Determination of melting point of n-alkanes by means of light scattering technique

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Abstract. A modified droplet technique, an optical method, was used to determine the melting temperature of several n-alkanes. The authors prepared emulsions of n-alkanes in water by means of ultrasound dispersing without the use of surfactants. The average size of the paraffin cluster measured by dynamic light scattering had a radius of about 100 nm for all the samples. During heating, n-alkanes in the emulsion melt changing the optical properties of the emulsions. The sharp variation of light scattering intensity for a relatively small change in temperature corresponds to a phase transition of the n-alkane. Using the described principles, the authors determined the melting temperatures for n-alkanes from C₁₉H₄₀ (n-Nonadecane) to C₂₈H₅₈ (n-Octacosane). The obtained results are in good agreement with data of other works.

1. Introduction
One of the major physical properties of n-alkanes and any other materials is melting temperature. There are a lot of articles in which one of the results is the determination of the melting temperature of pure n-alkanes or their mixtures [1–4]. Paraffins are a promising substance for phase-change materials (PCMs) [5, 6]. For such application of paraffins, they have to be prepared in the form of an emulsion or encapsulated inside submicron-sized particles [3, 4, 7–9]. The finite size can strongly influence the physical property of n-alkanes in the encapsulated form and in the form of emulsion. Both first- and second-order phase transitions get smeared and shifted due to the finite size of a sample.

It is common sense that such experimental methods as calorimetry and x-ray diffraction are used to determine the melting point of n-alkanes [1–3]. In spite of this, there are several articles in which the determination of the melting point is made by means of other experimental techniques, sometimes exotic enough. Jung et al. [10] used an atomic force microscope to determine the temperatures of phase transitions for several paraffins. In their experiment, nanogram amounts of paraffin were coated onto a silicon cantilever, and the resonance frequency and deflection of the cantilever were measured as a function of temperature. Nowak and Severtson [11] used dynamic mechanical spectroscopy (DMS) to study the plastic crystalline region of several model n-alkane systems and commercial paraffin wax. Johnson [12] investigated several paraffins with dilatometry and refractometry. It should be noted that each experimental method has its advantages and disadvantages.
In this work, the authors used the approach similar to the droplet technique [13, 14] and applied it for investigating the phase behavior of pure n-alkanes from $C_{19}H_{40}$ (n-Nonadecane) to $C_{28}H_{58}$ (n-Octacosane) excluding n-Docosane and n-Heptacosane because they were not available. Earlier, the same technique was used to investigate the phase behavior of DODAB aqueous solution [15] and the mixture of n-alkanes [16]. The authors developed a method for the preparation of a stable n-alkane emulsion in water without the use of surfactants. In this case, it is possible to avoid the impact on the phase transition of surfactant.

2. Materials and methods
In this work, the authors studied the phase behavior of 8 n-alkanes: $C_{19}H_{40}$ (n-Nonadecane), $C_{20}H_{42}$ (n-Icosane), $C_{21}H_{44}$ (n-Heneicosane), $C_{22}H_{48}$ (n-Tricosane), $C_{24}H_{50}$ (n-Tetracosane), $C_{25}H_{52}$ (n-Pentacosane), $C_{26}H_{54}$ (n-Hexacosane) and $C_{28}H_{58}$ (n-Octacosane). The n-alkanes with a purity of 98–99% were acquired from Acros Organics. Bi-distilled medical water for injections sealed in plastic ampoules of 5 mL (Solopharm) was used. The components were not additionally purified. To prepare the emulsion, 10 ml of water were mixed at room temperature with 1 mg of n-alkane; the mixture was heated up to 80°C in a water bath and dispersed during 30 seconds (disperser UZDN-A, 75 W, 22 kHz). Then the sample was cooled down to room temperature (25°C). At room temperature, the considered samples are suspensions (solid particles in liquid). After heating above their melting point, they became emulsions (liquid droplets in liquid). Dispersing was performed with both components at their liquid state. The average size of droplets and particles in the samples is about 100 nm (by DLS).

This original concentrated preparation was diluted 100-fold, and by filtering through Chromafil Xtra PET syringe filters of 0.2 micrometers, samples of about 2 ml were prepared for the dynamic light scattering (DLS) device Photocor Compact-Z (laser 654 nm, 25 mW, scattering angle 90 degrees). With the samples so prepared, several heating/cooling cycles were performed.

An avalanche photodiode was used as a photon counting system in the DLS device used by the authors. Measurements were done in the automatic regime with a heating and cooling rate of about 2°C per hour and a temperature step 0.1°C. The authors did more than one heating/cooling cycle on each sample and did not use for analysis the first one. The second and successive cycles had a good reproducibility in the results. To determine the melting temperature on light scattering temperature dependence, the derivative of light scattering with respect to temperature ($dI/dT$) was obtained for each sample under investigation. Peaks in the derivatives correspond to the change in the optical property of the emulsion, and it can be assumed that these changes are due to phase transitions of the dispersed-phase particles because water does not have phase transitions in the considered working temperature range (5–70°C).

3. Results
The dependence of light scattering intensity $I$ on the temperature for the samples ($C_{19}H_{40}$ to $C_{28}H_{58}$) under investigation was measured. They present a behavior similar to $C_{25}H_{52}$ shown as an example in figure 1.

Heating the sample from the lower temperature, one can notice a light linear dependence, almost constant, on $T$. At one point, specific for the n-alkane under investigation, the intensity of light scattering drops by 10–30% of its initial value $I_0$. Then a new plateau is reached and continues till a second temperature, $T_m$ where again the light scattering intensity decreases abruptly, reaching a value of around 0.5$I_0$. The slope of the falls, the average values of the plateau and the final value of $I$ are different for different species even if they present the same general behavior. Figure 2 presents the light scattering intensity derivative $I'$ ($T$) for the same paraffin and dataset of figure 1. It is possible to note how two peaks exit from the fluctuation of the linear regime corresponding to the two falls of $I(T)$. From the plots of $I(T)$ and $I'(T)$ and
similar plots for other studied n-alkanes, it is possible to determine the melting temperatures ($T_m$). Determined $T_m$ are reported in table 1.

![Figure 1](image1.png)

**Figure 1.** Light scattering intensity $I(T)$.

![Figure 2](image2.png)

**Figure 2.** Derivative of light scattering with respect to temperature.

4. Discussion
It is known that between the fully ordered crystalline phases of n-alkanes and the isotropic liquid phase, a series of phases occurs, known as rotator phases [1]. In figure 2, the lower temperature peak corresponds to the temperature of phase transition from the fully ordered crystalline phase to the rotator phase. The studies of rotator phases will be carried out in future publications. The n-alkanes under investigation with odd and even numbers of carbon atoms are known to
Table 1. Melting temperature $T_m$ determination for several n-alkanes (°C).

| n-alkane | Sirota E.B. [17] | Open Melting Point Dataset [18] | Our work |
|---------|----------------|-------------------------------|----------|
| 19      | 31.8           | 32.1                          | 31       |
| 20      | 36.3           | 36.7                          | 36.1     |
| 21      | 40.1           | 40.5                          | 39.8     |
| 22      | 43.8           | 44.4                          | –        |
| 23      | 47.2           | 47.6                          | 47.6     |
| 24      | 50.4           | 51                            | 50.2     |
| 25      | 53.3           | 53                            | 53.6     |
| 26      | 56             | 56.4                          | 56.2     |
| 27      | 58.6           | 59.5                          | –        |
| 28      | 60.9           | 64.5                          | 62.9     |

have different phase diagrams and to melt from different rotator states. The differences in the slopes and in their regularity can be related to the different nature of the rotator phases from which they are originated, with the presence of additional metastable phases and with their formation dynamic. Moreover, it has not to be underestimated that in the emulsion/suspension the droplets present a size distribution, around an average measured size of 100 nm, and that the phase transition can occur in the droplet of different sizes at slightly different temperatures giving a not negligible different contribution to the less neat transitions. As one can see in table 1, the performed measurements are in good agreement with the ones obtained with other instruments and techniques as reported in literature.

5. Conclusions
The authors used light scattering intensity measurements to determine the melting temperature of several n-alkanes with the number of carbon atoms between 19 and 28. The obtained results are in good agreement with the ones obtained in literature via different instruments and investigation techniques.

It was shown how the light scattering technique can be used for the investigation of substances of fundamental relevance in the oil and gas industry. Indeed, this kind of investigation can be applied to a wide range of materials and such technique could be useful in the area of phase-change materials (PCMs). The successful determination of $T_m$ for several n-alkanes encourages further investigations aimed to achieve a deeper understanding of the whole phase diagram and of the phase transition mechanism.

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