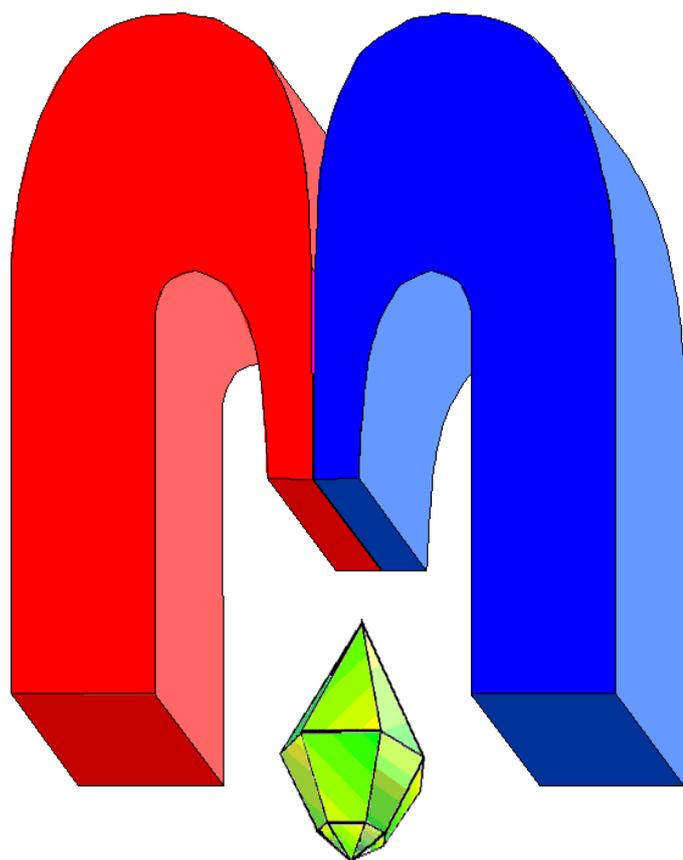


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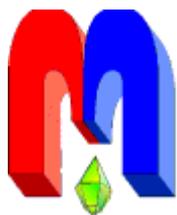
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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Size effect for asphaltene particles in the resin by NMR

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The resin-asphaltene model systems with different sizes of asphaltenes are studied by nuclear magnetic resonance (NMR) using the solid-echo sequence. For systems with particle sizes of asphaltenes greater than 50 μm , the form of relaxation attenuation consists of two components, one of which is characterized by a typical asphaltene relaxation time of about 20 μs . In this case, the Gaussian form describes the relaxation attenuation of this component, which is typical for the NMR signal in disordered solids. At the same time, it is found that the share of the solid component in the NMR signal decreases with decreasing particle size of asphaltenes. The signal drops to zero when the size of asphaltene particles reaches 10 microns. Based on the estimates of the rotational motion correlation time for an asphaltene particle in a dispersion medium (resin) with a known viscosity value, the influence of two factors is discussed: the difference in the values of macro- and microviscosity of the resin, as well as the possibility of partial dissolution of asphaltene particles in the resin. The results of repeated measurements for a long time indicate the existence of a reverse process in the system, leading to the aggregation of asphaltene particles.

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Keywords: NMR, solid-echo, spin-spin relaxation, correlation time, asphaltene, resin, aggregation.

1. Introduction

A characteristic feature of natural bitumen and heavy oil is the high content of asphaltene-resin substances (ARS) [1]. The high content of ARS in general and asphaltenes, in particular, is the main cause of the problems that arise not only at the stage of production but also at the stages of transportation and processing of high-viscosity oil [2].

Extensive literature is devoted to the study of the structure of asphaltenes and their ability to aggregate [3-6]. At the same time, it was found that asphaltenes are characterized by an extremely rich set of chemical and supramolecular structures. Many, including rheological, characteristics of oil are associated with the chemical composition of asphaltenes [7-9]. According to the most well-established opinion [10], it is asphaltenes surrounded by resins which primarily affect the dynamic viscosity.

In most cases, asphaltenes previously separated from oil are investigated in low molecular weight solvents. At the same time, it is noted in [11] that the size of asphaltene particles released from oil by precipitation, for example, in heptane, may not correspond to the initial size in crude oil and often leads [12-14] to their deposition even insolvent.

It can be considered unambiguously established [15] that in oil asphaltenes are dispersed only due to interaction with resin as one of the main components of hydrocarbon raw materials. Asphaltenes do not interact with the rest of the oil components and precipitate when mixed. At the same time, there is practically no work in which the issues related to the study of the properties of asphaltenes directly in interaction with resin molecules would be studied.

In work [16], it is shown that the nuclear magnetic resonance (NMR) technique also allows studies of the dynamics of hydrocarbons in proximity of asphaltene nano-aggregates and macro-aggregates in heavy crude oils as a function of the concentration of asphaltenes. It is useful for understanding the relations and correlations between NMR relaxation times T_1 and T_2 , diffusion coefficients D , and viscosity of heavy crude oils. It is evident that prediction of crude oil stability and solubility of asphaltenes under specified conditions requires the fundamental knowledge of the character of intermolecular interactions between asphaltenes and other heavy oil components present in the local

environment. This knowledge can be gained only by means of in situ studies of local rheological properties of crude oils and molecular dynamics of asphaltenes under various conditions [17].

Thus, an important stage on the way to obtaining information about the state of asphaltenes in petroleum is the study of model systems for asphaltenes-resins, which was the purpose of this work. As the primary research method the method of NMR was chosen, it was proven itself in the best way in the investigation of complex molecular systems, which is certainly true of the oil [18, 19]. Further in the text, the words "molecule" will use as a fraction the components of the model system, which refers to resins or asphaltenes.

2. Experimental methods

Petroleum asphaltenes and resins were obtained from petroleum field of the Republic of Tatarstan in the laboratory of the A.E. Arbuzov Institute of organic and physical chemistry, Kazan scientific Centre Russian Academy of Sciences. Asphaltenes are obtained from oil by precipitation from petroleum solution in petroleum ether. According to the data of optical measurements on the MTI EQ-MS microscope, the initial size of the asphaltenes particles obtained in this way is estimated to be approximately 1 mm. To prepare a series of model systems of asphaltene-resin with different sizes of asphaltene particles, the initial asphaltenes were ground using a disk eraser LDI, manual agate mortar and further sieved through a set of sieves. Because of this operation, powders of asphaltenes with the size (diameter) of particles of 1000, 51, 38, 22 and 10 microns were prepared. The size of the obtained particles was controlled by measurements on the MTI EQ-MS microscope.

By mechanical mixing of resin and asphaltene powders with a given mass concentration (5 %), five samples of asphaltene-resin with different particle sizes of asphaltenes were prepared. The mass content of asphaltenes in the samples was calculated by the ratio:

$$\omega = \frac{m_{\text{asph}}}{m_{\text{asph}} + m_{\text{resin}}} \cdot 100\%,$$

where m_{asph} is mass content of asphaltenes, m_{resin} is mass of resin in the model sample. The measurements were carried out on the NMR analyzer "Proton-20M" with a resonance frequency of $^1\text{H} = 20$ MHz protons with a characteristic time of "paralysis" of the receiving path $\tau_p = 10$ μs . In order to obtain the most complete information about the NMR signal at times commensurate with the paralysis time τ_p , the solid-echo pulse sequence [20, 21] shown in figure 1 was used.

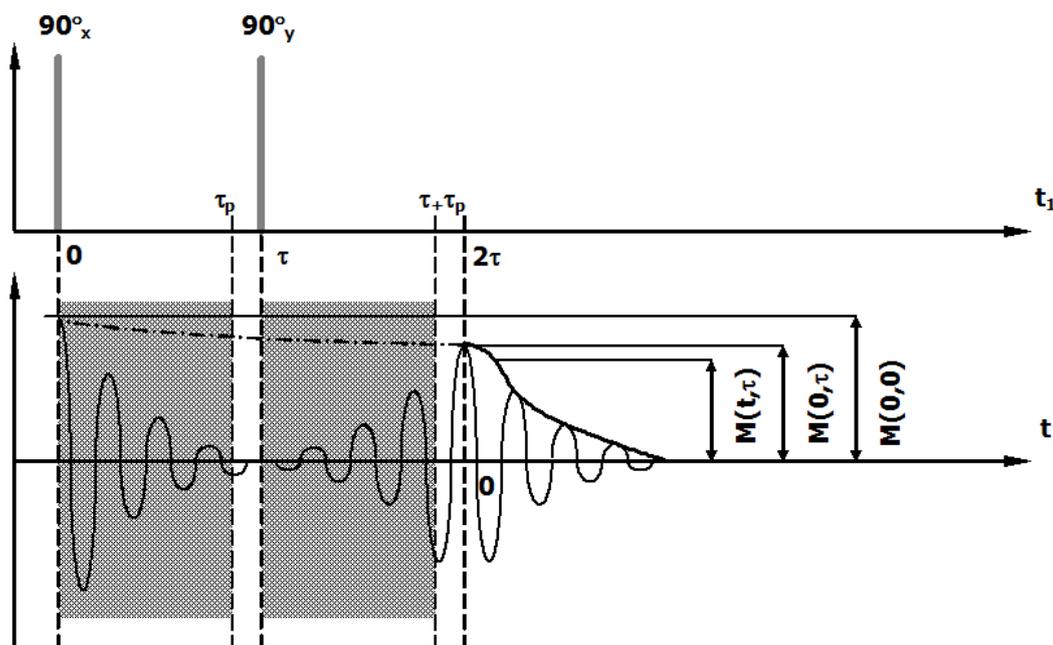


Figure 1. Solid-echo pulse sequence [19].

All experiments were carried out with a duration of $\pi/2$ radio frequency (RF) pulse of $2.7 \mu\text{s}$, and a value of $\tau = 13 \mu\text{s}$ at temperature $T = 310 \text{ K}$. The viscosity of the resin measured on the viscometer Fungilab Expert rotary type at a temperature of $T = 310 \text{ K}$.

3. Experimental results and discussion

Figure 2 shows relaxation attenuations normalized to the initial amplitude corresponding to the minimum and maximum particle size ($d_{\text{asph}} = 10$ and $1000 \mu\text{m}$) in a series of prepared asphaltene samples. The solid line in figure 2 shows the approximation of the experimental data by the equation with the Gaussian form of the line:

$$A(t) = A(0) \times \exp\left(-\left(\frac{t}{T_{2s}}\right)^2\right), \quad (1)$$

where $A(t)$ is a function describing the evolution of the NMR signal in time, $A(0)$ is the initial amplitude of the relaxation attenuation, T_{2s} is the spin-spin relaxation time corresponding to the Gaussian component.

The equation (1) is usually true for the case of so-called solids with disordered structure in the arrangement of atoms. According to the theory [17] to register the so-called "solid-state" NMR signal satisfying the equation (1), the following condition is sufficient:

$$\tau_c \gg T_{2s}, \quad (2)$$

where T_{2s} is the recorded spin-spin relaxation time and τ_c is the correlation time of local magnetic fields due to the interaction between neighboring nuclei. In most cases, the specified correlation time is controlled by rotational and translational modes of molecular motion.

Thus, relaxation attenuations for asphaltene particles are described quite satisfactorily by the equation of type (1), as it was shown in earlier works [21, 22], and are characterized by a fairly short time of spin-spin relaxation. As it can be seen from figure 2, relaxation attenuations for both sizes of asphaltene particles coincide up to the experimental error, which indicates, in particular, the absence of any mechanical destruction effects because of the grinding procedure of the initial asphaltene particles applied by us.

Figure 3 shows the free induction declines normalized to the initial amplitude on a semi-logarithmic scale, registered by the solid-echo sequence for the resin and the model system consisting

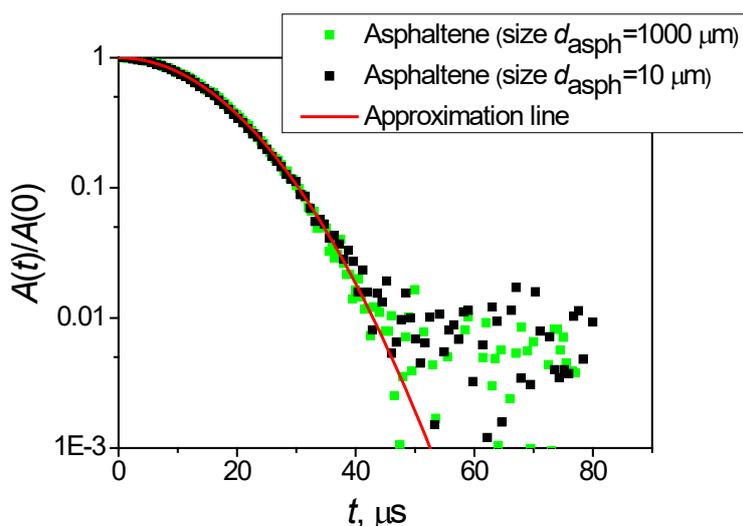


Figure 2. Relaxation attenuations for asphaltene obtained by the solid-echo pulse technique. Particle size of asphaltene $d_{\text{asph}} = 10 \mu\text{m}$ is the black symbols, $d_{\text{asph}} = 1000 \mu\text{m}$ is the green symbols. The solid line shows the result of approximation of the experimental results by the equation (1) at the value $T_{2s} = 20 \mu\text{s}$. Measurement temperature 310 K .

of a mixture of resin and asphaltenes (weight 5 %) with the initial particle size of ≈ 1 mm. The same figure 2 shows for comparison the relaxation decay for Mordovian-Karmal bitumen with the same content (weight 5 %) asphaltenes.

It can be seen that the decay of free induction for the resin sample (red symbols) in semi-logarithmic coordinates is approximated by a straight line, which corresponds to the equation usually used to describe the Lorentz form of relaxation attenuation in liquids:

$$A_l(t) = A(0) \times \exp\left(-\frac{t}{T_{2l}}\right), \quad (3)$$

where $A_l(t)$ is a function describing the signal with the Lorentz form, $A(0)$ is the initial amplitude corresponding to the time $t = 0$, T_{2l} is the transverse relaxation time.

At the same time, for the model sample containing 5 % asphaltenes and Mordovian-Karmal bitumen, a more complex type of relaxation attenuation is observed, which is satisfactorily approximated by the following equation (4):

$$\frac{A(t)}{A(0)} = p_s \times \exp\left(-\left(\frac{t}{T_{2s}}\right)^2\right) + p_l \times \exp\left(-\frac{t}{T_{2l}}\right), \quad (4)$$

where $A(t)$ is a function describing relaxation attenuation, $A(t = 0)$ is the initial amplitude, p_s and T_{2s} is the population and characteristic relaxation time components with Gaussian attenuation form, p_l and T_{2l} are the population relaxation time of the Lorentz (liquid phase) part of the NMR signal.

The dotted lines in figure 3 show the behavior of the Lorentzian components in the approximation of the relaxation attenuation of the equation (4). The resulting approximation of the value of p_s for the model sample of the resin and asphaltenes Mordovian-Karmal bitumen amounted to $p_s = 4.8$ and 4.9 % respectively. This is slightly lower than the expected value of 5 % and it is due to the lower proton density of asphaltenes compared to the proton density of the resin. Thus, in [23] according to elemental analysis and ^1H NMR spectroscopy, it is shown that the hydrogen content in asphaltenes can vary from 6.5 to 7.8 %. Whereas for resins the hydrogen content depending on the structural-group composition reaches values from 6.9 to 10 % [24, 25].

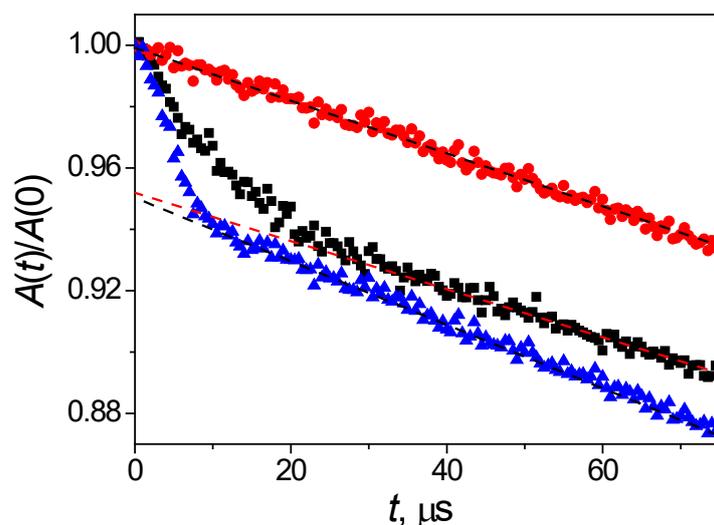


Figure 3. Normalized to the amplitude at the initial time ($t = 0$) free induction decay, obtained by using the pulse sequence solid-echo, pulse sequence parameters: RF pulse duration is the $2.7 \mu\text{s}$, $\tau = 13 \mu\text{s}$, the number of accumulations is the 1000. Dotted lines represent contributions to the decay of free induction from the liquid-phase components of the system under study. Red symbols are resin; black symbols are resin with 5 % asphaltene content (particle size ≈ 1 mm), blue symbols are Mordovian-Karmal bitumen with 4.8 % asphaltene content. Measurements were made at room temperature 310 K.

Thus, by the example of the study of the model system of asphaltene-resin with particle sizes of 1 mm, it can be concluded that the recorded p_s values with accuracy to the error of determining the proton density of the oil components are well correlated with the mass content of asphaltenes in the samples. This, in particular, confirms the applicability of the proposed in [21] method for determining the content of asphaltenes in oil samples based on NMR data.

This conclusion, in fact, is based on the fact that the NMR signal for asphaltenes has distinct characteristics. It is small (of the order of ten μs), the transverse relaxation time and a Gaussian, or close to it, the form of the relaxation attenuation.

For the colloid asphaltene-resin system, the correlation time τ_c in condition (2) should be understood as the correlation time of the rotational motion of the asphaltene particle as a whole. It is obvious that for the considered system, resins-asphaltenes with particle sizes of the order of about 1 mm, the fulfillment of the condition (2) is not in doubt. However, it is a priori unclear to what extent this condition will remain true in a situation where the particle sizes of asphaltenes in the resin will be significantly reduced.

As it turned out, for all the studied samples, except for the sample in which the particle size of asphaltenes was 10 μm , the relaxation attenuation is satisfactorily described by the equation (4), which assumes the presence of both the Lorentz and Gaussian components in the relaxation attenuation. The dotted lines in figure 4 show the behavior of the Lorentz components. An attempt to approximate the data for the asphaltene-resin mixture with a particle size of 10 μm is also formally possible by the equation (4). However, a good approximation result is achieved by assuming a (4) zero value for p_s . Figure 5 shows the dependence of the values of the p_s is the fraction of solid component in the relaxation attenuation of the solid-echo from the diameter of the particles dispersed in the resin particles of asphaltenes.

As it can be seen from figure 5, the proportion of the Gaussian component does not differ much from the expected about 5 % only for the asphaltene-resin system with a particle size of 51 μm . At the same time, for samples with smaller values of asphaltene particle sizes, the underestimated value of the p_s fraction is clearly visible. Moreover, for a sample with a particle size of 10 μm , there are no signs of asphaltenes in the system at all in the experimentally recorded relaxation attenuation. Thus, for the obtained model samples, an effect is found that indicates the dependence of the fraction of the registered Gaussian component with a small relaxation time T_{2s} on the particle size of asphaltenes

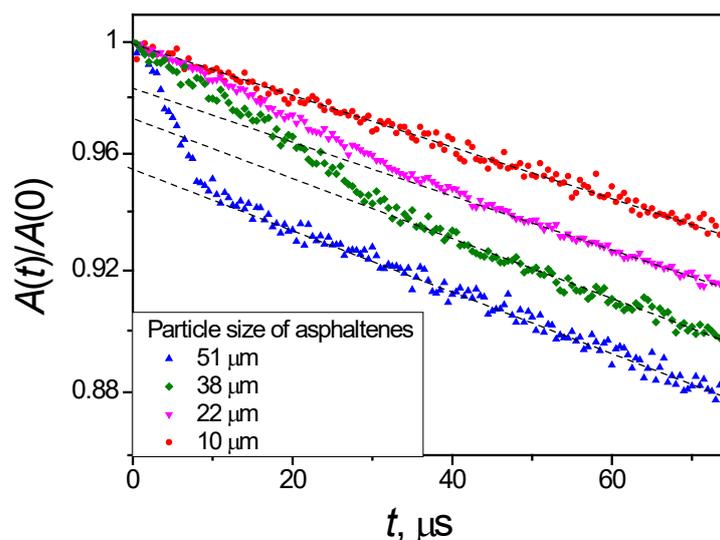


Figure 4. Normalized by amplitude at the initial time ($t=0$) free induction decreases for samples with 5 % asphaltenes content with different particle sizes in the resin obtained by the solid-echo pulse technique. Dotted lines represent the contributions to the decay of free induction of liquid-phase components of oil (Lorentz components) in the approximation of the data by the equation (4). Measurements were made at room temperature 310 K.

dispersed in the resin. The obtained result is quite unexpected and, at first, glance, calls into question the previously published works [26, 27] on the study of oil samples by NMR method. The same works include patents [28-30], in which it is proposed to determine the share of asphaltenes in oil samples by registering the solid component in the relaxation attenuation. However, during repeated experiments, we observed that the form of relaxation attenuations tends to change over time. Therefore, in figure 6 shows the results of the study of the sample asphaltene-resin with a particle size of 10 microns, obtained at different times after sample preparation, are shown.

It can be seen that over time the system begins to form a Gaussian (solid) component. The approximation of the experimental data by the equation (4) showed that after 10 days the initial zero value of p_s in percentage terms became equal to 1.6 %, after 55 days it reached the level of 4.2 %. At the same time, the relaxation time T_{2s} characteristic for this component is 20-25 μs , which, along with the Gaussian form of relaxation attenuation for this component, corresponds to the conditions of the solid (2).

In general, the results shown in figure 6 indicate the existence of a certain process, because of which the asphaltene-resin system according to the characteristics of the solid component tends to an equilibrium state:

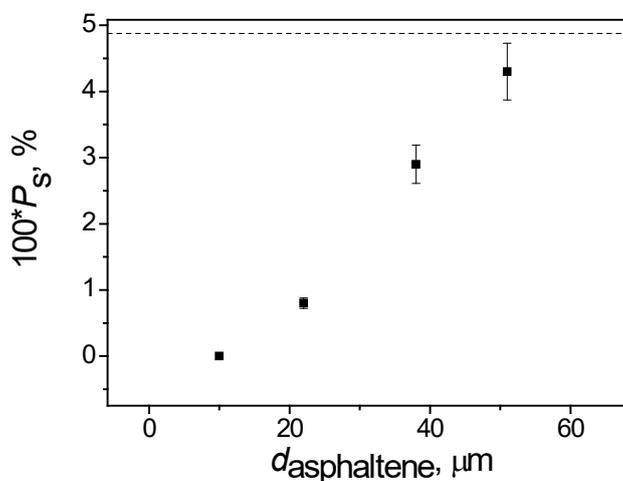


Figure 5. The dependence of the proportion of solid components in the relaxation attenuation of the solid-echo from the diameter of the particles dispersed in the resin asphaltenes. The dotted line shows the level of p_s (%) obtained by approximating the experimental data for the resin-asphaltene mixture with a particle size of 1 mm.

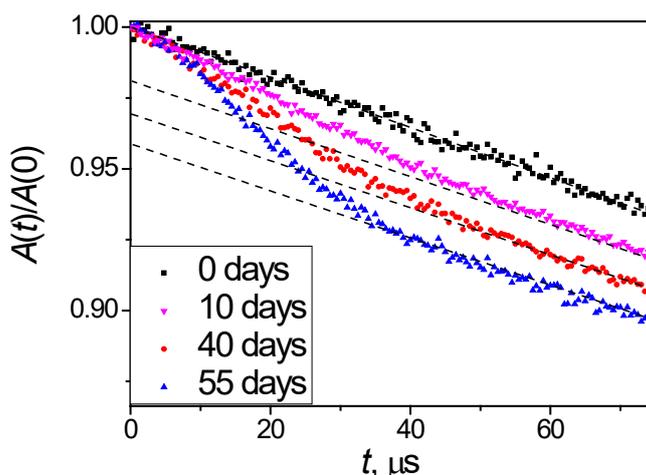


Figure 6. Relaxation attenuations normalized by the amplitude at the initial time ($t = 0$) for the model sample resin-asphaltenes (weight 5 %) with a particle size of 10 μm obtained at different times after sample preparation: 0 days are the black symbols, 10 days are the pink symbols, 40 days are the red symbols, 55 days are the blue symbols. Dotted lines represent the contributions to the decay of free induction of liquid-phase components of oil (Lorentz components) in the approximation of the data by the equation (4). Measurement temperature and sample storage temperature 310 K.

$$\frac{\lim_{t \rightarrow \infty} p_s(t) - p_s(t)}{\lim_{t \rightarrow \infty} p_s(t)} = P_s(t), \quad (5)$$

where as $p_s(t)$ at $t \rightarrow \infty$ the value $p_s = 0.048$ obtained by us for a mixture of asphaltene-resin with a particle size of 1 mm is taken, P_s is a function designation introduced for brevity. Figure 7 shows the time dependence of the solid component.

In fact, the dependence presented in figure 7 shows the kinetics of the process associated with the achievement of a certain equilibrium state in the asphaltene-resin system according to the characteristics of the solid component, namely, its value. In our opinion, this result correlates with the statements of many researchers [3-5] about the tendency of asphaltenes to aggregation. In other words, the result can be interpreted as a gradual increase in the size of asphaltene units. The growth of asphaltene aggregates should be accompanied by an increase in the correlation time in (2) and at the same time a decrease in the relaxation time for asphaltene protons. As a result, when a certain size of the aggregate is reached, the condition (2) begins to be fulfilled, which makes it possible to fix the characteristic features of the solid component in the NMR signal: a small relaxation time T_{2s} and a Gaussian form of relaxation attenuation of type (1). The straight line shown in figure 7 is calculated according to the equation

$$\frac{\lim_{t \rightarrow \infty} p_s(t) - p_s(t)}{\lim_{t \rightarrow \infty} p_s(t)} = \exp\left(-\frac{t}{t_{agr}}\right), \quad (6)$$

where $t_{agr} = 28$ days.

The parameter t_{agr} is a time characterizing the aggregation process. Thus, the presented data clearly indicate that they reflect a certain process of relaxation of the system in an equilibrium state with a characteristic time of about 30 days.

Thus, on the basis of the above reasoning, it should be assumed that the absence of the NMR signal characteristic of asphaltenes in a freshly prepared asphaltene-resin system with particle sizes of 10 μm is due to the short correlation time of rotational motion for a particle with such sizes and, consequently, to the failure of the condition (2). We will try to confirm this by calculations.

The value of the rotational correlation time τ_c for solid particles dispersed in a dispersion medium is associated [18] with the particle size a and viscosity η . The most common equation for determining the correlation time is [21, 31] following:

$$\tau_c = \frac{4\pi\eta r^3}{3kT}, \quad (7)$$

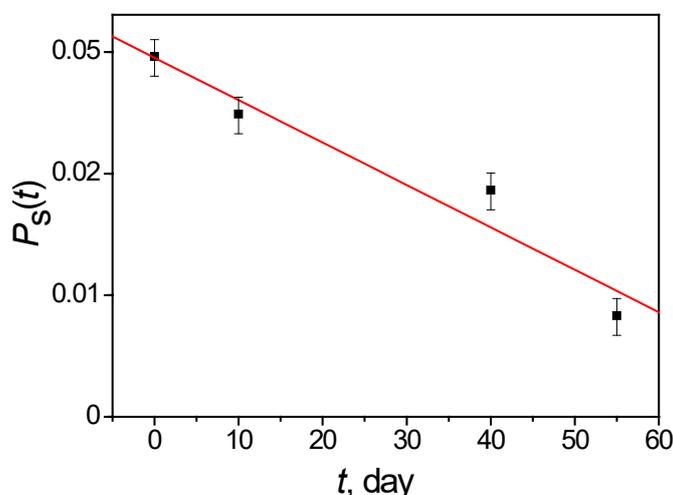


Figure 7. The dependence of the proportion of solid-state component p_s , recorded at a time interval of 55 days. The solid line shows the result of approximation of experimental data.

Size effect for asphaltene particles in the resin by NMR

where r is the radius of the particle; η is the viscosity of the dispersion medium; k is the Boltzmann constant; T is the absolute temperature.

Setting for the model system asphaltene-resin with the particle size (diameter) of $10\ \mu\text{m}$ $r = 5\ \mu\text{m}$, $T = 300\ \text{K}$ and the value of the dynamic viscosity of the resin $\eta = 10\ \text{MPa}\cdot\text{s}$ (according to measurements on the rotational viscometer Fungilab Expert) we obtain:

$$\tau_c = \frac{4\pi\eta r^3}{3kT} = \frac{4 \times 3.14 \times 10 \times 10^{-3} \times (5 \times 10^{-6})^3}{3 \times 1.38 \times 10^{-23} \times 300} \approx 10^3\ \text{s}.$$

As it can be seen from the calculation results, the obtained estimate of the τ_c value for the taken values of the parameters indicates just a very good fulfillment of the condition (2), but and not Vice versa. Therefore, for given the particle sizes of asphaltenes and the viscosity of the resin, a Gaussian component with $p_s \approx 5\%$ and a short relaxation time T_{2s} had to be registered at the initial site of relaxation attenuation. However, this is contrary to the experimental data.

At first glance, the only parameter in formula (6) the value of which can be questioned is the dynamic viscosity η . The value $\eta = 10\ \text{MPa}\cdot\text{s}$ used in the calculation was measured by the Fungilab Expert viscometer and, in fact, characterizes the macro viscosity of the system. At the same time, it is shown in [32, 33] that the values of macro- and microviscosity in complex molecular systems can be very different, although it is the latter that makes sense to use in calculations by the ratio (6). Direct estimation of the value of microviscosity from any independent measurements is, in this case, a certain difficulty. Therefore, we will try to calculate it from the following considerations. From the analysis of the data shown in figure 5, it follows that at a particle size of about $30\ \mu\text{m}$, the recorded p_s fraction will reach the level of the mean value between the zero level and the maximum $4.8\ \%$ measured for the resin-asphaltene system with particle sizes of $1\ \text{mm}$. Then it can be assumed that it is at this particle size for the correlation time τ_c that the condition is met: $\tau_c \approx T_{2s} \approx 2 \cdot 10^{-5}\ \text{s}$. Then, substituting in (6) the value of the radius of the particle $r = 15\ \mu\text{m}$, we can calculate the value of the microviscosity η at the requirement: $\tau_c = 2 \cdot 10^{-5}\ \text{s}$. However, the calculation result showed, that to fulfill this requirement, the viscosity value in (6) should be about $10^{-12}\ \text{Pa}\cdot\text{s}$, which is eight (!) decimal orders of magnitude smaller than the viscosity of water ($\eta_{\text{water}} = 1.004\ \text{MPa}\cdot\text{s}$) at normal conditions. Thus, an option based only on the assumed difference between macro- and microviscosity in formula (6) is at least insufficient to explain the experimental results. Formally, the radius of the particle r remains the only parameter on which the required result of calculating the correlation time τ_c of the asphaltene particle can still depend. Indeed, the requirement $\tau_c = 2 \cdot 10^{-5}\ \text{s}$ is satisfied if the equation (6) substitute the value $r = 14\ \text{nm}$. The result is, in fact, the lower estimate for the particle size of asphalt, since it was calculated under the condition that the measured value of macro viscosity ($10\ \text{MPa}\cdot\text{s}$) of the resin is preserved for parameter η . It is clear that the value of the parameter r can be slightly increased if in (6) substitute a reasonable value of microviscosity η . However, on the one hand, the value of microviscosity for the system under study is unknown to us, and on the other hand, the use of this value, it will not change any fundamentally overall result. Formally, it consists in the need for the assumption for the parameter r in (6) significantly lower values compared to the size of the particles of asphaltenes introduced into the resin at the stage of preparation of model samples.

4. Conclusion

The need to mutually agree of all the results obtained to recognize that the introduction of asphaltene particles in the resin can be a process of crushing them into smaller particles or, possibly, partial dissolution. The assumption of partial dissolution of asphaltenes in the resin is justified by some similarity of the chemical structures of resin molecules and asphaltenes, as it was already noted in [1, 25, 26]. At the same time, it is impossible not to take into account the possibility of violation of some integrity of asphaltene particles at the stage of their mechanical grinding.

Along with the above, an important result of the study is to establishment of the process of aggregation of asphaltenes over time. This is evidenced by the data shown in figures 6 and 7. On the one hand, the evidence of asphaltene aggregation contradicts the above hypothesis of crushing or partial dissolution of asphaltene particles in the resin, since these processes have the opposite direction. On the other hand, according to the data obtained, the aggregation process is rather slow (typical time is about 30 days). Therefore, its background may manifest the mentioned signs of partial dissolution particles of asphaltene.

In general, the results of the study of model asphaltene-resin systems indicate the existence of nontrivial mechanisms of interaction between the molecules of these components of oil.

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