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KINETICS OF DISSOLUTION OF ASPHALT-RESIN-PARAFFIN DEPOSITS WHEN ADDING DISPERSING AGENTS

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The study is devoted to the determination of kinetic parameters of the process of asphalt-resin-paraffin deposits dissolution by oil fractions, solvents and compositions based on them. The study of the kinetics of deposits dissolution and the effect of additives on this process is relevant, as the use of solvents will reduce the cost of cleaning and repairing process equipment of refineries. A series of experiments was performed to determine the kinetic regularities of dissolution of different types of asphalt-resin-paraffin deposits in petroleum solvents of different fractional composition and the effect of dispersing agents on this process. Crude distilled oil fractions 110–150^{0}C, 150–200^{0}C and 140–243^{0}C were shown to be the most effective for dissolving the asphalt-resin-paraffin deposits. The use of dispersant agents increases the degree of solubility of the components of the asphalt-resin-paraffin deposits. The kinetics of dissolution process obeys the Erofeyev-Kolmogorov equation.

Keywords: asphalt-resin-paraffin deposits, solvent, tank, dispersant, kinetics, fuel.

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Introduction

Asphalt-resin-paraffin deposits (ARPDs) are accumulated during storage, transportation of oil and oil products in tanks, especially of large volumes. Sometimes, ARPDs form a layer on the bottom of the tank up to 10% of the volume in a few months [1].

The presence of deposits leads to a decrease in the volume of oil tanks, to the emergence of corrosion-hazardous areas under the deposit and to a complication of the inspection of the tank. In addition to reducing the useful volume of tanks, the accumulation of deposits impedes the process of their operation, complicates the quantitative and qualitative accounting of oil, and reduces the technical and economic performance of oil tanks and the transport system as a whole. To increase the efficiency of oil tank capacity, it is necessary to preserve their useful volume.

The aim of the study is the selection of solvents that allow effectively removing various types of ARPDs. The object of the study is the process of dissolution of ARPDs and the factors that affect its rate. The subject of the study is the influence of the nature of the solvent, as well as the addition of additives to the rate of dissolution of deposits.

ARPDs have different components and are complex systems that include petroleum products, water, inorganic compounds and mechanical impurities, the ratio of which varies widely.

High-molecular-weight paraffinic hydrocarbons, which are a part of the ARPD, have high pour point, and under normal conditions form highly viscous precipitates, which sometimes turn into a solid state. The composition of resins and asphaltenes includes polycyclic aromatic structures that contain sulfur, oxygen, nitrogen, and various trace elements.

The process of preparation for the removal of deposits is the most time-consuming. Pumping requires compliance with increased requirements for safe operation. To perform these works, a number of methods are used as follows [2]:

– using a jet of water under high pressure for erosion of deposits;

– erosion of the deposit by oil;

– dilution of sludge with solvents;

– heating of bottom deposits.

To study the process of dissolution of ARPDs, two types of deposits were selected, which are different in the composition and structure: the first group of samples was with a high content of paraffins (ARPDp), and the second group of samples was with a high content of asphaltenes (ARPDa). The main characteristics of the deposits are given in Table 1 [1].

Table 1

Characteristics of ARPD [1]

Property	Value	
	ARPDp	ARPDa
organic part, wt.%	93.12	94.90
content of inorganic substances, wt.%	0.98	1.83
density, g/cm^3	0.87	0.94
pour point, ^{0}C	56	46
content of resins, wt.%	6.88	14.12
content of asphaltenes, wt.%	7.12	18.45
content of paraffins, wt.%	56.22	24.92

Dissolution and dispersion of ARPDs is a rather complex process that in influenced by a number of various factors, the most important of which are the fllowing: temperature, interaction time, composition and physicochemical properties of the solvent, and the composition and structure of ARPD.

The selection of reagents was mainly aimed at increasing the solubility of the components of ARPDs, which are a complex dispersed system of refractory substances both in composition and structure with intramolecular bonds. From this point of view, the greatest effect on dissolution is achieved if the reagents contain components similar in composition and structure to the components of the deposits (according to the principle «like dissolves like»).

Gasoline fractions (50–85^{0}C; 85–110^{0}C; 110–150^{0}C; and 150–200^{0}C), kerosene (140–243^{0}C) and diesel (182–351^{0}C) were studied as solvents, since they are the most affordable and relatively cheap. The fractions were obtained at the crude distillation unit of PJSC «Ukrtatnafta» (Table 2).

To increase the efficiency of solvents of this type, the following compositions based on them with additives-dispersants of paraffin deposits were studied: sodium sulfosuccinate based on mono- and diglycerides of fatty acids, and phosphatide concentrate [3].

Experimental

The efficiency of solvents was determined under the laboratory conditions by the methods described elsewhere [4].

The research was carried out by the method of «baskets» using cartridges made of filter paper. The experiments were performed in static and dynamic modes.

In the static method, the volume of the solvent, its composition, temperature and duration of the experiment did not change. The cartridge with the ARPD sample was immersed in a solvent of 40 ml for 1.5–2 hours. At the end of the specified time, the sample was removed, dried in the open air and weighed.

The efficiency of the solvent was evaluated by the degree of dissolution by the following formula:

$$\alpha = \frac{m_1 - m_2}{m_1}, \qquad (1)$$

where α is the degree of dissolution (the fraction of the unit); m_1 is the mass of the sample of ARPD before dissolution (g); and m_2 is the mass of the sample of ARPD after dissolution (g).

Dissolution was performed at fixed temperatures of 10, 25 and 35^{0}C, which was stabilized by a thermostat. The maximum value of temperature and duration of research are determined by the necessity of development of utilization of ARPD suitable for industrial conditions.

In the dynamic mode method, the efficiency of the solvents was evaluated depending on the duration of exposure. For each experiment, six samples of ARPD weighing up to 1 g were prepared. Each sample was wrapped in a cartridge made of filter paper. The solvent was poured into six beakers. An ARPD sample cartridge was immersed in each beaker and the time was recorded. Every 20–30

Table 2

Physicochemical characteristics and group composition of crude distilled oil fractions

Hydrocarbon fraction	Density at 20^{0}C, kg/m^3	Group composition, wt.%		
		paraffins	naphthenes	arenes
gasoline 50–85^{0}C	671	90.12	9.88	2.12
gasoline 85–110^{0}C	682	81.09	18.91	2.86
gasoline 110–150^{0}C	701	80.41	19.59	3.39
gasoline 150–200^{0}C	741	68.18	18.8	13.02
kerosene 140–243^{0}C	778	61.2	22.11	16.69
diesel 182–351^{0}C	823	–	–	28.21

minutes, one cartridge was removed in turn. After complete drying, the weight of the cartridge was determined. The degree of dissolution was determined by the formula (1).

The process of dissolution of ARPDs, which from the standpoint of formal kinetics corresponds to the first order reaction, is well described by the Erofeyev-Kolmogorov equation [5]:

$$\alpha = 1 - e^{-k\tau}, \quad (2)$$

where k is a rate constant of the dissolution process; and τ is the duration of the process.

To characterize the rate of first-order reactions, along with the rate constant, we used the quantity of the half-life. This value does not depend on the initial concentration of the starting material and is calculated according to Sakovich's formula [5]:

$$\tau_{1/2} = \frac{\ln 2}{k}, \quad (3)$$

The formula (3) allows determining the time during which the half of the initial amount of an ARPD dissolves.

To enhance the ability to dissolve and destroy ARPDs into small fragments, create around the already dispersed particles of solvate shells that prevent their integration into the original conglomerates and reduce the interfacial tension at the boundary ARPD/solvent, the described above additives (5 wt.%) were introduced into the base solvent.

Results and discussion

At the first stage, the efficiency of light hydrocarbon fractions in the processes of dissolution of deposits by static and dynamic methods of ARPD samples was investigated. The experimental results are summarized in Fig. 1 (static mode) and Fig. 2 (dynamic mode).

At the temperatures of 10 and 25^{0}C, the solution action of all crude distilled fractions for the samples of ARPDp and ARPDa is insignificant (Fig. 1). The best result in terms of the degree of dissolution does not exceed 0.25 for the sample ARPDp. The 50–85^{0}C hydrocarbon fraction showed a greater ability to dissolve the sample of paraffin-type ARPD. However, a relatively low degree of dissolution (0.041) and the slow rate of the process of dissolving the organic part of the ARPDa indicate the futility of using the gasoline fraction and hydrocarbon solvents of a similar nature for this type of sediment.

The solubility was affected by temperature. With increasing temperature, the solubility of the deposits improved, but the degree of dissolution for the sample ARPDa was only 0.45 for the fraction 140–243^{0}C. When tested on paraffin-type deposits, the degree of dissolution reached 0.55 for the fractions 110–150^{0}C and 150–200^{0}C.

The degree of dissolution of the ARPDa samples in the gasoline fraction 110–150^{0}C is lower than that of the ASPVp samples by almost 1.6 times. This fact is explained by the insufficient content of arenes in this fraction (Table 2), which are characteristic solvents for asphaltenes. The analysis of the action of solvents with a boiling point of 200^{0}C and above revealed greater efficiency in the destruction of asphalt-type deposits: the degree of dissolution was increased to 0.45.

Thus, crude distilled fractions 150–200^{0}C and 140–243^{0}C show the maximum solubility in relation to ARPD of both types.

The process of dissolution of both types of ARPD in the dynamic mode at the temperature of 35^{0}C in crude distilled oil fractions (Table 2) were studied according to the method described elsewhere

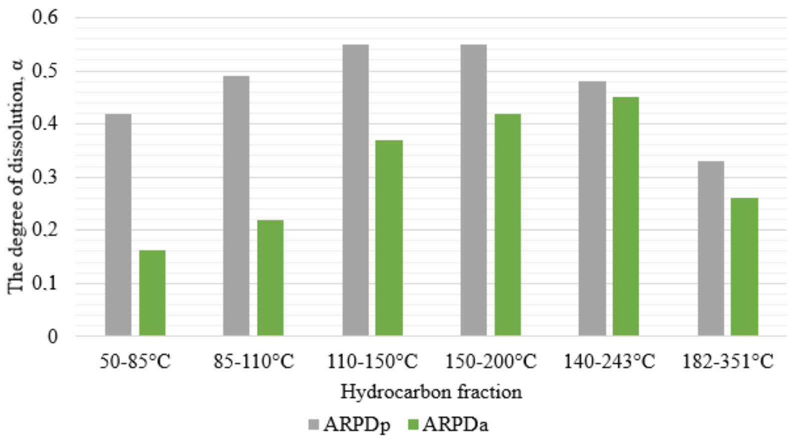

Fig. 1. The efficiency of light hydrocarbon fractions in dissolving ARPD in static mode

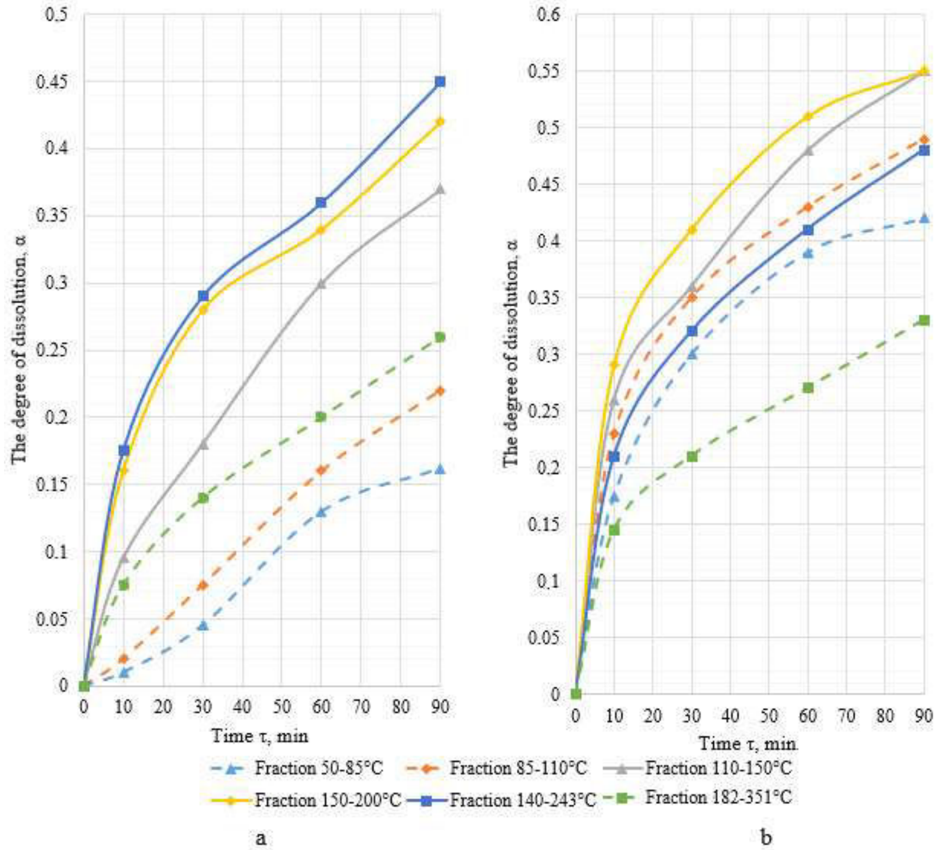

Fig. 2. Kinetic curves of dissolution of ARPDa (a) and ARPDp (b) in crude distilled oil fractions

[4]. The results are shown in Fig. 2.

Dissolution of ARPD of both types in the dynamic mode at 35⁰C is more intense in the gasoline fraction 150–200⁰C and kerosene 140–243⁰C and includes two stages. At the first stage, the ARPD swells and absorbs the solvent. This is followed by dissolution and dispersion. The maximum dissolution rates were 0.42 and 0.45 for ASPVa and 0.55 for ASPVp, respectively. The kinetics of change in the degree of dissolution in both cases is exponential. The maximum dissolution rate was observed in the first minutes of the process. After 30 minutes, the dissolution rate gradually decreases. The hydrocarbon composition of hydrocarbon fractions is characterized only by solubility and equilibrium is quickly established at the solvent/ARPD phase boundary. Complete destruction of deposits is not achieved, because dispersion does not occur under the conditions of the experiment.

Such components of ARPD as resins and asphaltenes are characterized by complexity of structure, low stability, high reactivity, polarity and surface activity, which is generally characteristic of heterocyclic compounds. Asphaltenes are lyophilic in relation to aromatic solvents, but lyophobic with respect to gasoline fractions [6].

Analysis of the obtained data showed that the use of crude distilled oil fractions for dissolution does not provide the required efficiency. To increase it, kinetic studies of the dissolution of ARPD in the fraction 140–243⁰C with the addition of dispersing agents were performed. The choice of this fraction is due to the relatively high solubility of ARPD and the greatest ability to mix with additives.

ARPDp is a type of deposit with a high content of hard paraffins; in the presence of asphaltenes and resins, it is capable of forming a stable bond with high molecular weight hydrocarbons. More dispersed paraffin particles pass into the solution and a high content of additives (up to 5 wt.%) is required to prevent their re-aggregation.

With increasing concentration of additives above 5 wt.%, there is an increase in the surface layers of associates with additive molecules, which reduce the surface activity due to weak affinity with the nucleus of deposit aggregates and, accordingly, less effect of interaction with paraffin-asphaltene components. In addition, at excessive concentrations of additives more than 5 wt.%, they are adsorbed on the surface of the ARPD, and the resulting

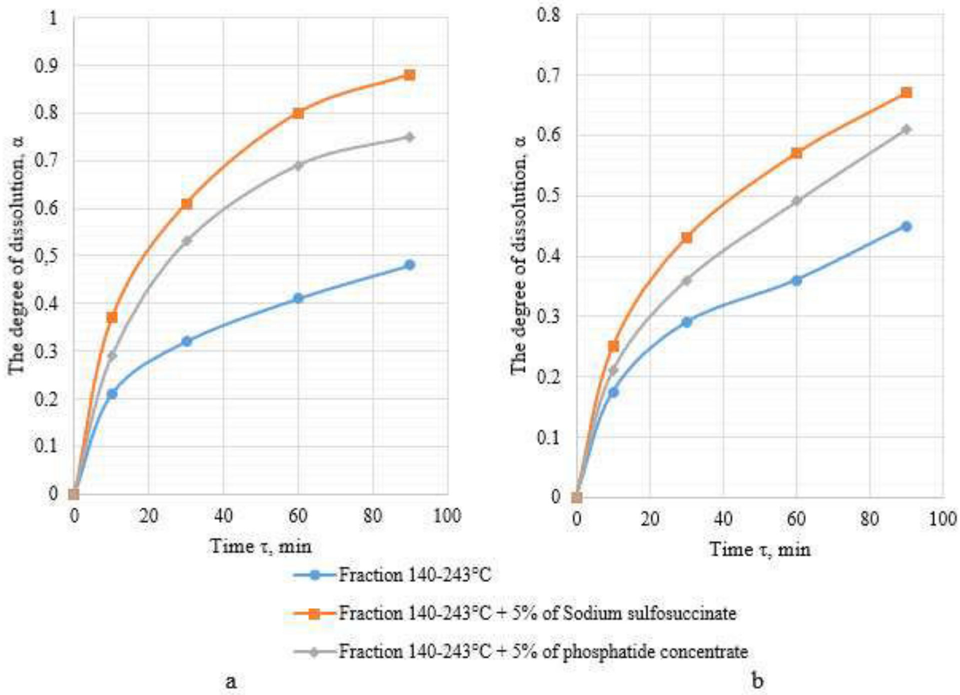

Fig. 3. The degree of dissolution of ARPDp (a) and ARPDa (b) in pure crude distilled fraction 140–243^{0}C and in crude distilled fraction 140–243^{0}C with 5 wt.% additives

polymolecular layer prevents the penetration of the active ingredients of the additives into the surface of the ARPD. The results obtained are presented in Fig. 3.

Additives are not solvents, but their introduction leads to an increase only in the «true» solubility of the components, but also in the dispersing ability of ARPD. This is evidenced by an increase in the degree of solubility for ARPDa: from 0.45 to 0.61 (phosphatide concentrate), to 0.67 (sodium sulfosuccinate); and for ARPDp: from 0.48 to 0.75 (phosphatide concentrate), to 0.88 (sodium sulfosuccinate).

To determine the constants of the dissolution rate of ARPD, we used equation (2), which after taking a logarithm has the following form:

$$-\ln(1-\alpha)=k\tau. \quad (4)$$

The results of experimental kinetic studies of dissolution of samples of ARPD deposits in the fraction 140–243^{0}C depending on the duration of contact were processed by formula (5) and presented graphically (Figs. 4, 5) to calculate the dissolution rate constant.

The graphical dependence according to equation (5) is a straight line (Figs. 4, 5), which is the main criterion that confirms the assumption that the dissolution of ARPD obeys the first order kinetics. The calculated values of the dissolution rate constant of ARPD are given in Table. 3.

The possibility of effective use of the kerosene fraction with the addition of sodium sulfosuccinate as a solvent for the extraction of ARPD of both types is confirmed by the values $\tau_{1/2}$ (60 and 30 min for ARPDa and ARPDp, respectively). In the first period of time, resins and low-melting paraffins are mainly dissolved. Then the rate of destruction and dissolution of ARPD is reduced. Probably, the solvent–ARPD system approaches the state of saturation in a thin solvent layer of solvent, which is formed around the conglomerates of ARPD. In addition, it is possible to re-aggregate (stick together) the dispersed particles of ARPD (especially asphaltene particles that have swelled), which reduces the possibility of penetration of the solvent into the conglomerates of ARPD [7].

At a fixed contact time for deposits of asphaltene and paraffin types, similar dependences are observed: the dissolution rate gradually decreases with increasing the duration of contact.

The effective influence of dispersant additives on ARPD is primarily due to the increased solubility of resins and asphaltenes present in the deposits, which are cementing agents of hard paraffin crystals. The obtained results confirm the expediency of the use of dispersant additives for the destruction of ARPD due to the joint process of dissolution and

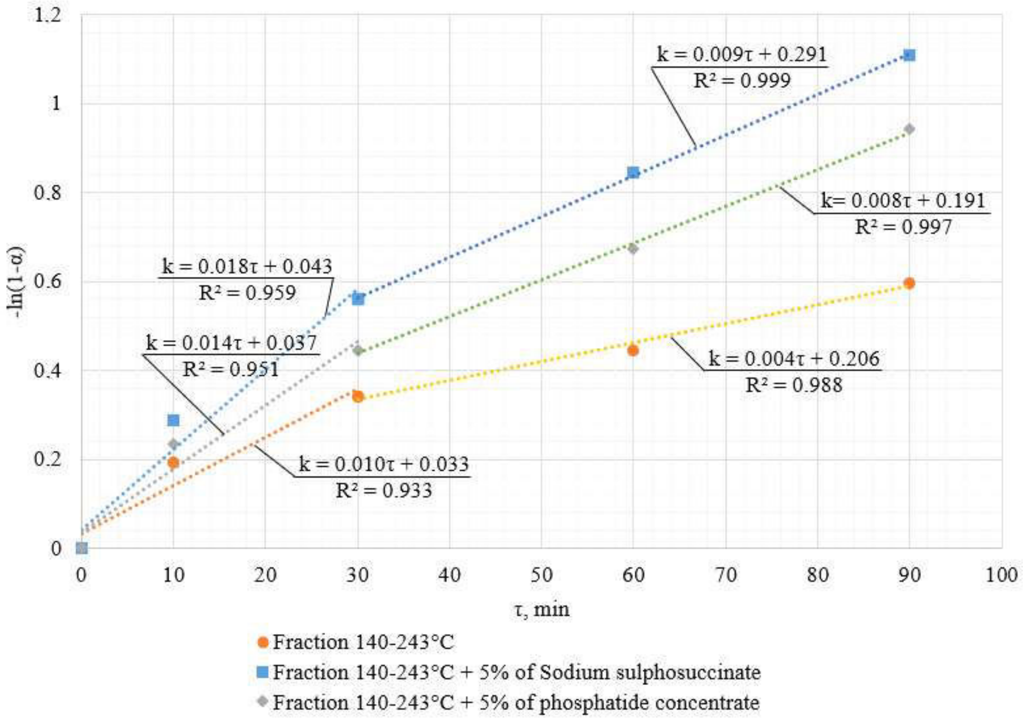

Fig. 4. Graphical determination of the constant of the dissolution rate of ARPDa in different solvents for the first and second stages of the process

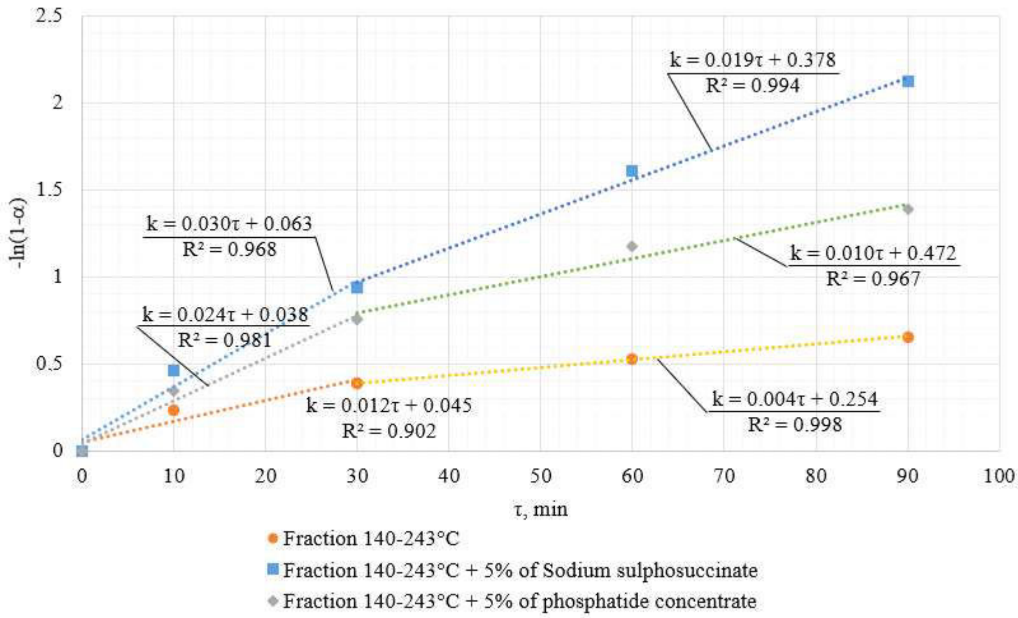

Fig. 5. Graphical determination of the constant of the dissolution rate of ARPDp in different solvents for the first and second stages of the process

dispersion.

Conclusions

1. Mechanical disposal of oil deposits does not solve the problem of their rational utilization, environmental and economic aspects of the problems associated with their use as a potential, valuable source of additional hydrocarbons.

2. Crude distilled oil fractions 110–150^{0}C, 150–200^{0}C and 140–243^{0}C proved to be the most effective for dissolving ARPD. To increase the efficiency of solvents, it is advisable to use dispersing agents.

3. It is shown that the use of dispersant additives

Table 3

Determination of the dissolution rate constant of ASP depending on the solvent composition and nature of deposits

The nature of ARPD and solvent	Stage of dissolution	The constant of the dissolution rate k, min^{-1}	$\tau_{1/2}$, min
ARPDa, fraction 140–243^{0}C	first	$1.09\cdot10^{-2}$	64
	second	$4.30\cdot10^{-3}$	
ARPDa, fraction 140–243^{0}C+5% of sodium sulphosuccinate	first	$1.80\cdot10^{-2}$	39
	second	$9.10\cdot10^{-3}$	
ARPDa, fraction 140–243^{0}C+5% of phosphatide concentrate	first	$1.43\cdot10^{-2}$	48
	second	$8.30\cdot10^{-3}$	
ARPDa, fraction 140–243^{0}C	first	$1.21\cdot10^{-2}$	57
	second	$4.50\cdot10^{-3}$	
ARPDa, fraction 140–243^{0}C+5% of sodium sulphosuccinate	first	$3.03\cdot10^{-2}$	23
	second	$1.96\cdot10^{-2}$	
ARPDa, fraction 140–243^{0}C+5% of phosphatide concentrate	first	$2.45\cdot10^{-2}$	28
	second	$1.05\cdot10^{-2}$	

increased the degree of solubility of the components of the ARPD due to the dispersing ability (for ARPDp from 0.48 to 0.88 and up to 0.75, for ARPDa from 0.45 to 0.61 and 0.67 at use of sodium sulfosuccinate and phosphatide concentrate as additives, respectively).

4. The Erofeyev-Kolmogorov equation can be used to calculate the kinetic parameters of ARPD dissolution. The kinetics of changes in the degree of ARPD dissolution is exponential. The maximum dissolution rate was observed in the first minutes of the process. After 30 minutes, the dissolution rate gradually decreases. Processing of experimental data allowed establishing the rate constants.

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КІНЕТИКА РОЗЧИНЕННЯ АСФАЛЬТО-СМОЛО-ПАРАФІНОВИХ ВІДКЛАДІВ ПРИ ДОДАВАННІ ДИСПЕРГУЮЧИХ ПРИСАДОК

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Робота присвячена визначенню кінетичних параметрів процесу розчинення асфальто-смоло-парафінових відкладів нафтовими фракціями, а також розчинниками та композиціями на їх основі. Вивчення кінетики розчинення відкладів і впливу присадок на цей процес є актуальним, оскільки застосування розчинників дозволить зменшити витрати на очищення та ремонт технологічного обладнання нафтопереробних підприємств. Здійснено серію дослідів для визначення кінетичних закономірностей розчинення асфальто-смоло-парафінових відкладів різних типів в нафтових розчинниках різного фракційного складу та впливу додавання диспергуючих присадок на цей процес. Показано, що прямогонні нафтові фракції 110–150^{0}С, 150–200^{0}С і 140–243^{0}С виявились найбільш ефективними для розчинення асфальто-смоло-парафінових відкладів. Використання диспергуючих присадок підвищує розчинність компонентів асфальто-смоло-парафінових відкладів. Кінетика розчинення підкорюється рівнянню Єрофеєва-Колмогорова.

Ключові слова: асфальто-смоло-парафіновий відклад, розчинник, резервуар, диспергуюча присадка, кінетика, паливо.

KINETICS OF DISSOLUTION OF ASPHALT-RESIN-PARAFFIN DEPOSITS WHEN ADDING DISPERSING AGENTS

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Keywords: asphalt-resin-paraffin deposits; solvent; tanks; dispersant; kinetics; fuel.

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