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INFLUENCE OF OPEN-POROUS SYSTEM ON THE SOLID-STATE PHASE TRANSITION IN 1-OCTADECENE

The solid-state phase transition in the silica gel–1-octadecene system has been studied at various temperatures with the help of differential scanning calorimetry and FTIR spectroscopy. Silica gels KSK-2.5, KSS-4, and Silica Gel 60 with different surface parameters are used. The temperature of the solid-state phase transition in the silica gel–1-octadecene system is shown to linearly depend on the ratio between the pore surface area and the pore volume. The energy characteristics of 1-octadecene nanocrystals in the surface layer are calculated in the framework of a thermodynamical model of crystal melting in pores.

Keywords: solid-state phase transition, nanocrystals, porous silica gel.

1. Introduction

The properties of substances located in nano-sized pores play an essential role in the phenomena associated with clay swelling, soil frost heaving, oil production, colloidal stability, and drug transport through biomembranes [1]. The configuration of nanopores has a significant effect on the physical properties of solids in them [2–4]. In particular, the melting temperature and the temperature of solid-state phase transition are changed in nanocomposite materials [5]. The reduction of the melting temperature was considered in many works [1–5].

The solid-state phase transition in systems of aliphatic molecules is a transition from the crystalline phase to the rotational one. The understanding of the mechanism of this phase transition has a large practical importance to the physics of condensed systems and materials science. The solid-state phase transition in such systems occurs at temperatures that are only a few degrees lower than the melting ones. This circumstance complicates its experimental research. Therefore, the number of publications where this transition was studied under confinement conditions is much less than the number of works dealing with the melting under the same conditions [6].

The microscopic mechanism of solid-state transitions in alkanes – both in bulk systems and in pores – is not understood yet in full and requires to be studied further [7, 8]. The influence of a nanopore morphol-

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ogy on this solid-state transition has to be analyzed as well.

In this work, the influence of the silica gel matrix morphology on the solid-state phase transition in 1-octadecene, $\text{CH}_3(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$ (Fig. 1), has been studied. 1-octadecene belongs to the class of α -olefins (they have an aliphatic chain), in which there is a methyl group ($-\text{CH}_3$) at one end and a vinyl one ($-\text{CH}=\text{CH}_2$) at another one. The vinyl group can serve as a marker, when studying the thermal motion of an aliphatic molecule. A 1-octadecene molecule has 18 carbon atoms. When being cooled down, the substance concerned forms crystals created by straightened molecular chains, whose axes are oriented perpendicularly to the crystalline plane [9].

In our previous work [10], it was shown that, when being heated, bulk crystalline 1-octadecene undergoes the transition from the orthorhombic crystalline phase, Or_{crys} , to the orthorhombic rotational-crystalline one, Or_{rot} . This is a phase transition of the first kind in the solid phase. At a further heating, the melting of the substance takes place.

Some researches concerning the influence of the pore morphology in silica gel on the melting of 1-octadecene crystals were carried out in our previous works [11, 12]. Owing to a small difference between the temperatures of indicated phase transitions, there arose a necessity to apply other experimental methods in order to correctly separate the contributions of those processes. In particular, IR spectra of SiO_2 -1-octadecene systems were registered in a wide temperature interval that included the indicated phase transitions [11]. The available structurally sensitive absorption bands allowed the temperature of each phase transition to be determined separately and more accurately.

The aim of this work is to study the phase transition in 1-octadecene in the solid state located in a porous silica gel matrix and experimentally determine the corresponding energy (the difference between the surface tensions of the crystalline and rotational phases) and entropy (the difference between the surface entropies of the crystalline and rotational phases) characteristics.

2. Experimental Part

2.1. Research methods

For the research of phase transformations, a differential scanning calorimeter DSC Q200 (TA Instru-



Fig. 1. Molecule of 1-octadecene

ments, USA) was used. The temperature calibration was carried out with the help of sapphire disks (supplied by TA Instruments) in standard aluminum crucibles. The studies were performed in the temperature interval from $-90\text{ }^\circ\text{C}$ to $120\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ in a nitrogen flux of $50\text{ ml}/\text{min}$. Infrared transmission spectra were registered on a Nicolet-Nexus Fourier Infrared Spectrometer in the spectral interval $625\text{--}4000\text{ cm}^{-1}$ with a spectral resolution of 1 cm^{-1} . The registration was carried out in the transmission mode immediately from the “free layer”. In order to compare the intensities of absorption bands in the spectra, the following conditions were obeyed: (i) the size of the aperture, with respect to which the background spectrum was recorded, corresponded to the size of the specimen, so that the specimen completely covered the aperture, and (ii) the sensitivity intervals of the device were identical, when recording the background and specimen spectra. The spectra were recorded in the temperature interval from $-150\text{ }^\circ\text{C}$ to $50\text{ }^\circ\text{C}$ with the increment $\Delta T = 5\text{ }^\circ\text{C}$ in the transmission mode with the help of a Variable Temperature Cell P/N 21525 (Specac company) with the windows from sodium chloride. In the course of spectrum registration, the cell was pumped out by means of a backing pump. The specimens were first cooled down in liquid nitrogen. Then they were heated up at a rate of $2\text{ }^\circ\text{C}/\text{min}$, and the spectra were registered.

2.2. Raw materials and specimen preparation

Silica gels with various pore sizes were used. The specimen characteristics were determined by analyzing the nitrogen adsorption isotherms measured at $-196\text{ }^\circ\text{C}$ on a high-vacuum adsorption device Sorptomatic 1990 (see Table 1).

To fill the silica gel pores with 1-octadecene, the silica gel specimens were embedded into the 20% solution of 1-octadecene in hexane. The indicated silica gel-to-solution ratio was so selected that 1-octadecene should fill 75–80% of the silica gel pore volume in the resulting composite. The mixtures of silica gel

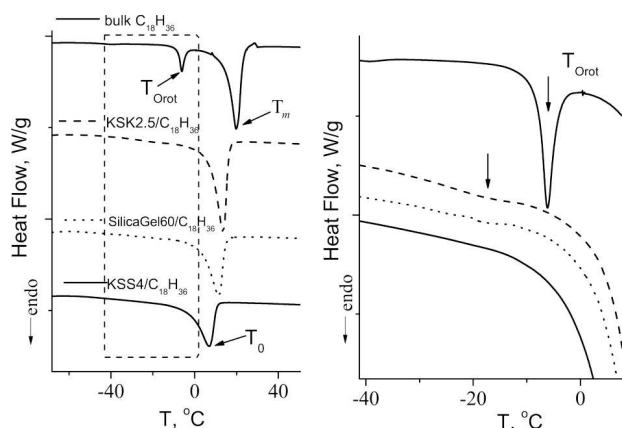


Fig. 2. Temperature dependences of the heat flux for examined specimens. T_{Orot} is the temperature of the phase transition from the orthorhombic crystalline phase Or_{crys} into the orthorhombic rotational-crystalline phase Or_{rot} , T_m the melting temperature of bulk 1-octadecene, and T_0 the melting temperature of 1-octadecene in silica gel pores

with 1-octadecene hexane solutions were irradiated with ultrasound in order to remove air remnants from the pores and then dried in air at a temperature of 90 °C. The resulting specimens were loose powders, whose particles did not stick together. The latter fact confirmed that the total amount of 1-octadecene was absorbed into the pores of silica gel particles.

To determine the content of 1-octadecene in porous matrices, the thermogravimetric researches using a Derivatograph Q1500D device were performed. The results of those studies are quoted in Table 2. One can

Table 1. Parameters of porous silica gels

Silica gels	$V, \text{cm}^3\text{g}^{-1}$	$S, \text{m}^2\text{g}^{-1}$	D, nm	$S/V, \text{nm}^{-1}$
KSK 2.5	0.926	311	11.93	0.33
Silica Gel 60	0.755	426	7.10	0.56
KSS 4	0.260	229	4.54	0.88

Table 2. Contents of adsorbed water, 1-octadecene, and surface -OH groups in specimens (in percent)

Silica gels	$m(\text{H}_2\text{O})$	$m(1\text{-octadecene})$	$m(-\text{OH})$
KSK 2.5/ $\text{C}_{18}\text{H}_{36}$	2.3	32.3	5
Silica Gel 60/ $\text{C}_{18}\text{H}_{36}$	3.3	32.1	3.4
KSS 4/ $\text{C}_{18}\text{H}_{36}$	4.7	22.4	4.3

see that silica gel pores contained adsorbed moisture (H_2O), 1-octadecene, and surface groups $-\text{OH}$.

2.3. Calorimetry

We measured the temperature dependences of the thermal flux in bulk 1-octadecene and 1-octadecene in silica gel pores in a temperature interval from $-80\text{ }^\circ\text{C}$ to $120\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ (Fig. 2). In our previous research of bulk 1-octadecene, it was shown that if 1-octadecene polycrystals are heated, then, starting from a temperature of about $T_{bOrot} = -30\text{ }^\circ\text{C}$, they undergo the phase transition from the orthorhombic crystalline phase, Or_{crys} , into the orthorhombic rotational-crystalline one, Or_{rot} , with a maximum at $T_{Orot} = -6\text{ }^\circ\text{C}$. This is a solid-phase transition of the first kind. When reaching the temperature $T_{bm} = 0\text{ }^\circ\text{C}$, 1-octadecene polycrystals begin to melt with a maximum at $T_m = 20\text{ }^\circ\text{C}$. At $T_{em} = 35\text{ }^\circ\text{C}$, the melting process comes to an end.

The temperature dependences of the heat flux obtained for nanostructured 1-octadecene in various porous silica gel matrices (Fig. 2) demonstrate the same phase transitions as in bulk 1-octadecene. One can see that the phase transition temperature decreases together with the pore size. Characteristic temperatures of the solid-phase transition T_{Orot} can be determined from the temperature dependences of the heat flux, but only with a low accuracy. Therefore, the method of infrared spectroscopy of specimens was additionally applied at various temperatures.

2.4. IR spectroscopy

The infrared transmission spectra of 1-octadecene were registered at various temperatures (see Fig. 3). When 1-octadecene polycrystals are heated up, the band changes can be observed (i) in a region of 720 cm^{-1} corresponding to pendulum vibrations of CH_2 groups ($\Delta\nu_{1,2}$), (ii) in a region of 908 cm^{-1} corresponding to deformation vibrations of the double bond $-\text{CH}=\text{CH}_2$ ($\nu_{\rho(=\text{CH}_2)}$), and (iii) in regions of 2845 and 2929 cm^{-1} (Fig. 3) corresponding to symmetric ($\nu_{s(-\text{CH}_2)}$) and antisymmetric ($\nu_{as(-\text{CH}_2)}$) valence vibrations of C-H groups [13].

One of the structurally sensitive bands in the IR spectrum of molecules with aliphatic chains is the band in a vicinity of $\nu = 720\text{ cm}^{-1}$ stemming from pendulum vibrations of CH_2 groups. At tempera-

tures below the phase transition ones, this band is split by $\Delta\nu_{1,2}(T)$ (this is inherent only to the orthorhombic subcell of the Or_{cryst} crystal [14]). Figure 3 demonstrates fragments of the IR spectra of bulk 1-octadecene registered at various temperatures. In the region of $\nu = 720 \text{ cm}^{-1}$, a splitting of the band is observed at the temperature $T = -80 \text{ }^\circ\text{C}$. As the temperature grows, two peaks approach each other, and, in a vicinity of the phase transition, they merge into a single peak. To resolve the two maxima and determine the value of $\Delta\nu_{1,2}(T)$ in the region of $\nu = 720 \text{ cm}^{-1}$, we approximated the peak profiles by the Voigt distribution.

The temperature dependences of the splitting magnitude $\Delta\nu_{1,2}(T)$ for the band of pendulum vibrations of CH_2 groups in a vicinity of $\nu = 720 \text{ cm}^{-1}$ are shown in Fig. 4 for bulk 1-octadecene and 1-octadecene in various matrices. In order to determine the temperatures of the phase transitions more accurately, we plotted the temperature dependences of the splitting derivative with respect to the temperature, $d\nu/dT$. A typical dependence of $d\nu/dT$ on T obtained for $\text{KSS4}/\text{C}_{18}\text{H}_{36}$ is shown in Fig. 4. One can see that the splitting $\Delta\nu_{1,2}(T)$ is practically constant in the temperature interval from $-100 \text{ }^\circ\text{C}$ to T_{bOrrot} . When the beginning of the phase transition in the solid state (T_{bOrrot}) is reached, the splitting magnitude drastically decreases in two stages: from T_{bOrrot} to T_{bm} , and from T_{bm} to T_{m} . A conclusion can be drawn that, when being cooled down to $-150 \text{ }^\circ\text{C}$, both bulk 1-octadecene and 1-octadecene in various matrices crystallize with the orthorhombic symmetry of the Or_{cryst} cells. When the commencing temperature of the phase transition T_{bOrrot} is attained, the phase transition into the orthorhombic rotational-crystalline phase Or_{rot} takes place. This transition is accompanied by a partial decrease of the Davydov splitting magnitude $\Delta\nu_{1,2}(T)$, because the azimuthal correlation between 1-octadecene molecules becomes partially lost. When the temperature T_{bm} is reached, the splitting magnitude $\Delta\nu_{1,2}(T)$ sharply vanishes. This behavior testifies that the azimuthal correlation between the molecules becomes completely lost, i.e., the specimen undergoes the melting.

In Figs. 5 and 6, the temperature dependences of the shifts of the symmetric ($\nu_{\text{s}}(-\text{CH}_2)$, Fig. 5) and antisymmetric ($\nu_{\text{as}}(-\text{CH}_2)$, Fig. 6) valence vibration bands with respect to their positions at $-150 \text{ }^\circ\text{C}$ are exhibited for all examined specimens. The de-

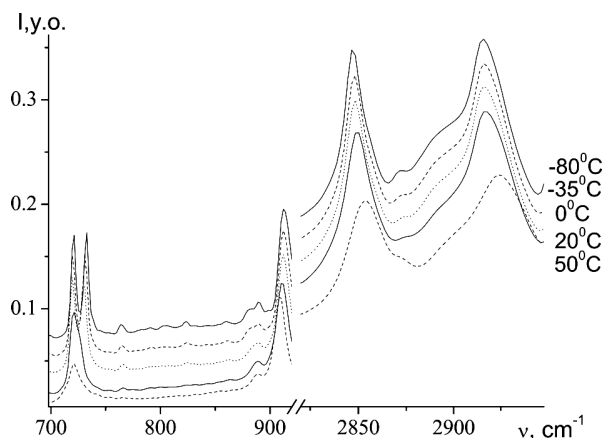


Fig. 3. Infrared transmission spectra of 1-octadecene at various temperatures

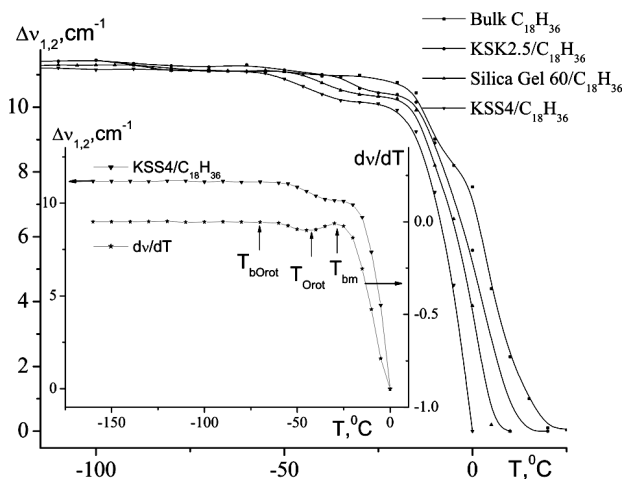


Fig. 4. Temperature dependences of the splitting $\Delta\nu_{1,2}(T)$ of the band of pendulum vibrations of CH_2 groups in a vicinity of $\nu = 720 \text{ cm}^{-1}$ for bulk 1-octadecene and 1-octadecene in various matrices. The indicated temperature dependence for $\text{KSS4}/\text{C}_{18}\text{H}_{36}$ and the temperature dependence of its derivative with respect to the temperature are shown in the inset

pendences demonstrate a few inflection points that coincide with the phase transition temperatures. To analyze the temperature behavior of the band position for symmetric and antisymmetric valence vibrations, we plotted the temperature dependences of the derivative $d\nu/dT$. The corresponding plots are shown for the specimens $\text{SilicaGel60}/\text{C}_{18}\text{H}_{36}$ (Fig. 5) and $\text{KSK2.5}/\text{C}_{18}\text{H}_{36}$ (Fig. 6). Two maxima are observed in those dependences. One of them is associated with the phase transition in the solid state, and the other

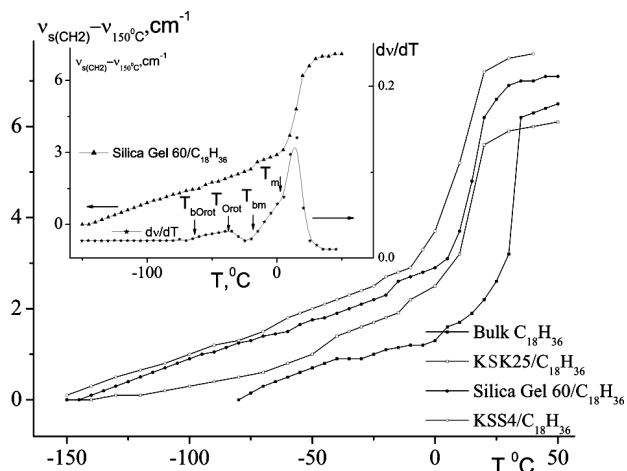


Fig. 5. Temperature dependences of the shift $\nu_s(-CH_2)$ of the band of symmetric valence vibrations with respect to its position at -150°C for bulk 1-octadecene and 1-octadecene in various matrices. The indicated temperature dependence for SilicaGel60/ $C_{18}H_{36}$ and the temperature dependence of its derivative with respect to the temperature are shown in the inset

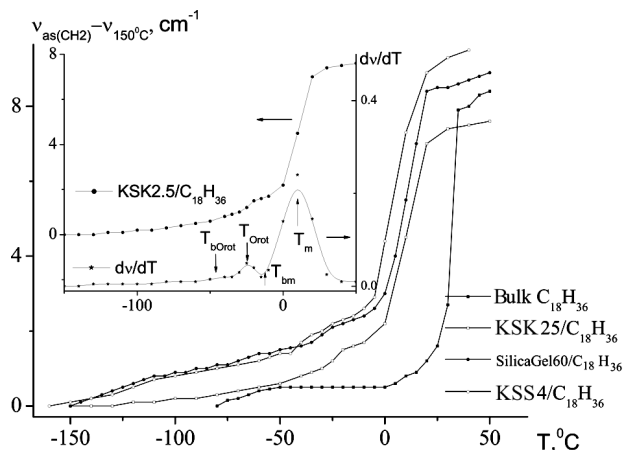


Fig. 6. Temperature dependences of the shift $\nu_{as}(-CH_2)$ of the band of antisymmetric valence vibrations with respect to its position at -150°C for bulk 1-octadecene and 1-octadecene in various matrices. The indicated temperature dependence for KSK2.5/ $C_{18}H_{36}$ and the temperature dependence of its derivative with respect to the temperature are shown in the inset

with the melting. All other specimens also demonstrated two phase transitions, whose temperatures decreased together with the pore size.

The band at 912 cm^{-1} (Fig. 3) is associated with deformational atomic vibrations of the end vinyl group. It is known [13] to be one of the most suitable

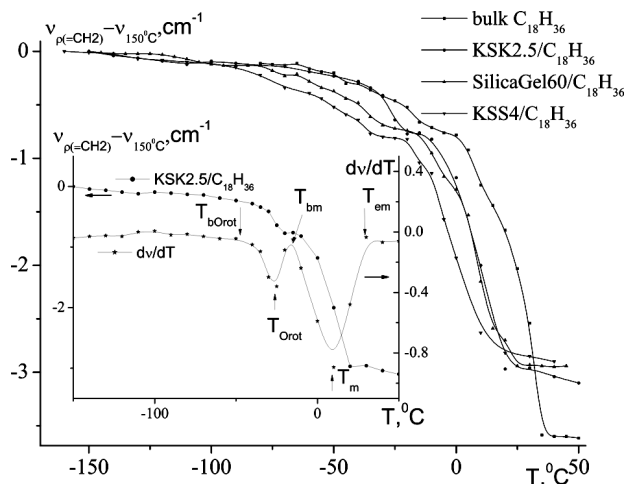


Fig. 7. Temperature dependences of the shift of the band of deformational vibrations of the double bond $-CH = CH_2$ with respect to its position at -150°C for bulk 1-octadecene and 1-octadecene in various matrices. The indicated temperature dependence for KSK2.5/ $C_{18}H_{36}$ and the temperature dependence of its derivative with respect to the temperature are shown in the inset

bands for studying the character of molecular motion in olefins. We plotted the temperature dependences of the shift of the band of deformation vibrations of the double bond $-CH = CH_2$ ($\nu_{\rho}(-CH_2)$) with respect to its position at -150°C for bulk 1-octadecene and 1-octadecene in various matrices. In order to exactly determine the phase transition temperatures for 1-octadecene and 1-octadecene in various matrices, we also plotted the temperature dependences of the temperature derivative dv/dT of the shift of the band of deformation vibrations of the double bond $-CH = CH_2$. For KSK2.5/ $C_{18}H_{36}$, this dependence is shown in Fig. 7. One can see that the band position practically is not changed within the temperature interval from -100°C to T_{bOrot} . When reaching the beginning of the phase transition (T_{bOrot}), the band position drastically decreases in two stages: from T_{bOrot} to T_{bm} , and from T_{bm} to T_m . In the same intervals, two minima are also observed in the dependences of the temperature derivative of the band position for deformational vibrations of the double bond $-CH = CH_2$. All other specimens also demonstrated two phase transitions, whose temperatures decreased together with the pore size.

The band at 1378 cm^{-1} is associated with umbrella vibrations of the end methyl group. This band

is known [15, 16] to be also suitable for studying the character of molecular motion in aliphatic chains. The temperature dependences of the shift of the band of umbrella vibrations of the final methyl group $-\text{CH}_3$ ($\nu_{\delta(-\text{CH}_3)}$) with respect to its position at -150°C were plotted for 1-octadecene and 1-octadecene in various matrices (Fig. 8). One can see that every dependence has a maximum in the temperature interval from -150°C to T_{bOrrot} . At the temperature when the phase transition begins (T_{bOrrot}), the band shift magnitude $\Delta\nu_{\delta(\text{CH}_3)}$ starts to drastically increase. This growth continues up to T_{bm} . After reaching a maximum value at T_{bm} , the value of $\Delta\nu_{\delta(\text{CH}_3)}$ for the umbrella vibrations of the final methyl group decreases and has a minimum at T_{m} . As the temperature increases further, the magnitude of $\Delta\nu_{\delta(\text{CH}_3)}$ grows monotonically.

3. Discussion of Results

By studying the infrared spectra of 1-octadecene in pores of porous silica gel, the temperatures of the solid-state phase transition, T_{Orrot} , are determined. In our previous works [12, 17], it was shown that it is expedient to describe the open-porous systems, with porous silica gels belonging to them, by the ratio S/V between the silica gel surface area S and the silica gel pore volume V rather than by the pore radius. Therefore, the dependences of the solid-phase transition temperature T_{Orrot} on this ratio are plotted for bulk 1-octadecene and 1-octadecene in various silica gel matrices (Fig. 9).

To describe the dependence of the solid-phase transition temperature T_{Orrot} on the S/V ratio, we use the following formula obtained in our previous work [12]:

$$T_0 = T_\infty \left(1 + \frac{\alpha_B(T_\infty) - \alpha_A(T_\infty)}{\Lambda} \frac{S}{V} \right), \quad (1)$$

where T_∞ is the temperature of the phase transition in a macroscopic-sized crystal; T_0 is the temperature of the phase transition for the crystalline substance in pores; $\alpha_A(T_\infty)$ and $\alpha_B(T_\infty)$ are the surface tension coefficients at the crystalline phase–matrix and rotational phase–matrix interfaces, respectively; and Λ is the specific heat of the phase transition in a macroscopic-sized crystal. The experimental dependence $T_{\text{Orrot}}(S/V)$ in Fig. 9 is approximated by formula (1), which gave us the values

$$T_\infty \frac{\alpha_B(T_\infty) - \alpha_A(T_\infty)}{\Lambda} = 25 \text{ K nm}$$

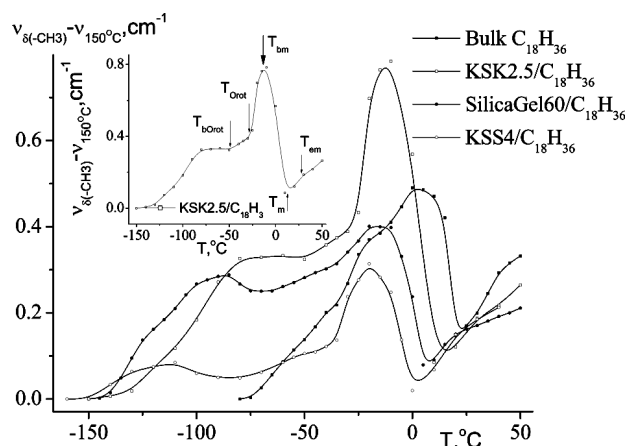


Fig. 8. Temperature dependences of the shift $\nu_{\delta(-\text{CH}_3)}$ of the band of umbrella vibrations of the final methyl group $-\text{CH}_3$ with respect to its position at -150°C for bulk 1-octadecene and 1-octadecene in various matrices. The dependence for KSK2.5/ $\text{C}_{18}\text{H}_{36}$ is repeated in the inset

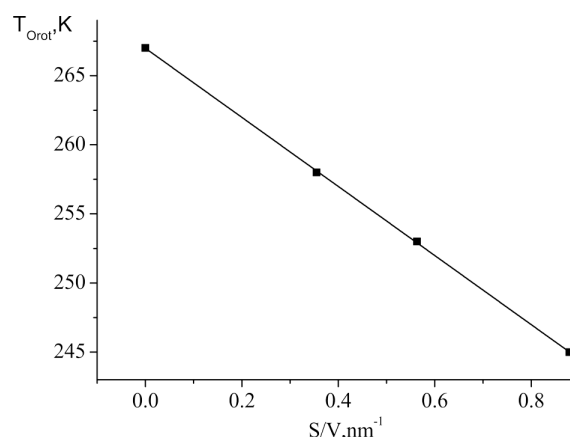


Fig. 9. Dependence of the temperature T_{Orrot} of the solid-phase transition from the orthorhombic crystalline phase Or_{crys} into the orthorhombic rotational crystalline one Or_{rot} on the ratio S/V for bulk 1-octadecene and 1-octadecene in various silica gel matrices

and $T_\infty = 267 \text{ K}$. The approximated temperature T_∞ coincides with the temperature of the solid-phase transition in bulk 1-octadecene, i.e., the same 1-octadecene crystalline structure is formed both in the bulk substance and in the pores of porous silica gel.

To find the surface tension difference $\alpha_B(T_\infty) - \alpha_A(T_\infty)$, we have to know the melting heat of bulk 1-octadecene. Experimentally (see Fig. 2), we obtained the specific heat value $\lambda = 159.5 \text{ kJ/kg}$, which included the heat of the phase transition from the

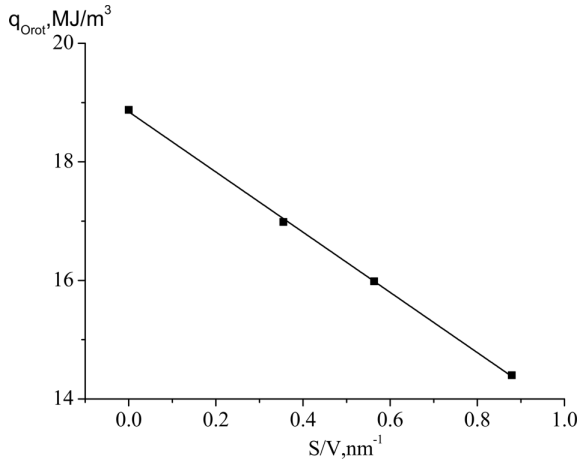


Fig. 10. Dependence of the heat q_{Orot} of the phase transition from the orthorhombic crystalline phase into the orthorhombic rotational crystalline one of 1-octadecene on the ratio S/V

orthorhombic crystalline phase to the orthorhombic rotational-crystalline one and the melting heat. Resolving the areas under the peaks in the temperature dependence of a heat flux for bulk 1-octadecene (Fig. 2), we found that the first peak included about 15% of the total area, whereas the second one about 85%. Then, the specific heat of the solid-phase transition in bulk 1-octadecene amounts to $\lambda = 24$ kJ/kg.

In formula (1), Λ is the phase transition heat per unit volume. Taking into account that the 1-octadecene density $\rho = 789$ kg/m³, the heat of the solid-phase transition per unit volume equals $\Lambda_{\text{Orot}} = 19$ MJ/m³, and the solid-phase transition temperature for bulk 1-octadecene equals $T_\infty = T_{\text{Orot}} = 267$ K, we obtain that the difference between the surface tension coefficients at the crystalline phase–matrix and rotational phase–matrix interfaces is

$$\alpha_B(T_\infty) - \alpha_A(T_\infty) = -1.8 \times 10^{-3} \text{ N/m.}$$

By comparing this value with the difference between the surface tension coefficients at the rotational phase–matrix and melt–matrix interfaces, which is equal to [12]

$$\alpha_B(T_\infty) - \alpha_A(T_\infty) = -4.7 \times 10^{-3} \text{ N/m,}$$

we see that the difference in the latter case is much larger.

Let us determine the specific heat of the solid-phase transition for 1-octadecene in various porous

silica gel matrices. From the experiment, we obtain the values of the specific heat for 1-octadecene in various porous silica gel matrices, which include the specific heat of the phase transition from the orthorhombic crystalline phase to the orthorhombic-rotational-crystalline one and the specific heat of the melting. To resolve the contributions from those transitions, we assume that their relative contribution is the same as was in the case of bulk 1-octadecene (15% and 85%, Fig. 2). With regard to the mass of 1-octadecene in the porous matrix (Table 2), we can plot the dependence of the solid-phase transition heat per unit volume of 1-octadecene on the ratio S/V (Fig. 10).

To describe the dependence of the solid-phase transition heat q_{Orot} on the ratio S/V , we use the following formula obtained in our previous work [12]:

$$q = \Lambda - T_\infty \left[\frac{\partial \alpha_B}{\partial T}(T_\infty) - \frac{\partial \alpha_A}{\partial T}(T_\infty) \right] \frac{S}{V}. \quad (2)$$

Here, the parameters T_∞ and Λ are the same as in formula (1), and the derivatives $\frac{\partial \alpha_A}{\partial T}$ and $\frac{\partial \alpha_B}{\partial T}$ are the surface entropies at the crystalline phase–matrix and rotational phase–matrix interfaces, respectively. By approximating the temperature dependence of the heat $q_{\text{Orot}}(S/V)$ (see Fig. 10) using formula (2), we obtain the value

$$\frac{\partial \alpha_B}{\partial T}(T_\infty) - \frac{\partial \alpha_A}{\partial T}(T_\infty) = -0.2 \times 10^{-3} \text{ N/mK.}$$

By comparing it with the surface entropy difference between the rotational phase–matrix and melt–matrix interfaces,

$$\frac{\partial \alpha_B}{\partial T}(T_\infty) - \frac{\partial \alpha_A}{\partial T}(T_\infty) = -0.9 \times 10^{-3} \text{ N/mK,}$$

one can see that the difference between the surface entropies of the phases at the melting is much larger than the corresponding difference at the solid-state transition.

Therefore, the processing of obtained experimental data enabled us to calculate both the difference between the surface energies and the difference between the surface entropies of the phases, which makes it possible to determine the energy parameters of the surface layer, when the pore surface is modified by various functional groups.

4. Conclusions

The structure of 1-octadecene crystals that are formed in silica gel pores is the same as in bulk 1-

octadecene. Both the difference between the surface tensions and the difference between the surface entropies of the phases at the melting are larger than the corresponding differences at the phase transition from the orthorhombic crystalline phase into the orthorhombic rotational-crystalline one.

1. P. Huber. Soft matter in hard confinement: phase transition thermodynamics, structure, texture, diffusion and flow in nanoporous media. *J. Phys.: Condens. Matter* **27**, 103102 (2015).
2. Q. Jiang, M.D. Ward. Crystallization under nanoscale confinement. *Chem. Soc. Rev.* **43**, 2066 (2014).
3. M. Sliwinska-Bartkowiak, A. Sterczynska, Y. Long, K.E. Gubbins. Influence of microroughness on the wetting properties of nano-porous silica matrices. *Mol. Phys.* **112**, 2365 (2014).
4. J. da Silva Buriti, M.E.V. Barreto, K.O. Santos, M.V.L. Fook. Thermal, morphological, spectroscopic and biological study of chitosan, hydroxyapatite and wollastonite biocomposites. *J. Therm. Anal. Calorim.* **134**, 1521 (2018).
5. Dongqing Wang, Jian Sui, Di Qi, Shuping Deng, Yongteng Wei, Xin Wang, Xiao Zheng Lan. Phase transition of dodecane in nanopores. *J. Therm. Anal. Calorim.* **135**, 2869 (2018).
6. K. Jiang, B. Xie, D. Fu, F. Luo, G. Liu, Y. Su, D. Wang. Solid-solid phase transition of n-alkanes in multiple nanoscale confinement. *J. Phys. Chem. B* **114**, 1388 (2009).
7. K. Nozaki, M. Hikosaka. Mechanism of primary nucleation and origin of hysteresis in the rotator phase transition of an odd n-alkane. *J. Mater. Sci.* **35**, 1239 (2000).
8. A.B. Herhold, H.E. King, Jr, E.B. Sirota. A vanishing nucleation barrier for the n-alkane rotator-to-crystal transformation. *J. Chem. Phys.* **116**, 9036 (2002).
9. H. Gang, O. Gang, H.H. Shao *et al.* Rotator phases and surface crystallization in eicosene *J. Phys. Chem. B* **102**, 2754 (1998).
10. O.M. Alekseev, S.O. Alekseev, L.A. Bulavin, M.M. Lazarenko, O.M. Maiko. Phase transitions in chain molecular polycrystals of 1-octadecene. *Ukr. J. Phys.* **53**, 882 (2008).
11. M.M. Lazarenko, A.N. Alekseev, S.A. Alekseev, Yu.E. Grabovsky, M.V. Lazarenko. Phase transitions of some aliphatic molecular crystals in confined space. *Khim. Fiz. Tekhnol. Poverkhn.* **2**, 128 (2011) (in Ukrainian).
12. L.A. Bulavin, O.M. Alekseev, Y.F. Zabashta, M.M. Lazarenko. Phase equilibrium, thermodynamic limit, and melting temperature in nanocrystals. *Ukr. J. Phys.* **63**, 1036 (2018).
13. L.M. Babkov, G.A. Puchkovskaya, S.P. Makarenko, T.A. Gavrilko. *IR Spectroscopy of Molecular Crystals with Hydrogen Bonds* (Naukova Dumka, 1989) (in Russian).
14. E.N. Kotelnikova, S.K. Filatov. *Crystal Chemistry of Paraffins* (Zhurnal-Neva, 2002) (in Russian).
15. M. Del Zoppo, G. Zerbi. Surface melting in crystalline polymethylene systems. *Polymer* **31**, 658 (1990).
16. S.Y. Tkachev, O.M. Alekseev, M.M. Lazarenko, M.V. Lazarenko *et al.* Topological solitons in branched aliphatic molecules. *Mol. Cryst. Liq. Cryst.* **665**, 166 (2018).
17. L.A. Bulavin, O.M. Alekseev, Y.F. Zabashta, M.M. Lazarenko. Melting thermodynamics of nanocrystals. *J. Phys. Stud.* **22**, 2601 (2018).

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ВПЛИВ ВІДКРИТО-ПОРИСТОЇ СИСТЕМИ НА ТВЕРДОФАЗНИЙ ПЕРЕХІД В 1-ОКТАДЕЦЕНІ

Резюме

За допомогою диференціальноскануючої калориметрії та ІЧ-спектрів при різних температурах проводились дослідження твердофазного переходу в системі силікагель – 1-октадецен. Використовувались силікагелі марок KSK 2.5, Silica Gel 60, KSS 4, які мають різні характеристики поверхні. Показано, що температура твердофазного переходу систем силікагель – 1-октадецен лінійно залежить від відношення площі до об'єму пор. За допомогою термодинамічної моделі плавлення кристалів у порах розраховані енергетичні характеристики поверхневого шару нанокристалів.