MORFOLOGIA E CINÉTICA DA DISSOLUÇÃO DE CERA DE PETRÓLEO EM SISTEMAS DE HIDROCARBONETOS

MORPHOLOGY AND KINETICS OF PETROLEUM WAX DISSOLUTION IN HYDROCARBON SYSTEMS

МОРФОЛОГИЯ И КИНЕТИЧЕСКИЕ ПАРАМЕТРЫ РАСТВОРЕНИЯ НЕФТЯНЫХ ПАРАФИНОВ В РАЗЛИЧНЫХ УГЛЕВОДОРОДНЫХ СИСТЕМАХ

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RESUMO

Este trabalho estuda o efeito da natureza química do solvente nos parâmetros cinéticos de dissolução e na morfologia das ceras de petróleo. A cinética da dissolução da cera de petróleo em condensado de gás e na mistura hexano-ciclo-hexano-benzeno foi examinada na balança de torção dentro da faixa de temperatura de 10 a 40 °C. O processo foi descrito usando a equação de Erofeev-Kolmogorov. Os seguintes parâmetros cinéticos foram calculados: taxa de reação, ordem de reações e energia efetiva para ativar a dissolução de cera nos solventes estudados. Verificou-se que a taxa de dissolução de cera no composto ternário é uma ordem de magnitude maior e a energia de ativação é três vezes menor em comparação com o processo de dissolução de cera no condensado de gás. As características morfológicas das amostras de cera, tratadas por estes solventes, foram examinadas por meio de microscopia eletrônica de varredura. Verificou-se que no composto ternário, a cera possui uma estrutura porosa e no condensado do gás é comprimida. Assim, o comportamento cinético e morfológico identificado das ceras de petróleo indica a influência da natureza química do solvente. Os achados deste estudo podem ser úteis na escolha do solvente para a remoção dos depósitos de parafina.

Palavras-chave: Parafina de petróleo, taxa de dissolução, modo cinético e de difusão, microscopia eletrônica de varredura, solventes de hidrocarbonetos.

ABSTRACT

This paper studies the effect of solvent chemical nature on the kinetic parameters of dissolution and the morphology of the petroleum waxes. The kinetics of the petroleum wax dissolution in gas condensate and the hexane-cyclohexane-benzene mixture was examined on the torsion balance within the temperature range from 10 to 40°C. The process was described using the Erofeev-Kolmogorov equation. The following kinetic parameters were calculated: reaction rate, the order of reactions and effective energy for activation the wax dissolution in the studied solvents. It was found that the wax dissolution rate in the ternary composite is an order of magnitude greater and the activation energy is three times less in comparison with the process of wax dissolution in the gas condensate. The morphological features of the wax samples, treated by these solvents, were examined by means of scanning electron microscopy. It was found that in the ternary composite, wax has a porous structure and in the gas condensate, it is compressed. Thus, the identified kinetic and morphological behavior of petroleum waxes indicates the influence of the chemical nature of the solvent. The findings of this study can be useful when choosing a solvent for the paraffin deposits removal.

Keywords: Petroleum paraffin, the rate of dissolution, kinetic and diffusion mode, scanning electron microscopy, hydrocarbon solvents

АННОТАЦИЯ

Цель работы – исследование влияния химической природы растворителя на кинетические параметры растворения и морфологию нефтяных парафинов. Кинетика растворения нефтяных парафинов в газовом конденсате и гексан-циклогексан-бензольной смеси исследовалась на торсионных весах в интервале температур от 10 до 40 °С. Кинетическое описание процесса выполнено при помощи уравнения Ерофеева-Колмогорова. Рассчитаны кинетические параметры: константы скоростей, порядок реакций и эффективная энергия активации растворения парафинов в исследуемых растворителях. Установлено, что скорость растворения парафинов в тройном композите на порядок выше, а энергия активации в три раза меньше, по сравнению с процессом растворения парафинов в газовом конденсате. Методом сканирующей электронной микроскопии изучены морфологические особенности обработанных этими растворителями образцов парафина. Установлено, что в тройном композите парафин имеет пористую структуру, а в газовом конденсате происходит его уплотнение. Таким образом, выявленные кинетические и морфологические особенности поведения нефтяных парафинов указывают на влияние химической природы растворителя, что позволяет осуществить целенаправленный выбор растворителя для удаления парафиновых отложений.

Ключевые слова: нефтяные парафины, порядок и константа скорости реакции, диффузионный и кинетический режим, алифатические, нафтеновые и ароматические углеводороды

INTRODUCTION

In the world's oil fields, the problem of asphaltene-resin-paraffin deposits (ARPD) is solved mainly by the thermal and chemical methods. However, systematic thermal treatment to remove ARPD in a large number of wells leads to considerable material costs. Therefore, the chemical methods are considered to be the most promising, universal and cost-effective. The essence of the chemical disposal techniques is in the preliminary destruction or dissolution followed by removal of the deposits. The methods of targeted selection and assessment of the ARPD solvent efficiency are rather well understood. The studies by Savinykh *et al.* (2007), Kamenshchikov (2008), Glushchenko *et al.* (2009), and Ibragimov *et al.* (2010) determined that the main criterion for choosing a solvent is the ARPD type. Depending on the components contained in ARPD in high concentrations, ARPD can be of paraffin, asphaltene and mixed type. Ragulin *et al.* (2001) showed the effective solvents for paraffin ARPD are low-boiling aliphatic hydrocarbons (HC) such as pentane, hexane, and heptanes. Khisamutdinov *et al.* (1990) proved that, for asphaltene ARPD removal, the solvents based on aromatic hydrocarbons should be used. However, using reagents, selected only on the basis of the ARPD type, does not always give positive results in the oilfields. This is because the reagents for paraffin

deposits removal are assessed and selected without regard to the physical and chemical nature and the diversity of the intermolecular interactions of the multicomponent solvents with the high molecular weight compounds of oil; lack of information on the properties of reagents, included in solvent composition, also plays a role (Dolomatov *et al.*, 1991, Kamenshchikov, 2008).

Thus, this paper aims to study the effect of solvent chemical nature on the kinetic parameters of dissolution and the morphology of the petroleum waxes. This work is a continuation of research on assessment and selection of the effective reagents for paraffin deposits (Ivanova *et al.*, 2014, Ivanova *et al.*, 2015). Previously, it was determined that the degree of petroleum wax crystallinity in various model solvents increases in the solvents series: aliphatic-naphthenic-aromatic → aliphatic-aromatic → aliphatic-naphthenic → aliphatic. It was also found that the temperature of the crystallization and melting of wax in the aliphatic and aliphatic-naphthenic-aromatic solvents is characterized by maximum values as compared to the aliphatic-aromatic systems.

MATERIALS AND METHODS

Since the ARPD in the Irelyakhskoe field (Yakutia, Russia) belong to paraffin type, the B2 petroleum wax (GOST 23683-89, 2007) was selected as the model of paraffin ARPD. This highly-purified paraffin contains no water or

mechanical impurities that may distort the experimental results. The following was studied as solvents of paraffin: gas condensate of alkane base, which is currently used in the Irel'yakhskoe field for removing ARPD deposits, and composite mixture, consisting of hexane, benzene and cyclohexane (HBCG) in ratios 1:1:1. The kinetics of paraffin dissolution in hexane and hexane-benzene mixture was examined by Ivanova (2014). The kinetics of paraffin dissolution in these HC was studied gravimetrically on the VLKT 500 torsion balance at temperatures 10 and 25°C, which correspond to the seasonal operating conditions at the Irel'yakhskoe field, and 40°C to determine the overall dependency of paraffin dissolution rate from temperature. The degree of dissolution (α) was calculated as the ratio of melted paraffin to its original total mass in the sample. The amount of solvent in the experiments was 70 cm³. The statistical calculation of the kinetic model parameters, expressed in linear form, was carried out by the least squares method using t-distribution with a confidence probability of 0.95 (Klinger, 1972). At least three tests of each sample were conducted.

In order to study the morphology of the samples in the pre-weighted weighing bottles, 10% paraffin solutions were prepared in the HC systems under study. The weighing bottles with the contents were brought to the permanent weight in the drying oven. The microphotographs of the samples were obtained by the JCM-7800F Jeol scanning electron microscope (Japan). The sample was secured on the two-sided conducting adhesive tape pasted to a metal substrate. The samples were studied by means of secondary electrons at a low accelerating voltage (a Schottky cathode), which provides a quality image without the conducting surface layer and helps to avoid distortion of the structure at a high magnification.

RESULTS AND DISCUSSION:

Figure 1 shows the kinetic curves of paraffin dissolution in HC solvents.

Figure 1. Kinetic curves of the petroleum wax dissolution in the gas condensate (A) and the hexane-cyclohexane-benzene mixture (B) at 10, 25 and 40°C, where α is the dissolution degree and τ is the time (min).

It is evident that the paraffin dissolution rate in the gas condensate is significantly dependent on temperature, as compared to the composite mixture. The curves geometry indicates that the paraffin dissolution in the studied reagents proceeded from the maximum initial rate. In case of HBCG, this could be explained by a sufficiently high chemical activity of the solvent, and in the case of gas condensate, by the influence of temperature. Rozovsky (1974) showed that such processes are well described by the Erofeev-Kholmogorov equation (Eq.1):

$$\alpha = 1 - e^{-kt^n} \quad (\text{Eq. 1})$$

where α is the degree of paraffin dissolution; k is the invariant defining the reaction rate constant; n is the invariant defining the process nature: at $n < 1$, it is the diffusion process; at $n > 1$, it is the kinetic process; at $n = 1$, it is the first order reaction, and the chemical reaction rate is comparable with the diffusion rate.

The dissolution rate constants were found by the Sakovitch formula (Eq.2):

$$K = nk^{\frac{1}{n}} \quad (\text{Eq. 2})$$

To characterize the rate of the first-order reaction, together with the rate constant, we used the half-life value. This value does not depend on the initial concentration of the source substance and is described by Eq.3 (Delmon, 1972):

$$\tau_{\frac{1}{2}} = \frac{\ln 2}{K} \quad (\text{Eq. 3})$$

According to the obtained experimental data, the logarithmic anamorphoses of the kinetic curves were plotted in coordinates $\lg[\lg(1-\alpha)] - \lg\tau$ (Figure 2). Parameter n , defined as the trend line slope ratio, allows establishing the order of reaction and the rate-controlling step of paraffin dissolution in the HC systems under study. The rectification of the experimental curves in a wide range of time indicates a fair choice of the equation to describe the kinetics of dissolution.

Figure 2. Logarithmic anamorphoses of the kinetic curves for petroleum wax dissolution in the gas condensate (A) and hexane-cyclohexane-benzene mixture (B) at 10, 25 and 40°C.

The kinetic parameters of the paraffin dissolution in the HC systems, determined by Equations 1, 2 and 3, are given in Table 1.

Table 1 shows that the process of paraffin destruction in the gas condensate at 10°C is diffusion controlled ($n < 1$), but when heated to 25°C or above, the process shifts to the kinetic model ($n \geq 1$). In the hexane-cyclohexane-benzene

mixture, the process proceeds in the kinetic area ($n > 1$) at different temperatures. The paraffin destruction is most likely to take place in the ternary composite, as the process is characterized by a low value of $\tau_{\frac{1}{2}}$ and an

efficient energy of activation (34.6 kJ/mol), while in hexane the energy of paraffin destruction activation is 125.2 kJ/mol (Ivanova, 2014). In the gas condensate and in the hexane-benzene mixture, the activation energy has intermediate values: 106.9 and 90.3 kJ/mol respectively. The obtained results agree with the findings of Ivanova *et al.* (2014), where it was found that the dissolution rate constants for the oilfield paraffin type ARPD in the ternary solvent is an order of magnitude greater, as compared to the aliphatic systems, and the process is characterized by a lower effective energy of activation. The studies of paraffin destruction kinetics at higher temperatures made it possible to establish the dependence of logarithm of the dissolution rate constant on the value of the reciprocal temperature (Figure 3).

Figure 3. Dependence of the dissolution rate constants K in the gas condensate and the hexane-cyclohexane-benzene mixture on $1/T$

It can be seen that for the models under study, the experimental data on the graph in coordinates $\lg K - 1/T$ are placed on the fractured lines, indicating the deviation from the temperature dependence of the dissolution rate constants in these systems on the Arrhenius equation. This can be explained by the fact that the measured rate constant refers to more than one stage of the reaction.

Thus, based on the kinetic studies, the composite solvent, consisting of aliphatic, aromatic and naphthenic HC, can be recommended for the removal of paraffin deposits, since in this solvent, the dissolution rate constant has maximum values and the process of paraffin destruction is characterized by the minimum value of effective activation energy.

The influence of the solvent chemical nature on the paraffin crystals morphology was examined by scanning electron microscopy. The microphotographs of the paraffin samples, treated with the studied solvents, are shown in Figures 4 and 5.

According to the microscopy data, the petroleum paraffin (Ivanova *et al.*, 2015) has a dense thin-layered structure; the distance between the layers is 7-12 nm; the thickness of the layers is 25-28.4 nm. In aliphatic solvents, paraffin has a predominantly monolithic structure: in the gas condensate (Figure 4) the thickness of the layer reaches 76.9 nm and the distance between layers 163 nm, in hexane (Ivanova *et al.*, 2015) these parameters are 44.2 nm and 20.6 nm, respectively. Hence the process of paraffin dissolution in aliphatic solvents can be characterized by the highest values of effective activation energy. After the treatment with an aliphatic-aromatic solvent (Ivanova *et al.*, 2015), the paraffin crystal formed a large number of cracks, whose width varies from 87 to 573 nm. In the ternary composite (Figure 5), the layer thickness is 57.6 nm, and the distance between layers varies from 46.5 to 427 nm. In this case, the pores are clearly visible on the crystal surface. The pores have 24-29.3 nm in diameter, and the distance between them is from 32.5 to 33.9 nm.

The specified structural features adequately correlate with the kinetic studies and together show the effects of the solvent on the morphological and kinetic parameters of the wax samples dissolution: in the series of aliphatic-naphthenic-aromatic → aliphatic-aromatic → aliphatic solvents the reagents' effectiveness for the paraffin removal is reduced. Therefore, a composite solvent, consisting of aliphatic, aromatic and naphthenic HC should be recommended for the paraffin deposits removal, as in this solvent the paraffin obtains a porous structure and the paraffin destruction proceeds at a high speed and with a low activation energy.

It should be noted, however, that when selecting a solvent to remove paraffin deposits in

the conditions of low climatic temperatures and permafrost, it is necessary to take into account the temperature of paraffin crystallization in potentially effective solvents. Thus, Ivanova *et al.* (2015) found that the temperature of petroleum and oilfield paraffin crystallization in the aliphatic-naphthenic-aromatic solvents has maximum values, as compared to the aliphatic-aromatic solvents. In the gas condensate (Ivanova *et al.*, 2015) which is currently used in the Irelyakhskoe field to clean the oil extraction equipment from paraffin deposits, the petroleum paraffin crystallites appear at 30.1°C, and when the aromatic components are added, the crystallization temperature decreases to 24.1°C. For the field of paraffin, these temperatures are 21.8 and 9.1°C, respectively. The findings testify in favor of the use of aliphatic-aromatic reagents in the permafrost conditions.

CONCLUSIONS:

This study confirmed that the solvent chemical nature influences the morphological and kinetic parameters of the paraffin dissolution. The kinetic and morphological studies, as well as the comparison with the findings of Ivanova *et al.* (2014) and Ivanova *et al.* (2015), showed that the use of gas condensate to clean the oil extraction equipment from paraffin is less effective. A better solution for this purpose would be the aliphatic-aromatic-naphthenic solvent. Also, the composite binary aliphatic-aromatic solvents can be recommended to remove the paraffin deposits generated during oil-field development in the permafrost conditions.

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Table 1. Rates constants $\tau_{\frac{1}{2}}$ and energy for activation of paraffin dissolution in the gas condensate and HBCG.

Sample	T (°C)	N	K (min ⁻¹)	$\tau_{\frac{1}{2}}$ (min)	Ea (kJ/mol)
Paraffin + Gas condensate	10	0.89±0.12	1.84*10 ⁻²	37.67	106.9
	25	1.44±0.21	1.81*10 ⁻¹	3.83	
	40	0.93±0.17	2.18*10 ⁻¹	3.18	
Paraffin + Hexane + Benzene + Cyclohexane (1:1:1)	10	1.92±0.09	1.47*10 ⁻¹	-	34.6
	25	1.25±0.15	3.08*10 ⁻¹	2.25	
	40	1.86±0.15	1.32	-

Figure 4. Microphotographs of the crude oil paraffin B2 sample treated with the gas condensate; scale leg: a, b – 10 μm; c, d – 100 nm

Figure 5. Microphotographs of the crude oil paraffin B2 sample treated with the hexane-benzene-cyclohexane mixture; scale leg: a, b – 10 μm ; c, d – 100 nm