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Thermal properties of dimethylsulfoxide under confined geometry conditions

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The phase transitions of melting and crystallization of dimethylsulfoxide in porous glasses with different pore sizes have been studied using differential scanning calorimetry. The influence of size effects on characteristics of the transitions is revealed. The linear nature of the dependence of the melting temperature shift on the inverse pore radius is established.

Keywords: Dimethylsulfoxide, phase transitions, nanoparticles, size effects.

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Dimethylsulphoxide (DMSO) is widely used in contemporary science and engineering, in particular, as component of cryoprotectors in cryobiology (see paper [1] and references therein), as well as dissolvent [2,3], so, physical and chemical properties of bulk DMSO were intensively studied. Most recently there is interest in properties study of DMSO [4–6] and of some other materials under conditions of limited geometry, i.e. in case, when the material is in pores of nanoporous matrices. The paper [4] studied change in properties of inverted photonic crystal upon DMSO introduction, in [5] by methods of NMR and impedance spectroscopy the aqueous solutions of DMSO, introduced into glass matrix with average radius of pores of about 1.5 nm. In paper [6] the acoustic methods and method of differential scanning calorimetry (DSC) studied the phase transitions (PTs) of melting and crystallization in eutectic solutions water–DMSO of different composition introduced into porous glasses. Together with size effects typical for the single-component systems, the significant difference in PT intervals was identified by the above methods, which is explained by authors under a phenomenological model [7] previously suggested to melt decane in pores.

In present paper by DSC method we studied the processes of DMSO introduced into the porous matrices with different average size of pores.

The matrices were made of the preliminary heat treated blanks of sodium borosilicate glasses of two types: DV-1M and DV-1Sh (they differ by heat treatment conditions). Matrices of type 1 were manufactured of DV-1M by chemical treatment in 3M solution of hydrochloric acid for 120 h at temperature of 50°C, and then washed in distilled water and dried. Matrices of type 2 were made of DV-1Sh using the same procedure. To manufacture the matrices of type 3 part of matrices of type 2 was additionally treated in 0.5M solution of KOH for 25 h at temperature of 4–6°C. Characteristics of the manufactured porous matrices were determined by method of nitrogen sorption-desorption in device Quadrasorb SI. The porous matrices of type 1 had bimodal distribution of pores with basic maximum corresponding to radius of pores 3.2 ± 0.3 nm, and additional peak at 5.5 ± 0.5 nm (about 10% of pores by volume). Matrices of type 2 had single mode, but rather wide distribution of pores with average radius 6.4 ± 0.6 nm. For both types of matrices the specific porosity (i.e. ratio of pores volume to sample volume) was 26 ± 1%. For matrices of type 3 the sorption-desorption isotherms has no area of capillary condensation. Radius of pores for them can be calculated in the approximation of cylindrical pores as per formula $r = 2V/S$, where V and S — specific volume and specific area of surface of pores, respectively. The specific area was determined by BET-section of isotherm, and was $6.8 \pm 0.7\,\mathrm{m^2/g}$. The specific volume of pores was determined by weighing of empty and water filled matrix, and was $0.168 \pm 0.005\,\mathrm{cm^3/g}$, porosity was 27 ± 0.5%. The calculated effective radius of pores for matrices of type 3 was equal to 50 ± 5 nm.

Samples for measurements were prepared by porous matrices immersion in pure DMSO. Samples № 1–3 are designated by type of appropriate matrix. Degree o pores filling (on supposition of permanent density of DMSO) was close to 100%. Sample № 4 was a bulk DMSO. Its study is necessary due to contradictions in available literature data on melting heat [8–11].

Studies by DSC method were performed in microcalorimeter DSC-111 (Setaram). The sensitivity of the instrument was $\sim 3 \cdot 10^{-5}$ J/s. The instrument calibration and correction of system errors were performed in accordance with the method described in paper [12]. Calibration was performed such that temperatures of maxima (minima) of peaks in curves of heat capacity corresponded to temperatures T_m (T_c) of melting (crystallization) PT. Temperature of PT were determined with accuracy of ±2 K.

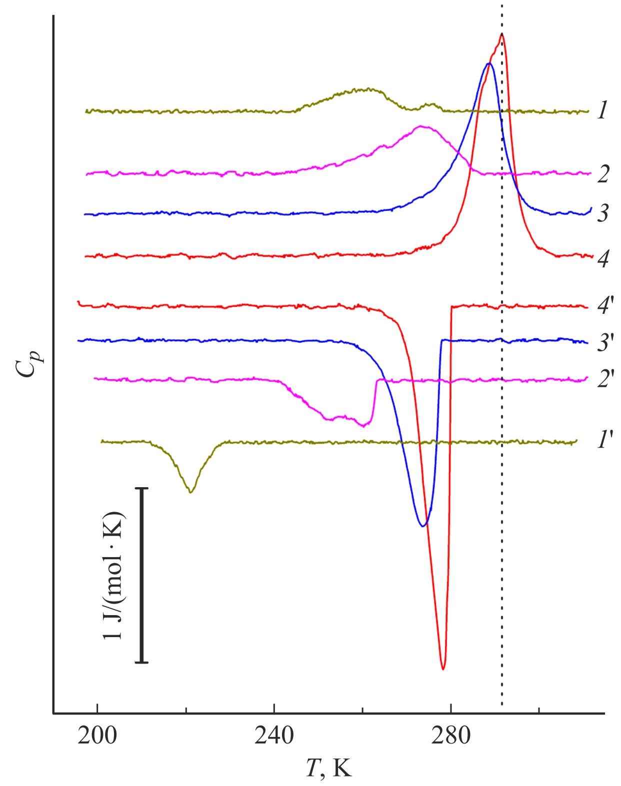

Figure 1. Temperature dependences of specific heat capacity of DMSO under conditions of limited geometry and bulk DMSO, measured during heating (*1–4*) and cooling (*1′–4′*). The numbers next to curves correspond to the numbers of samples. For visualization the curves are shifted relative each other along the axis of ordinates.

Melting (crystallization) heats Q_m (Q_c) were calculated by integration of the corresponding peaks. Scanning speed for samples № 2–4 was 5 K/min, for sample № 1–2 K/min.

Fig. 1 shows the temperature dependences of specific heat capacity of DMSO samples, the dependences were obtained during heating and cooling modes.

In cooling mode on the temperature dependences of heat capacity there are exothermic peaks corresponding to crystallization PT. The peaks have asymmetric form. When pore radius decreases the curve maxima shift to region of low temperatures, their amplitude decreases, and width increases. In heating mode there are endothermic peaks corresponding to melting. Their form is asymmetric also. With pore radius decreasing the amplitude, width and position of peak maxima change similarly to hat in case of crystallization. Note that in curve *1* there are two peaks. Generally, this can be associated with both bimodal distribution of radiuses of pores and, appropriately, of nanoparticles, and with presence of several crustal phases of substance, as it was observed, for example, in gallium alloys [13]. Since in matrix of type 1 the bimodal distribution of pores is observed, and presence in DMSO of polymorphs is unknown, for the studied system the first supposition is more probable. Presence of only one peak on the crystallization curve can be explained by the fact that, as crystallization occurs under the conditions of strong overcooling, the crystallization front arising in some portion of sample quickly spreads on all pores regardless of their size.

Parameters of phase transitions of melting and crystallization for system DMSO–porous matrix

Sample number	T_m, K	T_c, K	Q_m, kJ/mol	Q_c, kJ/mol
1	261, 276	228	6.3	6.2
2	274	262	5.3	3.7
3	289	274	9.9	9.6
4	291	279	12.8	12.7

Fig. 1 shows presence of prominent hysteresis between crystallization and melting processes, at that its temperature interval ($T_m - T_c$) increases when average radius of pores decreases.

Table shows PT parameters for all studied samples.

Note that measured herein melting heat for bulk sample was 12.8 kJ/mol, which is in good agreement with value given in [9]. In case of nanocomposites the obtained melting heat and crystallization heat are significantly lower than in bulk sample.

Said above manifestations of size effects during aggregate PTs are quite well known. For isolated small particles the shift of transition temperature can be described by simple thermodynamic models [14], major part of which is based on Gibbs–Thomson equation

$$\frac{\Delta T}{T_m^{bulk}} = \frac{CM\sigma_{sl}}{r\rho Q_{bulk}}, \qquad (1)$$

where $\Delta T = T_m^{grain} - T_m^{bulk}$ — temperature deviation of phase transition of particles with radius r (T_m^{grain}) from its value for bulk material (T_m^{bulk}), ρ — density, σ_{sl} — surface tension at interface solid body/liquid, Q_{bulk} — specific heat of transition, M — mole mass, C — dimensionless coefficient depending on particle form. So, Gibbs–Thomson equation predicts the linear dependence of transition temperature shift on reverse size of particle, which in our case is determined by size of matrix pore.

Opposite to case of isolated particles under conditions of limited geometry we need to consider particles interaction with matrix and with each other, so simple thermodynamic models can be considered as rather coarse approximation only. The matter of its accuracy and applicability of Gibbs–Thomson equation shall be considered separately in each case.

For studied herein nanocomposites the dependence of shift of ΔT melting temperature on reverse mean radius of pores is shown in Fig. 2. Figure shows that this dependence with good accuracy is linear one:

$$\Delta T = Ar^{-1}. \qquad (2)$$

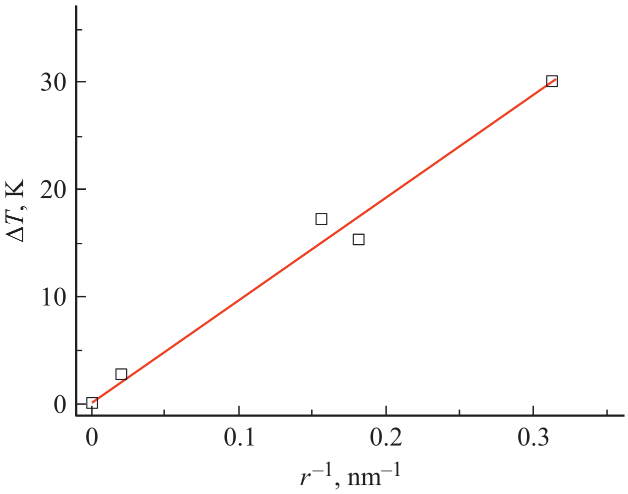

Figure 2. Relative change in T_m DMSO in nanopores vs. reverse mean radius of pores.

Coefficient of proportionality is $A = 96 \pm 5\,\mathrm{K \cdot nm}$. So, we can say on applicability of Gibbs–Thomson equation in case of DMSO in pores of glass matrices. In accordance with equation (1) $A = CT_m^{bulk}M\sigma_{sl}/\rho Q_{bulk}$. Neglecting the dimensional dependence of density we find that $C\sigma_{sl} = 59 \pm 3\,\mathrm{mN/m}$.

Note that models based on Gibbs–Thomson equation suppose that transition heat does not depend on radius of nanocrystal, and has permanent value typical for the bulk material. At the same time, see literature [15,16] and data obtained by us, with decrease in average size of pores the significant decrease in heat of phase transition occurs. We can suppose that permanent coefficient A in equation (2) is due to simultaneous change in melting heat and surface energy of nanoparticles, at that $C\sigma_{sl}/Q_{bulck} = 0.466 \pm 0.002$.

Thus, made studies of processes of melting and crystallization of DMSO in porous glasses identified temperature decrease of phase transitions, their broadening, decrease in transition heats. The linear nature of dependence of melting temperature shift on reverse mean radius of pores was identified.

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Conflict of interest

The authors declare that they have no conflict of interest.

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