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Structure-Dynamical Investigations of Heavy Oil Residues of Different Chemical Nature

Annotation (Abstract)

It is known [1], [2], [3], [4], [5], [6], [7], [8], that the most appropriate raw material for a wide range of bitumen products as a whole, and for bitumen insulation materials (BIM) in particular, are the flux oils of heavy crude oils with naphthene-aromatic base, distinguished by high content of resinous-asphaltene materials (RAM) and low content of high-molecular paraffins. Due to output limitations of such kinds of oil, heavy petroleum residues (HPR) of paraffin and high-paraffin crude oils are often used. It shall be noted, that in production of high-melting special bitumens during high-temperature oxidation of residual stock, there emerge nonhydrocarbon compounds, insoluble in hot benzol - carbenes and carboids, as well as the compounds of paraffin-naphthene base, initially contained in crude oil. If considering HPR as a thermodynamic system of phases A, B and C, it is necessary to point out, that, based on molecular mobility and structural-dynamical parameters of phases, it is possible to assume the structure of their carbon components with much assurance. As a source raw material for oxidation process, structural-dynamical states of HPR were studied on relaxometer YAMR 08BK/RS at different temperature regimes.

Key words: Heavy petroleum residues, paraffin-asphaltene associates, physical-chemical modification, oxidative polymerization, complex structural units, NMR-relaxometry, infrared spectrometry.

Main part

As per the works of A.S. Kolbanovskaya [9], bitumen disperse structure is mainly determined by the content of direct-chain paraffin hydrocarbons (HC) [10]. If their content exceeds 3%, there emerge a crystal paraffin frame, which provides hardness of the system and reduces the plastic range, having a negative impact on physical mechanical properties of BIM. Therefore, when processing the HPR of paraffin-naphthene base, there is a need in its activation by using such chemically active modifiers, which would subject the segments of paraffin chains to chemical structuring due to effective intermolecular diffusion during oxidation with further formation of macromolecular polycyclic naphthene-aromatic fragments.

It is known that the impact on supermolecular structure of magnetic, electromagnetic and acoustic fields, and the injection of different additives to HPR, allows to resize a disperse phase in wide range and to regulate its properties intentionally [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20]. It was found out, that this effect is achieved by size control of CSU, the core of which is a gas bubble during oxidation. Syunaev Z.I., Apostolov S.A., and Kemalov A.F. /4-6/ found out, that the disperse state of HPR has an impact on the speed of process and quality of the obtained bitumen. This proposition was disregarded previously in solving the optimization problems of bitumen production engineering, however, at the present time not all aspects are studied.

Based on such approach, HPR structure in oxidation process shall get a high-resin type; in the oxidation process, there emerge the structures, allied to asphaltenes in chemical composition, but having the physical-chemical properties of "heavy" resins. As a result, the obtained sample of special bitumen shall differ in high content of film forming agent - resins at low quantity of paraffin structures and asphaltenes.

To determine the degree of impact of HPR chemical structure on kinetics of oxidation and physical-mechanical properties of BIM, and also taking into consideration the results of preliminary investigations, testifying, that the process of oxidative polymerization, mainly, finishes at the stage of obtaining the bitumen, the flux oils (Table 1) of naphthene-aromatic (Karabashsky NBZ - flux oil-1) and paraffin-naphthene (ENPU OJSC "Tatneft" - flux oil-2) bases were used as a raw material for special bitumen production.

Table 1 - Physical-chemical properties of flux oils

Indices	Flux oil-1	Flux oil-2
Density, kg/m^3	0,9686	0,9878
Relative viscosity, RV_{80}	22,96	51,76
Content, %mass.:		
- CAB	18,25	28,23
- sulphur	0,492	0,887
- paraffins	less than 2	15
asphaltenes/resin	0,64	0,45

Flux oil oxidation was carried out on batch-operated laboratory unit at the process temperature equal to 250^0C and air flow rate equal to 3 l/min*kg of raw material.

The study of main physical-mechanical properties of bituminous lacquers, produced on the basis of special bitumens,

Fig.1 – Dependence of T_{soft} of bitumen on oxidation duration

showed the ambiguity of their assessment (Fig.2). So the coverings, based on oxidized flux oil-2, are characterized by high values of solidness, equal to 0,36 conv.unit (Fig.2a), and low adhesive-strength properties. Alongside with that, the coverings, based on special bitumen of KNBZ with T_{soft} equal to 110^0C, are characterized by less solidness (0,0619 conv.unit) and high adhesive-strength properties (Fig.2b).

It can be explained by high content of paraffin-naphthene HC and asphaltenes in the flux oil-2 as compared to the flux oil-1 (Table 1).
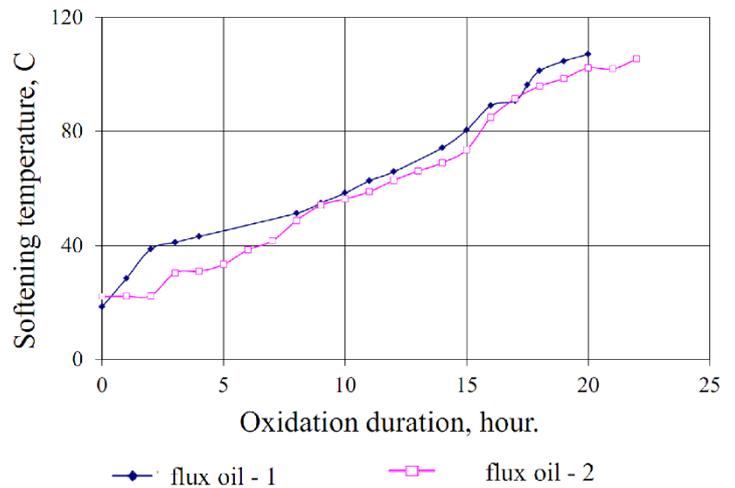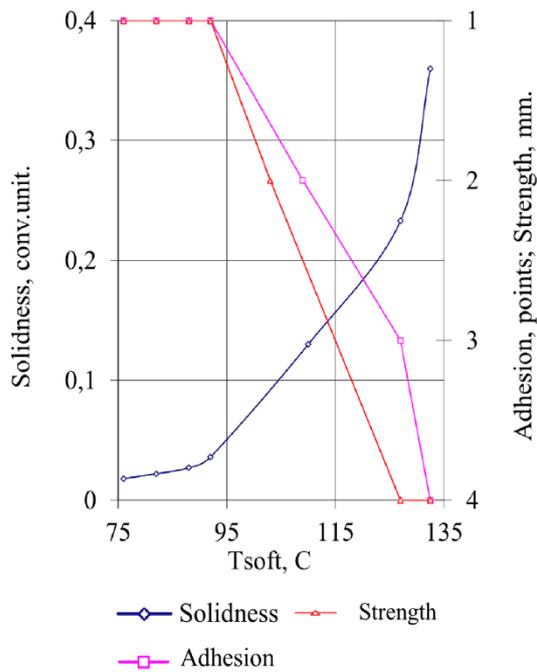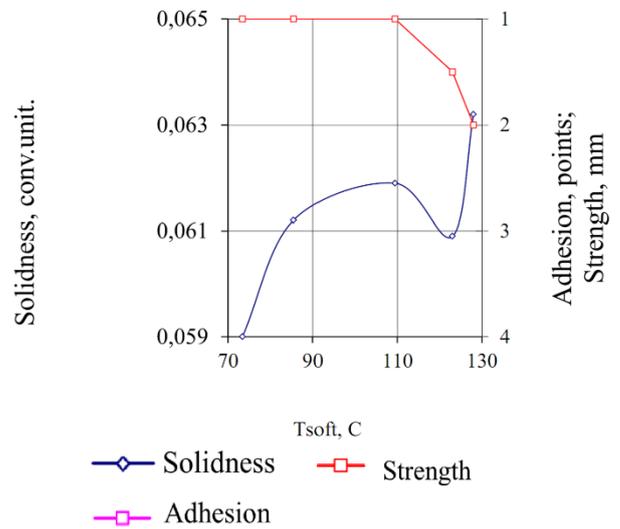
a - air-blown asphaltic bitumen of ENPU

b - air-blown asphaltic bitumen of KNBZ

Fig.2 - Dependence of physical-mechanical properties of BIM, produced on the basis of air-blown asphaltic bitumen, on T_{soft}

A directly-proportional dependence of paraffin HC and asphaltenes content on the values of density and relative viscosity of flux oil was determined. We consider, that during oxidation the high content of total sulphur in raw material results in the change of disperse colloid system, i.e. to the increase of disperse phase content - asphaltenes and reduction of disperse medium - maltene part, which is a film forming base for BIM.

It shall be noted, that the studied flux oils (Table 1) with various physical-chemical properties have different sulphur content and disperse phase concentration. Alongside with that, the study of kinetics of oxidation (Fig.1) testifies about similar reaction speed, resulting in high melting point bitumen (KNBZ and ENPU) with T_{soft} within the range from 80 to 130^0C, the BIM of which is characterized by different physical-mechanical properties.

To solve the revealed contradictions, firstly, it is necessary to study both the interconnection of physical-chemical nature of the raw material, ways of its modification and properties, and the final materials. That is why it is necessary to use such investigation

methods, which are able to forecast its reaction capacity and the characteristics of final product, taking into consideration the raw material chemical complexity.

Modern instrumental investigation methods of newly formed equilibrium structures in physicochemistry include nuclear magnetic relaxation [1], [8], [10], which is a foundation property of nuclear magnetism, characterizing the nuclear spin system dynamics in ODS - flux oils, bitumens etc. High information value of nuclear magnetic relaxation parameters about the properties of the investigated material, relative simplicity of experimental determination of these parameters, as well as the reliability of theoretical data interpretation separate it to an independent physical method of investigation.

The study of molecules and atoms motion in solid bodies, liquids and gases, the investigation of reactions of complexing, chemical exchange, solvation and intermolecular interactions in solutions, the determination of electronic structure parameters of metals and alloys, the study of electron-nuclear interaction, molecules structure and properties make an incomplete scope of tasks, available for solution by means of NMR-spectroscopy. Nowadays this method attracts not only physical and chemical scientists, but also the experts in technology; it is, firstly, explained by practical relevance of data about NMR, the processes of which depend on many physical-chemical properties of the investigated system and perfectly illustrate the dynamical phenomenon at molecular level.

The investigation of oil disperse systems (ODS) by means of NMR-relaxometry are carried out based on single complex structural unit (CSU), i.e. studying the temperature impact during the change of thermodynamic characteristics of spin-spin system, it can authentically assume the structural peculiarities of ODS in general.

Due to the work of magnetic field and alternating electromagnetic impulses, acting as per Kar-Parsel-Meybum-Gill method, nucleus magnetizing take place in spin system, resulting in their precessing with the definite frequency of vibration amplitudes, i.e. the molecular motion of paramagnetic nuclei increases. This phenomenon is expressed by *the spin-spin relaxation time $T_{2i.}$*

In a definite moment, at the constant temperature of experiment (T_{exp}) nuclei magnetization intensity of the **phase**[1] i reaches its constant discreteness, and the

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[1] **Phases** are the assemblies of system parts, identical in chemical composition, physical and thermodynamical properties, characterized by different molecular shifts at SDA

"interchange" of nucleus magnetization with the surrounding spin systems take It promotes the increase of molecular motion of the most active segments of the phase under study. The recorded thermodynamic "response" (TDR) of the neighboring CSU is expressed in sectional precession or vibration frequencies amplitudes of the most active magnetic nuclei and is named *the spin-lattice relaxation time T_{1i}*. A spin-lattice system of phases i in NMR-spectroscopy is a complex of spin-spin systems Σi.

It shall be noted, that the precessions of magnetic nuclei of structural units, characterized by spin-spin relaxation time T_{2i}, overlap the TDR of the spin-lattice system. The phenomenon is that the studied ODS is subjected to the outside forces - the magnetostatic field, alternating electromagnetic impulses and T_{exp}. Consequently, there is a directly-proportional dependence between the time of spin-spin and spin-lattice relaxation in CSU and ODS respectively.

That is why the presence of magnetostatic field during the study of structural-dynamical parameters in TDR is explained by obligatory equality of spin-spin relaxation time T_{2i} values of CSU in one of the phases. Otherwise, the activity of alternating magnetic field will change TDR due to decrease of T_{2i}, and, finally, T_{1i} value will tends towards zero ($T_{1i} \rightarrow 0$).

Based on the abovementioned arguments, the extremums of TDR in ODS will be observed in the more mobile phases *A* and *B*, i.e. $T_{1A} > T_{1B} > T_{1C}$.

Possible structural-dynamical states of ODS in initial time moment, at T_{exp} = t_{init}. Knowledge of structural-dynamical parameters, state of thermodynamic stability of RAM in ODS allows to use "express analysis" for its characterization, i.e. the data of NMR-relaxometry of oil system initial state allows to promote theoretical assumptions about its physical-chemical and thermodynamic activity at destructive heat treatment. Thus, based on the values of vibration frequency amplitudes of magnetic nuclei and occupancy of surrounding hydrogen protons, it is possible to determine the type of segment structure of carbon chain.

As per the system (I) in table 2 it can be assumed, that the response P_{1A} is provided by the most active substituted alkene chains (mainly short-chain, which can be methyl-, ethyl substitutes), but, taking into consideration low values of T_{2A} and T_{1A}, it follows, that the response reasons are the steric hindrances of the carbon chain.

Therefore, the segment structure of the phase **A** is mainly characterized by long-chain paraffin structure of segments.

It shall be noted, that the difficulties in determination of substitution degree and the length of aliphatic chain of the phase **A** in initial time moment are explained by its "frozen" state. At high values of T_{2A} and P_{2A} (II), conforming it with the data of P_{1A} and T_{1A}, where the response is $P_{1A} \sim P_{2A}$ (or a little lower), the structure of substitutes of the phase **A** can be characterized, with some probability, as a short-chain with high degree of branching.

Table 2 - Structural-dynamical states of ODS in initial time moment, at $T_{exp} = t_{init}$

System type	Structural-dynamical characteristics of spin-spin system		TDR degree in ODS
(I)	T_{2A} – low value		$T_{1A} \sim T_{2A}$ (or a little higher)
	P_{2A} – high (~80% mass.)		$P_{1A} > P_{2A}$ (up to 40-50%)
(II)	T_{2A} – high values		$T_{1A} \sim T_{2A}$ (or a little higher)
	P_{2A} – high (~80% mass.)		$P_{1A} \geq P_{2A}$ (up to 50-70%)

Olefinic links in alkene carbon chains can be determined from the values of T_{2A} and P_{2A}, taking into account, that the length of C=C link is less than the length of C-C, and the link energy (table 3) $\delta_{C=C}$ is more than δ_{C-C}. Table 3 – Characteristics of covalent link

Link	Carbon atom hybridization type	Link length, nm	Angle between hybrid orbitals	Link energy, kJ/mole	Molecular shape
C-C	sp^3	0,154	$109^0 28`$	350	Tetrahedral
C=C	sp^2	0,134	120^0	605	Plane
C≡C	Sp	0,120	180^0	825	Linear

It is proved by the fact, that at increase of the quantity of C=C olefinic links, the values of T_{2A} will sharply decrease, and, thus, the values of T_{2A} will be close to T_{2B}, P_{2B} in this case will have comparatively low values. Alongside with that, the values of T_{1A} can be multiply lower than the ones of T_{2A}, as the olefinic links in HPR provide

"the arrangement", i.e. shows a tendency to the further intermolecular structuring.

Considering HPR as a thermodynamic system of phases *A*, *B* and *C*, it shall be noted, that on account of molecular mobility and structural-dynamical parameters of phases, the structure of their carbon segments can be assumed with much assurance.

Formerly, it was determined, that the structural-dynamical analysis (SDA) of oil disperse systems has the phases *A*, *B* and *C*, which, due to their different content and molecular mobility, can be relatively classified as oils, resins and asphaltenes respectively.

The study of structural-dynamical parameters of flux oils of different chemical nature by means of impulse NMR. As a raw material of the oxidation process there were studied the structural-dynamical states of HPR on the relaxometer NMR 8BK/RS at different temperature regimes.

For the flux oils analysis the following measurement modes were used: the starting period T = 500 ms – 2 s, the interval between 90^0 and 180^0 impulses N = 5 – 1000, the accumulation quantity n = 3 – 50. The analysis time did not exceed 3 minutes.

As per Fig.3 the flux oils have the straight-line dependence between T_{exp} and relaxation time T_{2i}, i.e. $10^3/T$ is directly-proportional to T_{2i}, however, T_{2C} for the flux oil-1 differs significantly from T_{2C} for the flux oil-2.

Primarily, in Fig.3 there can be found the slight differences in molecular mobility of the studied flux oil components, characterized by the spin-spin relaxation time T_{2i}. However, more detailed analysis of the experimental data shows, that T_{exp}, at which the phase *C* develops, is different for each flux oil. So, for the flux oil-2 it equals to 72^0C, and for the flux oil-2 it is $49,6^0C$.
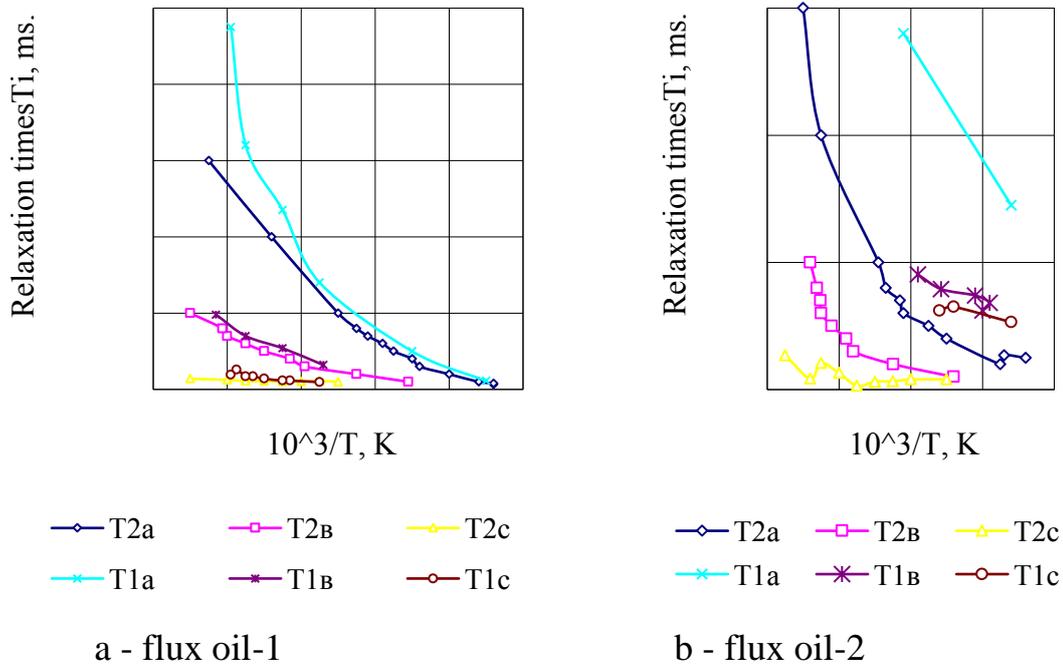
a - flux oil-1   b - flux oil-2

Fig.3 - Temperature dependencies of flux oils relaxation times

High T_{exp}, at which the phase *C* develops, is explained by steric hindrances of the molecular structure at its motion, i.e. it can be assumed, that the structure of asphaltene molecules of the flux oil-2 is more ordered than the one of the flux oil-1. Alongside with that, Fig.3 shows, that in the whole interval of T_{exp} of the flux oil-1 there are no sudden changes of relaxation time $T_{2C,}$ what points to thermodynamically stable structure, mainly consisting of the segments of polycyclic naphthene-aromatic structure with low substitution degree of alkene chains.

A comparative analysis in Fig.3 shows, that when T_{exp} exceeds 60^0C, the molecular motion of the substituted segments of the phase *C* increases in a different degree. The reason is both the structure of the disperse phase itself, and the degree of substitution, branching and substitutes chain length. By means of impulse NMR it was revealed, that the substitution character of the phase *C* is expressed by the long alkene chains with low degree of branching, what is proved by the values of protons P_{2C} occupation (Fig.4), where the low concentration of the phase *C* in the flux oil-1 is shown (within the limits of 20% mass.). Therefore, a comparative analysis of structural-dynamical parameters of flux oils shows the low degree of aromaticity and high content of paraffin-naphthene HC in the flux oil-2.

Based on the dependencies T_{2A} and T_{2B} on $10^3/T$ (Fig.3), let us note, that the time T_{2A} for the flux oil-2 is 2,5 ms., what significantly exceeds the time T_{2A} of the flux oil-1, equal to 0,65 ms. Alongside with that, $T_{exp,}$ at which the most mobile phase **A** develops, equals to 28,2^{0}C for the flux oil-,1 and it is 31,8^{0}C for the flux oil-2. It is necessary to point out, that at similar T_{exp} $10^3/T$ for the both flux oils– 3,28K, different relaxation times T_{2A} are observed: 1 ms for the flux oil-1 and 2,5 ms for the flux oil-2.

It shall be noted, that at 72^{0}C>T>55^{0}C, T_{2A} is higher for the flux oil-1, than for the flux oil-2 by 8%mass at the average. However, at T>72^{0}C there is an inverse dependence, explained by the phase transitions (PT), connected with the structural-dynamical reorganization of the molecular morphology. Thus, it can be concluded, that the most mobile phase **A** of the flux oil-2 is characterized by long-chain paraffin segments, and the one of the flux oil-1 is characterized mainly by short-chain aliphatic segments, which, in our opinion, are the structural segments of more high-molecular part of disperse medium and, respectively, less mobile - resins, characterized by the relaxation time T_{2B}. As per the data of molecular mobility of the phase **B**, it was determined, that in the whole interval $10^3/T$ the relaxation time T_{2B} for the flux oil-1 is less than the one for the flux oil-2.

This fact characterizes chemical composition of the phase **B** of the HPR under study, which, as we consider, consists mainly from polycyclic naphthene-aromatic structures in the flux oil-1; the phase **B** in the flux oil-2 is mainly characterized by polycyclic paraffin-naphthene structures, what is also proved by the values of spin-lattice relaxation time T_{1i} (Fig.3) and proton P_{1i} occupancy (Fig.4).
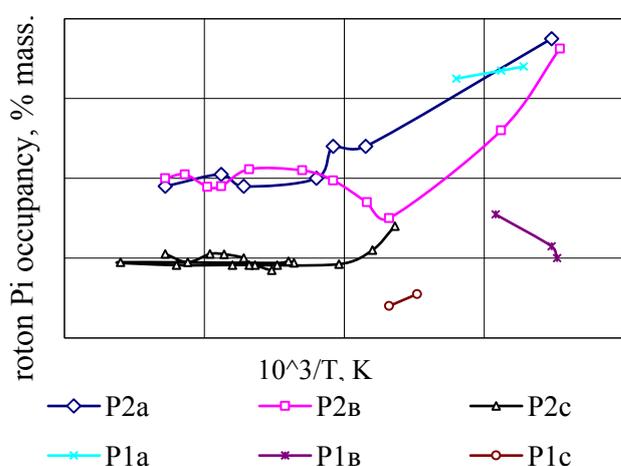

Fig.4 – Temperature dependence of proton occupancy of the phases in the flux oil-2

Thus, the revealed relaxation time differences of the most mobile phases T_{2A} and T_{2B} for the both flux oils prove the high content of paraffin structures in the flux oil-2 (Table 1), which is a significant disadvantage in BIM production (Fig.2).

The study of the most mobile phases **A** and **B** - P_{2A} and P_{2B} shows the simbasis of characteristic curves

(Fig.4). In initial time moment the measurement in the interval T_{exp} - 10^3/T 3,13–3,165K, P_{2A} of the flux oil-2 ($\approx$47,5%mass.) significantly exceeds the values of proton occupancy of the flux oil-1 ($\approx$62%mass.); there is observed a stepped variation of P_{2A} of the flux oil-2, stabilizing at temperature of 55^0C up to 50%mass., then it slightly varies within the limits of 40%mass.

When considering the changes of proton P_{2C} occupancy (Fig.5), it follows, that the phase C of the flux oil-1 is represented by the polycyclic naphthene-aromatic structures, and due to the fact, that in Fig.5a P_{2C} is characterized by thermal instability, unlike P_{2C} of the flux oil-2 (Fig.4), expressed by the extremums of the P_{2C} dependence on 10^3/T, high chemical affinity of the phase C with resin components can be assumed.

$$y = 18,543e^{0,2902x}$$
$$R^2 = 0,1357$$

a– spin-spin system   b – spin-lattice system
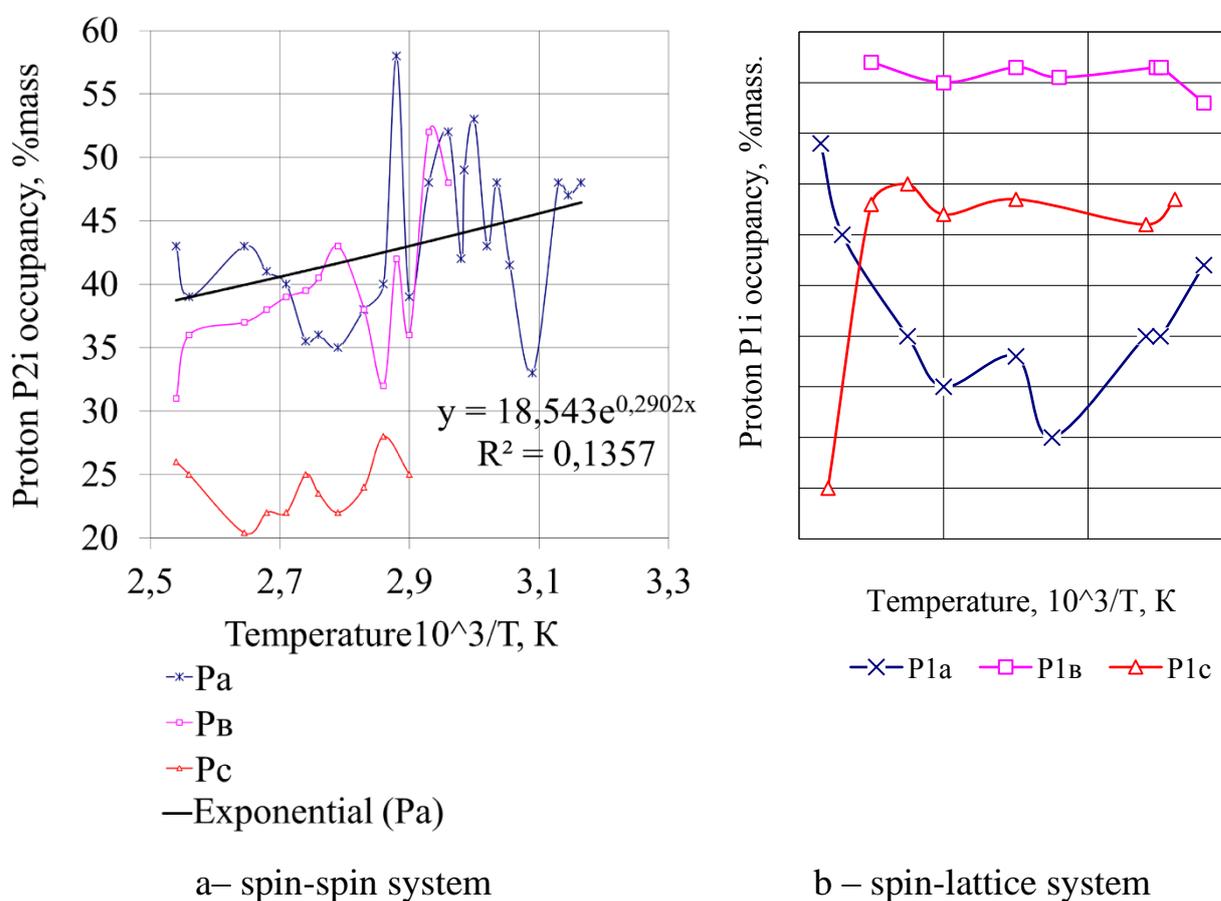
Fig.5 - Dependence of proton occupancy of phases P_i of the flux oil-1 on temperature

Measuring the value of the thermodynamic" response", i.e. the relations of times T_{1i} to the protons occupancies of the lattice P_{1i}, with the values of spin-spin relaxation times T_{2i} and the protons P_{2i} occupancies of the HPR under study, and also taking into consideration the activation energies (E_A), it is possible to characterize the segmental

thermodynamic activity of the lattice elements; together with that, by means of P_{1i} values it is possible to evaluate the order degree of the spin-lattice system. Thereby, the study of the spin-spin system of HPR magnetic nuclei and the investigation of T_{1i} and P_{1i} parameters will provide the revealing of quantitative distribution of phases in the spin-lattice system.

The values of E_A of molecular motion on the assumption of Arrhenius relation for correlation times $\tau_c = \tau_0 \exp(E_A/RT)$ were obtained using the following formula (1):

$$E_A = 19{,}13\left[T^{(1)}T^{(2)}\big/(T^{(2)} - T^{(1)})\lg\left(T_2^{(2)}\big/T_2^{(1)}\right)\right] \qquad (1)$$

where $T^{(1)}$, $T^{(2)}$ are the temperatures, at which the values of relaxation times $T_2^{(2)}$ and $T_2^{(1)}$ are determined. In this case only intermolecular contribution to relaxation is taken into consideration; it is determined by dipole-dipole interaction from the rotational diffusion, which in conditions of high-temperature approximating $\omega\tau_0 \ll 1$, ordinary for ODS, for the protons with the spin $I = \frac{1}{2}$ is written as: $(T_{2VN})^{-1} = 3\gamma^4 h^2 \tau_c / 2r^6$ (2)
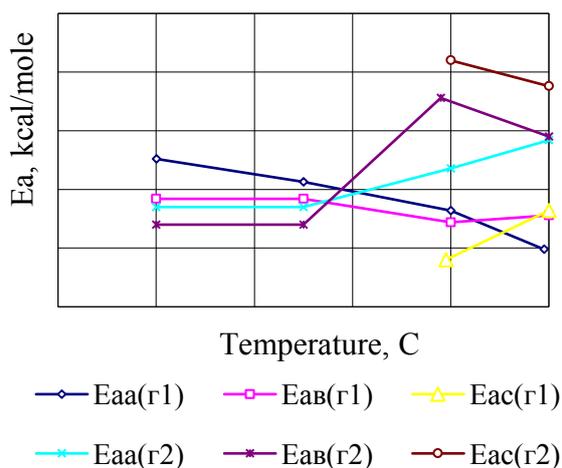

Fig.6 – Dependence of activation energy on temperature

That is why, graphic dependencies of spin-lattice relaxation times T_{1i} for the flux oil-1 are in plane parallel direction according to spin-spin relaxation dependencies T_{2i} (Fig.3), as well as the protons occupancies P_{1i}, are in parallel to each other. The presence of extremes (Fig.5b) for P_{1A} and P_{1C} is explained by the presence of PT. The increase of time T_{1C} in the temperature interval of 2,6–2,75K can also be a reason for PT, connected with structural-dynamical reorganization of the molecular morphology, and also the involvement of some structural segments of resins molecules, showing the most chemical affinity, to the molecular mobility of the phase C.

The results of the analysis (Fig.6) of the dependencies of E_A on T_{exp} for the flux oils are in keeping with the data of NMR-relaxometry, and fully support the previously introduces assumptions about possible chemical composition of CSU components of flux oils. Fig.6 shows that at low T_{exp} the activation energies in the flux oil-1 are higher,

and at high values they are lower, than in the flux oil-2. At this the maximum values of E_A are close to the values, typical of potential barriers at steric hindrances of molecular mobility of polyethylene type long-chain polymers with $E_{A\text{пол}} \approx 12\text{-}14$ kcal/mole /10/. The behavior of E_A for the flux oil-2 in dependence of T_{exp} is characterized at low T_{exp} by the "frozen" state of segments of long aliphatic chains with high mobility of end and side chains, and at high T_{exp} - by steric hindrances of molecular segmental mobility.

Conclusions.

Therefore, based on the results of the analysis of structural-dynamical characteristics of the initial HPR, it shall be noted, that the flux oil-1 is the most appropriate raw material for the special bitumen obtaining. It is proved by both NMR-relaxometry data and physical-chemical properties of BIM, obtained on its basis special bitumens. However, based on naphthene-aromatic base of the flux oil-1, characterized by low branching degree of end groups of short-chain aliphatic substitutes, it can be assumed, that its chemical modifying in the process of mutual oxidation with the additives will not initiate, in the required degree, the reactions of oxidative polymerization, which, as known, are the most favorable in obtaining the high-strength coverings.

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