Study of the phase behavior of \( n \)-pentacosane \( \text{C}_{25}\text{H}_{52} \) by optical method

V N Kuryakov and V A Dechabo
Oil and Gas Research Institute of the Russian Academy of Sciences, 3, Gubkin Street Moscow, 119991, Russian Federation

E-mail: vladimir.kuryakov@gmail.com

Abstract. For two samples of \( n \)-pentacosane dispersions in water with different average size of the dispersed phase, the melting, crystallization and rotator phase temperatures are determined by optical method. For particles, that have a radius of 100 nm, the temperatures of phase transition correspond with the published data. For particles with a radius, that is not exceeding 50 nm, a significant undercooling of \( n \)-pentacosan drops happens.

1. Introduction
The study of the phase behavior of \( n \)-alkanes in dispersed systems is important both for the fundamental science and for applications. Some \( n \)-alkanes may be in weakly ordered plastic crystalline phases called the "rotator" phases [1, 2]. This adds features to their phase behavior. Pure \( n \)-alkanes and their mixture are considered as one of the prospective materials for creating Phase Change Material (PCM) [3]. Phase change material is used to store or transport thermal energy. This process uses the heat of the phase transition of the phase transition material. In development of PCM-materials, among other things, it is necessary to be able to create them with specified temperatures of phase transition. The phase transition temperatures of PCM have to correspond to the operating temperatures of the process in which this PCM is used. For instance, some PCM-materials are responsible for accumulation of thermal solar energy, while others are needed to create air conditioning systems. Also, while developing PCM-materials in the form of a dispersed system, it is necessary to take into consideration the possible influence of a confined geometry on the phase behavior of a phase-transitive material. The phase behavior of \( n \)-alkanes in conditions of confined geometry is insufficiently studied. This article is devoted to the results of studying the phase behavior of \( n \)-pentacosane (\( \text{C}_{25}\text{H}_{52} \)) particles with an approximate drop size of 100 nm. The phase behavior of this particular \( n \)-alkane has been well studied for bulk samples experimentally as well as theoretically [1, 2, 4-8]. However, the influence of confined geometry conditions on the phase behavior of \( n \)-pentacosane has not been sufficiently studied.

2. Materials and Methods
The dispersions were produced from \( n \)-pentacosane (\( \text{C}_{25}\text{H}_{52} \)), purchased in Acros Organics with a purity of 99%, and medical double-distilled water for injection (Solopharm, Russia).

Using ultrasonic dispersion of the \( n \)-alkane/water mixture, at a temperature above the melting point of \( n \)-pentacosane (80°C), we prepared dispersion sample (OriginalSample) with a volume of 10 mL and concentration of \( n \)-alkane in the water of 0.01 mass%. Surfactants were not used in the preparation of dispersions. A more detailed description of the preparation of stable \( n \)-alkanes dispersions in water can
be found in earlier works [9-11]. For light scattering studies, this dispersion was previously diluted with water by 100 times. To produce a sample of dispersion with a particle size not exceeding 100 nm (Sample100), we filtered the original dispersion through the Sartoriuse Stedim Ministart PES 0.1-mkm pore size syringe filter.

Temperature dependences of the scattered light intensity were measured by Photocor Compact-Z (Photocor, Russia). The light scattering angle was 90°. Laser wavelength was 654 nm and power was 30 mW. The samples were heated and cooled at an approximate rate of 2 °C per hour and in temperature step of 0.1°C. For each sample at least two heating-cooling cycles were measured. We used the results of the second or third cycle for analysis.

It is well known that calorimetric methods are widespread for studying the phase behavior of substances. This technique measures the thermal effects that occur with a substance when, for example, the temperature changes. The experimental optical method proposed by the authors is based on measuring the changes in optical properties of the studied sample. Using the proposed optical method, it is possible not only to study the phase behavior of pure n-alkanes, but also to determine the temperatures of phase transitions of n-alkanes in oil systems [12]. It's necessary to note that this optical method for phase transition temperatures determination has a high sensitivity. It can be applied to dispersed systems with such a low concentration of the dispersed phase that micro-calorimetry is inapplicable due to insufficient sensitivity [13].

3. Results and discussion
The average hydrodynamic radius in the samples was measured by means of dynamic light scattering (DLS). The average hydrodynamic radius of the particles in OriginalSample is 104 ±5 nm. The zeta potential of the particles in this sample is -34±1 mV. The average hydrodynamic radius of the Sample100 particles is 51±5 nm, and the zeta potential is -7±1 mV. During the heating-cooling cycles, the size of the particles was not changing within the accuracy of measurements. Furthermore, for n-nonadecan (C_{19}H_{40}) which is close to the n-pentacosane the density in the liquid phase is 0.7752 g/cm$^3$ at 35 °C and 0.7720 g/cm$^3$ at 40 °C and the density in the solid phase is 0.786 g/cm$^3$ at 25 °C [14-16]. It is possible to estimate the change of particle size during melting. This change is connected with the difference in the density of the liquid and solid phases. According to our estimates, the ratio of the radiuses of particles in liquid and solid phases will be about 1.005. Such small changes in particle size are difficult to detect by dynamic light scattering.

![Figure 1. The temperature dependence of the scattered light intensity for the OriginalSample during heating (red circles) and cooling (blue squares).](image-url)
Figure 1 shows the temperature dependence of the scattered light intensity for the OriginalSample. One can see that this dependence has special features. Drastic changes of it are connected with changes of the optical properties of the dispersed system. Thus, it is well known that there should not be such changes in the optical properties of the dispersion medium (water) in the studied temperature range. Changes in the optical properties of the studied samples are associated with changes in the optical properties of the dispersed phase (n-alkane particle). During phase transitions of melting, crystallization, and crystal-to-crystal phase transitions (rotator phases), the refractive index of n-alkanes changes abruptly. For instance, the results of measurements of the temperature dependence of the refractive index for C_{28}H_{58} are given in [17]. We assume that the temperature dependence of the refractive index for the studied n-alkane C_{25}H_{52} has a similar behavior at phase transitions. Also, it is necessary to underline that changes in the refractive index of n-pentacosane in the studied sample are connected with its phase transitions. These changes are the leading cause for the existence of features on the temperature dependence of the scattered light intensity.

In order to determine the temperature of the phase transitions in Figure 1, it is necessary to take a derivative of the smoothed data of temperature dependence of the scattered light intensity on temperature. The temperatures that correspond to the peaks on such a derivative will be the temperatures of phase transitions. Hence, due to the analysis of experimental data during heating, the melting temperature (53.4±0.2 °C) and the temperature of the crystal-to-crystal phase transition (46.1±0.2 °C) can be determined. During cooling process, the crystallization temperature (liquid-solid phases) (50.6±0.2°C) and two crystal-to-crystal phase transitions (39.1±0.2 °C and 42.4±0.2 °C) can be determined too. The temperatures of melting and phase transition from the crystalline phase to the rotator phase, determined by this way, coincide with the published data with good accuracy [1, 2]. Certain temperatures of phase transitions during cooling process are slightly different from the published data. This may be due to the fact that the effect of slight undercooling can be observed upon cooling n-alkanes [1, 2, 4].

The temperature dependence of the scattered light intensity measured on the Sample100 is slightly different (Figure 2). The particle size in this sample is not exceeding 100 nm.

![Figure 2](image.png)

**Figure 2.** The temperature dependence of the scattered light intensity for the Sample100 during heating (red circles)-cooling (blue squares) cycle.

Figure 2 shows that when this sample is heated, two special temperatures can be determined on the temperature dependence of the scattered light intensity, as for the OriginalSample. The melting temperature is 53.2±0.5 °C and temperature of the phase transition from the crystal phase to the rotator phase is 44.2±0.5 °C. These temperatures are close to the corresponding phase transition temperatures.
in the OriginalSample. The temperature dependence of the intensity of scattered light in the studied samples during cooling process differs significantly. For the Sample100, only one special temperature (38.0±0.2 °C) can be detected during cooling process, according to Figure 2. Most likely, it is the crystallization temperature. At the same time, upon subsequent heating of this sample, the temperature dependence of the scattered light intensity will have a form similar to this dependence at heating in Figure 2. During subsequent heating, two phase transitions will occur in n-pentacosane particles: crystal-crystal and melting.

The effect of confined geometry on the phase behavior of n-pentacosane is observed, which manifests itself in significant undercooling. A similar effect of strong undercooling of submicron n-nonadecane (C_{19}H_{40}) particles was observed in [18].

4. Conclusions
Two samples of n-pentacosane dispersions in water with a drop size of about 100 nm and 200 nm were prepared without adding surfactants. For these samples, the phase transition temperatures (melting, crystallization, rotator phases) of n-pentacosane in dispersion were determined by an optical method. For n-pentacosane droplets about 100 nm in size, the effect of strong undercooling is observed experimentally.

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