Determination of phase transition temperatures (melting, crystallization, rotator phases) of \( n \)-alkanes by the optical method

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Abstract. The temperatures of phase transitions (melting, crystallization, rotator phases) were determined for a number of individual \( n \)-alkanes from \( \text{C}_{19}\text{H}_{40} \) (\( n \)-nonadecane) to \( \text{C}_{28}\text{H}_{58} \) (\( n \)-octacosane) by the optical method, a modified droplet technique. For this research, \( n \)-alkanes were presented as an emulsion in water without the addition of surfactants. Emulsions were prepared by ultrasonic dispersion of a small amount of \( n \)-alkane in water at a temperature above the melting point of the investigated \( n \)-alkane. The hydrodynamic radius of the dispersions measured by the dynamic light scattering (DLS) method was about 100 nm and did not change within a wide temperature range within the measurement accuracy. The temperatures of melting, crystallization, and rotator phase transitions of pure \( n \)-alkanes in the form of emulsion were determined from temperature-dependent measurements of the light scattering by the dispersions. The supercooling values for studied \( n \)-alkanes were also determined.

1. Introduction
An emulsion is a mixture of two liquids that do not mix under normal conditions. Emulsions belong to the class of colloidal systems in which both the dispersed phase and the dispersion medium are liquids. The use of emulsions is diverse: in the agricultural industry they are used as carriers for insecticides, fungicides, and pesticides, in the cosmetic industry – emulsions are used for hair and skin care, in pharmaceuticals they are used to increase the efficiency of delivery of active ingredients in the human body, in the food industry fat emulsions, such as milk, mayonnaise. Currently, one of the promising objects of research is paraffin emulsions. They are interesting in that they are emulsions at temperatures above the melting point and are sols (solid particles in liquid) at temperatures below the
melting point. This property determines the scope of their application. A paraffin emulsion in water can be used as a phase-change material (PCM) [1–3].

When the paraffin in the emulsion crystallizes, the stored energy is released in the form of latent heat of phase transition. Conversely, when the paraffin in the emulsion melts, energy is absorbed. This property of PCM materials can be used to store thermal energy, provide thermal barriers or thermal insulation. PCM materials are used, for example, in the transportation of chilled food and drinks, the transport of medicines and vaccines, in conditioning, the accumulation of solar energy.

Conventional methods for studying the phase transitions of n-alkanes are adiabatic and differential scanning calorimetry [4, 5]. Furthermore, X-ray diffraction methods [6, 7], the Dynamic mechanical spectroscopy (DMS) method [8], and the recently proposed atomic force microscopy approach [9] are used to study the rotator phases of n-alkanes.

In this work, we propose a new method for determining the temperatures of phase transitions of n-alkanes, based on dynamic and static light scattering technique – a powerful experimental methods for studying microheterogeneity and phase equilibria in various fluid samples including microcapsules [10], emulsions [11], protein solutions [12], near-critical ternary systems [13], and near-critical polymer solutions [14]. This methods feature the study of n-alkane emulsion in water. Such a technique is, in fact, a well-known droplet technique with modifications [15, 16], and has been already used to study phase transitions of pure n-alkanes and their mixtures [17–20].

2. Experimental section
Emulsions were prepared from n-alkanes (C$_{18}$H$_{36}$, C$_{20}$H$_{42}$, C$_{21}$H$_{44}$, C$_{22}$H$_{48}$, C$_{23}$H$_{50}$, C$_{25}$H$_{52}$, C$_{26}$H$_{54}$ и C$_{28}$H$_{58}$) purchased from Acros Organics with a purity of 98-99% 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 the used n-alkane, we prepared emulsion samples with a weight concentration of n-alkane in water of 0.01%. Surfactants were not used in the preparation of emulsions. Sartorius BP 301S analytical balance (0.1 mg) was used for sample component weighing. Ultrasonic dispersion of the water/n-alkane mixture was carried out for 30 seconds on an ultrasonic disperser UZDN-A (Russia) with an operating frequency of 22 kHz and a power of 75 watts. Measurements by dynamic light scattering showed that the characteristic hydrodynamic radius of the particles in the resulting dispersions was about 100 nm. Dynamic and static light scattering measurements were performed using Photocor Compact-Z equipment (Russia). The measurements were carried out at a scattering angle of 90 degrees. For measurements by dynamic and static light scattering, the samples were diluted 100 times with double-distilled water. The heating and cooling during the experiment were carried out at a speed of about 6 K/h and the temperature step was 0.1 K. The obtained samples, both in an emulsion state and in a sol state, did not coalesce. More details on the sample preparation procedure can be found in the articles [18–20].

3. Results and discussion
For all the emulsions studied, the temperature dependences of the intensity of the scattered light during heating and cooling were measured. At least two heating-cooling cycles were measured for each sample. Figure 1 shows a typical temperature dependence of the intensity of the scattered light on the dispersion of n-alkane in water.

The light scattering intensity, in this case, is determined by the size of the emulsion droplets, their concentration, and the difference in the refractive indices of the n-alkane phase and water. Phase transitions of melting and crystallization of n-alkane in the emulsion lead to a change in the refractive index of the n-alkane phase, which, in turn, leads to a change in the measured intensity of the scattered light. For example, for n-alkane C$_{18}$H$_{36}$ (T$_{Mel}$ ~ 31 °C), the refractive index at 20 °C (solid phase) and at a temperature of 40 °C (liquid phase) is 1.4409 [21] and 1.43095 [22], respectively. The concentration of particles during the experiment does not change. The contribution to the change in the intensity of the scattered light from the change in particle size associated with different densities of the liquid and solid phases is about 2-3%.
For \( n \)-alkane emulsions \( \text{C}_{20}\text{H}_{42} \) and \( \text{C}_{28}\text{H}_{58} \), temperature dependences of the intensity of the scattered light were measured at different rates. Figure 2 shows the temperature dependences of the intensity of the scattered light during heating and cooling of the emulsions of these two \( n \)-alkanes. From the results obtained, it can be concluded that the measurement results of the temperature dependences of the scattered light intensity at different heating rates are well reproducible.

**Figure 1.** Temperature dependence of the scattered light intensity during heating and cooling for the dispersion of \( n \)-alkane \( \text{C}_{28}\text{H}_{58} \) in water.

**Figure 2.** Temperature dependence of the intensity of the scattered light during heating and cooling for the dispersion of \( n \)-alkane \( \text{C}_{20}\text{H}_{42} \) and \( \text{C}_{28}\text{H}_{58} \) in water at different rates of temperature change.

Thus, from measurements of the scattered light intensity during heating and cooling of emulsions of individual \( n \)-alkanes in water, it is possible to determine the temperature of phase transitions (melting, crystallization, rotator phases) of \( n \)-alkanes. In this work, the phase transition temperature was determined as the maximum of the peak of the derivative of the intensity of the scattered light with respect to temperature.

Figure 3 shows the melting and crystallization temperatures of the studied \( n \)-alkanes measured by the optical method. The melting temperatures measured by the optical method are in good agreement with the melting temperatures of bulk samples measured in [23] by scanning calorimetry. The
difference between the crystallization temperatures measured by the optical method and the crystallization temperatures of emulsified n-alkanes samples in [23] is probably due to the use of surfactants for emulsification of n-alkanes in [23]. Surfactants can lead to a significant undercooling of the n-alkane drops in the emulsion.

**Figure 3.** Melting and crystallization temperatures of n-alkanes measured in this work (red circles and blue squares) and data from Sirota E.B. work [23] (crosses and stars).

Figure 4 and Figure 5 show the temperatures of phase transitions of the crystal-crystal type (rotator phases), measured by the optical method, during heating and cooling of the samples under study.
Figure 4. The temperatures of crystal to rotator phase transition measured in this work (black circles) and data from Sirota E.B. work [5] (red squares).

Figure 5. The temperatures of rotator to crystal phase transition measured in this work (black circles) and data from Sirota E.B. work [5] (red squares).

Figure 6 shows the dependence of the magnitude of undercooling ($T_{\text{Melt}} - T_{\text{Crystal}}$) on the number of carbon atoms in the $n$-alkane molecule.

Figure 6. Dependence of the magnitude of undercooling ($T_{\text{Melt}} - T_{\text{Crystal}}$) on the number of carbon atoms in the $n$-alkane molecule, this work (black circles) and data from Sirota E.B. work [23] (red squares).
Figure 6 shows that for the studied emulsion samples, the undercooling value is significantly less than the undercooling value for \( n \)-alkane emulsions prepared using surfactants in [23].

Table 1 presents the temperatures of phase transitions measured by the optical method.

| Chain length | \( T_{\text{Crystal-Rot}} \), \(^\circ\text{C} \) | \( T_{\text{Rot-Rot}} \), \(^\circ\text{C} \) at heating | \( T_{\text{Melt}} \), \(^\circ\text{C} \) | \( T_{\text{Crystallization}} \), \(^\circ\text{C} \) | \( T_{\text{Rot-Rot}} \), \(^\circ\text{C} \) at cooling | \( T_{\text{Rot-Crystal}} \), \(^\circ\text{C} \) | \( T_{\text{Melt}} \) | \( T_{\text{Crystallization}} \), \(^\circ\text{C} \) |
|-------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 19          | 20                              | 31.5                          | 26                              | 14.5                          | 5                              | 5                              |
| 20          | 25                              | 36                            | 32                              | 20                            | 4                              |
| 21          | 30                              | 40                            | 35                              | 25                            | 5                              |
| 23          | 40                              | 47.5                          | 44                              | 35                            | 3.5                            |
| 24          | 43.5                            | 46.5                          | 50                              | 47                            | 36                            | 39                            | 3                              |
| 25          | 46.5                            | 53.5                          | 51                              | 39                            | 42                            | 47                            | 1                              |
| 26          | 49.5                            | 51.5                          | 56                              | 55                            | 42                            | 47                            | 1                              |
| 28          | 56                              | 62.5                          | 61                              | 46                            | 53                            | 53                            | 1.5                            |

4. Conclusion
Optical methods were used to determine the temperatures of phase transitions (melting, crystallization, rotator phases) of \( n \)-alkanes. It is shown that the method of dynamic and static light scattering can measure not only the size of paraffin emulsions but also determines the temperature of the phase transitions of \( n \)-alkanes. The proposed methodology allows studies of the influence of various factors on the phase transition temperatures of \( n \)-alkanes in emulsions, such as impurities to \( n \)-alkanes, emulsion droplet size, surfactants, pressure, and impurities in a dispersion medium.

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References
[1] Du K, Calautit J, Wang Z, Wu Y and Liu H 2018 A review of the applications of phase change materials in cooling, heating and power generation in different temperature ranges Appl. Energy 220 242–73
[2] Kahwaji S, Johnson M B, Kheirabadi A C, Groulx D and White M A 2018 A comprehensive study of properties of paraffin phase change materials for solar thermal energy storage and thermal management applications Energy 162 1169–82
[3] Bukhalkin D D, Semenov A P, Novikov A A, Mendgaziev R I, Stoporev A S, Gushchin P A and Shchukin D G 2019 Phase change materials in the energy sector: current state of research and application prospects Chemistry and Technology of Fuels and Oils 55 685–97
[4] Voronov V P 2000 Surface precrystallization of normal C24 alkane in porous glass J. Exp. Theor. Phys. 91 144–9
[5] Sirota E B and Singer D M 1994 Phase transitions among the rotator phases of the normal alkanes J. Chem. Phys. 101 10873–82
[6] Sirota E B, King H E, Singer D M and Shao H H 1993 Rotator phases of the normal alkanes: an X-ray scattering study J. Chem. Phys. 98 5809–24
[7] Cholakova D and Denkov N 2019 Rotator phases in alkane systems: In bulk, surface layers and micro/nano-confinements Adv. Colloid Interface Sci. 269 7–42
[8] Craievich A F, Denicolo I and Doucet J 1984 Molecular motion and conformational defects in odd-numbered paraffins Phys. Rev. B 30 4782–7
[9] Jung N, Yun M and Jeon S 2012 Phase transitions between the rotator phases of paraffin investigated using silicon microcantilevers J. Chem. Phys. 136 104903
[10] Trushina D B, Bukreeva T V, Borodina T N, Belova D D, Belyakov S and Antipina M N 2018
Heat-driven size reduction of biodegradable polyelectrolyte multilayer hollow capsules assembled on CaCO$_3$ template *Colloids Surf. B.* **170** 312–21
[11] Cabaleiro D, Hamze S, Agresti F, Estellé P, Barison S, Fedele L and Bobbo S 2019 Dynamic Viscosity, Surface Tension and Wetting Behavior Studies of Paraffin–in–Water Nano–Emulsions *Energies* **12** 3334
[12] Nikfarjam S, Ghorbani M, Adhikari S, Karlsson A J, Jouravleva E V, Woehl T J, & Anisimov M A 2019 Irreversible Nature of Mesoscopic Aggregates in Lysozyme Solutions *Colloid Journal* **81** 546–54.
[13] Novikov A A, Semenov A P, Monje-Galvan V, Kuryakov V N, Klauda J B and Anisimov M A 2017 Dual action of hydrotropes at the water/oil interface *J Phys Chem C* **121** 16423–31
[14] Zheng X, Anisimov M A, Sengers J V and He M 2017 Mesoscopic Diffusion of Poly (ethylene oxide) in Pure and Mixed Solvents *J Phys Chem B* **122** 3454–64
[15] Turnbull D 1949 The Subcooling of Liquid Metals *J. Appl. Phys.* **20** 817–817
[16] Vonnegut B 1948 Variation with temperature of the nucleation rate of supercooled liquid tin and water drops *J. Colloid Sci.* **3** 563–9
[17] Kuryakov V N and Ivanova D D 2019 Determination of melting point of n-alkanes by means of light scattering technique *J. Phys. Conf. Ser.* **1385** 12045
[18] Kuryakov V N and Ivanova D D 2019 Crystallization Behavior of Pure n-Alkane (n-Nonadecane) in a form of Nanoemulsion *Int. J. Nanosci.* **18** 1940032
[19] Kuryakov V N, De Sanctis Lucentini P G and Ivanova D D 2018 Tricosane (C23H48) and Octacosane (C28H58) mixture phase transition insight via Light scattering techniques *IOP Conference Series: Materials Science and Engineering* **347** 012034
[20] Kuryakov V N, Ivanova D D, Novikov A A, Ivanov E V, Gushchin P A, Semenov A P, Yusupova T N, & Shchukin D G 2019 The study of phase transitions in n-tricosane/bitumen aqueous dispersions by the optical method *Energy & Fuels* (in Press) DOI:10.1021/acs.energyfuels.9b03566
[21] Haynes W M 2014 CRC Handbook of Chemistry and Physics, 95th Edition (Florida: CRC Press)
[22] Lechner M D 1996 Refractive Indices of Inorganic, Organometallic, and Organononmetallic Liquids, and Binary Liquid Mixtures vol 38A (Berlin/Heidelberg: Springer-Verlag)
[23] Kraack H, Sirota E B and Deutsch M 2000 Measurements of homogeneous nucleation in normal-alkanes *J. Chem. Phys.* **112** 6873–85