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Study of the Impact of Nonionic Additives on the Composition and Structure of Petroleum Dispersed Systems by IR Spectroscopy

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Abstract: The article describes a technique for obtaining a quantitative assessment of the composition and structure of the petroleum dispersed system (PDS) and its individual structural formations based on the data of the component composition and infrared spectroscopy. In the PDS of heavy petroleum feedstock modified with a mixture of unsaturated carboxylic acids and four atomic alcohols, the components of the core and the inner solvation shell are different in structure. The degree of affinity of the components of the inner and outer solvation shells of the complex structural unit (CSU), as well as that of the outer solvation shell and the hydrocarbon components of the dispersion medium, increases. Nonionic additives are involved, to a greater degree, in structuring the solvation shell of the CSU and also increase the degree of its affinity with the hydrocarbon components, which leads to an increase in the dispersion of the system and a decrease in its mobility.

Keywords: petroleum dispersed systems; complex structural unit (CSU); asphaltene; component composition; IR spectroscopy; spectral coefficients

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1. Introduction

Among the existing variety of dispersed systems found in nature, there are petroleum dispersed systems, as well. Currently, their popularity is growing, which is associated with an increase in the production of hard-to-recover heavy oil in the world, as well as marketable products obtained from heavy oil residual feedstock. Petroleum dispersed systems are formed due to the presence of asphaltenes. According to the data of physico-chemical methods of analysis, asphaltenes are identified as a mixture of molecules having polyaromatic and naphthenic rings with aliphatic chains and heteroatoms, such as nitrogen, oxygen, sulfur and metals (for example, nickel, vanadium [1]). Besides the fact that the molecular structure of asphaltenes is very complex, they tend to aggregate. The aggregates of asphaltenes are polydisperse [2,3].

Based on the concept of petroleum dispersed systems, aggregates of asphaltenes form the core of the dispersed phase, and they are surrounded by lighter high-molecular weight and less polar compounds that form a solvation layer, while the composition of the dispersion medium includes low-molecular weight oil components [4–6]. For the petroleum dispersed system (PDS) with asphaltenes as the nuclei of the complex structural units (CSU), various models of the nucleus have been proposed [5].

The colloidal properties of asphaltenes are demonstrated by their aggregation, flocculation, sedimentation and adsorption on surfaces, which lead to significant complications in the oil industry [7]. Phase inversion in the petroleum dispersed system leading to sedimentation of asphaltenes and the formation of asphaltene deposits presents one of the main problems that occurs at all stages of the technological process, including production (extraction through production wells), transportation (through oil pipelines), processing and operation of commercial products (bitumen binders, bituminous products).

Mainly due to the negative effects of asphaltenes, understanding the chemistry of asphaltenes and the fundamental principles of the colloid formation mechanism has been the driving force of scientists in recent years [8]. More and more works have appeared on the study of structural transformations of complex structural units of PDS during aggregation, flocculation and sedimentation of particles of the dispersed phase. In [9], the effect of an additive containing amino and phosphate groups on the processes of flocculation and sedimentation of asphaltenes in the petroleum dispersed system was studied. A decrease in the rate and constant of sedimentation and a decrease in the size of associates of resinous–asphaltene substances, which lead to an increase in the aggregate and stability of the petroleum system, were established. Mitusova T.N. et al. [10] proposed improving the stability of residual oil fractions based on their modification with the addition of ethoxylated amines and alkylnaphthalenes, as well as the determination of the resistance of heavy oil residues to stratification during storage, transportation and operation from the point of the petroleum dispersed system concept by preparing benzene solutions. Using the lattice model of diffusion-limited aggregation of Witten–Sander in [11], data on the dimension of the asphaltene core of complex structural units (CSU) of various oils were presented, and a decrease in the fractal density of the core with an increase in its radius was established. In [12], the authors proposed using the method of inverse gas chromatography to determine the parameters of the petroleum dispersed system, which, based on the retention volume, makes it possible to calculate the surface energy, entropy and enthalpy of dispersions. In order to optimize the processing of heavy petroleum feedstock based on the data of molecular motion and physicochemical characteristics of the petroleum system, the possibility of using the analytical method of pulsed NMR was shown in [13]. In [14], Fourier IR spectroscopy and thin-layer chromatography were used to establish the interaction of cationic and nonionic surfactants with the surface of the dispersed phase in the petroleum dispersed system, which made it possible to assess their stability. One paper proposed a method for studying the structure of heavy oil feedstock, being a sediment from the bottom of an oil reservoir, by the APPI UHR-MS method [15].

The main approach which allows creating binding materials with specified performance characteristics by compounding heavy oil feedstock with various modifying additives is the theory based on oil dispersed systems [16–25]. However, analytical methods that allow comparative analysis of the composition and structure of individual structural formations—CSU and PDS—in compounded heavy oil feedstock are at an early stage of their development.

The present work is devoted to obtaining data on the structure and quantitative and qualitative compositions of structural formations of the PDS of heavy petroleum feedstock by its modification with nonionic compounds.

For the first time, the study of the component composition and IR spectral coefficients of structural formations of the PDS of heavy petroleum feedstock compounded with pentaerythritol and a mixture of unsaturated carboxylic acids of distilled tall oil in the presence of manganese oxide was carried out. According to the data of the component composition, the proportion of a complex structural unit (CSU) in relation to the dispersion medium of the PDS was estimated, as well as the composition of the CSU consisting of a core and a solvation shell. Based on the IR spectroscopy data, the proportion of paraffinic structures relative to aromatic ones (aliphaticity) was calculated using the ratio of optical absorption densities $(D_{720} + D_{1380})/D_{1600}$; using this parameter, the structural affinity coefficients of neighboring structural formations of the PDS were calculated. The combination of the selected research methods made it possible to quantitatively characterize the changes occurring in the composition and structure of the PDS of heavy oil feedstock modified with nonionic compounds.

2. Experimental

2.1. Materials

As a heavy oil feedstock (HOF) used as a binding material for the preparation of crushed stone–mastic asphalt concrete mixtures, tar was chosen, produced during atmospheric-vacuum distillation of the mixture of oils from the Romashkinskoye and Prikamskoye fields, obtained at NGDU "Elkhovneft" of PJSC "Tatneft". The additives were: a mixture of unsaturated carboxylic acids of distilled tall oil (DTO) of TU 13-4000177-26-85 "Oil tall distilled", $C_{17}H_{33}COOH$, $C_{17}H_{31}COOH$, $C_{17}H_{29}COOH$; branched polyhydric alcohol, pentaerythritol $C(CH_2OH)_4$ (PE) of GOST 9286-89 "Pentaerythritol for industrial use. Specifications"; pyrolusite (P) of GOST 4470-70 "Reagents. Manganese (IV) oxide. Specifications", containing dioxide of 80% wt. manganese. The choice of unsaturated monobasic acids and four atomic alcohols as the main modifying components was based on the revealed convergence with heavy petroleum feedstock compounds. In [26,27], it was shown that pentaerythritol intensified the process of structure formation in the PDS of heavy petroleum feedstock. Pyrolusite at a temperature of 240 °C and above formed salts with organic acids, soluble in the resins of heavy petroleum feedstock. When heavy petroleum feedstock is modified with pentaerythritol and unsaturated carboxylic acids of distilled tall oil, esters are formed; manganese oxide in pyrolusite presents an active catalyst for this esterification reaction. The resulting esters are capable of structuring and stabilizing the PDS of heavy petroleum feedstocks.

2.2. Experimental

The modification of heavy petroleum feedstock was carried out by compounding it with selected additives in a heated mixer with a volume of 500 cm^3 equipped with a thermocouple. The additives were introduced in a predetermined amount into heavy oil feedstock dehydrated and heated to a temperature of 100 °C, with its intensive stirring, and then the mixture was heated to 240 °C and kept at this temperature for 1 h. The first control experiment (1) involved heavy oil feedstock (HOF). In the second experiment (2), the content of pyrolusite (P.) in the HOF was 4% wt. In the third experiment (3), DTO content was 12.6% wt. In the fourth experiment (4), pentaerythritol (PE) was added to DTO in an amount of 1.5% wt. In the fifth experiment (5), pyrolusite (P.) was added to DTO in an amount of 0.5% wt. In the sixth experiment (6), HOF was modified with pentaerythritol in the same amount. In the seventh experiment (7), HOF was modified with a complex additive consisting of DTO (12.6% wt.), PE (1.5% wt.) and pyrolusite in an amount of 0.5% wt.

2.3. Analysis

The component composition was determined according to the standard method [1]. The precipitation of asphaltenes was carried out with a 40-fold excess of petroleum ether (40–70 °C). Saturated and aromatic hydrocarbons (HC) from resins were separated by liquid adsorption column chromatography on ASK silica gel (fraction 0.25–0.5 mm) using the following solvents: petroleum ether and carbon tetrachloride in a ratio of 4:1, benzene and a mixture of benzene and isopropyl alcohol in a 1:1 ratio.

The structure of the PDS components was determined by infrared spectroscopy using a Bruker Vector IR Fourier spectrophotometer in the range of 2000–650 cm^{-1}. A sample of heavy oil feedstock was provided as a thin film between two parallel KBr plates. To study asphaltenes, the latter were ground into powder with optically pure KBr, and then the mixture of powders was pressed. From the IR spectroscopy point of view, the presence of paraffinic and aromatic structures is common in the structure of the PDS components of heavy hydrocarbon feedstock. Thus, the results of IR spectroscopy are given in the form of spectral coefficients, which present the ratio of the optical densities of absorption bands at frequencies D_{1380} (-CH_3) and D_{720} (-CH_2-) to the optical density of C = C_{arom} bonds at D_{1600} using a common baseline for a group of bands in the range of 1850-650 cm^{-1}: Al = (CH_2 + CH_3)/C = C_{arom} presents aliphaticity, which characterizes the proportion of paraffinic fragments (fragments) in relation to aromatic ones; B = CH_3/CH_2—branching, which characterizes the structure of paraffinic structures.

3. Results and Discussion

3.1. Component Composition

When modifying heavy oil feedstock (HOF), the additive, depending on its nature, is concentrated in a certain group of compounds: hydrocarbons (HC), benzene resins, alcohol-benzene resins and asphaltenes, or forms an insoluble residue. The effect of the distribution of additives in the composition of heavy oil feedstock is presented by the data on the component composition, where the ratio of resinous–asphaltenic components (RAM) to hydrocarbons is shown by the RAM/HC parameter (Figure 1).

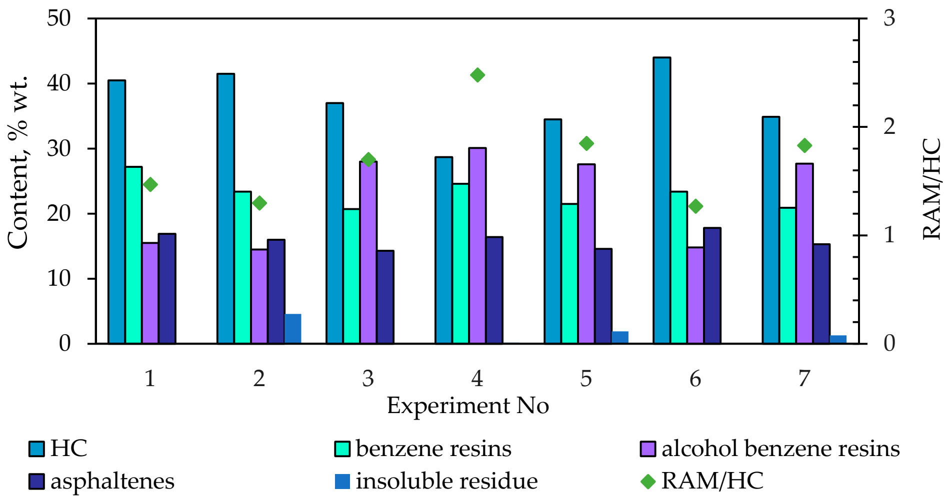

Figure 1. Component composition of the original and modified heavy oil feedstocks.

Compared with the initial heavy oil feedstock, the introduction of pyrolusite into its composition does not change the ratio of resinous–asphaltene compounds (RAM) and hydrocarbon components (HC) (Figure 1). When distilled tall oil (DTO) is introduced into heavy oil feedstock, this ratio increases due to an increase in the contribution of alcohol-benzene resins, that is, tallow oil appears in alcohol-benzene resins. This is also confirmed by the data on the component composition when distilled tall oil and pyrolusite are added to heavy oil feedstock. The introduction of pentaerythritol (PE) into heavy oil feedstock, on the contrary, lowers this ratio, since it becomes an integral part of hydrocarbon components (HC). The combined use of distilled tall oil and pentaerythritol significantly changes the ratio of resinous–asphaltene substances and oil in the tar sample. Of all the samples, this sample is characterized by the maximum content of alcohol-benzene resins and the minimum content of hydrocarbon components (HC). Under the modified conditions (intensive stirring at a temperature of 240 °C for an hour), a partial interaction of the acids of distilled tall oil and pentaerythritol occurs. The resulting product becomes an integral part of alcohol-benzene resins. Pyrolusite is separated into a separate phase, since it is insoluble in the compounds of heavy oil feedstock. The use of a complex additive (HOR + DTO + PE + P.) in the modification leads to a decrease, in comparison with the initial heavy oil feedstock, in less polar components—hydrocarbon components (HC) and benzene resins—and an increase in the content of the most polar components—alcohol-benzene resins.

3.2. The Composition of PDS

The presence of additives in the composition of heavy petroleum feedstock significantly affects the composition and structure of the PDS (Figure 2). The structure of CSU is similar to the structure of a micelle in colloidal chemistry. However, the fundamental difference between the CSU and the micelle is the absence of a strictly pronounced boundary between the core, the solvation shell and the dispersion medium in the oil dispersed system. Pyrolusite is not included in the PDS; therefore, heavy oil feedstock modified with it is excluded from consideration. The share of complex structural units (CSU) in the PDS of heavy oil feedstock before and after modification was estimated as the content of resinous–asphaltene components (RAM), and the dispersion medium (DM) as the content of hydrocarbon components (HC) (Figure 2). Based on the existing concepts of the PDS, the CSU core consists of asphaltenes (A), and the solvation shell comprises resins. The soma solvation shell consists of an inner and an outer layer containing alcohol-benzene resins (R_{ab}) and benzene resins (R_b), respectively.

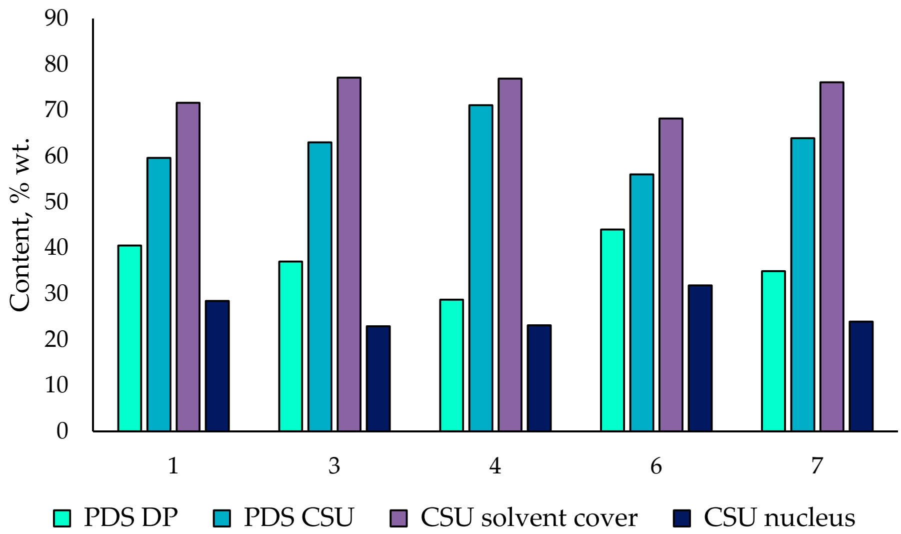

Figure 2. Composition of the petroleum dispersed system of the original and modified heavy oil feedstocks (HOFs).

Only the addition of pentaerythritol (PE) leads to an increase in the proportion of the dispersion medium in heavy oil feedstock and a decrease in the proportion of CSU. In this case, the core of the CSU increases and the solvation shell decreases. The rest of the additives lead to a decrease in the contribution of the dispersion medium and an increase in the CSU content. In their composition, the core decreases and the solvation shell increases.

3.3. The Structure of PDS Components

The durability of crushed stone–mastic asphalt concrete pavements is influenced by the structure and affinity of PDS components in modified binders. The structure of the PDS components was evaluated based on the data of FTIR spectroscopy. The content of structural groups was calculated from the absorption of the corresponding absorption bands relative to the C=C bonds of the aromatic ring [28]. To characterize the PDS components of the initial and modified heavy petroleum feedstock, the spectral coefficients were calculated based on the obtained absorption values (Figure 3).

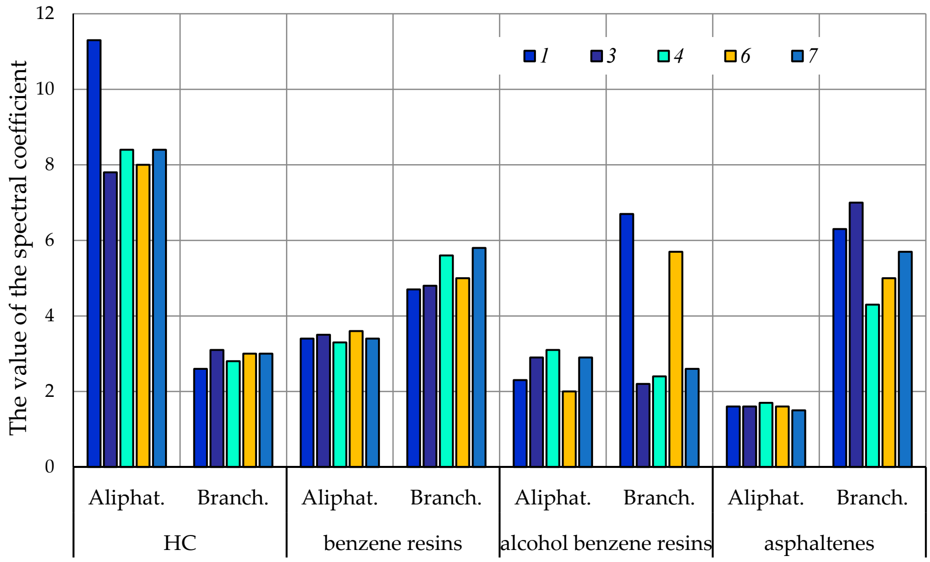

Figure 3. Spectral coefficients of petroleum dispersed system (PDS) components based on IR spectroscopy data.

The aliphaticity of PDS components decreases in the sequence hydrocarbon components (HC)—benzene resins—alcohol-benzene resins—asphaltenes. Noteworthy is the increase in the proportion of paraffinic structures in heavy oil feedstock and a threefold decrease in their branching in alcohol-benzene resins, if the modification is made with PE or PE is a component of the additive. The acids contained in PE are close in polarity to alcohol-benzene resins; therefore, they are released with them during adsorption chromatography. Probably, their aliphatic part is weakly branched; therefore, the branching of paraffinic structures of alcohol-benzene resins decreases.

To determine the degree of affinity (homogeneity) of the structure of PDS components [29], the following parameters were used: aliphaticity (A) and branching of paraffinic structures (B). Based on the values of the aliphaticity of the PDS components, the structural affinity coefficients of neighboring structural formations of PDS were calculated (Figure 4). The affinity coefficients include three structural parameters—methylene groups with more than four atoms in the chain, methyl groups and aromatic structures; therefore, they are representative parameters:

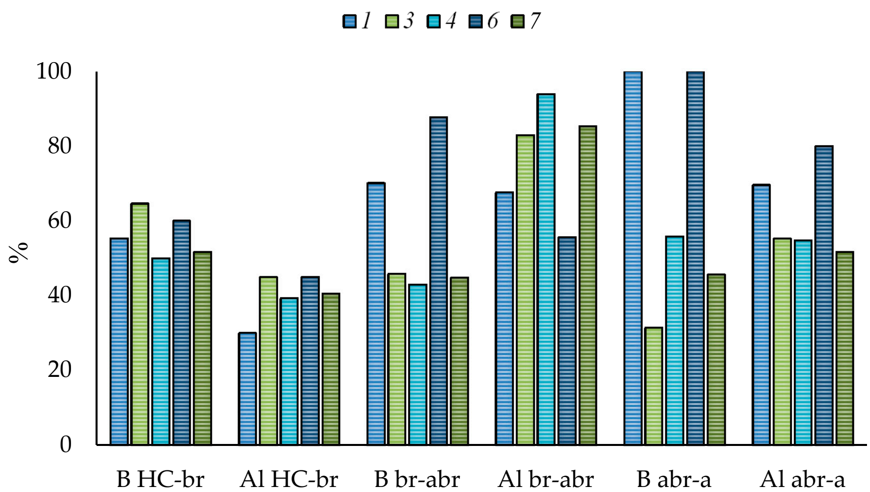

Figure 4. Coefficients of the degree of affinity of PDS components.

$A_{HC\text{-}br} = Al_{br}/Al_{HC} \times 100\%$—the affinity of the structure of the outer solvation shell and the dispersion medium;

$A_{br\text{-}abr} = Al_{br}/Al_{abr} \times 100\%$—the affinity of the structure of the outer and inner solvation shells;

$A_{abr\text{-}A} = Al_{abr}/Al_{A} \times 100\%$—the affinity of the structure of the inner solvation shell and the nucleus.

Similar coefficients were also calculated for the branching of paraffinic structures: $B_{HC\text{-}br}$, $B_{br\text{-}abr}$, $B_{abr\text{-}A}$.

With the introduction of additives, the affinity of the aliphaticity of the hydrocarbon components (HC) of the dispersion medium and benzene resins of the outer solvation shell of CSU increases. In this case, in the CSU, the affinity of the components forming the solvation shell increases, but the affinity of the aliphaticity of the inner solvation shell and the core decreases. The exception is heavy oil feedstock modified with pentaerythritol (PE)—the degree of affinity of the components of the outer and inner solvation shells is significantly higher, and that of the inner solvation shell and core is lower than in the original HOF. The higher the degree of affinity of the aliphatic components of the solvation shell, the higher its content.

The lowest degree of affinity of the structure of the inner solvation shell and the core is observed for heavy oil feedstock modified with a complex additive (experiment 7). This is due to the fact that alcohol-benzene resins of the solvation shell have a low dissolving power (53%) with respect to the core asphaltenes. The degree of affinity of the PDS components of the modified heavy oil feedstock by the complex additive increases in the series $A_{abr\text{-}A} < A_{br\text{-}abr} < A_{HC\text{-}br}$. An increase in the solvation shell in the PDS of the modified HOF with distilled tallow oil and pentaerythritol is associated with the immobilization of the hydrocarbon components of the dispersion medium due to the affinity of their structure with the structure of benzene resins of the outer solvation shell exceeding 52%. The composition of the PDS of heavy oil feedstock contains associative combinations, the proportion of which exceeds the proportion of the dispersion medium. A high proportion of the solvation shell in the composition of associative combinations and an increase in the degree of affinity of the structure of the molecules of the hydrocarbon components of the dispersion medium and the peripheral part of the solvation shell of complex structural units indicate the low molecular mobility and high stability of the PDS of the modified heavy oil feedstock.

Therefore, under the conditions of compounding of heavy petroleum feedstock with nonionic additives, a regular redistribution in its component composition occurs. The introduction of PE into heavy oil feedstock most effectively reduces the RAM/HC ratio, and the introduction of distilled tall oil and PE leads to a maximum increase in the content of alcohol-benzene resins against the background of a decrease in the amount of HC due to the occurrence of esterification reactions with the formation of high molecular compounds containing oxygen functional groups. The high content of high-molecular weight polar components in heavy oil feedstock favorably increases the adhesive properties of the binder to mineral fillers in crushed stone–mastic asphalt concrete mixtures. A distinctive feature of the PDS of heavy petroleum feedstock compounded with DTO and PE is an increased proportion of CSU in the dispersion medium, which indicates partial transition of the dispersion medium components into CSU. In the composition of CSU, fewer components fall on the core and more fall on the solvation shell, which indicates the formation of associative combinations (local structural formations) from the CSU with the maximum degree of ordering of the structural elements of the system. The degree of affinity of the components of the inner and outer solvation shells of the CSU is lower, while that of the outer solvation shell and the HC components of the dispersion medium is the highest.

The obtained results in the future will make it possible to identify patterns and build correlation dependences of the structure and quantitative and qualitative compositions of structural formations of CSU with the physicochemical properties of binders based on them. This will make it possible to create structural materials based on heavy oil feedstock with improved operational parameters.

4. Conclusions

During transportation and processing of oils, as well as the production of petroleum products with specific properties, theoretical concepts of petroleum dispersed systems are widely used, and the importance of taking into account the colloidal-chemical properties of oils is noted; however, there is a lack of experimental data that allow assessing the structure of the PDS and the composition and structure of its individual structural formations—complex structural units and dispersion medium. It has been established by Fourier IR spectroscopy and liquid adsorption chromatography that the modification of heavy oil feedstock with pentaerythritol and distilled tallow oil in the presence of pyrolusite leads to a redistribution of the composition and structure of the components of the petroleum dispersed system. The combination of the selected research methods made it possible to characterize the changes occurring in the quantitative composition and structure of the PDS of modified heavy oil feedstock with nonionic compounds.

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