Tricosane \((\text{C}_{23}\text{H}_{48})\) and Octacosane \((\text{C}_{28}\text{H}_{58})\) mixture phase transition insight via Light scattering techniques

V N Kuryakov\(^1\), P G De Sanctis Lucentini\(^2\) and D D Ivanova\(^3\)

\(^1\) Oil and Gas Research Institute of RAS (OGRI RAS), Gubkina Street, 3, 119333, Moscow, Russia.
\(^2\) Gubkin Russian State University of Oil and Gas (National Research University), Department of Physics, Leninskiy prospect, 65, Moscow, 119991 Russia.
\(^3\) D. Mendeleev University of Chemical Technology of Russia Minusskaya pl., 9, Moskva, 125047 Russia.

Abstract. In this study we analyse several emulsion samples of pure Tricosane \((\text{C}_{23}\text{H}_{48})\) and Octacosane \((\text{C}_{28}\text{H}_{58})\) paraffins as well as their mixtures with different component concentrations, prepared by means of ultrasonic dispersion without the addition of surfactants. We show that from the measurements of Static Light Scattering temperature dependences it is possible to determine the phase transition temperatures of the paraffins emulsion during the heating and cooling cycles (melting, crystallization and rotator phases). The results for the pure paraffin are in good agreement with the literature data. We produce the outcomes of the Dynamic Light Scattering technique to determine the cluster size of the obtained emulsions (radius 70-120 nm). Those emulsions proved to remain stable during several months.

1. Introduction

The \(n\)-Alkanes melting and crystallization temperatures take great importance in many research and applied works as, for example, in the Oil and Gas or in the phase change material world. Furthermore we have an unusual family of plastic-crystalline bulk phases enriching the phase diagrams in-between the liquid and the lower crystal phases temperature, often called rotator or Cristal-Rotator phases.

As evidence of the wide interest aroused, we can find experiment performed with different methods with details on the different phase diagram zones. Among the methods commonly used for studying the phase transitions, we would like to mention the result of the adiabatic scanning calorimetry and the differential one \[1\] \[3\]. There are indeed other stimulating results from the study of the paraffins rotator phases via the well established X-ray diffraction methods \[2\] \[4\], from the Dynamic mechanical spectroscopy (DMS) \[3\] and from the recently proposed use of atomic force microscope cantilever \[5\].

In this paper we propose a technique for determining the phase transitions temperatures of the paraffins and of their mixtures based on optical methods. The studied paraffins are nanoemulsions in water prepared by ultrasonic dispersion without the addition of surfactants. A similar technique was already successfully used to determine the phase transitions in the DODAB vesicles \[6\] and the light scattering technique is a well established method for the critical phenomena investigation \[7\] \[8\].
2. Materials and methods
For this experiment we prepared emulsions in water from pure paraffins (C\text{23}H\text{48}, C\text{28}H\text{58}) and from their mixtures with 17, 33, 50, 67 and 83 weight percent of the components. The heating and cooling rate in all the experiments was fixed at 2 K h\textsuperscript{−1} and it was explored the range of temperatures in which the water remain in its liquid state, from the temperature at which the paraffins are completely solid to the one at which they are completely liquid.

\textit{Materials and instruments.} We prepared the samples with Tricosane (C\text{23}H\text{48}, 98\% pure), and Octacosane (C\text{28}H\text{58}, >99\% pure), purchased from Acros Organics and bi-distilled water purified by reverse osmosis at production time (mean conductivity 10 mS cm\textsuperscript{−1}). To prepare new emulsion samples and to dilute the highly concentrated ones, we used each time only water from new ampoules. We did not make use of any surfactants.

To prepare the nanoemulsion of paraffin in water, we used an ultrasonic disperser model UZDN-A (USSR, 22 kHz, 75 W) with an immersion transducer. We weight the components of the prepared mixture on a Sartorius BP301S balance (max weight 303 g, \(\sigma = 0.1\) mg). The measurements of light scattering temperature dependence, the hydrodynamic radius (by DLS) and the zeta potential of the emulsions were performed on particle size and zeta potential analyzers Photocor Complex and Photocor Compact (Russia).

\textit{Samples preparation.} We used the ultrasonic dispersion method to prepare the emulsions of the pure paraffins and their mixtures in water. The dispersing was carried out at a temperature substantially higher than the melting point of the paraffin in use. Before starting the dispersion operations, we visually verified that the paraffin on the surface of the hot water was completely passed into the liquid state. During the dispersion process, the temperature of the water-paraffin mixture did not drop below the crystallization temperature of the used n-Alkane.

To prepare emulsions from a mixture of two paraffins, we preliminarily took samples of the pure species in the right proportions, melted them in one vial, stirred intensively in the liquid state and after cooling the necessary amount of such a mixture was used for the mixture-sample preparation.

To carry out the emulsification, we used the ultrasonic disperser up to the power of 75 W. There were prepared samples of about 10 ml each time. The initial paraffin concentration in water was about 0.01\% in weight.

3. Results and discussion
We performed Dynamic Light Scattering (DLS) measurements at 25 \textdegree C to determine the hydrodynamic radius \(R_h\) of the paraffin clusters. For each sample it was in the range \(R_h = 70 \sim 120\) nm. The zeta potential in emulsions of the single paraffins C\text{23}H\text{48} and C\text{28}H\text{58} was close to \(-35\) mV.

We present, in figure 1 the scanning electron microscope (SEM) image of a sample obtained drying the sample studied with the DLS. We chose the paraffin with the higher melting point (C\text{28}H\text{58}) in order to avoid any accidental melting of the clusters during the SEM measurement.

It should be noted that on the dried sample there are no separate particle clusters. Indeed, being the solvent removed, all the clusters stuck together.

The visual hindrance caused by the three-dimensionality of the resulting structure, the impossibility of focusing of different plans and measuring the sizes only on such plans with the images at our disposal, the drying procedure itself that lead to clump together the different clusters of the solution, are all elements that impair the possibility to have a precise and complete reconstruction for the particle size distribution and the relative average.

Taking for example the minimum and the maximum radius of the more evident and peripheral structures, we obtain an average radius of respectively \(R_{\text{SEM}}^{\text{min}} = 55 \pm 20\) nm and \(R_{\text{SEM}}^{\text{Max}} = 78 \pm 19\) nm. Both results are quite in agreement with the DLS one, considering
that the manual selection procedure of the ellipses for the SEM image is prone to introduce a systematic error avoiding to count the bigger structures below the peripheral ones.

Further study with different preparation methods of the SEM specimens have to be implemented to avoid that all the clusters clump together and to allow more informative particle counts.

For each sample we studied the temperature dependence of the scattered light intensity $I_s = I_s(T)$ upon heating and cooling. In figure 2 we show the results for the $C_{28}H_{58}$ emulsion. The intensity $I_s(T)$ shows a linear behaviour and a weak dependence in some temperature ranges, remaining practically constant. Then at special temperatures, or temperature ranges, a significant change occurs.

**Figure 1.** SEM image of paraffin ($C_{28}H_{58}$) particles dried from the studied emulsion.

**Figure 2.** Temperature dependence of the scattered light intensity $I_s$, upon (a) heating and (b) cooling, for the paraffin emulsion $C_{28}H_{58}$.
In general the intensity $I_s$ in an emulsion may depend on the concentration of the droplets, on their size, their shape, on the surface properties and on the difference in the refractive indices between the dispersion medium and the dispersed phase.

We assume that the marked change of $I_s$ in our samples is due to the phase transitions of the paraffin in the emulsion.

The low-temperature intensity gap corresponds to the phase transitions from the Crystal ($Cr$) to the Crystal-rotator ($RCr$) phase and vice versa upon heating and cooling, respectively. In figure 2 these temperatures are marked as $T_{Cr-RCr}$ and $T_{RCr-Cr}$.

The changes in the scattering intensity $I_s$ at higher temperatures correspond instead to phase transitions phase Crystal-rotator to liquid ($L$) (melting point) and vice versa, upon heating and cooling respectively. In the figure these temperatures are denoted as $T_{RCr-L}$ and $T_{L-RCr}$.

Upon cooling, b-panel on the right of the figure 2 it is possible to note another characteristic temperature corresponding to a change in the slope of $I_s$ (marked with $T^*$) in the temperature interval between the Liquid and the Crystal-Rotator phases.

The temperature $T^*$ may be correlated to a phase transition from the rotator phase III [2] or the temperature range $T_{L-RCr}-T^*$ may be connected to the range in which a surface crystallization happens in the paraffin emulsion droplets [9]. Further analysis are needed to investigate this zone.

We observed similar temperature dependences of $I_s$ for each of the studied emulsions. From these dependences, we determined the characteristic temperature assumed as the phase transition ones.

The figure 3 shows the temperatures of phase transitions for the mixtures of two n-Alkanes, determined according to the procedure described above.

A number of studies in the field of n-Alkanes binary mixture for bulk samples [10–12] presented analogous forms of the phase transition temperature dependence on the concentration.

It should be noted that in all samples in our study we were able to measure the melting temperature with a good reproducibility. Indeed during this phase transition the refractive index ($RI$) of the paraffin in emulsion changes greatly, which causes a strong change in the scattered light intensity $I_s$ within a little temperature increment.

For the paraffin mixture emulsion samples, not all the phase transitions have a clearly determined temperature: the intensity of the scattered light during heating and cooling are blurred in a certain temperature ranges. When we prepare an emulsion from a mixture of paraffins we are fixing the overall percentage of each species on the total. Nonetheless it is not possible to obtain the same concentration of paraffins in each drop of the emulsion, which leads to phase transitions in different drops at different temperatures and cause the blurred data reading.

The temperatures of all the phase transitions of the pure paraffin emulsion samples were also determined with good reproducibility.

In the table 1 we report the experimental data of the phase transition temperatures taken from [9] for the pure paraffins, $C_{23}H_{48}$ and $C_{28}H_{58}$, and the ones determined in this study. The used symbols are $T^*_m$ for the melting temperature (solid to liquid phase transition), $T^*_s$ for the temperature of Crystal to Crystal-rotator phase transition in the emulsion samples. $T^*_s$ is the temperatures of solidification for the bulk, non-emulsified samples. With the symbols $T_{RCr-Cr}$, $T_{Cr-RCr}$, $T_{RCr-L}$, are indicated the phase transitions between crystal (Cr), rotator crystal (RCr) and liquid (L) phases determined in this work and introduced above.

4. Conclusion

We prepared by means of ultrasonic dispersion several samples nanoemulsion in water from two pure n-Alkanes ($C_{23}H_{48}$ and $C_{28}H_{58}$) and their mixtures with different relative percentage, without the addition of surfactants.
(a) $RCr \rightarrow L$ (Melting point) upon heating.

(b) $L \rightarrow RCr$ upon cooling.

(c) $Cr \rightarrow RCr$ upon heating.

(d) $RCr \rightarrow Cr$ upon cooling.

**Figure 3.** Phase transitions temperatures of the binary n-alkane mixture ($C_{23}H_{48},C_{28}H_{58}$) versus the concentration of the components as determined from the LS measurements for the nanoemulsions samples. Crystal (Cr), Crystal-rotator (RCr) and Liquid (L) phases.

We propose a method to determine the phase transition temperatures of those samples observing the scattered light intensity temperature dependence.

**Table 1.** The comparison of the phase transition temperature of pure n-Alkanes from [9] (with an asterisk) with the ones determined in this work. All the reported temperatures are in Celsius degrees.

| n     | $T^*_m$ | $T_{RCr-L}$ | $T^*_x$ | $T_{Cr-RCr}$ | $T^*_s$ | $T_{RCr-Cr}$ |
|-------|---------|-------------|---------|---------------|---------|--------------|
| $C_{23}H_{48}$ | 47.2    | 48          | 40.6    | 39            | 33.4    | 34           |
| $C_{28}H_{58}$ | 60.9    | 62          | 57.7    | 56            | 45.4    | 45           |
The phase transition temperatures of the two pure paraffins so determined are in a good agreement with the previous literature data.

The n-Alkanes Crystal-rotator phase transition presents an intrinsic complexity. We believe that the percentage fluctuation of the two types of paraffin in the binary mixture drops may cause a different transition temperature for each drop and a complex pattern of the scattered light temperature dependence of the whole emulsion. The eventual influences of the heating and cooling rates on the metastable phases, moreover, may play an additional role in the Rotator-Crystal phase.

The previous ones are all elements that drive us to consider interesting further future studies, applying new methods for the sample preparation, comparing the results of other instruments measurements on the same samples, and applying different methods of data analysis and data acquisition in order to obtain a deeper knowledge of the applicability of this technique for a broader phase transitions comprehension.

Acknowledgments
Authors are grateful to Alexey D.Yapryntsev from Kurnakov Institute of General and Inorganic Chemistry Russian Academy of Sciences for the SEM analysis of samples.

References
[1] Voronov V P 2000 Journal of Experimental and Theoretical Physics 91 144–149 ISSN 1090-6509 URL https://doi.org/10.1134/1.1307242
[2] Sirota E B and Singer D M 1994 The Journal of Chemical Physics 101 10873–10882 URL http://doi.org/10.1063/1.467837
[3] Sirota E B, Jr H E K, Singer D M and Shao H H 1993 The Journal of Chemical Physics 98 5809–5824 (Preprint https://doi.org/10.1063/1.464874) URL https://doi.org/10.1063/1.464874
[4] Craievich A F, Denicolo I and Doucet J 1984 Phys. Rev. B 30(8) 4782–4787 URL https://link.aps.org/doi/10.1103/PhysRevB.30.4782
[5] Jung N, Yun M and Jeon S 2012 The Journal of Chemical Physics 136 104903 (Preprint https://doi.org/10.1063/1.3692296) URL https://doi.org/10.1063/1.3692296
[6] Voronov V P, Kuryakov V N and Muratov A R 2012 Journal of Experimental and Theoretical Physics 115 1105–1110 ISSN 1090-6509 URL https://doi.org/10.1134/S106377611211012X
[7] Robertson A E, Phan D H, Macaluso J E, Kuryakov V N, Jouravleva E V, Bertrand C E, Yudin I K and Anisimov M A 2016 Fluid Phase Equilibria 407 243 – 254 ISSN 0378-3812 aqueous Solutions URL [8] Belyakov M, Gorodetskii E, Kulikov V, Kuryakov V and Yudin I 2011 Chemical Physics 379 123 – 127 ISSN 0301-0104 URL http://www.sciencedirect.com/science/article/pii/S0378381211006487
[9] Kraack H, Sirota E B and Deutsch M 2000 The Journal of Chemical Physics 121 6873–6885 (Preprint https://doi.org/10.1063/1.481263) URL https://doi.org/10.1063/1.481263
[10] Ungar G and Masic N 1985 The Journal of Physical Chemistry 89 1036–1042 (Preprint http://dx.doi.org/10.1021/j100252a030) URL http://dx.doi.org/10.1021/j100252a030
[11] Hammami A and Mehrotra A K 1995 Fluid Phase Equilibria 111 253 – 272 ISSN 0378-3812 URL http://www.sciencedirect.com/science/article/pii/037838129502777C
[12] Mazee W 1957 Analytica Chimica Acta 17 97 – 106 ISSN 0003-2670 URL http://www.sciencedirect.com/science/article/pii/S0003267000870026
Tricosane \((C_{23}H_{48})\) and Octacosane \((C_{28}H_{58})\) mixture phase transition insight via Light scattering techniques

V N Kuryakov\(^1\), P G De Sanctis Lucentini\(^2\) and D D Ivanova\(^3\)

\(^1\) Oil and Gas Research Institute of RAS (OGRI RAS), Gubkina Street, 3, 119333, Moscow, Russia.
\(^2\) Gubkin Russian State University of Oil and Gas (National Research University), Department of Physics, Leninskiy prospect, 65, Moscow, 119991 Russia.
\(^3\) D. Mendeleev University of Chemical Technology of Russia Minuskaya pl., 9, Moskva, 125047 Russia.

Abstract. In this study we analyse several emulsion samples of pure Tricosane \((C_{23}H_{48})\) and Octacosane \((C_{28}H_{58})\) paraffins as well as their mixtures with different component concentrations, prepared by means of ultrasonic dispersion without the addition of surfactants. We show that from the measurements of Static Light Scattering temperature dependences it is possible to determine the phase transition temperatures of the paraffins emulsion during the heating and cooling cycles (melting, crystallization and rotator phases). The results for the pure paraffin are in good agreement with the literature data. We produce the outcomes of the Dynamic Light Scattering technique to determine the cluster size of the obtained emulsions (radius 70-120 nm). Those emulsions proved to remain stable during several months.

1. Introduction

The n-Alkanes melting and crystallization temperatures take great importance in many research and applied works as, for example, in the Oil and Gas or in the phase change material world. Furthermore we have an unusual family of plastic-crystalline bulk phases enriching the phase diagrams in-between the liquid and the lower crystal phases temperature, often called rotator or Cristal-Rotator phases.

As evidence of the wide interest aroused, we can find experiment performed with different methods with details on the different phase diagram zones. Among the methods commonly used for studying the phase transitions, we would like to mention the result of the adiabatic scanning calorimetry and the differential one \([1-3]\). There are indeed other stimulating results from the study of the paraffins rotator phases via the well established X-ray diffraction methods \([2-4]\), from the Dynamic mechanical spectroscopy (DMS) \([3]\) and from the recently proposed use of atomic force microscope cantilever \([5]\).

In this paper we propose a technique for determining the phase transitions temperatures of the paraffins and of their mixtures based on optical methods. The studied paraffins are nanoemulsions in water prepared by ultrasonic dispersion without the addition of surfactants. A similar technique was already successfully used to determine the phase transitions in the DODAB vesicles \([6]\) and the light scattering technique is a well established method for the critical phenomena investigation \([7,8]\).
2. Materials and methods
For this experiment we prepared emulsions in water from pure paraffins (C$_{23}$H$_{48}$, C$_{28}$H$_{58}$) and from their mixtures with 17, 33, 50, 67 and 83 weight percent of the components. The heating and cooling rate in all the experiments was fixed at 2 K h$^{-1}$ and it was explored the range of temperatures in which the water remain in its liquid state, from the temperature at which the paraffins are completely solid to the one at which they are completely liquid.

**Materials and instruments.** We prepared the samples with Tricosane (C$_{23}$H$_{48}$, 98% pure), and Octacosane (C$_{28}$H$_{58}$, > 99% pure), purchased from Acros Organics and bi-distilled water purified by reverse osmosis at production time (mean conductivity 10 mS cm$^{-1}$). To prepare new emulsion samples and to dilute the highly concentrated ones, we used each time only water from new ampoules. We did not make use of any surfactants.

To prepare the nanoemulsion of paraffin in water, we used an ultrasonic disperser model UZDN-A (USSR, 22 kHz, 75 W) with an immersion transducer. We weight the components of the prepared mixture on a Sartorius BP301S balance (max weight 303 g, $\sigma = 0.1$ mg).

The measurements of light scattering temperature dependence, the hydrodynamic radius (by DLS) and the zeta potential of the emulsions were performed on particle size and zeta potential analyzers Photocor Complex and Photocor Compact (Russia).

**Samples preparation.** We used the ultrasonic dispersion method to prepare the emulsions of the pure paraffins and their mixtures in water. The dispersing was carried out at a temperature substantially higher than the melting point of the paraffin in use. Before starting the dispersion operations, we visually verified that the paraffin on the surface of the hot water was completely passed into the liquid state. During the dispersion process, the temperature of the water-paraffin mixture did not drop below the crystallization temperature of the used n-Alkane.

To prepare emulsions from a mixture of two paraffins, we preliminarily took samples of the pure species in the right proportions, melted them in one vial, stirred intensively in the liquid state and after cooling the necessary amount of such a mixture was used for the mixture-sample preparation.

To carry out the emulsification, we used the ultrasonic disperser up to the power of 75 W. There were prepared samples of about 10 ml each time. The initial paraffin concentration in water was about 0.01% in weight.

3. Results and discussion
We performed Dynamic Light Scattering (DLS) measurements at 25 $^\circ$C to determine the hydrodynamic radius $R_h$ of the paraffin clusters. For each sample it was in the range $R_h = 70 - 120$ nm. The zeta potential in emulsions of the single paraffins C$_{23}$H$_{48}$ and C$_{28}$H$_{58}$ was close to $-35$ mV.

We present, in figure 1, the scanning electron microscope (SEM) image of a sample obtained drying the sample studied with the DLS. We chose the paraffin with the higher melting point (C$_{28}$H$_{58}$) in order to avoid any accidental melting of the clusters during the SEM measurement.

It should be noted that on the dried sample there are no separate particle clusters. Indeed, being the solvent removed, all the clusters stuck together.

The visual hindrance caused by the three-dimensionality of the resulting structure, the impossibility of focusing of different plans and measuring the sizes only on such plans with the images at our disposal, the drying procedure itself that lead to clump together the different clusters of the solution, are all elements that impair the possibility to have a precise and complete reconstruction for the particle size distribution and the relative average.

Taking for example the minimum and the maximum radius of the more evident and peripheral structures, we obtain an average radius of respectively $R_{\text{SEM min}} = 55 \pm 20$ nm and $R_{\text{SEM Max}} = 78 \pm 19$ nm. Both results are quite in agreement with the DLS one, considering
that the manual selection procedure of the ellipses for the SEM image is prone to introduce a systematic error avoiding to count the bigger structures below the peripheral ones.

Further study with different preparation methods of the SEM specimens have to be implemented to avoid that all the clusters clump together and to allow more informative particle counts.

For each sample we studied the temperature dependence of the scattered light intensity $I_s = I_s(T)$ upon heating and cooling. In figure 2 we show the results for the $C_{28}H_{58}$ emulsion. The intensity $I_s(T)$ shows a linear behaviour and a weak dependence in some temperature ranges, remaining practically constant. Then at special temperatures, or temperature ranges, a significant change occurs.

**Figure 1.** SEM image of paraffin ($C_{28}H_{58}$) particles dried from the studied emulsion.

**Figure 2.** Temperature dependence of the scattered light intensity $I_s$, upon (a) heating and (b) cooling, for the paraffin emulsion $C_{28}H_{58}$. 
In general the intensity $I_s$ in an emulsion may depend on the concentration of the droplets, on their size, their shape, on the surface properties and on the difference in the refractive indices between the dispersion medium and the dispersed phase.

We assume that the marked change of $I_s$ in our samples is due to the phase transitions of the paraffin in the emulsion.

The low-temperature intensity gap corresponds to the phase transitions from the $Crystal$ ($Cr$) to the $Crystal$-rotator ($RCr$) phase and vice versa upon heating and cooling, respectively. In figure 2 these temperatures are marked as $T_{Cr-RCr}$ and $T_{RCr-Cr}$.

The changes in the scattering intensity $I_s$ at higher temperatures correspond instead to phase transitions phase $Crystal$-rotator to liquid ($L$) (melting point) and vice versa, upon heating and cooling respectively. In the figure these temperatures are denoted as $T_{RCr-L}$ and $T_{L-RCr}$.

Upon cooling, b-panel on the right of the figure 2, it is possible to note another characteristic temperature corresponding to a change in the slope of $I_s$ (marked with $T^*$) in the temperature interval between the $Liquid$ and the $Crystal$-Rotator phases.

The temperature $T^*$ may be correlated to a phase transition from the rotator phase III [2] or the temperature range $T_{L-RCr} - T^*$ may be connected to the range in which a surface crystallization happens in the paraffin emulsion droplets [9]. Further analysis are needed to investigate this zone.

We observed similar temperature dependences of $I_s$ for each of the studied emulsions. From these dependences, we determined the characteristic temperature assumed as the phase transition ones.

The figure 3 shows the temperatures of phase transitions for the mixtures of two n-Alkanes, determined according to the procedure described above.

A number of studies in the field of n-Alkanes binary mixture for bulk samples [10–12] presented analogous forms of the phase transition temperature dependence on the concentration.

It should be noted that in all samples in our study we were able to measure the melting temperature with a good reproducibility. Indeed during this phase transition the refractive index ($RI$) of the paraffin in emulsion changes greatly, which causes a strong change in the scattered light intensity $I_s$ within a little temperature increment.

For the paraffin mixture emulsion samples, not all the phase transitions have a clearly determined temperature: the intensity of the scattered light during heating and cooling are blurred in a certain temperature ranges. When we prepare an emulsion from a mixture of paraffins we are fixing the overall percentage of each species on the total. Nonetheless it is not possible to obtain the same concentration of paraffins in each drop of the emulsion, which leads to phase transitions in different drops at different temperatures and cause the blurred data reading.

The temperatures of all the phase transitions of the pure paraffin emulsion samples were also determined with good reproducibility.

In the table 1 we report the experimental data of the phase transition temperatures taken from [9] for the pure paraffins, $C_{23}H_{48}$ and $C_{28}H_{58}$, and the ones determined in this study. The used symbols are $T_m^*$ for the melting temperature (solid to liquid phase transition), $T_{zr}^*$ for the temperature of $Crystal$ to $Crystal$-rotator phase transition in the emulsion samples. $T_s^*$ is the temperatures of solidification for the bulk, non-emulsified samples. With the symbols $T_{RCr-Cr}$, $T_{Cr-RCr}$, $T_{RCr-L}$, are indicated the phase transitions between crystal (Cr), rotator crystal (RCr) and liquid (L) phases determined in this work and introduced above.

4. Conclusion

We prepared by means of ultrasonic dispersion several samples nanoemulsion in water from two pure n-Alkanes ($C_{23}H_{48}$ and $C_{28}H_{58}$) and their mixtures with different relative percentage, without the addition of surfactants.
(a) $RCr \rightarrow L$ (Melting point) upon heating.

(b) $L \rightarrow RCr$ upon cooling.

(c) $Cr \rightarrow RCr$ upon heating.

(d) $RCr \rightarrow Cr$ upon cooling.

**Figure 3.** Phase transitions temperatures of the binary n-alkane mixture ($C_{23}H_{48}, C_{28}H_{58}$) versus the concentration of the components as determined from the LS measurements for the nanoemulsions samples. *Crystal* ($Cr$), *Crystal-rotator* ($RCr$) and *Liquid* ($L$) phases.

We propose a method to determine the phase transition temperatures of those samples observing the scattered light intensity temperature dependence.

**Table 1.** The comparison of the phase transition temperature of pure n-Alkanes from [9] (with an asterisk) with the ones determined in this work. All the reported temperatures are in Celsius degrees.

| n     | $T^*_m$ | $T_{RCr-L}$ | $T^*_{xfr}$ | $T_{Cr-RCr}$ | $T^*_s$ | $T_{RCr-Cr}$ |
|-------|---------|-------------|-------------|--------------|---------|--------------|
| $C_{23}H_{48}$ | 47.2    | 48          | 40.6        | 39           | 33.4    | 34           |
| $C_{28}H_{58}$ | 60.9    | 62          | 57.7        | 56           | 45.4    | 45           |
The phase transition temperatures of the two pure paraffins so determined are in a good agreement with the previous literature data. The n-Alkanes Crystal-rotator phase transition presents an intrinsic complexity. We believe that the percentage fluctuation of the two types of paraffin in the binary mixture drops may cause a different transition temperature for each drop and a complex pattern of the scattered light temperature dependence of the whole emulsion. The eventual influences of the heating and cooling rates on the metastable phases, moreover, may play an additional role in the Rotator-Crystal phase.

The previous ones are all elements that drive us to consider interesting further future studies, applying new methods for the sample preparation, comparing the results of other instruments measurements on the same samples, and applying different methods of data analysis and data acquisition in order to obtain a deeper knowledge of the applicability of this technique for a broader phase transitions comprehension.

Acknowledgments
Authors are grateful to Alexey D.Yapryntsev from Kurnakov Institute of General and Inorganic Chemistry Russian Academy of Sciences for the SEM analysis of samples.

References
[1] Voronov V P 2000 Journal of Experimental and Theoretical Physics 91 144–149 ISSN 1090-6509 URL https://doi.org/10.1134/1.1307242
[2] Sirota E B and Singer D M 1994 The Journal of Chemical Physics 101 10873–10882 URL http://doi.org/10.1063/1.467837
[3] Sirota E B, Jr H E K, Singer D M and Shao H H 1993 The Journal of Chemical Physics 98 5809–5824 (Preprint https://doi.org/10.1063/1.464874) URL https://doi.org/10.1063/1.464874
[4] Craievich A F, Denicolo I and Doucet J 1984 Phys. Rev. B 30(8) 4782–4787 URL https://link.aps.org/doi/10.1103/PhysRevB.30.4782
[5] Jung N, Yun M and Jeon S 2012 The Journal of Chemical Physics 136 104903 (Preprint https://doi.org/10.1063/1.3692296) URL https://doi.org/10.1063/1.3692296
[6] Voronov V P, Kuryakov V N and Muratov A R 2012 Journal of Experimental and Theoretical Physics 115 1105–1110 ISSN 1090-6509 URL https://doi.org/10.1134/S106377611211012X
[7] Robertson A E, Phan D H, Macaluso J E, Kuryakov V N, Tourajeva E V, Bertrand C E, Yudin I K and Anisimov M A 2016 Fluid Phase Equilibria 407 243 – 254 ISSN 0378-3812 aqueous Solutions URL http://www.sciencedirect.com/science/article/pii/S0378381215003490
[8] Belyakov M, Gorodetskii E, Kulikov V, Kuryakov V and Yudin I 2011 Chemical Physics 379 123 – 127 ISSN 0301-0104 URL http://www.sciencedirect.com/science/article/pii/S0301010410005240
[9] Kraack H, Sirota E B and Deutsch M 2000 The Journal of Chemical Physics 112 6873–6885 (Preprint https://doi.org/10.1063/1.481263) URL https://doi.org/10.1063/1.481263
[10] Ungar G and Masic N 1985 The Journal of Physical Chemistry 89 1036–1042 (Preprint http://dx.doi.org/10.1021/j100252a030) URL http://dx.doi.org/10.1021/j100252a030
[11] Hammami A and Mehrotra A K 1995 Fluid Phase Equilibria 111 253 – 272 ISSN 0378-3812 URL http://www.sciencedirect.com/science/article/pii/037838129502777C
[12] Mazee W 1957 Analytica Chimica Acta 17 97 – 106 ISSN 0003-2670 URL http://www.sciencedirect.com/science/article/pii/S0003267000870026