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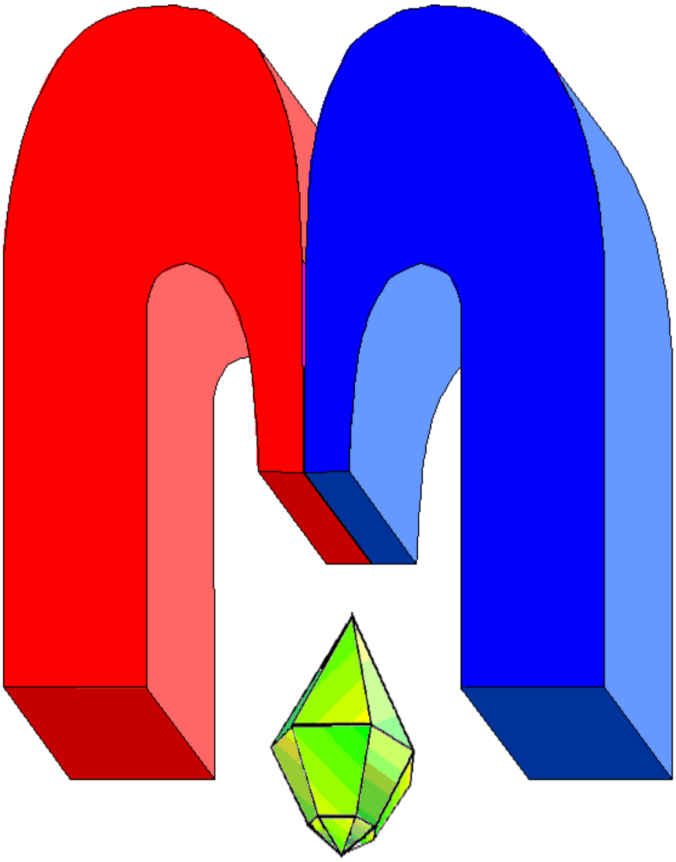

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

The processes of aggregation and dissolution in model systems resin-asphaltene by NMR

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The resin-asphaltene model samples are studied by nuclear magnetic resonance (NMR). According to the differences in spin-spin relaxation times, we are able to distinguish two components of the resin in the mixture. The first component with slower relaxation rate corresponds to the resin in bulk. The second component with the much higher relaxation rate conforms to the resin interacting with the asphaltene particles. The dependence of the ratio between the contributions of these functions on the particle size of asphaltenes is found. It is shown that the fraction of resin molecules interacting with asphaltenes is described by the power dependence on the particle size in terms of one particle. In this case, the proportionality to the volume is given by the value of the exponent (0.9) that is closer to unity, while this exponent is 1.33 for the particle surface. This result is not consistent with the conventional simple model of an asphalt particle surrounded by a solvate resin layer. A hypothesis is formulated about the partial dissolution of asphaltene molecules in the resin is formulated, which is also confirmed by the dependence in the NMR signal of the fraction of the solid component on the particle size of asphaltenes. It is shown that the kinetic dependences of the fraction of the solid component, as well as the fraction of the resin molecules in the state of interaction with asphaltenes, reflect in general the opposite processes, although they are characterized by a close time value of 20 days.

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Keywords: NMR, solid-echo, CPMG, spin-spin relaxation, asphaltene, resin, aggregation, dissolution.

1. Introduction

A significant amount of work is devoted to the study of the state of asphaltenes in oil. In 1961, Yen proposed a pocket model of asphaltenes, based on the study of X-ray diffraction [1]. Later S.R. Sergienko [2] was able to describe the thermal decomposition of asphaltenes, presenting a model of asphaltenes as a set of aromatic cycles. However, this model did not agree with the experimental results obtained by nuclear magnetic resonance (NMR) spectroscopy. Further studies of asphaltenes by various physical and chemical methods led to the creation of the Speight model [3]. This model was proposed according to the analyzed results of the study of asphaltenes by mass spectroscopy and X-ray diffraction (XRD). In contrast to the models of Yen and Sergienko Speight model takes into account the location of the condensed aromatic fragments at the periphery of the interaction of aromatic resins with asphaltenes. Moreover, in the following J. Speight concluded that the fragmented composition of asphaltene molecules and resin molecules played a key role in the deposition of asphaltenes in various hydrocarbon solvents. Further, in the text, the words "molecule" will use as a fraction the components of the model system, which refers to resins or asphaltenes.

Along with the studies of the condensed state of asphaltenes [4, 5], the issues of asphaltene-resin interactions remain debatable. Some of the studies, for example, [6, 7] investigated the thermodynamic characteristics and interaction potentials of asphalt and resin. In other papers [8, 9] the question of dynamic influence of solvate layer of resin on the processes of stabilization and exchange in water-oil emulsion is studied.

In [10, 11] the effects of the addition of resins on aggregation and stability of petroleum asphaltenes in hydrocarbon solutions were studied by dynamic light scattering. However, the system that was studied contains heptane. In oil, the aggregation of asphaltenes goes without heptane. Therefore, the application of these results to the real object is not entirely legitimate. An interesting

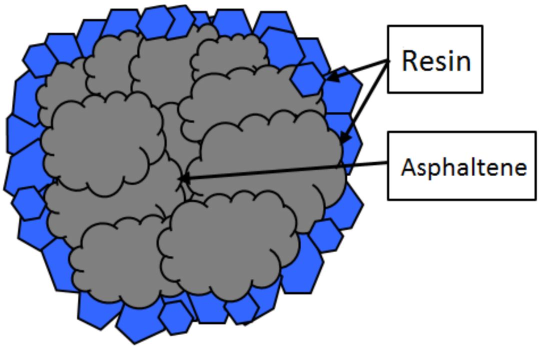

Figure 1. Schematic representation of the aggregate "asphaltene-resin". Color-coded molecules of resins and asphaltenes: asphaltenes is the gray, resins is the blue.

result was obtained in [12]. Authors consider experimentally proven that the association of the major part of vanadyl porphyrins with asphaltenes in oil systems was likely related to the functional groups attached to the porphyrin macrocycle rather than the π - π - interaction of the aromatic rings with porphyrin ones. Unfortunately, asphaltene aggregation was research without resin. Therefore, the question of the effect of tar on the processes of asphaltene aggregation remains open.

As it was shown by the results of studies, for example [13], resins along with asphaltenes are the most polar and aromatic compounds of oil. It is believed that due to the related chemical structure, resins cover the active areas of asphaltenes and thereby isolate them from each other. To describe the results obtained in the course of studies of the interactions between asphaltene and resin, a model [14] is used in which asphaltene is represented by a solid core surrounded by a solvate layer of resin (figure 1).

One of the methods that have proven themselves in the study of complex molecular systems, which undoubtedly include asphaltenes and resins, is the method of NMR [15, 16]. It is known [17] that the use of the NMR method provides a fundamental opportunity to separate the contributions to the resulting signal from the solid and liquid phases. At the same time, analyzing the form of relaxation attenuation for resin molecules, we can hope to obtain information about the characteristics of the proposed solvate layer around the asphaltene particles. Thus, the main purpose of this work is to study the features of resin molecules relaxation characteristics in the presence of asphaltene particles with the help of NMR.

2. Experimental methods

Oil asphaltenes and resins were obtained from Yelkhovskoye oil field of the Republic of Tatarstan in the laboratory of the A.E. Arbuzov institute of organic and physical, Kazan scientific centre Russian Academy of Sciences. The size of the asphaltenes was ~ 1 mm. To prepare the experimental samples, asphaltene particles were crushed to medium size (diameter d) about 10, 22, 38, 51, 200 and 1000 microns. The size of the milled particles of asphaltenes was monitored on the microscope, MTI EQ-MS with the Digital Camera DCM310, a device for video and photography.

In [18] we have described the method of samples preparation and processing of experimental results by a set of Gaussian and Lorentz forms in resin samples with 5 % asphaltene content.

In this work, samples of the resin were studied in which asphaltenes with different particle sizes were added at their mass content in the sample of 10 %. The measurements were carried out on a NMR analyzer with a resonant frequency at $^1H = 20$ MHz protons, the time of "paralysis" of the receiving path $\tau_p = 10$ μs. The NMR signal at times commensurate with the paralysis time τ_p was recorded using the pulse technique solid-echo at a time interval between two $\pi/2$ radio frequency (RF) pulses $\tau = 13$ μs [18, 19]. The correctness of the results obtained using the solid-echo technique is limited in the time domain of the experiment to 100 μs. The main reason for this restriction is associated with the inhomogeneity of the magnetic field, which leads to a rapid loss of phase coherence of the precessing nuclei ensemble. Therefore, to obtain information about the relaxation times of the order of 10^{-4} s or more, which are typical for resin molecules, a pulse sequence of

Carr-Parsell-Meibum-Gill (CPMG) was used, in which the time interval (2τ) between π RF pulses varied from 30 to 1000 μs. Thus, complete relaxation attenuation for each sample was obtained by combining the results of measurements by solid echo and CPMG at different values of 2τ. The measurements were made at a temperature of 310 K.

3. Experimental results and discussion

In this paper, the resin samples were studied in which asphaltenes with different particle sizes were added at their mass content in the sample of 10 %. Figure 2 shows the relaxation attenuation normalized to the initial amplitude received for the resin sample. The form of the experimentally obtained relaxation attenuation for the resin is typical, as it can be seen from the figure 2a, for the so-called multiphase [14, 18] systems in terms of NMR. It can be described by either a continuous or a discrete set of relaxation times. The experimental relaxation attenuation for a resin sample with a good degree of accuracy (solid curve) is approximated by the equation (1):

$$F_{\text{resin}}(t) = \sum_{i}^{n} P_i \times \exp\left(\frac{t}{T_{2i}}\right), \tag{1}$$

for the following parameter values: $n = 5$, $P_1 = 0.596$, $P_2 = 0.01$, $P_3 = 0.133$, $P_4 = 0.019$, $P_5 = 0.242$, $T_{21} = 103$, $T_{22} = 50$, $T_{23} = 36$, $T_{24} = 26$ and $T_{25} = 8$ ms.

Figure 2b shows the result of subtraction from the experimental data (figure 1a) of the curve corresponding to the equation (1). It can be seen that the approximation error of the experimental results on the entire time interval in which the relaxation attenuation was recorded does not exceed 1 %.

Thus, the experimental result presented in figure 1 gives grounds to consider the following: the relaxation attenuation for a resin sample with a good precision ratio is approximated by a discrete spectrum of relaxation times. In this case, the minimum transverse relaxation time is 8 ms, which is significantly longer than the relaxation time $T_{2s} = 20$ μs, characteristic of asphaltenes [18, 20]. This circumstance suggests that in studies of samples prepared from a mixture of resin and asphaltenes, the contributions of asphaltenes protons and resin protons in the total NMR signal can be divided, first of all, on the basis of a significant difference in the values of the corresponding spin-spin relaxation times.

Figure 3 shows the results of a study of the spin-spin relaxation resin samples, each of which was added asphaltenes with different particle sizes (d): from 10 to 1000 microns. It is easy to see that for all the curves shown in figure 3a, the same form of relaxation attenuations characterizes the time

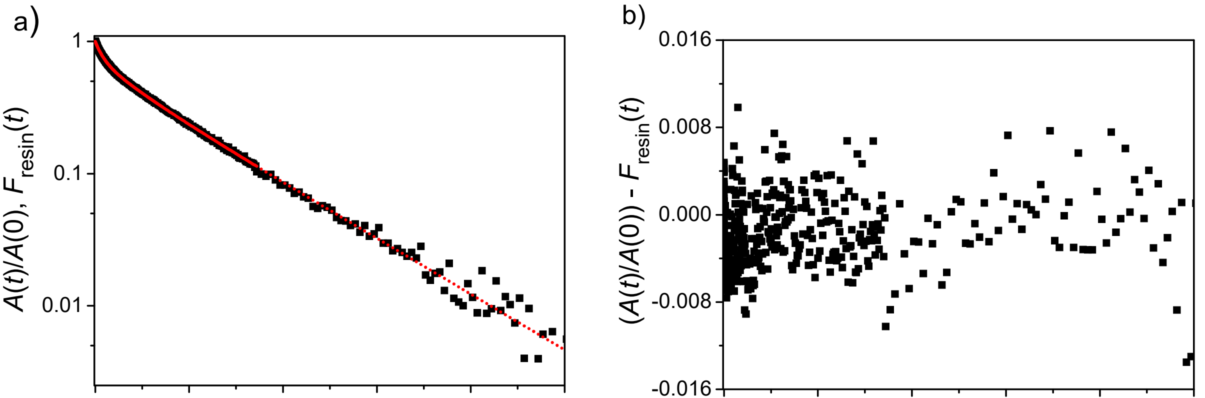

Figure 2. a) The relaxation attenuation for the resin normalized to the initial amplitude for the resin obtained by using the CPMG pulse sequence. The measurement temperature is 310 K; a solid line shows the result of approximated experimental results by expression (1) for the values of the parameters specified in the text. b) The result of subtraction from the experimental curve for the resin of the curve corresponding to the equation (1).

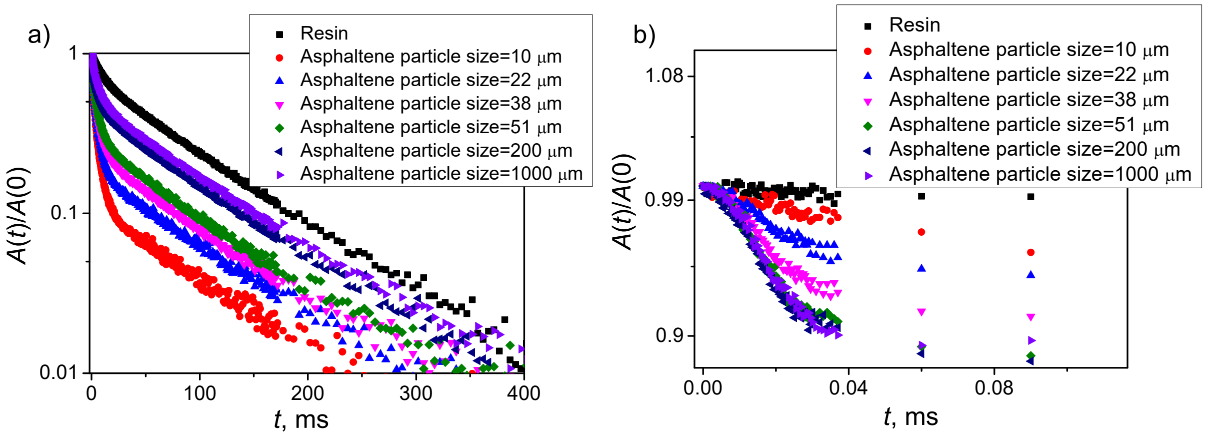

Figure 3. a) Normalized to the amplitude at the initial moment of time ($t = 0$) relaxation attenuations for the resin and resin samples containing 10 % asphaltenes with different particle sizes (shown in the figure) obtained by using the pulse sequences solid-echo and CPMG; b) The initial areas of relaxation attenuations shown in figure 3a. Measurements were made at a temperature of 310 K.

domain above 25 ms with a difference only in the signal level. In addition, most importantly, the signal of NMR is similar to the form of relaxation attenuation obtained for the resin sample. Relying additionally on the overall presentation of the [21, 22] and following the model in figure 1, it can be assumed that not all resin molecules are involved in the formation of a solvate layer around the asphaltene particle. In other words, some of them should be free and, therefore, should have the same characteristics of molecular motion as in the original resin sample. Then, it is reasonable to expect that the part of the relaxation attenuation in the resin-asphaltene system will be described by the $F_{\mathrm{resin}}(t)$ function in eq. (1) at the values of the parameters P_i and T_{2i} set above for the initial resin sample.

The validity of this assumption, in our opinion, is convincingly demonstrated in figure 3, where the relaxation attenuation for the resin-asphaltene system (weight 10 %) with particle sizes of 1000 μm. The solid line in this figure is calculated by the equation (2):

$$F_{\text{resin-asph}}(t,d) = p_{\mathrm{s}} \times \exp\left(-\left(\frac{t^2}{T_{2\mathrm{s}}}\right)^2\right) + P_{\text{resin-sol}} \times \sum_i^n \exp\left(-\frac{t}{T_{2i\_\text{resin-sol}}}\right) + P_{\text{resin-free}} \times F_{\text{resin}}(t), \tag{2}$$

for the following parameter values: $p_{\mathrm{s}} = 0.09$, $T_{2\mathrm{s}} = 21$ μs, $n = 1$, $P_{\text{resin-sol}} = 0.18$, $T_{21\_\text{resin-sol}} = 3.2$ ms and $P_{\text{resin-free}} = 0.73$.

As it can be seen from figure 4, the calculated curve well approximates the relaxation attenuation for a given asphaltene-resin sample, both in the region of large and in the region of minor (see tab in figure 4a). In this case, the graph in figure 4b confirms the good description quality of the experimental data by the equation (2). It is seen that the average error of approximation of the experimental results for the entire time interval in which the relaxation attenuation was recorded does not exceed 1%.

Therefore, the first term in (2) obviously describes the solid-state component of relaxation attenuation. The value of relaxation time $T_{2\mathrm{s}} = 21$ μs is characteristic [23, 24] for asphaltenes and the signal share $p_{\mathrm{s}} = 0.09$ practically corresponds to the quantitative (weight 10 %) the content of asphaltenes in the model system asphaltene-resin. Thus, the first term in (2) can be unambiguously attributed to the NMR signal from protons that are part of asphaltenes.

The presence of the third term (2) in the form containing the $F_{\mathrm{resin}}(t)$ function indicates the presence in the considered resin-asphaltene system of a sufficiently large part of the resin molecules that did not change their nuclear magnetic relaxation characteristics when adding asphaltenes. In the general NMR signal the fraction of such molecules in (2) is characterized by the value of the parameter $P_{\text{resin\_free}} = 0.73$. At the same time, the second term in (2) makes sense to refer to those resin molecules

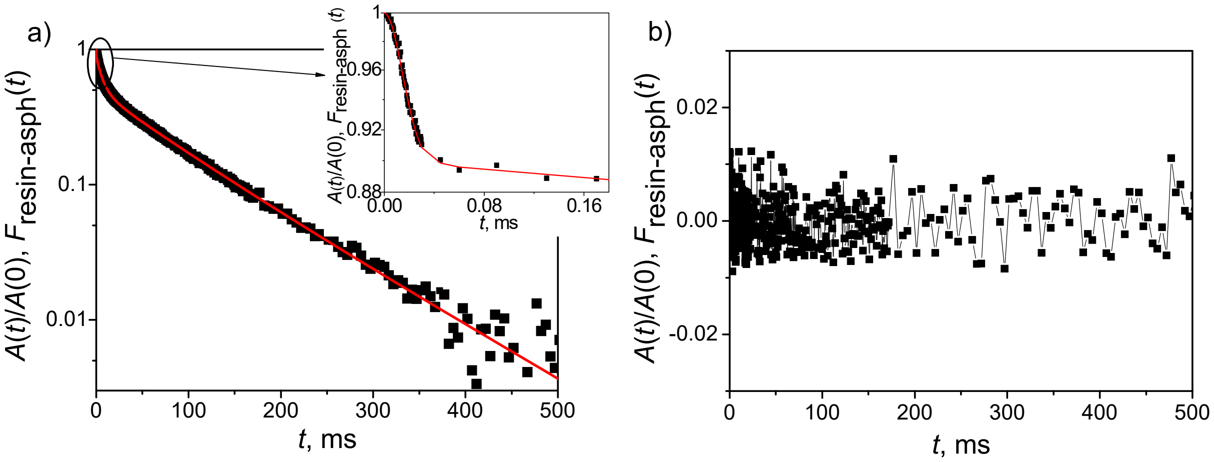

Figure 4. a) Normalized relaxation attenuation to the initial amplitude for the resin, to which 10 % of asphaltenes with particle size $d = 1000$ μm were added, obtained by using solid-echo and CPMG pulse sequences. The insert shows the initial area of relaxation attenuation. The solid line shows the approximation of experimental results by the equation (2) for the values of the parameters given in the text. Measurement temperature 310 K; b) the result of subtracting from the experimental curve for a resin containing asphaltenes a curve corresponding to the equation (2).

that, one way or another, interact with molecules of asphaltenes. According to the model in figure 1, it can be resin molecules that form a solvation layer on the surface of the asphaltene particle.

For further reasoning, the proportion of free resin molecules and resin molecules associated with the interaction with asphaltenes is more logical to consider only with respect to the volume of the resin, and not the entire resin-asphaltene sample. To do this, it is enough to carry out the appropriate renormalization of the $P_{\text{resin-free}}$ parameter. Due to insignificant differences in proton density between the asphaltene-resin system components, the normalized value can be found from the mass composition of the system. For greater accuracy, we use the results of the relaxation attenuation description shown in figure 3, in which the solid component proportion related to asphaltenes is defined as $p_{\text{s}} = 0.09$. Then, the fraction of free resin molecules, normalized to the entire volume of resin in the sample, is from the ratio:

$$\left|P_{\text{resin-free}}\right|_{\text{norm}} = \frac{P_{\text{resin-free}}}{0.91}\,. \tag{3}$$

The fraction of resin molecules that interact with the asphaltenes, it is easy to identify:

$$\left|P_{\text{resin-sol}}\right|_{\text{norm}} = 1 - \left|P_{\text{resin-free}}\right|_{\text{norm}}\,. \tag{4}$$

Therefore, in any case, it is important to establish the fact that the introduction of asphaltenes in powder form with different particle sizes into the resin leads to the fact that only part of the resin molecules are in a state of interaction with asphaltenes. The other part of the molecules does not change the characteristics of NMR relaxation and therefore remains free. Since the NMR characteristics of such resin molecules are set and determined by the function of $F_{\text{resin}}(t)$, the type of relaxation attenuation for the remaining part of the NMR signal in resin-asphaltene samples is of interest. The desired result can be obtained by subtracting from the experimental data presented in figure 3, the function $P_{\text{resin-free}}(d)\times F_{\text{resin}}(t)$. In this case, the fraction of $P_{\text{resin-free}}(d)$, at which the best approximation of the experimental data by the equation of type (2) was achieved, was dependent on the particle size of asphaltene d and will be discussed below.

Figure 5 shows the relaxation attenuations obtained by subtracting the $F_{\text{resin}}(t)$ function with the weight coefficient $P_{\text{resin-free}}(d)$ from the normalized experimental relaxation attenuations. The curves shown in the semi-logarithmic coordinates of figure 5 demonstrate that the resin molecules in the state of interaction with asphaltenes are characterized by approximately the same slope of

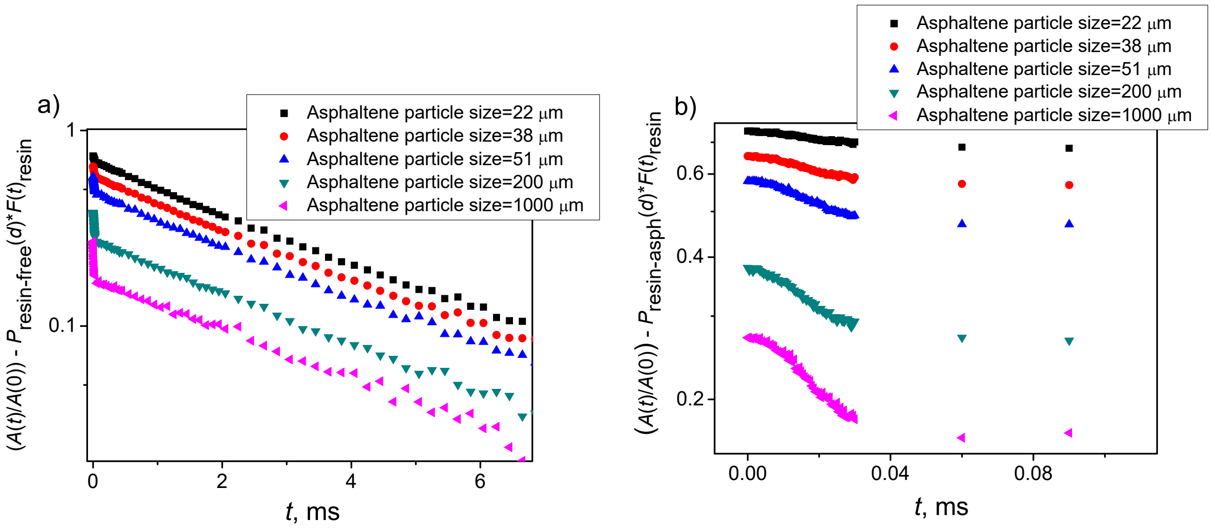

Figure 5. a) Relaxation attenuation obtained by subtracting from the experimental data presented in figure 3, the function $P_{\text{resin-free}}(d)$; b) The initial areas of relaxation attenuations shown in figure 5a.

relaxation attenuations. This means that regardless of the size of the asphaltene particles, the interacting resin molecules are characterized by approximately the same spin-spin relaxation time $T_{21\_\text{resin-sol}} \approx 3.2$ ms. It should be noted (see figure 5b) that the fraction of p_s characterizing the solid-state component in the NMR signal decreases with decreasing particle size of the asphaltene and, as already noted in [18], becomes zero at $d = 10$ μm. Possible causes of $p_s(d)$ dependence have been discussed in [18].

As the part of the results presented in figure 5a, attention should be paid to the absence of any obvious signs of a strong difference in the spin-spin relaxation times for the resin molecules with $T_{21\_\text{resin\_sol}} \approx 3.2$ ms and the part of the asphaltene molecules that did not give a signal to the solid-state component. In other words, the dynamic characteristics of the resin molecules and the asphaltenes in interaction with each other were so close that it was difficult to distinguish them by the time of spin-spin relaxation. Typically, so it can be [25, 26] only in a molecular solution. Thus, this result does not contradict the hypothesis formulated in [18] on the possibility of dissolving asphaltene molecules in the resin.

Now let us return to the analysis of data on the dependence of resin molecules fraction in the free $P_{\text{resin-free}}(d)$ or conditionally solvated $P_{\text{resin-sol}}(d)$ States on the particle size of asphaltenes. Figure 6 shows the dependence of the fraction of resin molecules $\left|P_{\text{resin-sol}}\right|_{\text{norm}}$ in the state of interaction with asphaltenes on the particle size of asphaltenes after the corresponding normalization (3). It is easy to notice that with the increasing asphaltenes particle size there is a decrease in the fraction of solvated resin molecules. This result in principle does not contradict the classical ideas about the structure of the asphaltene-resin aggregate (see figure 1). Indeed, according to this model, the fraction of resin molecules taken together is determined by the value of the surface of the asphaltene particle, which, of course, should decrease with the growth of the particle size. For a better understanding of the dependence presented in figure 6, it makes sense to consider the fraction of the so-called solvated resin molecules, in terms of one particle of asphaltene. Such a transition is easy to make, as we know, and the mass content of asphaltenes in the sample, and the diameter of asphaltene particles. To establish a correlation between the main characteristics (surface area S and volume V) of the asphaltene particle size and the number of resin molecules associated with it, when calculating the fraction of the bound resin per particle, it is possible to limit the value not to the exact value, but to the value proportional to it. Since the mass content of asphaltenes is the same for all the studied model resin-asphaltene systems, the data presented in figure 6, it is sufficient to additionally normalize the value d^3, proportional to the volume of one asphaltene particle with a diameter d.

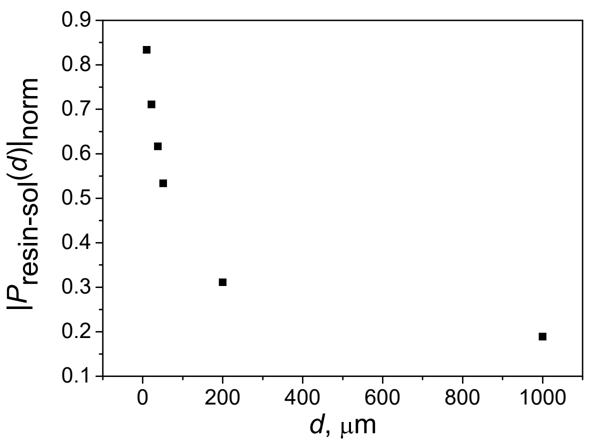

Figure 6. Dependence of the asphaltene on the fraction $\left|P_{\text{resin-sol}}\right|_{\text{norm}}$ of the resin involved in the interaction with asphaltenes, from the particle size *d*.

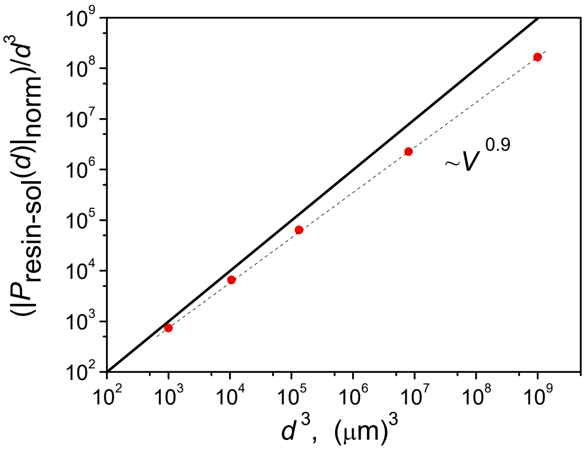

Figure 7. Correlation between the volume of resin per asphaltene particle and the volume of asphaltene particle. The solid line shows the absolute correlation of the values deferred along the axes.

As a result, we found that the relationship between the surface area S of the asphaltene particle and the fraction of resin molecules associated with it was characterized by a power dependence of the type:

$$\frac{|P_{\text{resin-sol}}(d)|_{\text{norm}}}{d^3} \propto S^{1.33\mp 0.03}.$$

At the same time, for volume V, a similar correlation (see figure 7) corresponds to the equation:

$$\frac{|P_{\text{resin-sol}}(d)|_{\text{norm}}}{d^3} \propto V^{0.9\mp 0.03}.$$

It can be seen that there is a better correlation between the number of resin molecules acting with one asphaltene particle and its volume compared to that for the surface area.

Formally, the obtained result allows us to make an assumption that the resin can be not only on the surface of the asphaltene particle, but also in its volume. In our opinion, this result is primarily due to the genetic affinity of asphaltenes and resins molecules, which, in turn, allows the possibility of their interpenetration or partial dissolution. In favor of the hypothesis of asphaltene molecules dissolution in the resin, the data obtained, including in [18], on the decrease in the fraction of the NMR signal characteristic of solid asphaltenes with a decrease in the particle size of asphaltenes.

In [18] we noted that the form of relaxation attenuation for the resin into which asphaltenes were added tends to change over time. Let us analyze the change in the time fraction of the solid component p_{s}.

$$P_{\text{s}}(t) = \frac{\lim\limits_{t\to\infty} p_{\text{s}}(t) - p_{\text{s}}(t)}{\lim\limits_{t\to\infty} p_{\text{s}}(t)} = \exp\left(-\frac{t}{t_{\text{agr}}}\right), \tag{5}$$

where as $p_{\text{s}}(t)$ by $t \to \infty$ accepted value $p_{\text{s}} = 0.09$ we obtained for the sample resin-asphaltene with a particle size of 1 mm, P_{s} is the function designation introduced for brevity, aggregation time $t_{\text{agr}} = 20$ days. At the same time, the aggregation time for all three asphaltene-resin systems are shown in the figure 8 was within the same error limit and equal to $t_{\text{agr}} = 22 \pm 2$ days.

In fact, the dependence presented in figure 8 reflects the kinetics of the process of achieving a certain equilibrium state in the asphaltene-resin system on the basis of the solid-state NMR signal share. In the work [18] because of similar studies in the model systems of asphaltene-resin with a mass content of the last 5 %, it was found that the characteristic aggregation time is about 30 days. For the

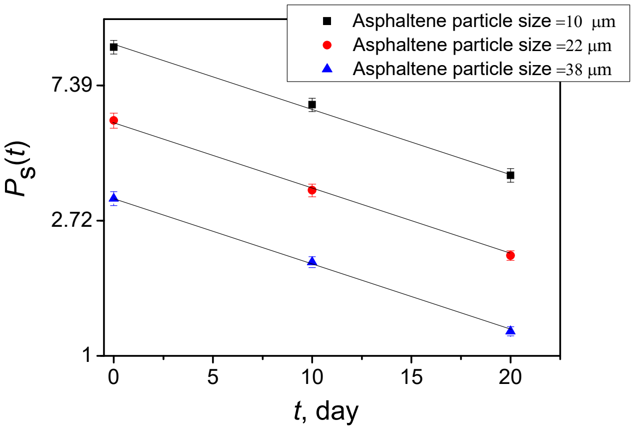

Figure 8. Dependence of solid-state component's share p_s (in %) obtained in the first 20 days after sample preparation. Solid lines show the result of experimental data approximation by the equation (5).

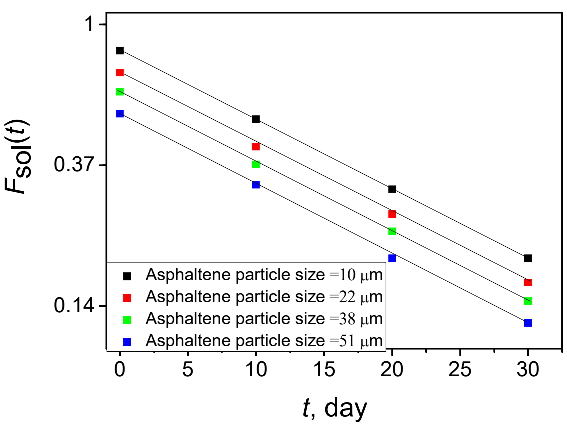

Figure 9. Dependence of the share of $F_{sol}(t)$, obtained from studies during the first 30 days after the resin-asphaltene samples preparation. The solid line shows the result of the experimental data approximation by the equation (6).

concentration of asphaltenes weight 10 %, the $t_{agr} \approx 22 \pm 2$ days was obtained. That is, with the increase in the content of asphaltenes in the dispersion environment of resin, the process of asphaltenes aggregation is faster, which is quite expected. At the same time, the characteristic aggregation time does not depend on the initial particle size of asphaltenes.

We have found the kinetics of change for both the p_s and the fraction of resin molecules $\left|P_{\text{resin-sol}}\right|_{\text{norm}}$ that interact with asphaltene. This relationship is due to a change over time (sample exposure). Moreover, if grows over time, the fraction of resin molecules associated with asphaltenes interaction decreases. Figure 9 shows the kinetics of change in the time fraction under the assumption of the following ratio:

$$F_{\text{sol}}(t) = \frac{\left|P_{\text{resin-sol}}(t)\right|_{\text{norm}} - \lim\limits_{t\to\infty}\left|P_{\text{resin-sol}}\right|_{\text{norm}}(t)}{\left|P_{\text{resin-sol}}(t=0)\right|_{\text{norm}} - \lim\limits_{t\to 0}\left|P_{\text{resin-sol}}\right|_{\text{norm}}(t)} = \exp\left(-\frac{t}{t_{sol}}\right), \tag{6}$$

where as $\left|P_{\text{resin-sol}}\right|_{\text{norm}}$ by $t \to \infty$ accepted value 0.17 we obtained for the sample resin-asphaltene with a particle size of 1 μm, $F_{\text{sol}}(t)$ is the function designation introduced for brevity, the characteristic time of formation of a constant solvate $t_{\text{sol}} = 21$ days. It is easy to notice the proximity of characteristic times values for both kinetic processes. Thus, the process of asphaltenes aggregation and the time dependence of resin molecules fraction associated with asphaltenes are in the optimum correlation.

At first glance, this result seems trivial. However, that is it, if our data did not contradict the classical model of asphaltene-resin unit (figure 1). However, according to the findings of [18], the observed kinetics of the p_s fraction change is due to the mechanism of molecules transition to the aggregated state from a state close to the state of the solution. In other words, our studies have not been able to establish a direct relationship between the value of p_s and the size of asphaltene particles in the sense in which they are presented in figure 1.

Conclusion

As a result of the NMR spin-spin relaxation study in the model samples of asphaltene-resin, it was shown that the input of an asphaltenes system for a sufficiently large part of the resin molecules, the structural and dynamic characteristics remain unchanged. At the same time, another part of the resin molecules with shorter relaxation time reflects the relaxation characteristics of the resin molecules in a state of interaction with asphaltenes. The dependence of the ratio between the contributions of these functions on the asphaltenes particle size was found. It was shown that the fraction of resin molecules in the state of interaction with asphaltenes is described, in terms of one particle, by the strong addiction on the particle size characteristics. In this case, the volume proportionality is established closer to unity, the value of the exponent is 0.9, and for the particle surface this indicator is more than one and is 1.33. This result is not consistent with the classical simple model of an asphaltene particle surrounded by a solvate resin layer. The hypothesis of asphaltene molecules partial dissolution in the resin is confirmed by the dependence of the solid component fraction in the NMR signal of asphaltenes particle size. It is shown that the kinetic dependences of the solid component fraction and the fraction of resin molecules in the state of interaction with asphaltenes reflect in general the opposite processes. Nevertheless, the kinetics of these are characterized by almost the same values of characteristic times and this time is about 20 days. This is a nontrivial result since the p_s fraction characteristic of solid asphaltenes is not directly related to the size of the asphaltene particles introduced into the resin at the sample preparation stage.

To confirm the hypothesis that the observed process of asphaltenes aggregation may be preceded by a stage of partial or complete dissolution of the initial asphaltenes, additional studies are necessary.

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