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Study of Octadecane and Docosane droplets melting

The alkanes melting (n-Octadecane, n-Docosane) is studied experimentally. The droplets size and shape histories are analyzed and compared with the characteristics of n-alkanes phase transition solid-liquid. It is found that the droplet equivalent diameter increases significantly due to melting and thermal expansion. At the same time its shape evolves continuously: initially elongated droplet becomes almost spherical then elongates again. The droplet aspect ratio non-monotonic change correlates with surface tension temperature dependence.

Introduction. Melting of n-alkanes is of great interest for fundamental science (theory of phase transitions) as well as for industrial applications. The heat accumulation and storage is an important area of energy saving. Thermal storage devices can provide an efficient utilization of solar energy and waste heat power plant, smooth daily and seasonal fluctuations in energy consumption. A phase change materials (PCM) are capable to accumulate considerable quantity of energy when melting and then release stored latent energy while solidifying [1]. The use of latent heat of paraffin melting for heat accumulation is very promising because the enthalpy of melting is sufficiently high, besides paraffin is chemically inert and safe in usage, inexpensive substance. The melting point of n-alkanes, which are solid under normal conditions, rises gradually with molecular weight from 22°C (heptadecane $C_{17}H_{36}$) and to 75°C (pentatriocontane $C_{35}H_{72}$), providing a wide range of possible applications. For example, the melting point of n-Octadecane (28.1°C) slightly exceeds the optimal temperature for human comfort, so it can be used as component of PCM for everyday use ("smart" wall-paper and textiles, and so on). The melting point of n-Docosane is higher (44°C), so it can be used for providing thermal conditions of electronic equipment and aeronautical engineering. so they are considered as main component of PCM.

Peculiarities of Alkanes melting. Development of heat storage devices on the basis of phase-change materials (PCM) requires the accurate data on melting characteristics of the materials. In this paper the peculiarities of melting kinetics of Octadecane and Docosane are described.

Nowadays, the solid-liquid phase transitions are investigated widely due to promising applications, because the successful way to develop new products implies availability of reliable data on melting characteristics of n-alkanes and their mixtures. At the present time it is established that melting of alkanes has some peculiarities [2-4]:

– a pronounced change of physical properties during a phase transition;

– an existence of one or more intermediate phases (rotator phases);

Table. The thermophysical properties of Octadecane and Docosane [4, 6].

n-alkane	Octadecane, $C_{18}H_{38}$		Docosane, $C_{22}H_{46}$	
t_{melt}, °C	27.5		44.6	
Phase state	solid	liquid	solid	liquid
ρ, кг/м3	930	771	910	778
$\sigma_{\max}$, mN/m	26.2 (28.2 °C)	27.5 (30.0°C)	23.8 (44°C)	27.6 (48°C)
k ,Wt/mK	0.32	0.16	0.26	0.13

– a surface freezing at temperature some degree above alkane melting point;
– a temperature hysteresis of melting and crystallization processes.

The phenomena listed above reflect a complex nature of the melting and crystallization processes. This complexity leads to dependence of the kinetic characteristics on a number of factors: the nature of heat source, heating rate and specific surface of a sample (surface/volume ratio). That is why one should study the melting kinetics under operating conditions. In our study we investigate melting of pendant droplets of Octadecane and Docosane because very few literature data are available on pendant droplets melting.

The pronounced changes of physical properties are used to control process of droplet melting. For example, the specific gravity of alkane substantially reduces during melting, as a result the size of droplet increases visibly. After melting completion the droplet diameter grows slightly with temperature due to thermal expansion, but soon begins to decrease because of intensive evaporation. In so way we can determine a melting time by dependence $d_{eq}(t)$. Solid alkane is opaque, but it becomes almost transparent when melted, so we can visually distinguish a solid and a liquid phases, and to estimate a volume fraction of solid residue. Also it should be noted that thermal conductivity of alkanes decreases twofold after melting.

In the Table below some physical properties of solid and liquid alkanes are presented. We can see, that they differ substantially. These differences are used for diagnostics of phase transition solid-liquid.

The intermediate states are the most distinctive feature of alkane melting. Let's consider them in details.

Surface freezing. N-alkanes with chain length from 16 to 50 are characterized by phenomenon known as 'surface freezing', which occurs at temperature some degrees above the bulk melting point. In the paper [5] the results of surface tension measurements on liquid n-alkanes are presented confirming the existence of a surface ordered layer at temperatures up to $\Delta T = 3$°C above the bulk freezing temperature. The surface tension data reveal that the structure of the surface layer is similar to the bulk rotator phase, where the molecular chains are vertically aligned and hexagonally packed with long-range positional order. In Fig.2 the graph of n-Docosane surface tension versus temperature $\sigma(T)$ is presented [5]. We can see that the surface tension

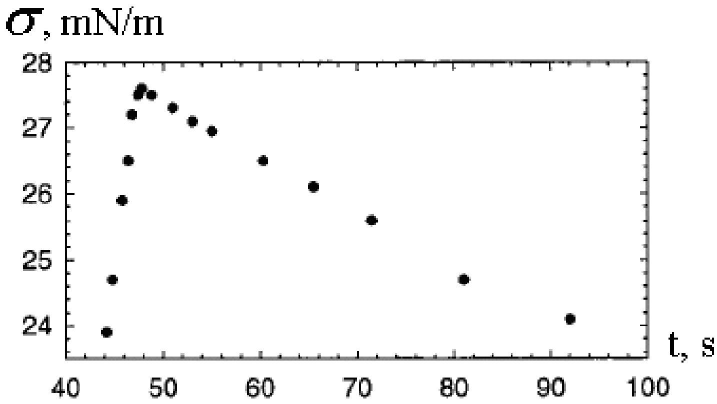

Fig.1. Surface tension of n-Docosane [6].

is about 23.8 mN/m at melting point, and rises quickly up 27.6 mN/m at ~ 48°C, then drops down fluently. In so way the maximum point on the graph $\sigma(T)$ corresponds to the state of surface freezing. As a result the droplet shape is almost spherical. In the Fig.1 the surface tension of Docosane versus temperature is presented.

Rotator phases. Rotator phases of normal alkanes and other hydrocarbon chain systems attract the attention of many researchers owing to their unique properties which include surface crystallization, anomalous heat capacity, negative thermal compressibilities and unusually high thermal expansions. As it is known, the molecules of n-alkanes form lamellae with long axes of the molecules parallel [6]. For $n < 30$ alkanes have a triclinic crystal structure for even n and an orthorhombic crystal structure for odd n.

Recently it was found that not only orthorhombic n-alkanes but also triclinic n-alkanes undergo consistent phase transitions from the crystal state to the low-temperature (rot.1) and high-temperature (rot.2) rotator states. Each of these states is characterized by a specific form of the molecular thermal oscillation motion.

Experiment and results. The droplets melting was studied by use the special setup described earlier [4]. As the alkanes concerned are solid at room temperature, at first a sample was melted in a water bath, then a droplet was formed with a syringe and suspended on a tungsten filament (d = 114 mcm). The solidified droplet was inserted in heated air, and the droplet history was recorded by camera through microscope objective.

The images obtained are processed to determine its size and to analyze shape evolution. To determine an equivalent diameter of a droplet we use the method developed earlier: at first we calculate surface area of a solid of revolution obtained by rotating a semi-perimeter of droplet image around the vertical line and then define a diameter of a sphere of the equal surface area.

Octadecan droplet melting. It is found that when heating an octadecane droplet its diameter firstly diminishes and then increases significantly due to thermal and melting expansion. At the same time its shape changes continuously: initially elongated droplet becomes almost spherical then stretched again. With a further tempera-

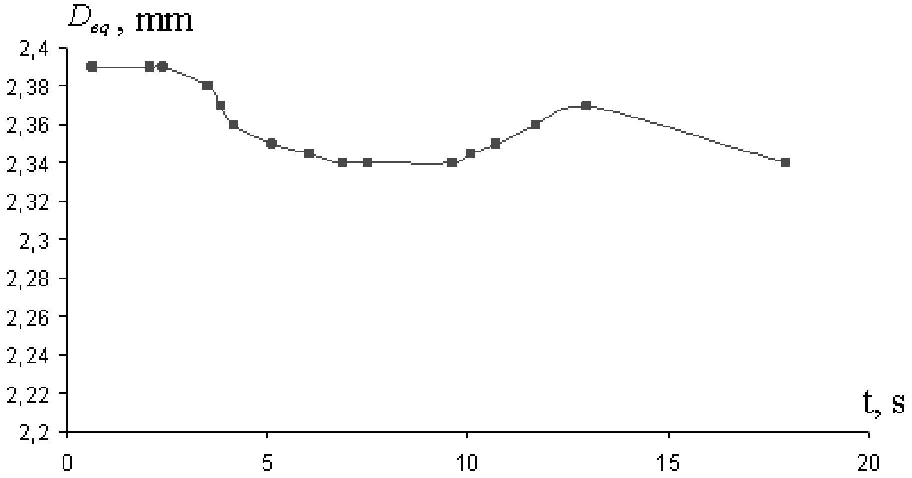

Fig. 2. The octadecane droplet history during melting under DC field d_0 = 2.4 mm.

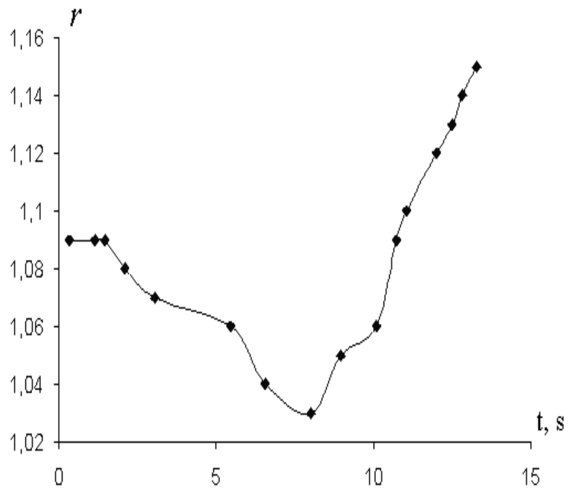

Fig.3a. Change of the droplet aspect ratio during melting under DC field. D_{eq}^{0} = 2.4mm

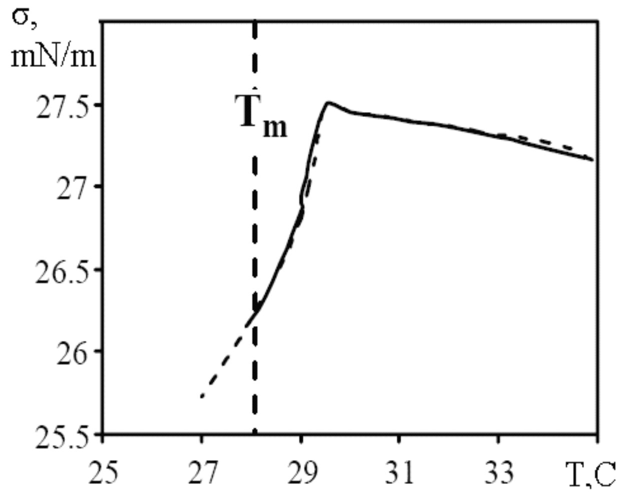

Fig.3b. Octadecane surface tension versus temperature [3].

ture rise the droplet's diameter diminishes due to intensive evaporation, when it goes down to 1 mm, droplet's shape becomes practically spherical.

In figure 2 the dependence of the droplet equivalent diameter on heating time is presented. Octadecane is a fusible alkane and melts quickly. Under constant electric field (E = 82 kV/m) melting duration is relatively long [8]. The possible cause of droplet size decrease at the beginning of melting is presence of voids formed during droplet preparation. Another possible cause is the phase transition to the rotator state.

There are a number of shape factors to describe a shape of droplet or particle. For example a 'circularity' (or isoperimetric quotient) is often used to analyze an image of droplet. The circularity is a function of the perimeter P and the area S of the droplet projection:

$$f_{circ} = \frac{4\pi S}{P^2}.$$

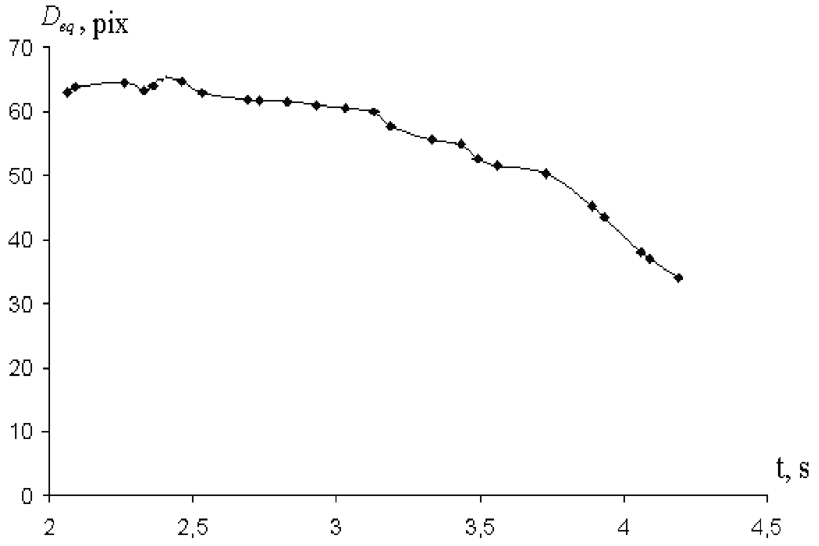

Fig. 4a. Docosane droplet melting and burning history. D^0_{eq} = 1.6 mm

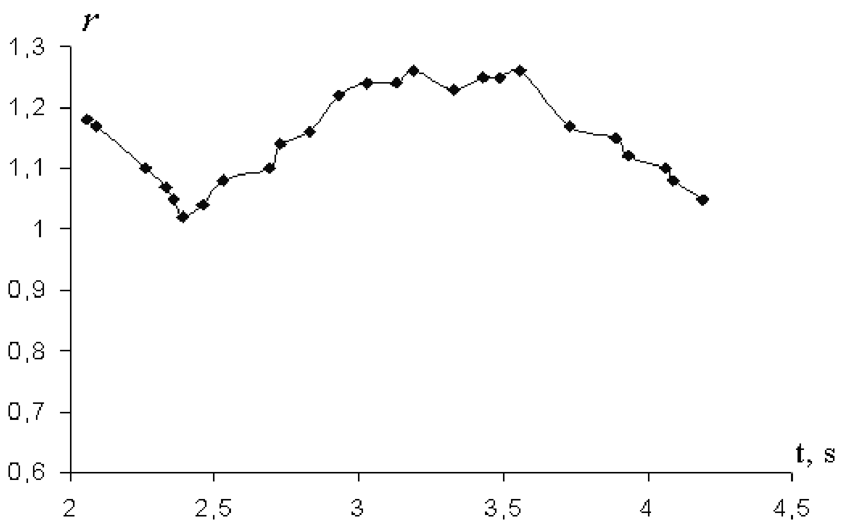

Fig.4b. Change of the droplet aspect ratio during melting and burning

The circularity of a circle is one, and less than one for an elongated circle. But in our study it is more appropriate to use 'aspect ratio', which equals to ratio of the largest droplet diameter *D* and the smallest diameter orthogonal to it *d*: $r = D/d$

For a pendant droplet *D* is a maximum vertical size (height) and *d* is a horizontal size.

Aspect ratio of a droplet is a function of the gravitational Bond number, which represents the ratio of gravitational-to-surface tension forces:

$$Bo = \frac{\Delta\rho g L^2}{\sigma}.$$

Here $\Delta\rho$ – difference in density of droplet and ambient medium, kg/m^3; g – gravitational acceleration, 9.81 m^2/c; L – characteristic length, m; σ – surface tension, N/m. In our conditions: $\rho_l \gg \rho_{air}$, $L \approx R$ – a droplet radius, so we have a next expression: $Bo = \rho g R^2 / \sigma$.

A simple linear function can be used to express an aspect ratio through gravitational Bond number [10]: $r = 1 + k \cdot Bo$. The coefficient k should be determined experimentally for each investigated material.

In Fig.3a the dependence of the aspect ratio on time is presented for Octadecan droplet with initial diameter 2.4 mm.

The correlation between $r(t)$ and $\sigma(T)$ curves leads us to the conclusion that local minimum of the aspect ratio corresponds to maximum value of the surface tension and to surface freezing state. In so way we observe a transitional state of surface freezing some degrees above melting point, which can be used as a reference temperature point.

Docosane droplet burning. The melting of Docosane droplet is similar to that of octadecane, so we present here the burning history of Docosane droplet to consider a melting as initial stage of combustion process.

In Fig. 4 the dependencies of size and aspect ratio on heating time are presented for Docosane droplet with initial diameter D_{eq}^{0} = 1.5 mm. We can observe a relatively small expansion during melting following by a fast size decrease due to intensive evaporation and burning. If we compare two graphs in Fig.4, we find out that maximum point on the curve $D_{eq}(t)$ corresponds to minimum point on the curve $r(t)$. So the moment t = 2.39 s is considered as time of the melting completion and droplet ignition. Thus pre-ignition time is determined by melting duration in the experimental conditions. In this case the pre-ignition time is comparable with burning duration.

Conclusions. The melting of the pendant droplets of n-alkanes is studied experimentally. The droplets size and shape evolution is analyzed. For the first time the state of surface freezing during melting of the pendant droplets of Octadecane and Docosane is confirmed experimentally, which corresponds to local minimum of a droplet aspect ratio. This fact can be used to determine a temperature reference point when studying droplet melting.

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Исследование плавления капель октадекана и докозана

АННОТАЦИЯ

Экспериментально исследовано плавление н-алканов (октадекан, докозан). Изучена эволюция диаметра и формы капель, полученные зависимости сопоставлены с характеристиками фазовых переходов solid-liquid нормальных алканов. Установлено, что при нагреве заметно увеличивается диаметр капли вследствие плавления и теплового расширения. Одновременно немонотонным образом меняется форма капли. Показано, что локальный минимум аспектного отношения капли соответствует состоянию поверхностного замерзания (surface freezing), что позволяет использовать его как реперную точку при измерении температуры капли.

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Дослідження плавлення крапель октадекану та докозану

АНОТАЦІЯ

Експериментально досліджено плавлення нормальних алканів (н-октадекан та н-докозан). Проведено аналіз еволюції розміру та форми краплі, отримані залежності зіставлено з характеристиками фазових перетворень. Встановлено, що у процесі плавлення діаметр краплі помітно зростає внаслідок розширення при плавленні та теплового розширення. Водночас немонотонним чином змінюється форма краплі. Доведено, що локальний мінімум аспектного відношення краплі відповідає стану поверхневого замерзання, що дозволяє використати його як реперну точку для виміру температури краплі.