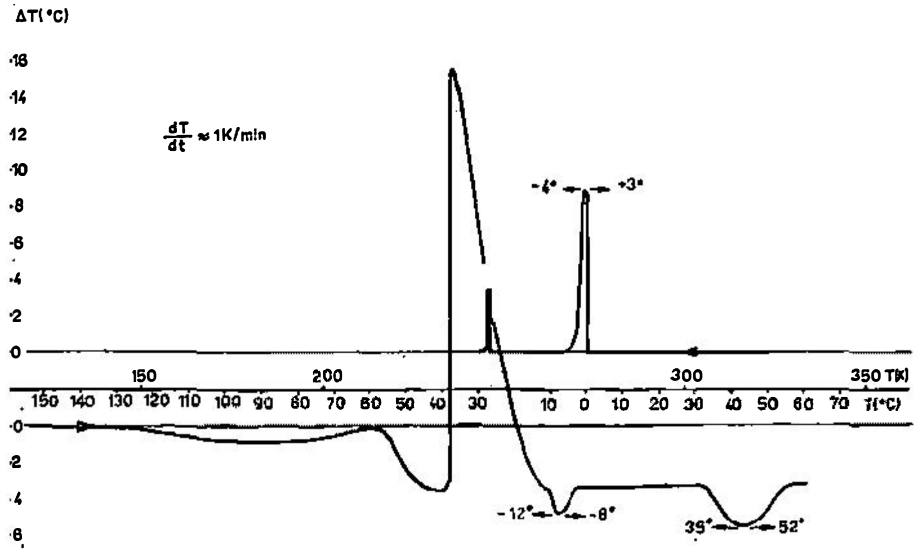

Fig. 1. Differential thermal analysis of STP samples.

tion to the so called unstable phase. Its melting is represented by the last minimum on the DTA curve. The minimum is a broad one, probably because STP, once melted, is not a single-phase system. The second phase is generated by dehydratation occuring near melting point.

The measurements of electrical conductivity shown in Fig. 2. offer almost identical conclusions. Again the upper curve was taken down in a cooling cycle, while the lower one in a heating cycle from —30°C. The freezing of the melt signalized by the abrupt decrease of conductivity is now observed at —24°C, showing a stable undercooling as large as 73K. The difference between ΔT s found by DTA and $\sigma(T)$ is probably caused by the different shapes and sizes of the cells used in the respective measurements. We will mention this observation later.

The second, more drastic decrease of conductivity σ is evidently a result of the transition into the stable modification. This transition was observed at the same temperature as registered by DTA. The conclusions from the measurements of $\sigma(T)$ in the heating cycle are also similar to those stemming from respective DTA curves and need no description of their own (see the lower curve in Fig. 2.). Thus, besides giving an insight in the magnitude of the stable undercooling, DTA and $\sigma(T)$ measurements show that the transition between two solid phases of STP is a reversible process. The disagreement between our findings and those in the old works is, however, of small significance for this report and we did not insist on explaining its cause.

More significant were the results of the critical cooling rate measurement. It was done by quenching the molten STP droplets in liquid nitrogen. A droplet having the temperature T_m at the moment $t = 0$ of diving into nitrogen will not

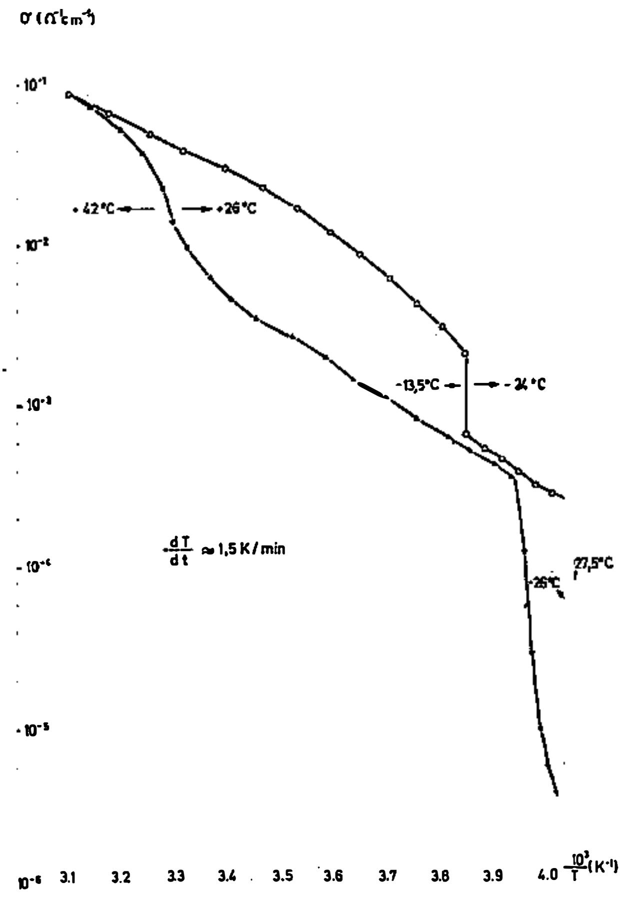

Fig. 2. Electrical conductivity of STP vs temperature.

be cooled uniformly. The hottest point will be the center of droplet, with temperature T_s. During the quenching this temperature decreases following the Newton's law of cooling

$$T_s = T_a + (T_m - T_a) \exp(-t/\tau_r), \tag{14}$$

in which T_a is the ambient temperature (77K — the boiling point of liquid nitrogen), and τ is the time constant. Supposing that the dissipation of heat occurs only by conduction and that droplets were spherical, τ_r is given by

$$\tau_r = \frac{d\, Cp\, r^2}{\tau \varkappa}. \tag{15}$$

Here r is radius of a droplet, C_p is thermal capacity of STP and $\varkappa$ its thermal conductivity. Thus, the center will be cooled faster the smaller is the droplet radius.

We assumed that a droplet will be transformed into glass only if its center is cooled at least to T_g in a time interval t_g too short for the formation of a nucleus and its spread through the entire volume of the droplet. Then the cooling rate may be expressed as Q K $(T_m - T_g)/t_g$. Since t_g may be obtained from (14) inserting $T_s = T_g$, we may write

$$Q = \frac{6 \varkappa (T_m - T_g)}{d C_p r^2 \ln [(T_m - T_a)/(T_g - T_a)]}. \tag{16}$$

To measure the critical cooling rate Q_c one has to determine the critical radius r_c. All droplets with $r < r_c$ will then be glassy and all those with $r > r_c$ will crystallize.

The determination of r_c for STP is quite easy since the states are visibly different: the glassy droplets are transparent and colorless and those in crystalline state are white. Varying the radii of droplets it was found that $r_c = 0.25$ cm. Taking besides $\varkappa = 3.24 \cdot 10^{-3}$ cal cm^{-1} K^{-1}s^{-1}, $d = 1.657$ g cm^{-3}, $C_p = 0.569$ cal g^{-1}K^{-1} and $T_g = 215$K, equation (16) gives 62K/s. However, although easy, the measurements of r_c were of limited accuracy so that Q_c can be approximated by the value 100 K/s.

The last quantity necessary for the analysis of glass transition in STP is the viscosity η and its temperature variations. We have taken very accurate and precise measurements of Moynihan$^{7)}$ who showed that η (T) as measured is identical with equation (3) with characteristic constants $A = 8.657 \cdot 10^{-5}$ PK$^{-1/2}$, $B = 583$K and $T_0 = 203$K. It is interesting that the extrapolation to $\eta = 10^{15}$ P gives the glass temperature $T_g = 217$K. This value is in very good agreement with 215K found in our DTA. It seems therefore that the value $T_g = 231$K obtained in an old measurement of Samsoen$^{8)}$ is too high.

4. Discussion and conclusion

As the first step in our mathematical analysis of glass transition in STP we have chosen the Uhlmann's calculation. In it, as in all others, the greatest problem is the constant α appearing in equation (1) for the nucleation frequency. As may be seen from (2) α is given by the interfacial tension S whose direct measurement is almost impossible. Thus it is necessary to have a theoretical or empirical relation for the prediction of α. Relying on numerous experimental facts Uhlmann introduces α equalizing $16\pi\alpha^3 \Delta H_m/3RT_m$, a part of exponent in (1), with 1.024. If one respects all the Uhlmann's arguments the equalization may give α if ΔH_m is known. Since for STP $\Delta H_m = 34$ cal g^{-1} and $R = 2$ cal mol^{-1} K^{-1}, one obtains $\alpha = 0.17$. The respective TTT curve calculated from (10) with $N = 6.02 \cdot 10^{23}$ mol^{-1} and $M = 248.2$ g mol^{-1} is represented in Fig. 3. As expected, the curve has a minimum in t-axis and its coordinates are $T_n = 254$K and $t_n = 0.34$ s. Critical cooling rate according to (13) is then 190 K/s. This value is in acceptably good agreement with our measurements.

The analysis according to recipe of Vreeeswijk et al. was more complicated. In the calculations of isothermal nucleation frequency (1) they have used $\alpha = 0.32$ basing this upon the data for approximately twenty liquids. Unfortunately, the calculation of I_0 and the integration of (9) was not possible for STP. For each reasonable undercooling the values of I_0 were under the lower limit of Hewlett-Packard 9820A, i.e. under 10^{-99}. The reason was evidently in an inadequate value of α: it was too large. Taking the gradually decreasing values of α however, integral (9) gave more and more reasonable values of Q_c (let us mention by the way that the integration was made between $T = T_0$ and $T = T_m$. Lower limit must be T_0 since only for $T > T_0$ viscosity (3) has meaningful values). Such a procedure may give any result, but we believe that it is not just a coincidence that $Q_c \approx 100$ K/s was obtained for $\alpha = 0.19$ which is near to previous value 0.17. It seems therefore that the experiment and calculations following Uhlmann's and Vreeswijk's approach give a group of consistent facts, so that $\alpha = 0.17—0.19$ and $Q_c \approx 100$ K/s may be accepted for STP.

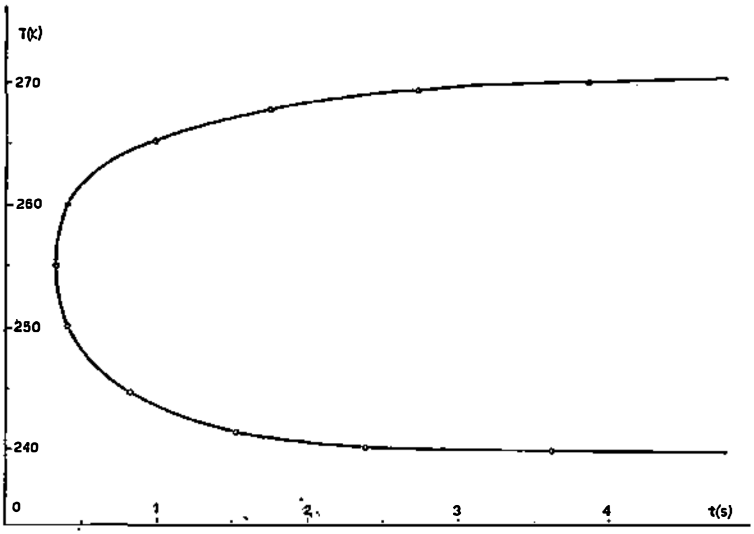

Fig. 3. TTT curve of STP.

Let us now concentrate on the question of the origin of large stable undercoolings in STP. The absolute magnitudes of α and Q_c do not give a direct answer because a material of such properties is quite resistent to glass formation. The critical cooling rate $Q_c \approx 100$ K/s, though small in comparison with that of metals or elemental semiconductors, is rather large comparing good glassformers. Besides, the parameter $\alpha = 0.17—0.19$ is extraordinary small. In fact, there is no material ever examined with so small a value of α. The minimal α which may be found, for example, in Turnbull's survey of data$^{1)}$ (which, nota bene, does not contain any hydratized salt) is 0.25. Since good glassformers that exhibit large stable undercoolings have large α (even 0.8—0.9) the effect in STP remains unexplained.

The reason for large ΔT in STP, from the standpoint of nucleation processes only, may lie in a favourable combination of α and η (T) which gives extraordinary steep dependence of nucleation frequency upon temperature. As may be seen

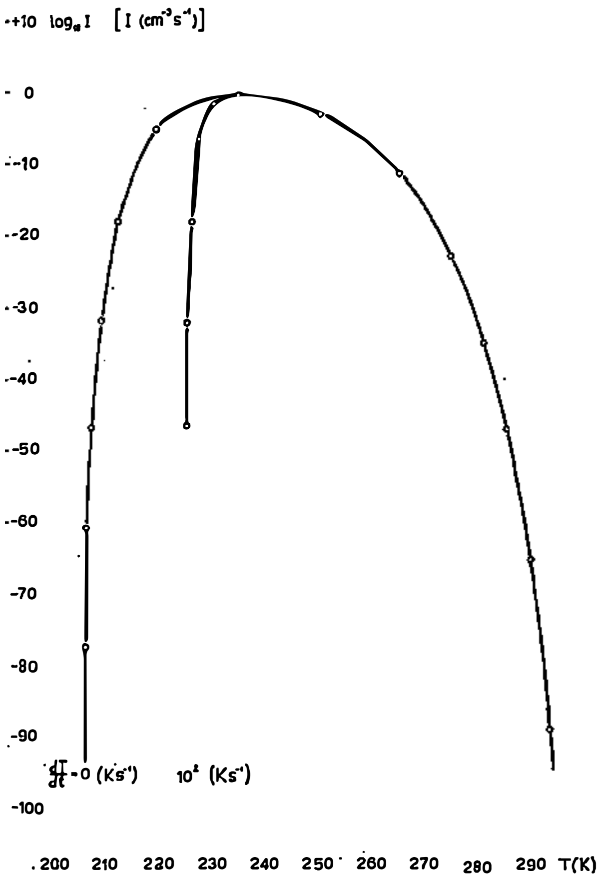

Fig. 4. Nucleation frequency of STP vs temperature.

from Fig. 4. where the equation (8) for $Q = 100$ K/s and $Q = 0$ is represented, the nucleation frequency has the maximum at about 235 K, while at 205 K and 295 K decreases for almost a hundred orders of magnitude. If we assume equation (5) in its simplest form $n = VI_0t_w$ and if we insert conventional values $V = 1$ cm^3 and $t_w = 10^5$ s, we will see that the condition $n < 1$ is fulfilled at all temperatures up to at least 250 K = −23°C. This gives the stable undercooling $\Delta T = 72$ K, also found in our experiment. Consequently, at room temperature liquid STP may exist almost indefinitely.

Nevertheless, the answer is still incomplete since we assumed only a homogeneous nucleation. In liquid STP there are certainly the heterogeneous nuclei, i.e. $d_s \neq 0$. Even in a very pure liquid such nuclei may be formed by dehydratation occuring at the melting point. As a consequence, the large undercoolings are better defined by the rate of crystal growth than by the nucleation. The evidence for this conclusion is also given by the observation that ΔT depends on the shape and dimensions of the measuring cell.

The rate of crystal growth is defined by equation (11). The only unknown parameter in it is f — the fraction of acceptor sites in the crystal surface. Let us examine briefly the results of the variation of this parameter. With $f = 1$ equation (11) gives $u \approx 1$ cm sec^{-1} at room temperature. This completely disagrees with the observations since liquid STP may persist for weeks at this temperature. Even the Uhlmann's suggestion (12) does not improve the results much because it gives $u \approx 0.02$ cm s^{-1}. It seems therefore that f in STP has an unusually small value: it must be much less than 1.

We have found the great support for this conclusion in the work of Jackson[10] who showed that all materials with parameter $\beta = \Delta H_m/RT_m > 2$ have smooth solid-liquid interface on the molecular scale, i.e. small number of acceptor sites, or, $f \ll 1$. This has been in accordance with the observations on glycerol ($\beta = 7.5$), salol ($\beta = 7$) and boron oxide ($\beta = 3.5$). Taking into account that β in STP is extraordinary high, i.e. 13, one has to expect unusually small values of f too.

Thus the reason for the large stable undercoolings in STP appears to be simple and understandable. We believe that the same arguments are valid for other similar substances mentioned in the Introduction.

Aknowledgement

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PRIJELAZ NATRIJ TIOSULFATA PENTAHIDRATA U STAKLASTO STANJE

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Sadržaj

Rezultati novijih istraživanja prijelaza u staklasto stanje mogu se primijeniti i na ispitivanje porijekla velikih stabilnih pothlađenja karakterističnih za neke materijale. Takva ispitivanja pokazuju, na primjer, da se stabilna pothlađenja natrij tiosulfata, pentahidrata, koja dosižu i do 70 K, mogu pripisati neobično strmoj ovisnosti nukleacione frekvencije o temperaturi i vrlo maloj vrijednosti omjera akceptorske i ukupne površine kristala.

Nađeno je da karakteristični alfa parametar za natrij tiosulfat pentahidrat iznosi 0.17—0.19, da je kritična brzina hlađenja oko 100 K/s i da je temperatura staklastog prijelaza tog materijala približno 215 K.