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microsecond range of spin-spin relaxation times**

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**The characterization of asphaltenes by ^1H NMR relaxation method:
microsecond range of spin-spin relaxation times**

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The asphaltene powders have been studied by ^1H NMR relaxation method, differential scanning calorimetry (DSC) and X-ray structure analysis. The asphaltene samples were extracted from three oils with different component and hydrocarbon-group compositions. It was found that free induction decays (FID) of various asphaltene samples contain Gaussian component with spin-spin relaxation times T_2 about $10\div 20$ μs , which was named a solid component. The detecting possibilities of equilibrium first-order phase transitions and non-equilibrium glass-transitions on temperature dependence of part P_s of solid component in the ^1H NMR signal are presented. The ^1H NMR relaxation and DSC methods to study temperature properties of asphaltenes are compared. The glass-transition temperatures of side aliphatic chains of asphaltene molecules are measured. We set up that crystallization of high-molecular side aliphatic chains of asphaltene molecules is possible.

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1. Introduction

The asphaltene is a general name of a great variety of high-molecular polycyclic compounds, containing heteroatoms N, S, O and impurities of metal atoms Ni, V and others. Practically, asphaltene is a substance, which precipitates out of oil when low-molecular *n*-alkanes are added in oil. The quantity of precipitated asphaltenes decreases and their chain-length distribution changes from bimodal to unimodal under increasing number of carbon atoms in the molecule of *n*-alkane solvent [1]. In most models the asphaltenes are defined as firm quasispherical colloidal particles consisting of condensed aromatic rings grouped one above another in a stack with approximately parallel planes and surrounded by chains of aliphatic (with number of carbon atoms 5-6 and more) and/or naphthene-aromatic systems on periphery [2-4]. The size and form of colloidal asphaltene particles in solutions depend on solvent and temperature. The sizes of colloidal particles can vary in the range from 14 to 30-50 Å. Initial colloidal particles can form more and more large aggregates as a result of coagulation/flocculation, up to sedimentary stability loss and settling-out.

Asphaltene play an important part in structure and properties formation of oil dispersed system, though, as a rule, the content of asphaltene in the oils is insignificant (about 5-7%). It is established that the tendency of oil to settling-out of asphaltene-resin-paraffin substances is defined basically by asphaltene characteristics, namely, high aromaticity, low content of hydrogen, high condensity of aromatic rings, high density [6, 7] and the absence of structural and chemical compatibility with corresponding resins. The authors [5] name similar asphaltene as the most polar fractions, they precipitate first during asphaltene precipitation out of oil by a standard technique. The natural oil contains insignificant quantities of the most polar fractions of asphaltene, which have smaller molecular weights, do not contain long side aliphatic chains and can have significant amounts of sulfoxide and carbonyl groups in own structure [1]. Powder particles of these asphaltene fractions are dense, glossy particles of black color and are characterized by some ordering of the structure. The least polar fractions of asphaltene represent a brown powder without gloss and have an amorphous structure [5].

It is noticed that paraffin hydrocarbons coprecipitate together with asphaltene during the standard procedure of asphaltene precipitation out of oil by low-molecular *n*-alkanes. There are some assumptions explaining this phenomenon. The authors [1] consider that complexity of structure and molecular weight of asphaltene aggregates increase approaching the boundary of flocculation during addition of low-molecular *n*-alkanes into the oil. Asphaltene possess superfluous ability to association through hydrogen bonds near the flocculation point that leads to coprecipitation of other oil components, in particular, high-molecular paraffin hydrocarbons. Philp and coworkers [8] believe that coprecipitation of high-molecular hydrocarbons, such as paraffins and asphaltene, occurs because of equally low solubility in low-molecular *n*-alkanes (solubility in *n*-pentane is equal 1.3 mg / 100 ml approximately). Recently, a number of publications [9, 10] appeared, whose authors claim that Van der Waals interactions between lateral side aliphatic chains of asphaltene molecules are responsible for the least thermally steady asphaltene aggregates formation [11]. Further, the same authors assume that asphaltene interact with *n*-alkanes (*n*-alkanes are dissolved in the solvation sphere of colloidal asphaltene aggregates), and this interaction causes flocculation of asphaltene molecules and its precipitation out of oil [12]. It is found that interaction between asphaltene and paraffins depends on the structure of asphaltene [13], concentration and dispersion degree of asphaltene [14].

The paper [15] claims that asphaltene aggregates can be in the three different phases. The heat capacity of asphaltene is similar to the heat capacity of solid crystal at the temperatures essentially below -30°C , until they do not undergo phase transition to the amorphous state at the heating above -30°C . The amorphous phase of asphaltene arises due to interactions polar side aliphatic chains and keeps up to temperatures $25-30^{\circ}\text{C}$. During further heating, asphaltene form more dense structures (stable up to temperatures of the order 100°C) due to bonding between pericondensed aromatic surfaces, and then asphaltene suffer phase transition to the ordering crystal phase in the temperature range $100-180^{\circ}\text{C}$. At more high temperatures, the amorphous phase of asphaltene is softened and the crystal phase of asphaltene begins to melt only at temperatures $220-240^{\circ}\text{C}$. Finally, at the temperature 350°C , asphaltene are destroyed forming mesomorphic anisotropic melt, which foregoes coke formation.

The authors [16] studied thermal properties of asphaltene in the stream of nitrogen by means of differential scanning calorimetry (DSC) and discovered two typical phase transitions for asphaltene. So their asphaltene samples suffer glass-transition in the range of temperatures $120-130^{\circ}\text{C}$, which relates to non-polar amorphous phase of asphaltene. The endothermic effect observed by authors at temperature 180°C under heating of asphaltene is explained as melting of crystal phase, which is characteristic for a polar asphaltene fraction.

Thus, from the above mentioned data follows that the composition and structure of asphaltene play an important part in structure and properties formation of oil disperse system. Studying asphaltene phase transitions mechanisms is necessary for understanding the internal structural organization of natural oil and its changes with temperature. This information is important for oilfield exploitation technologies optimization and also for oil refining and transportation.

The purpose of our work is to find structural features of different oil asphaltene using ^1H nuclear magnetic resonance (NMR) relaxation method. It is also supposed to give the analysis of ^1H NMR relaxation method opportunities in comparison with DSC method on the example of asphaltene.

2. Samples

The asphaltene samples (powders) extracted from three different oils, essentially differing in component and hydrocarbon-group compositions (Table I) have been chosen as objects of research. It is seen from Table I that the

Dachnaya oil is characterized by high content of asphaltenes, Mordovo-Karmal bitumen is characterized by high content of resins and Mamurinsk oil is characterized by high content of paraffins (wax contains paraffins).

Table I. Physical-chemical research data of the Mordovo-Karmal bitumen (Tatarstan; extracted by in-situ combustion method), Dachnaya oil well №3577 (Tatarstan) and Mamurinsk oil well №21 (Samara region)

Oil samples	Gasoline fraction, wt. %	Wax, wt. %	Benzene resins, wt. %	Alcohol-benzene resins, wt. %	Asphaltenes, wt. %
Dachnaya oil well №3577	18.8	55.7	16.4	2.0	7.1
Mordovo-Karmal bitumen	10.1	52.1	25.0	8.0	4.8
Mamurinsk oil well №21	21.2	60.2	13.7	3.6	1.4

The asphaltene precipitation was carried out by petroleum-ether (boiling temperature 40-70°C) with volume proportion: oil/solvent = 1/40. The precipitated asphaltenes were washed on the filter in the Soxhlet's apparatus by hot petroleum-ether until the solvent becomes colorless. Then obtained asphaltenes were dissolved in benzene to eliminate non-hydrocarbon impurity, after that benzene was removed. Finally, asphaltenes were dried up to constant weight in vacuum.

3. Experimental methods

Nuclear magnetic resonance (¹H NMR) relaxation

Free induction decays (FID) of various asphaltenes contain Gaussian component with spin-spin relaxation times T_2 about 10÷20 μs (see Fig.1). We are name the component with Gaussian form of FID a solid component, because immobile protons with high arrangement density can possess such a FID form. We believe that crystalline and amorphous solids, containing hydrogen, can possess such short spin-spin relaxation times T_2 . We choose part P_s of solid component in the ¹H NMR signal of asphaltenes as a parameter, which describes the content of solid-state formations [17, 18]. Its measurement is difficult to perform applying direct measurement from FID, because NMR equipment has

dead time τ_p (in our case $\tau_p = 13 \mu s$). Therefore it is necessary to use Solid-Echo pulse sequence ($90^\circ_x - \tau - 90^\circ_y - \tau$) [19-21] for correct measurement of parameter P_s . Transverse magnetization decay of asphaltenes in Solid-Echo pulse sequence is similar to FID and can be described by equation:

$$M(t, \tau) = M_l(t) + M_s(t, \tau),$$

$$M_l(t) = \sum_i M_{li}(0) \cdot \exp\left(-\frac{t}{T_{2li}}\right), \quad (1)$$

$$M_s(t, \tau) = M_s(0, \tau) \cdot \exp\left(-\left(\frac{t}{T_{2s}}\right)^2\right),$$

where $M_{li}(0)$ is magnetization of liquid component (Lorentzian component) at the maximum of solid-echo signal; $M_s(0, \tau)$ is magnetization of solid component (Gaussian component) at the maximum of solid-echo signal, which depends on time interval τ between RF-pulses; T_{2li} is spin-spin relaxation time of liquid component; T_{2s} is spin-spin relaxation time of solid component.

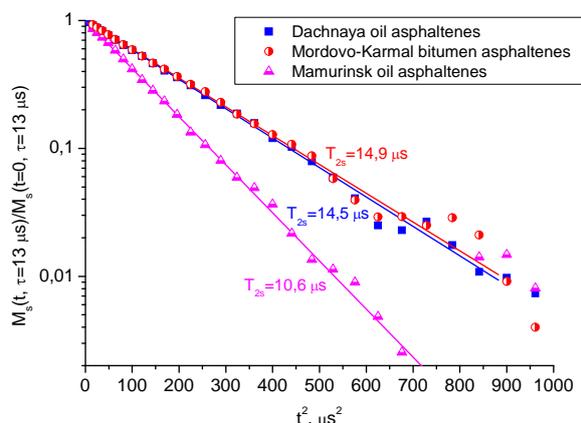


Fig.1. Transverse magnetization decay of solid component in the ¹H NMR signal for different oil asphaltenes at room temperature 24°C (solid-echo pulse sequence, $\tau = 13 \mu s$). Fitting curves computed on the basis of the equations (1) for experimental points are shown by solid curves.

Solid component magnetization dependence on time τ (see Fig.2) can be presented in the form:

$$M_s(0, \tau) = M_s(0, 0) \cdot \exp\left(-\left(\frac{\tau}{T_{2s}^{irr}}\right)^n\right), \quad (2)$$

where T_{2s}^{irr} is relaxation time of solid component magnetization caused by irreversible processes (flip-flop transitions, multi-quantum transitions); n is power parameter, for which the dependence of $\ln(M_s(0, \tau))$ from τ^n is a linear function. The value of parameter n is defined by the properties of dipole-dipole interactions and the nature of asphaltene solid-state formations.

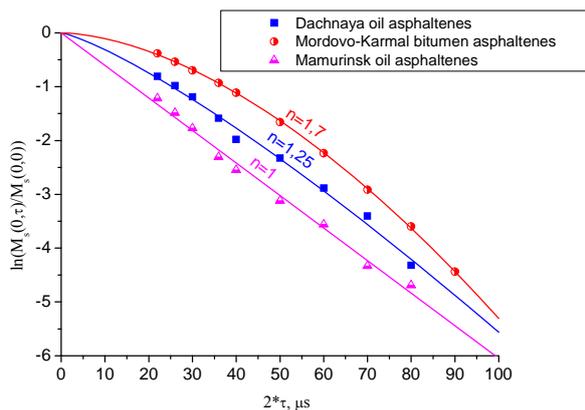


Fig.2. Solid component magnetization dependence on time interval τ in the pulse sequence Solid-Echo for different oil asphaltenes. Fitting curves computed on the basis of the formula (2) for experimental points are shown by solid curves.

where $\Delta P_{si}^{amorph/cryst}$ is increment of $P_s(T)$ due to mixture component vitrifying (devitrifying) or crystallizing (melting) at cooling (heating); T_{0i} is mean temperature of the phase transition; w_i is parameter, which characterizes the phase transition temperature interval; N is number of phase transitions.

In the equation (4) summation is made on a set of Fermi's functions, each of which relates to first order phase transition or to glass-transition. The opportunity of Fermi's function application for computation of observable phase transitions on $P_s(T)$ dependence can be explained by comparing derivative of Fermi's function with Gaussian distribution function (see Table II), because crystallizing and vitrifying processes are described by Gaussian distribution.

Table II. Ratio of the 4-th moment to the 2-nd moment squared for different distribution functions

Distribution function	Expression for function	$M_4/(M_2)^2$
Gaussian	$\frac{1}{w \cdot \sqrt{\pi/2}} \cdot e^{-\frac{(x-x_0)^2}{w^2}}$	3
Lorentzian	$\frac{2}{\pi} \cdot \frac{w}{4 \cdot (x-x_0)^2 + w^2}$	6.988 (for truncated function on the level 1%)
derivative of Fermi's function	$\frac{1}{w} \cdot \frac{1}{e^{\frac{x-x_0}{w}} + e^{-\frac{x-x_0}{w}} + 2}$	4.2

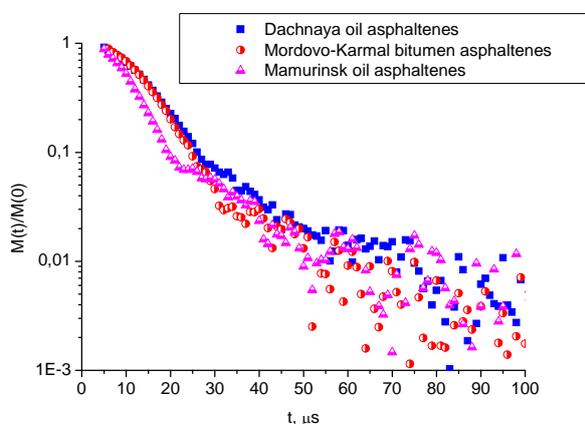


Fig.3. Transverse magnetization decay of 1H NMR signal for different oil asphaltenes at room temperature $24^\circ C$ (solid-echo pulse sequence, $\tau = 11 \mu s$)

company Setaram (France). The speed of scanning equals 1 K/minute, hanging weight equals 20 mg.

Thus, expressions to define part P_s of solid component in the 1H NMR signal of oil can be written down as follows:

$$P_s = \frac{M_s(t=0, \tau=0)}{M(t=0, \tau=0)},$$

$$P_{li} = \frac{M_{li}(t=0)}{M(t=0, \tau=0)},$$

$$\sum_i P_{li} + P_s = 1,$$

where P_{li} is part of liquid component in the 1H NMR signal of oil.

Temperature dependences of part P_s of solid component in the 1H NMR signal of different oil asphaltenes are well described by the equation:

$$P_s(T) = 100 - \sum_{i=1}^N \frac{\Delta P_{si}^{amorph/cryst}}{\exp\left(-\frac{T-T_{0i}}{w_i}\right) + 1},$$

It's possible to claim that derivative of Fermi's function is suitable for approximate computation of phase transition processes, because ratios of the 4-th moment to the 2-nd moment squared for derivative of Fermi's function and Gaussian distribution function are insignificantly different.

Temperature dependences of 1H NMR signal parameters of asphaltene powders were measured in the temperature range $-70 \div 150^\circ C$ using pulse NMR apparatus with resonance frequency 19.08 MHz on nuclei 1H , dead time $\tau_p = 13 \mu s$ of receiver and magnetic field homogeneity 0.01 gauss/cm of electromagnet. This pulse NMR apparatus is manufactured by scientists of molecular physics department of Kazan state university.

Differential scanning calorimetry (DSC)

Asphaltene phase transitions were additionally checked in the range of temperatures $20 \div 150^\circ C$ by differential scanning calorimeter C80 manufactured by

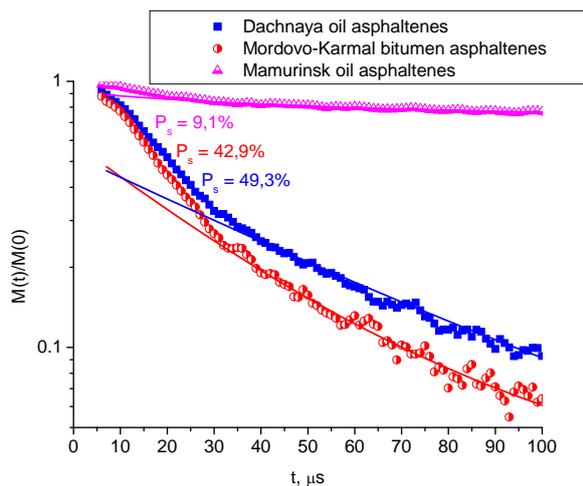


Fig.4. Transverse magnetization decay of ^1H NMR signal for different oil asphaltenes at high temperature 145°C (solid-echo pulse sequence, $\tau = 11 \mu\text{s}$)

X-ray structure analysis

X-ray diffractograms of asphaltene powders at room temperature were measured by diffractometer DRON-3M (Russia).

4. Results and discussion

Transverse magnetization decays of ^1H NMR signal of different oil asphaltenes at temperatures 24 and 145°C are presented in figures 3 and 4, respectively. It's possible to see that decays of all asphaltene samples at these temperatures contain Gaussian component (solid component) and at least one Lorentzian component (liquid component).

Results of exponential decomposition of ^1H NMR signals of asphaltenes at temperatures 24 and 145°C are presented in the tables III and IV, respectively. Notations in the tables are presented as follows: P_1 - total part of liquid components in the ^1H NMR signal of asphaltenes with average spin-spin relaxation time T_{2l} ; P_s - part of solid component in the ^1H NMR signal of asphaltenes with spin-spin relaxation time T_{2s} .

Table III. Decomposition of ^1H NMR signals of asphaltenes at room temperature (24°C) on exponential components with Lorentzian and Gaussian forms

Samples of oil asphaltene	$P_l, \%$	$T_{2l}, \mu\text{s}$	$P_s, \%$	$T_{2s}, \mu\text{s}$
Dachnaya oil, well №3577	34.7	16.5	65.3	14.9
Mordovo-Karmal bitumen	3.2	53.0	96.8	14.5
Mamurinsk oil, well №21	16.8	24.4	83.2	10.6

Table IV. Decomposition of ^1H NMR signals of asphaltenes at high temperature (145°C) on exponential components with Lorentzian and Gaussian forms

Samples of oil asphaltene	$P_l, \%$	$T_{2l}, \mu\text{s}$	$P_s, \%$	$T_{2s}, \mu\text{s}$
Dachnaya oil, well №3577	50.7	52.5	49.3	17.9
Mordovo-Karmal bitumen	57.1	33.4	42.9	16.8
Mamurinsk oil, well №21	88.7	455.8	11.3	18.2

Thus, the ^1H NMR signals of all asphaltene samples contain a solid component at room temperature (24°C) as well as at high temperature (145°C). It's possible to assume that components with Lorentzian decay form relate to mobile side aliphatic chains of asphaltene molecules.

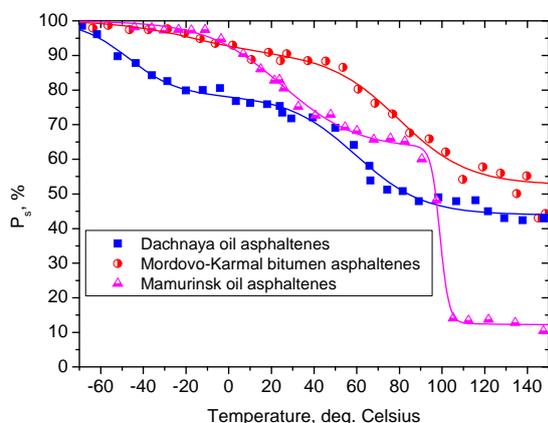


Fig.5. Temperature dependences of part P_s of solid component measured during heating for different oil asphaltenes (solid-echo pulse sequence, $\tau = 13 \mu\text{s}$). Fitting curves computed on the basis of the formula (4) for experimental points are shown by solid curves.

Temperature dependences of part P_s (Fig.5, 6) and spin-spin relaxation time T_{2s} (Fig.7) of solid component in the ^1H NMR signal were measured for investigated asphaltene samples. The part P_s of solid component for all asphaltene samples decreases during heating in the wide temperature range from -70 to 150°C. $P_s(T)$ dependence for Mamurinsk oil asphaltene only shows temperature hysteresis effect (Fig.6) during heating and cooling in the range of temperatures 90-105°C, that indicates the first order phase transition. This phase transition is characterized by the change of solid component magnetization $\Delta P_s^{\text{cryst}} = 52.5 \pm 3.5\%$ and the average temperature $98.8 \pm 2^\circ\text{C}$. Part P_s of solid component decreasing during heating with missing temperature hysteresis effect in this temperature range can be explained by devitrifying side aliphatic chains of asphaltene molecules and showing up their mobility. The glass-transition of Mamurinsk oil asphaltene is characterized by the change of solid component magnetization $\Delta P_s^{\text{amorph}} = 33.6 \pm 2.5\%$ with the average temperature 27.1°C . The glass-transitions of

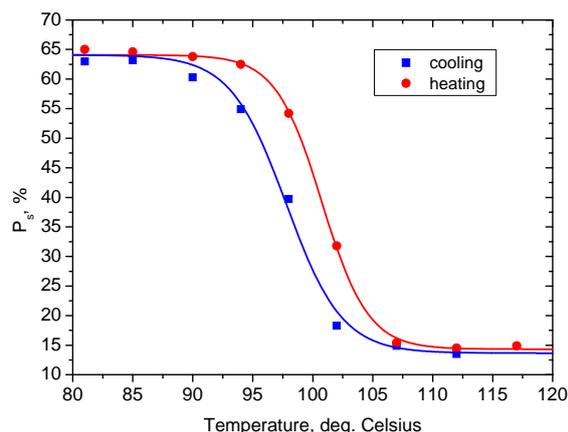


Fig.6. Temperature dependences of part P_s of solid component measured during heating and cooling for Mamurinsk oil asphaltenes (solid-echo pulse sequence, $\tau = 13 \mu\text{s}$). Fitting curves computed on the basis of the formula (4) for experimental points are shown by solid curves.

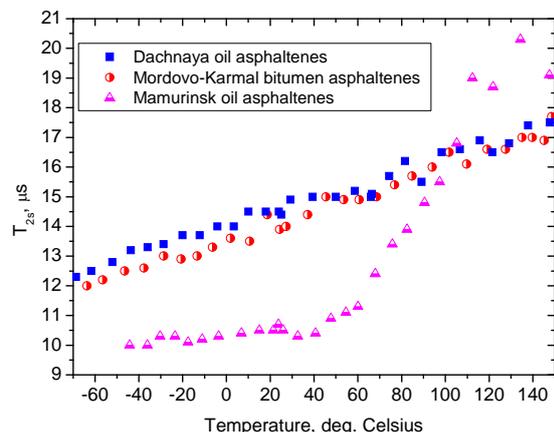


Fig.7. Temperature dependences of spin-spin relaxation time T_{2s} of solid component measured during heating for different oil asphaltenes (solid-echo pulse sequence, $\tau = 13 \mu\text{s}$)

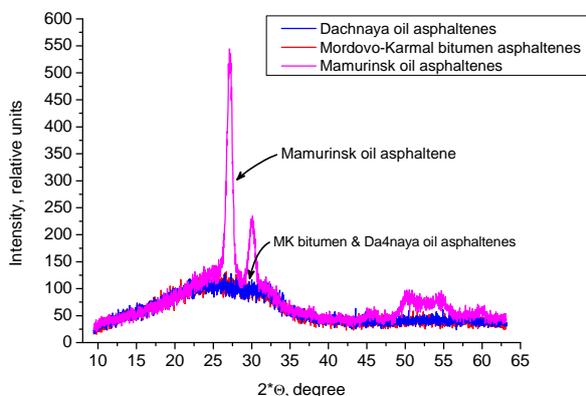


Fig.8. X-ray diffractograms for different oil asphaltene powders at room temperature 20°C

samples. An enormous endothermic effect in the temperature range $90\div 110^\circ\text{C}$ is observed for Mamurinsk oil asphaltenes, which can be attributed to melting crystal phase of high-molecular paraffins. It should be noted that paraffin crystal phase presence is additionally confirmed by IR spectroscopy data, according to which the Mamurinsk

Dachnaya oil asphaltenes are characterized by two changes of solid component magnetization $\Delta P_{s1}^{\text{amorph}} = 21.5 \pm 2.0\%$ and $\Delta P_{s2}^{\text{amorph}} = 34.5 \pm 2.5\%$ with the average temperatures -46.9 and 59.6°C , respectively. The glass-transitions of Mordovo-Karmal bitumen asphaltenes are characterized by two changes of solid component magnetization $\Delta P_{s1}^{\text{amorph}} = 12.6 \pm 1.5\%$ and $\Delta P_{s2}^{\text{amorph}} = 29.8 \pm 2.5\%$ with the average temperatures 2.0°C and 87.2°C , respectively.

It should be noted that so wide a range of glass-transition temperatures $-50\div 90^\circ\text{C}$ of side aliphatic chains of asphaltenes can be caused by distribution of their length, variation of their isomeric structure (saturated and unsaturated aliphatic chains) and the insertion of heteroatoms (O, N and others).

Temperature dependences of spin-spin relaxation time T_{2s} of solid component magnetization for Dachnaya oil asphaltenes and Mordovo-Karmal bitumen asphaltenes are changed in the same manner and do not show uneven changes. However, the spin-spin relaxation time T_{2s} for Mamurinsk oil asphaltenes during heating in the range of temperatures from 60 to 110°C sharply enough increases from 11 to $19 \mu\text{s}$, that is well explained by melting one of the components of multiphase system at these temperatures.

Thus, the observed first order phase transition at temperature $98.8 \pm 2^\circ\text{C}$ for Mamurinsk oil asphaltenes can be explained by the presence of high-molecular hydrocarbonic impurity. The data of temperature dependences of ^1H NMR relaxation show that there are no other impurities of high-molecular hydrocarbons in the Dachnaya oil asphaltenes and Mordovo-Karmal bitumen asphaltenes.

The measurements of X-ray diffractograms (see Fig.8) of investigated asphaltenes at room temperature have been performed to confirm this hypothesis. The data of X-ray structure analysis show that Dachnaya oil asphaltenes and Mordovo-Karmal bitumen asphaltenes have amorphous structure, and that Mamurinsk oil asphaltenes contain both amorphous and crystal phases.

X-ray diffractograms (Fig.9) of spectral pure graphite and pure paraffin (mixture of paraffin hydrocarbons $\text{C}_{18}\text{-C}_{35}$) were measured to establish the type of lattice for crystal phase of Mamurinsk oil asphaltenes. Figure 10 shows that X-ray diffractograms of Mamurinsk oil asphaltenes and pure paraffin are very similar. Now, we can conclude that the crystal phase of Mamurinsk oil asphaltenes is characterized by the same lattice spacing as crystal paraffin.

Referring to the DSC data for investigated asphaltene samples (Fig.11), we notice two regions on the thermograms of asphaltenes in the temperature range $90\div 110^\circ\text{C}$ and $110\div 130^\circ\text{C}$. Some doubts arise with regard to thermal processes taking place in the temperature range $110\div 130^\circ\text{C}$ for all asphaltene

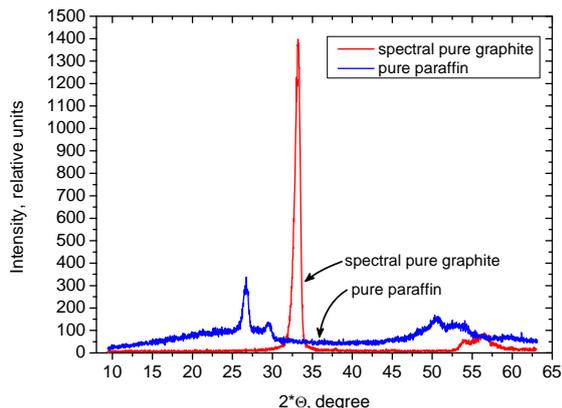


Fig.9. X-ray diffractograms for spectral pure graphite and pure paraffin at room temperature 20°C

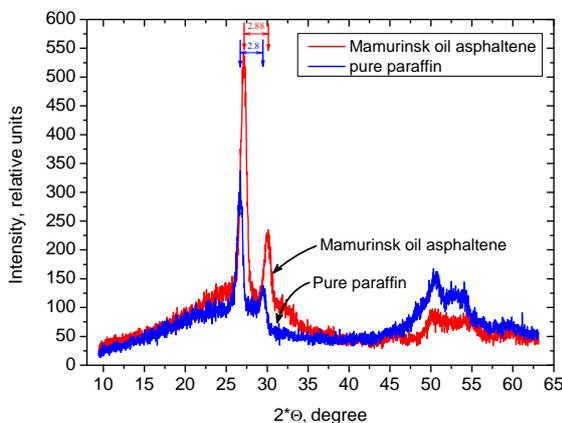


Fig.10. Comparison of X-ray diffractograms for Mamurinsk oil asphaltene and pure paraffin

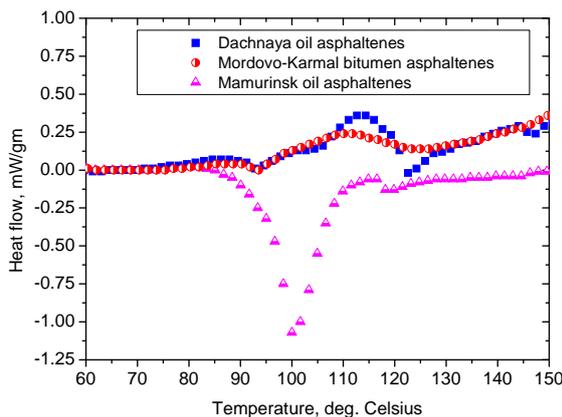


Fig.11. DSC curves of heating for different oil asphaltenes with asphaltenes [1, 8-14]. It is necessary to point out that high-molecular side aliphatic chain of asphaltene molecule is able to crystallize of its own at cooling. Also, the hypothesis about the opportunity of crystallization of high-molecular side aliphatic chains of asphaltene molecules is partially confirmed on the basis of the dissolution stage of investigated asphaltenes in benzene, which has to separate paraffin and asphaltene molecules.

Finally, it should be noted that low-molecular side aliphatic chain of asphaltene molecule is only able to vitrify at cooling. Such a wide range of glass-transition temperatures $-50\div 90^{\circ}\text{C}$ of side aliphatic chains of asphaltene molecules can be caused by distribution of their length, variation of their isomeric structure (saturated and unsaturated aliphatic

oil asphaltenes are characterized by high content of unbranched aliphatic chains. The presence of the ordered structures in the Mamurinsk oil asphaltenes is confirmed by the peak on frequency 888 cm^{-1} .

In conclusion, it's possible to evaluate the content of crystal phase of high-molecular paraffins in the Mamurinsk oil asphaltenes using the next equation:

$$\frac{m_{\text{asph}}^{\text{cryst}}}{m_{\text{asph}}^{\text{amorph}}} = \frac{\Delta P_s^{\text{cryst}}}{\Delta P_s^{\text{amorph}}} \cdot \frac{C_{\text{asph}}^{\text{Hamorph}}}{C_{\text{asph}}^{\text{Hcryst}}},$$

$$m_{\text{asph}} = m_{\text{asph}}^{\text{cryst}} + m_{\text{asph}}^{\text{amorph}}, \quad (5)$$

$$C_{\text{asph}}^{\text{Hamorph}} = C_{\text{asph}}^{\text{H}},$$

$$C_{\text{asph}}^{\text{Hcryst}} = C_{\text{paraff}}^{\text{H}},$$

where m_{asph} , $m_{\text{asph}}^{\text{cryst}}$, $m_{\text{asph}}^{\text{amorph}}$ are weights of asphaltenes, their crystal and amorphous phases; $\Delta P_s^{\text{cryst}}$ ($\Delta P_s^{\text{amorph}}$) is increment of $P_s(T)$ due to melting (devitrifying) of asphaltene components ($\Delta P_s^{\text{amorph}} = 100\% - \Delta P_s^{\text{cryst}}$; $\Delta P_s^{\text{cryst}} = 52.5 \pm 3.5\%$ for Mamurinsk oil asphaltene), $C_{\text{asph}}^{\text{H}}$ and $C_{\text{paraff}}^{\text{H}}$ are amounts of protons in asphaltene (about 8 wt.%) and paraffins (about 14.8 wt.%), respectively. It's possible to approximately estimate the weight content of crystal phase of high-molecular paraffins in the Mamurinsk oil asphaltene by using equations (5). The value 37.5 wt.% obtained from ¹H NMR data is in quite good agreement with the value 46 wt.% obtained from DSC data.

5. Summary

The comparison of ¹H NMR relaxation and DSC methods for studying temperature properties of asphaltene shows that temperature dependence of part P_s of solid component in the ¹H NMR signal allows to detect equilibrium first-order phase transitions (presence of temperature hysteresis effect) and non-equilibrium glass-transitions (absence of temperature hysteresis effect). However, we can identify only first-order phase transitions from DSC curves.

The results of the complex research of asphaltene, extracted from three different oil samples (Dachnaya oil with high content of asphaltene; Mordovo-Karmal bitumen with high content of resins and Mamurinsk oil with high content of paraffins), by ¹H NMR relaxation, DSC, X-ray structure analysis and IR spectroscopy methods show that asphaltene are able to contain the crystal phase of high-molecular paraffins. We believe there is no answer to the question: whether these paraffin chains are bonded to asphaltene, i.e. whether they are structural elements of asphaltene molecules, or these paraffin chains are individual paraffin molecules coprecipitated together

chains) and the insertion of heteroatoms (O, N and others). Additional research is needed to understand in detail the influence of side aliphatic chains structure of asphaltene molecules on their glass-transition temperatures.

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