Light mirror reflection combined with heating/cooling curves as a method of studying phase transitions in transparent and opaque petroleum products: Apparatus and theory

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Abstract

A portable low weight low cost apparatus "Phasafot" and method for determining pour and cloud points of petroleum products, as well as precipitation and melting temperatures of paraffins in both transparent (diesel fuels), semi-transparent (lube oils) and opaque (crude oils) samples are described. The method consists in illuminating the surface of a sample with an oblique light beam and registering the intensity of specularly reflected light while heating/cooling the sample in the temperature range of its structural transitions. The mirror reflection of a light beam from an ideally smooth liquid surface falls in intensity when the surface becomes rough (dim) due to crystal formation. Simultaneous recording of the temperature ramp curve and the mirror reflection curve enables the determination of the beginning and end of crystallization of paraffins in both transparent and opaque petroleum products. Besides, their rheological properties can be accurately determined by rocking or tilting the instrument while monitoring the sample movement via its mirror reflection.
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1. Introduction

The propensity of petroleum products to precipitate paraffins may cause the obstruction of crude oil pipe-line flow, plugging of filters in motor engines and in refining operations, gelation of fuels in car engines, etc. Therefore, the cloud point – the temperature at which the paraffin crystal formation becomes visible in a fuel, and the pour point – the temperature at which the product loses its mobility are important technological parameters for whose determination a number of instruments have been devised and marketed. Although these instruments serve their purpose in most cases, they have a number of shortcomings, among which is their inability to measure crystallization and melting temperatures of paraffins in opaque samples, e.g. crude oils and their heavy residues. Besides, the measurement of pour points of various petroleum products is often difficult to perform with sufficient precision, or the instrumentation is cumbersome and expensive. Therefore, attempts are constantly being made to develop new or upgrade the existing instruments. Methods based on DSC [1], thermal microscopy, viscometry, and DSC [2–4], DSC and viscometry [5] may be mentioned in this connection, as they permit a detailed and objective study of petroleum products by comparatively simple means. A wide range of tasks can be solved including the improvement of pour point depressant formulations and the study of the mechanism of pour point depression [4]. An added advantage of thermal microscopy is its ability to study opaque samples, e.g. the processes of paraffin crystal growth in crude oils [2,3]. Still, the instruments employed are expensive, and the analysis takes time.

Wax (paraffin) deposition is an ever present problem in pipelines and oil wells. In Ref. [6] application of CT imaging has been proposed as an alternative tool for cloud point determination. In Refs. [7,8] differential scanning calorimetry has been used to establish the wax content and wax appearance temperatures of crude oils. In Ref. [9] the limitations of the cloud point measurement techniques and the influence of the oil composition on its detection are discussed. Theoretical aspects of the problem of wax deposition in wells and pipelines can be found in Refs. [10,11].

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In the present communication a simple and rapid method to study the low temperature properties of various crude oils and related products is described.

2. Results and discussion

A method alternative to those used currently in the petroleum industry is presented hereinafter in some detail. It will be shown in what follows that the shortcomings of the known methods can be overcome by adopting a new technique of photometric signal generation and measurement. This consists in registering the light reflected from the surface of a liquid sample undergoing various phase transitions during heating or cooling. In the liquid state the opaque sample has an ideally smooth surface capable of specularly reflecting about 4–5% of the light falling on it for the incidence angle of about 30°. As soon as a phase transition, e.g. crystallization sets in, the crystals appearing in the bulk and hence on the surface of the sample make the surface rough due to chaotic orientation of the surface crystals. As a result the randomly scattered portion of the light increases, while the specularly reflected portion diminishes in proportion to the crystal density on the surface. Monitoring the intensity of the specularly reflected or randomly scattered light rather than that of the light transmitted (as in common methods) enables the study of phase transitions in samples of various nature, texture, and transparency.

The situation described above applies mainly to opaque or semi-opaque samples. In the latter case the use of cuvettes with blackened bottoms is recommended to reduce the light reflected from the bottom and leave only that reflected from the surface.

In the case of transparent and semi-transparent samples a different mode of operation is adopted. A liquid sample forming a 2–5 mm thick layer is placed in a metal cuvette with a flat polished bottom. The light is reflected back from the cuvette bottom to the photoreceptor, passing twice the sample, which enables operation in the conventional transmission mode in which the optical densities of liquid samples can be studied. In this case the specular component from the surface should be minimized as it serves no useful purpose, and that from the bottom maximized. The borderline between the two modes of operation is determined by the optical properties of the sample, viz. its optical density.

A schematic drawing of the apparatus "Phasafot" is presented in Fig. 1.

It consists of the following basic parts: outer jacket 1 and inner jacket 2 covered with lid 3: optical unit 4 housing reflectometer and temperature sensor (thermocouple); heating/cooling device based on Peltier elements 5 and 6 connected to temperature programmer 7. Inlet 8 and outlet 9 are provided in the jacket for passing the water cooling the Peltier elements.

A cup 10 with sample is put on the Peltier device and the optical unit 4 lowered into the thermostat. Simultaneously the thermocouple 11 protruding from the optical unit is immersed in the sample.

A light emitting device – LED 13 projects a beam of light onto the surface of the sample at an angle about 30° relative to the perpendicular to the surface plane; the beam of light is
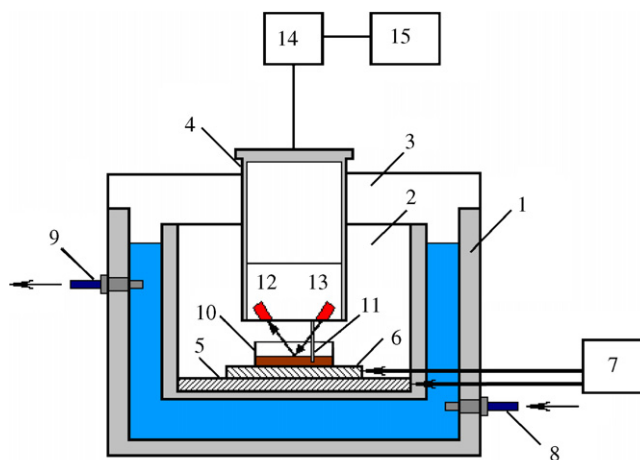

Fig. 1. Schematic drawing of apparatus "Phasafot".

reflected back at the same angle and falls on the photoreceptor 12 which generates a signal (voltage) proportional to the intensity of the reflected beam. The analogue signals (voltages) from the reflectometer and the thermocouple are fed into the ADB 14 where they are digitized and then passed on to the computer 15. The digitized signals are collected by the program "Thermo" and displayed on the monitor screen as two curves—the sample mirror reflection (MR) and the sample temperature (T) as functions of time (Fig. 2).

Heating/cooling rates may vary from 2 to 20 °C/min, the temperature range of the instrument is from −50 to 120 °C.

When determining crystallization temperatures of paraffins in petroleum products and their pour points the mode of the instrument operation is the following.

The cup is filled with 0.4–0.5 ml of the liquid under study and placed in the thermostat, the optical unit placed above the cup and the instrument positioned horizontally to obtain a maximal MR signal.

The sample is heated to 40–50 °C to eliminate its thermal history, then subjected first to a cooling and then to a heating cycle. The temperatures of phase transitions are noted visually using the changes in the MR signal in the course of the experiment or by recording the curves via the computer.

Below are given examples of the instrument operation.

2.1. Determination of crystallization/melting temperatures of samples transparent in the liquid state (e.g. individual paraffins)

In this example the sample is transparent in the liquid state, thus a cuvette with light reflecting bottom is used. The solid paraffin is loaded into the cup in the amount sufficient to form a film 2–3 mm thick completely covering the cup bottom on melting.

On Fig. 2 mirror reflection (MR) and heating/cooling (H/C) curves are presented as they are seen on the monitor screen after the run. Time is plotted on the X-axis and the sample temperature on the ordinate. The MR curve is dimensionless.

The temperature curve is composed of three cycles: heating, cooling, and then again heating. A horizontal step is
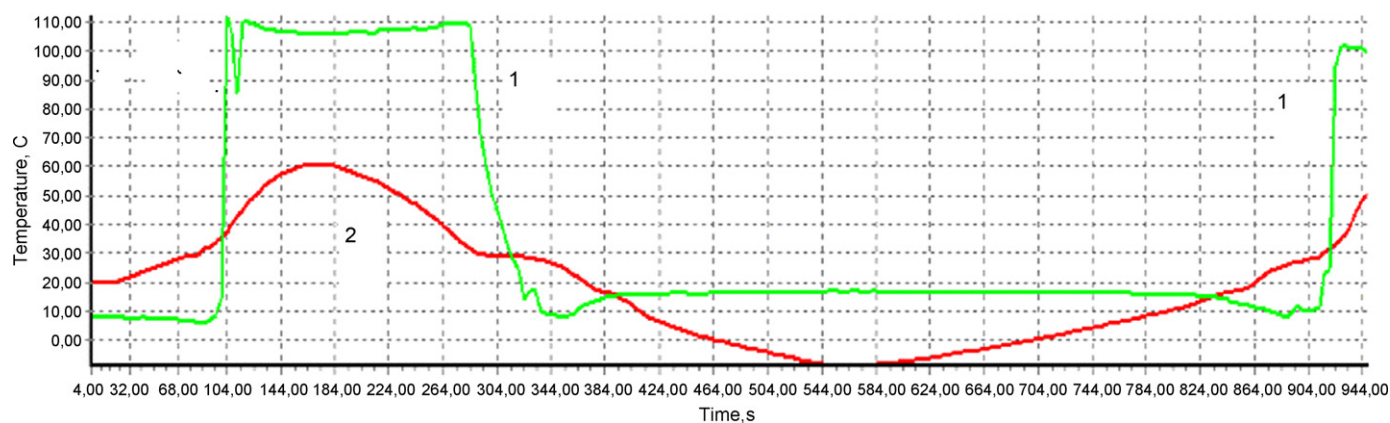
Fig. 2. Curve 1: mirror reflection (dimensionless), curve 2: temperature of nonadecane $C_{19}H_{40}$ (plotted on the *Y*-axis). The upward step on the MR curve indicates paraffin melting in the heating cycle, the downward step indicate freezing of the melt in the cooling cycle.

observed on the temperature curve and an upward step on the MR curve on the paraffin melting at 30 °C in the first heating cycle, see the left side of Fig. 2. On melting the solid paraffin forms a transparent film on the cup bottom, and the increased light reflected from the cuvette causes the rise of the MR signal.

In the cooling cycle the liquid paraffin begins to solidify at 30 °C and a horizontal step appears on the cooling curve. The downward step on the MR curve occurs just at the beginning of the horizontal step on the cooling curve. This is due to a rapid and uniform fall-out of paraffin crystal nuclei which make the sample opaque thus reducing the mirror reflection from the cuvette bottom. The further growth of the crystals within the duration of the horizontal step does not change the MR to any great extent.

In the second heating cycle (see the right side of Fig. 2) as the sample melts and becomes transparent again the MR signal rises causing an upward step on the MR curve. This step is found at the end of the quasi-horizontal (sloped) step on the heating curve. This is due to the opaque paraffin film persisting on the sample surface till its full melting.

A reversible rotatory phase transition can also be discerned on the cooling and heating curves marked by small sloped steps on the C/H curves at around 20 °C and corresponding upward/downward steps on the MR curve, due evidently to a better reflection ability of the paraffin non-rotatory phase formed below 20 °C on cooling.

In the above example the cooling/heating curves alone may be used for studying the paraffin crystal formation/melting due to the large heats absorbed/evolved at nearly constant temperature producing horizontal steps on H/C curves. In the case of mixtures (technical paraffins) or low purity specimens with broadened transition intervals or solutions with moderate paraffin content no well defined steps are observed on the temperature curve making them unusable for establishing transition temperatures. The MR curves of a technical paraffin are given below as a typical example (Fig. 3).

Although no steps can be discerned on the temperature curve there are well defined steps on the MR curve enabling the exact pinpointing of phase transition temperatures in the sample (if used together with the temperature curve). The irregular double-peak shape of the MR curve in the melting region of the second
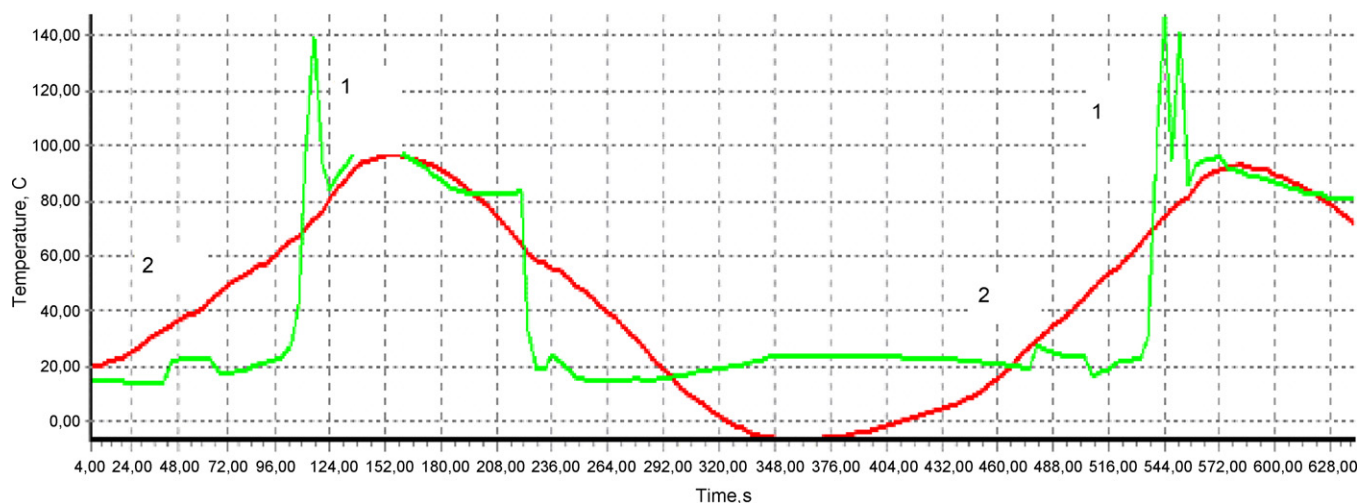

Fig. 3. Curve 1: mirror reflection, curve 2: sample temperature of a technical paraffin (presumably a $C_{22}H_{46}$–$C_{28}H_{58}$ mixture).
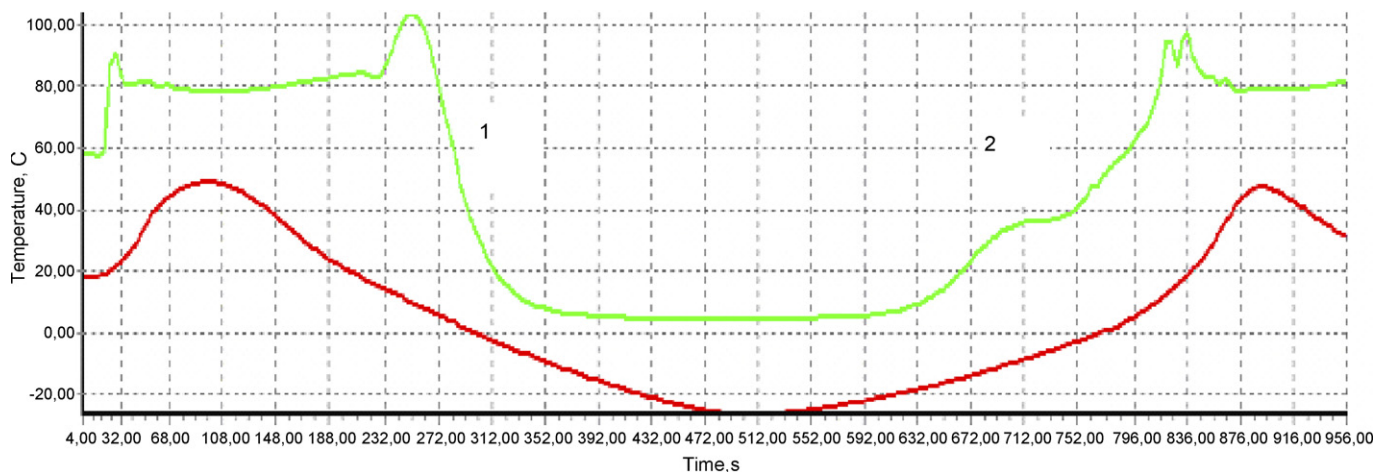
Fig. 4. MR cooling curve 1 and MR heating curve 2 of Kumkol crude oil.

heating cycle points to the presence in the sample of low and high-melting paraffin fractions with $T_m = 68\,°C$ and $T_m = 79\,°C$, respectively.

2.2. Determination of freezing/melting temperatures of paraffins in opaque solutions (e.g. crude oils)

In the case of opaque samples no light is reflected from the cuvette bottom and only that reflected from the sample surface comes into play. Although its intensity is small (4–5% of the total incident light) as compared to that reflected from the metal cuvette bottom (up to 99%), it can produce a high voltage signal (in our case 5–6 V) quite sufficient for very sensitive measurements.

The figure shows that the freezing and melting of paraffins in the crude can be very well seen due to the steep downward and upward steps on the MR curve in the region of crystal formation/melting (precipitation/dissolution), while not a trace of these events can be discerned on the ideally uniform C/H curves. Projecting the steps of the MR curve on the C/H curves allows pinpointing the temperatures of phase transitions in the sample.

Data of Fig. 4 was processed to obtain a graph giving the percent content D of the solid fraction as a function of the melt temperature (Fig. 5). It was calculated using the formula

$$D = 100 \left| \frac{\Delta h}{H} \right| \%$$

where Δh is the current height of the downward step on the MR curve and H is the full height of the step. The left curve on the graph refers to the cooling cycle; it is obtained on moving from high to low temperatures (from the right to the left on the figure), and the right curve refers to the heating cycle; it is obtained on moving from low to high temperatures, i.e. from left to right on the figure.

It is seen on Fig. 4 that paraffin precipitation begins just at the start of the downward deflection on the curve, occurring at $10\,°C$, which is the top point of the left portion of the curve on Fig. 4 and the right portion of the cooling curve on Fig. 5. The slight rise of MR just before its fall may be due to gel (glass) formation of the crude just preceding paraffin precipitation.

The paraffins in the crude precipitate in the interval 10 to $(-15)\,°C$ and melt in the interval -20 to $(+16)\,°C$, their being a negative hysteresis of $11\,°C$ between the freezing and melting curves at 80% conversion.

2.3. Determination of pour points of crude oils

The mirror reflection can also be used for studying the mechanistic (rheological) properties of petroleum products, viz. their ability to flow or solidify on heating/cooling. For this purpose the instrument is tilted periodically in the temperature range where the sample undergoes the process of solidification. For the liquid sample this results in a rough comb-like appearance of the MR curve due to the periodic violation of the parallel disposition of the planes of the liquid sample surface and that of the photoreceptor (the MR signal is maximal when these planes are parallel). On the sample becoming solid the MR curve becomes flat due to the said planes becoming fixed at some constant angle. The point on the cooling curve where the MR becomes constant despite the instrument rocking is the temperature T_g of the sample solidification (gelation), see Fig. 6.

After this the pour point of the sample can be determined in the heating cycle. If the sample-photoreceptor planes happened
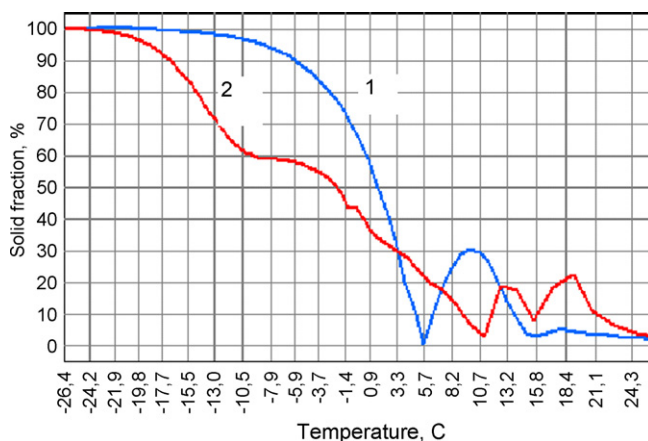

Fig. 5. Data of Fig. 4 presented as "solid fraction D, %; temperature, °C" graph. Curve 1: precipitation of paraffins, curve 2: their melting.
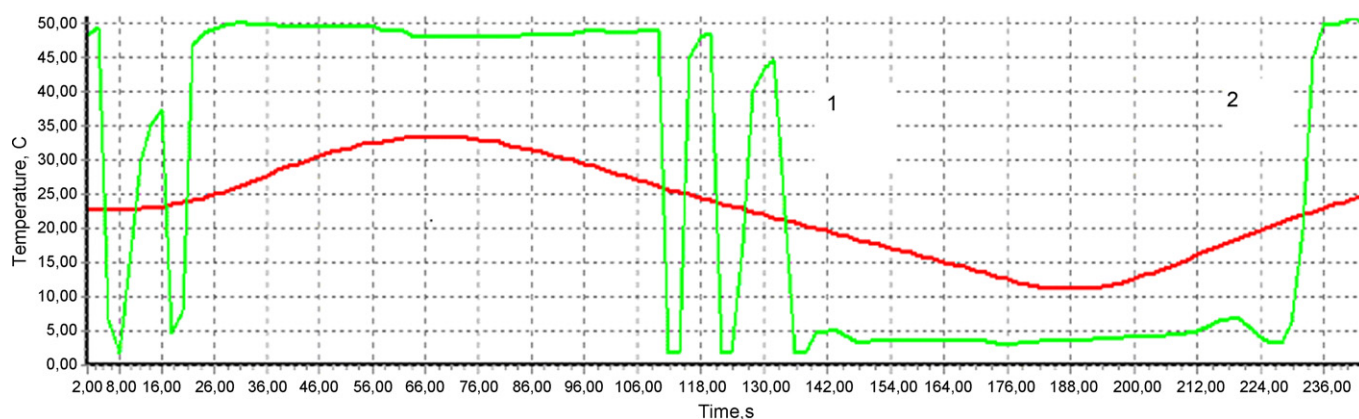
Fig. 6. MR cooling curve 1 of Kumkol crude oil obtained on rocking the instrument. Gelation point $T_g = 20\,^\circ\text{C}$. MR heating curve 2 obtained without rocking. Pour point $T_p = 20\,^\circ\text{C}$.

to be parallel on solidification causing a maximal MR signal, the instrument is left tilted during heating so that when the sample melts and flows at its pour point the MR signal falls, thus enabling the pour point identification. If, on the contrary, the sample-photoreceptor planes were not parallel when the sample became solid, and its MR was not maximal, the instrument is positioned horizontally during the heating cycle; on reaching the pour point the sample flows, the said planes become parallel and the MR signal returns to maximum, thus enabling the pour point (T_p) identification. The latter case is exemplified in Fig. 6 where the MR signal of the Kumkol crude oil happened to be at its lowest on the sample becoming solid. From the MR curve one finds the solidification (gelation) temperature of the crude $T_g = 20\,^\circ\text{C}$ and the pour point $T_p = 20\,^\circ\text{C}$, i.e. the temperatures T_g and T_p are identical (the transition from liquid to solid and from solid to liquid is quite reversible).

It should be noted in the present context that the term "solidification" is not equivalent to the term "crystallization". Comparing Figs. 5 and 6 one can see that the Kumkol crude solidifies at $20\,^\circ\text{C}$, but precipitation (crystallization) of paraffins in the crude occurs at much lower temperatures $T_{cl} = 10$ to $(-12)\,^\circ\text{C}$. Solidification of the crude is in fact gelation—the formation of a non-Newtonian liquid, otherwise immobile but capable of flow if a proper shearing stress is applied to it. The gel,

being a structured liquid, reflects light as a liquid and therefore is not accompanied by the fall of MR, in contrast to crystallization. On the contrary, a slight rise of the MR signal can be observed beginning from $17.4\,^\circ\text{C}$ (Fig. 5), which is close to $T_g = 20\,^\circ\text{C}$ of Fig. 6. Evidently, the gel reflects light slightly better than the liquid, and this produces a small upward deflection on the MR curve just before paraffin precipitation. Thus, from Figs. 5 and 6 it follows that gelation precedes paraffin precipitation in the cooled crude oil, and not vice versa, as is commonly thought.

From the above it follows that the cloud point of the Kumkol crude is $T_{cl} = 10\,^\circ\text{C}$ and its gelation and pour points are $T_g = T_p = 20\,^\circ\text{C}$.

2.4. Determination of cloud and pour points of a diesel fuel

In the present example the sample has solidified at a nearly maximum MR signal, and this has made possible monitoring the sample gelation and paraffin precipitation in the same run. The fall of MR in the interval $-9(-8)$ to $(-20)\,^\circ\text{C}$ shows that paraffin crystals form in this interval just after the sample has become solid. So its gelation $T_g = -8$ or $-9\,^\circ\text{C}$ and its cloud point $T_{cl} = -8$ or $-9\,^\circ\text{C}$ (Fig. 7).

After this the instrument was tilted and the heating cycle started. The formed crystals melt in the gel in the interval -18
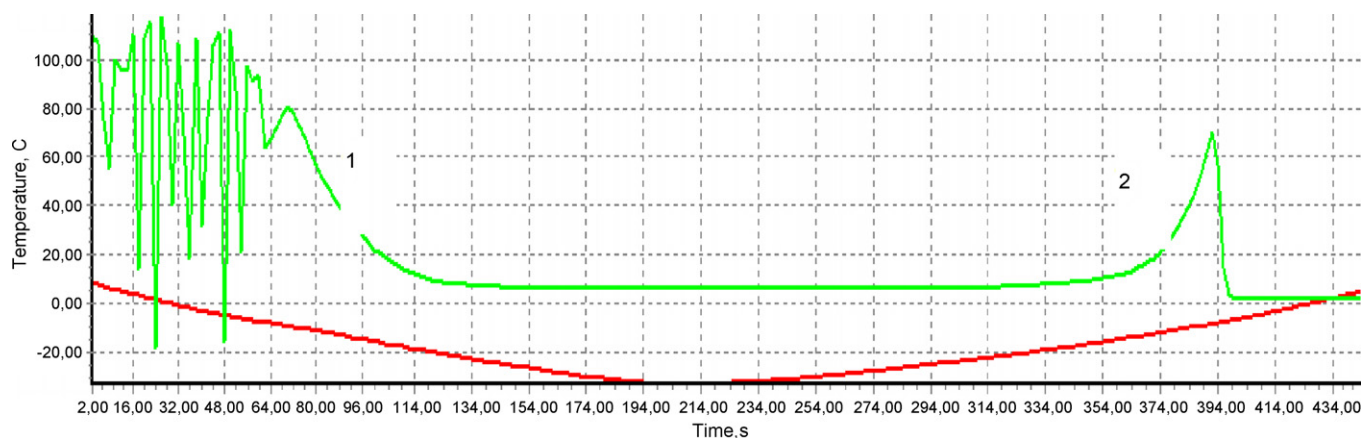

Fig. 7. MR cooling curve 1 of a summer diesel fuel obtained on rocking the instrument. Gelation point $T_g = -8\,^\circ\text{C}$. MR heating curve 2 obtained without rocking. Paraffins melting interval $\Delta T_m = -20$ to $(-8)\,^\circ\text{C}$, pour point $T_p = -8\,^\circ\text{C}$.
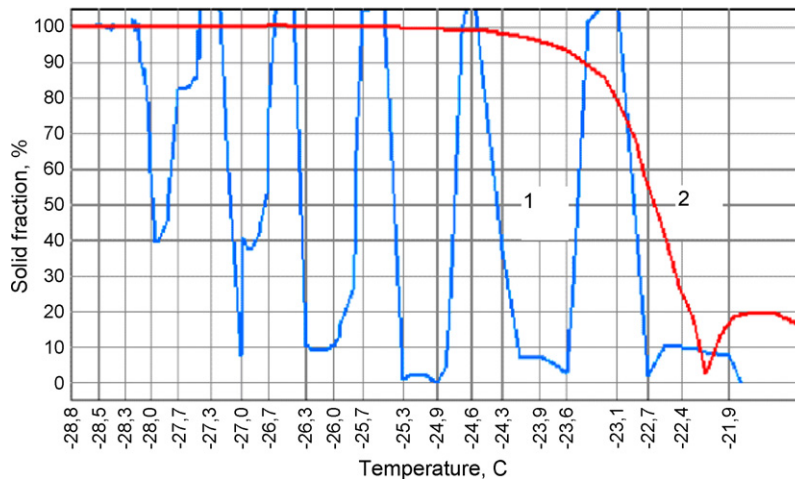
Fig. 8. MR cooling curve 1 and MR melting curve 2 of industrial base oil I-20A.

to $(-8)\,^\circ$C (the MR rises beginning from $-18\,^\circ$C), then the gel melts in its turn and the sample flows causing an abrupt fall of MR at $-8\,^\circ$C. So the sample pour point is $T_p = -8\,^\circ$C.

In this example paraffin precipitation begins immediately after gelation without overcooling (in contrast to crude oils) evidently due to the absence in the fuel of resins and asphaltenes—depressants of paraffin crystallization. Here both the fuel gelation and paraffin precipitation are fully reversible and very close to each other (proceed without overcooling).

2.5. Determination of lube base oil pour and cloud points

Cloud and pour points of a light industrial base oil were determined by the described method (Figs. 8 and 9).

The light base oil fully loses mobility at $-28\,^\circ$C; at this temperature the comb on the graph levels off. So its gelation point is $T_g = -28\,^\circ$C. On heating the gelled sample (without rocking) the latter melts in the interval -24 to $(-22)\,^\circ$C as is shown by the downward step on the MR heating curve. So its average pour point is $T_p = -23\,^\circ$C. Thus, there is a hysteresis of $5\,^\circ$C between the gel formation and gel melting temperatures T_g

and T_p. These may be considered as two pour points of the light base oil—one obtained on cooling (T_g), and the other on heating (T_p).

To study the paraffin precipitation and dissolution (melting) in the base oil the instrument was positioned horizontally to obtain a maximum MR signal (and thus maximum sensitivity of measurement), and the cooling cycle started.

Fig. 9 shows that the light reflecting ability of the base oil begins to rise from $-4\,^\circ$C. It begins to fall at $-15\,^\circ$C due evidently to the start of paraffin precipitation, so its cloud point is $T_{cl} = -15\,^\circ$C. The last fraction of small low melting paraffin crystals form in the interval -24 to $(-28)\,^\circ$C, which is close to the base oil gelation point $T_g = -28\,^\circ$C (temperature of its full immobilization). In the heating cycle the paraffins melt at -24 to $(-22)\,^\circ$C, which is close to the sample pour point $T_p = -23\,^\circ$C (the temperature of its liquefaction and flow).

In this example two distinct paraffin fractions are present in the sample: the high melting one with $T_{cl} = -15\,^\circ$C and the low melting one with $T_{cl} = -24$ to $(-28)\,^\circ$C. The precipitation of this fraction, predominant in the sample, coincides with its gelation, just as in the case of the diesel fuel discussed above. The same
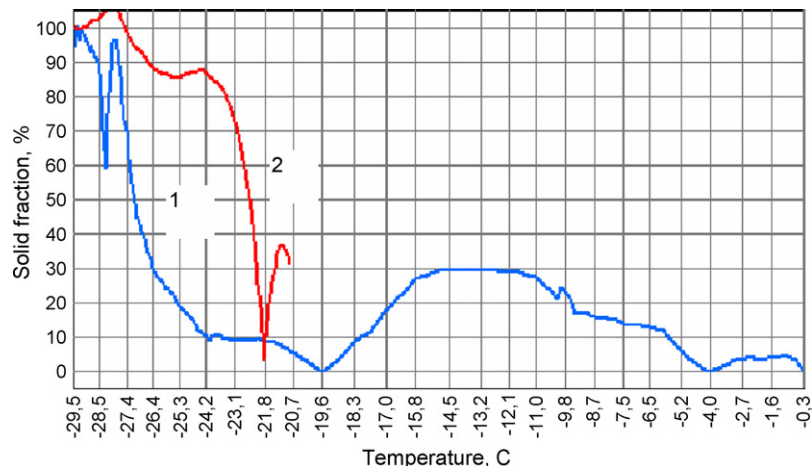

Fig. 9. Crystallization (curve 1) and melting (curve 2) of paraffins of base oil I-20.

refers to the temperatures of paraffin crystals melting (T_m) and the sample flow (T_p).

3. Conclusions

1. The method described above has a number of distinctive features offering the researcher quite a number of new possibilities as regards the study of low temperature properties, thermal as well as rheological, of various petroleum and not only petroleum products. For the first time mirror reflection from liquid opaque samples has been made full use of to obtain important information on events taking place in such nontransparent objects. On the other hand, its use in combination with light reflecting cuvettes has made possible work in transmission mode and thus enabled traditional optical density measurements, and its use in combination with mechanical perturbation of the sample has much simplified determination of the rheological properties of materials.
2. Application of the method to petroleum products has revealed the following sequence of events taking place in such products, e.g. crude oils. On cooling: gelation (glass formation) – paraffin nuclei fall-out (precipitation) – growth of nuclei (paraffin crystal formation). On heating: melting of paraffin crystals—melting of the gel leading to the sample liquefaction (flow).
3. The notions of pour point and cloud point of petroleum products should be reconsidered and made more meaningful and precise in the light of the obtained results. Actually, there are two pour points: one obtained on cooling (T_g) and the other on heating (T_p). They may or may not coincide depending on the nature of the product, e.g. absence or presence in it of resins and asphaltenes. The same applies to the cloud point. On cooling the cloud point T_{cl} is the temperature of the nuclei fall-out often occurring with considerable overcooling, and on heating it is the temperature T_m of the melting of the last paraffin crystals. These may be quite different temperatures. Besides, the cloud and pour points are not actually points, but intervals, whose breadth is proportional to the molecular and structural heterogeneity of the sample.
4. The universal character of the proposed method, its high precision and high through-put capacity recommend it well for use in laboratories of petroleum product quality assessment and control.

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