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USE OF A KINETIC STUDY FOR THE EFFECTIVENESS EVALUATION OF ASPHALTENE-RESIN-PARAFFIN DEPOSITS (ARPD) SOLVENTS

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***Abstract**. The process of the paraffin type asphaltene-resin-paraffin deposits dissolution in the alkane base gas condensate, hexane-benzene mixture (HBM) and hexane at 10 and 25°C is investigated. These deposits are formed during oil production in the Irelyakh field. The comparative effectiveness evaluation of studied solvents is performed by the widely used in practice "baskets" method and the results of kinetic studies.*

***Keywords:** asphaltene-resin-paraffin deposits, APRD, gas condensate, solvents, reaction order, rate constant, diffusion and the kinetic regime*

As the world's scientific and practical experience is shown, one of the promising directions in the fight against deposits of solid hydrocarbons (HC) and asphaltene-resin substances formed in the walls of oilfield equipment during production, collection and transportation of oil, is the use of different reagents – removers. Compositions of aliphatic and aromatic hydrocarbons are usually used as such removers [1]. This combination of components corresponds to the composition of the ARPD, and is most beneficial for their dissolution.

The problem of the ARPD formation in the Irelyakh gas and oil field has arisen since its operation in 1992. It should be noted that the deposit is located in the zone of continuous permafrost, so the reservoir temperature does not exceed 10 - 16 °C, and in the produced fluids is dominated by methane-naphthenic hydrocarbons [2]. These factors have led to intensive processes of crystallization and coagulation of the ARPD directly in the bed, his face zone and on the surface of oilfield equipment. To eliminate the negative ARPD effects every year about 300 m^3 of gas condensate is pumped into the elevator tubing, however, to completely clean the equipment from the sediments is not possible. For removal of the ARPD in the autumn-winter season it requires a larger volume of the condensate compared to the spring-summer period [3].

One of the most widely used methods for the effectiveness evaluating of solvents is a "method of baskets" [1]. But, often, well-proven in the lab solvents sediments often show poor performance in the fields. Mostly, this can be explained by the fact that the choice of solvent does not take into account the physical and chemical processes occurring at the interface solvent - ARPD [4]. In this regard need to search for a new approach to directional selection of solvents. In our view, the choice of reactant or compositions for removing deposits should take into account the kinetic aspects of the dissolution process. Exactly kinetic studies will find analytical expressions for the solvent effectiveness evaluating on the basis of ideas about nature, the sequence of stages and speeds of the dissolution process. This information will allow to carry out a purposeful selection of a reagent for the efficient removal of sediments and to optimize the conditions of this process.

The experimental part

The ARPD of the paraffin-type were used in the experiments [3], they are formed on the surfaces of the tubing in Irelyakh GOF. The surface temperature of the tubing in the autumn-winter period is not more than 10 °C, and in the spring and summer it does not exceed 25 °C, so that all research conducted at these temperatures.

As the ARPD solvents were studied: gas condensate, which is now used on Irelyakh field to remove the ARPD [3], hexane, as a model of the light fraction of the condensate and the composite mixture of hexane and benzene (HBM) in a 1:1 ratio.

The solvents effectiveness evaluation was made in two ways: "by the baskets," and the results of kinetic studies.

"The method of baskets", the effectiveness of the reagent was estimated from the change of the sediment mass when it is exposed to solvents: the temperature of the experiment, 10 and 25 °C, contact time – 4 hours, static conditions. The detergency solvents, as a universal indicator of efficiency, are shown in Table 1.

Table 1. The effectiveness of the ARPD destruction by various hydrocarbon solvents

Detergency, % mass.	*t*, ºC	Reagents		
		Gas condensate	Hexane	Hexane-benzene mixture
	10	38	87	100
	25	63	97	100

It is established that the use of gas condensate at any temperature is not the best choice for removing sediments from the surface of the oilfield equipment. Most effectively the structure of the paraffin ARPD is destroyed by hexane and HBM because the composition of these reagents contains low-boiling aliphatic hydrocarbons, which are quite good solvents of paraffin hydrocarbons. Thus, on the basis of the results obtained "by the baskets," to remove the paraffin on the Irelyakh field at low reservoir temperatures we can recommend the fractionated condensate or composite aliphatic-aromatic solvent.

Investigation of the ARPD dissolution kinetics in the above systems was carried out gravimetrically in static conditions at temperatures of 10 and 25 °C. The degree of dissolution was calculated as the ratio of the dissolved ARPD initially taken to its total mass in the sample. The volume of the solvent in the experiments was fixed and was 70 cm^3. Statistical calculation of kinetic models parameters, expressed in linear form was carried out the least squares method using the *t*-distribution at P = 0.95 [5].

There are obtained kinetic curves of the ARPD dissolution in the hydrocarbon solvents at different temperatures (Fig. 1) in the coordinates of the dissolution rate (α) - time (τ). It is seen that the dissolution rate of the ARPD in a gas condensate, as compared to hexane and HBM, essentially independent of temperature. Analysis of the shape of the curves showed that the dissolution of the ARPD in the studied solvents is characterized by the maximum initial velocity. In the case of hexane and HBM it can be explained by relatively high chemical activity of the solvent, and in the case of gas condensate - the influence of temperature. However, with the increasing dissolution the rate of the processes gradually reduced.

Similar processes [6], are well described by the Erofeev-Kolmogorov equation:

$$\alpha = 1 - e^{-kt^n}, \quad (1)$$

where the α – degree of the ARPD dissolution; k – a constant that determines the reaction rate constant; n – a constant, which determines the nature of the process: if $n < 1$ – a diffusion process; $n > 1$ – kinetic process; $n = 1$ – first-order reaction, the rate of chemical reaction comparable to the rate of diffusion.

To transfer rate constants in the dimension of the min^{-1} we used the formula of Sakovich [7], (Table 2):

$$K = n\,k^{\frac{1}{n}} \quad (2).$$

According to the experimental data the kinetic curves were constructed in coordinates lg[–lg(1–α)] - lg τ (Fig. 2). The parameter n, defined as the slope of the lines trend, allows us to establish the order of reaction and the limiting stage of the ARPD dissolution in the studied systems.

Defined by the equation (1) kinetic parameters of the process of the ARPD dissolution and the magnitude of the reliability of the approximation are given in Table 2.

High values of the magnitude the reliability of the approximation, as well as flattening of the experimental curves over a wide range of time testify to the choice of a just solution of the equation to describe the kinetics of dissolution.

It is evident that the ARPD destruction process in the gas condensate and in hexane as a model of the condensate light fraction, flows in the diffusion region ($n < 1$), so in the autumn and winter operation of wells to achieve the complete removal of the ARPD from the surface of oil drilling equipment, using as solvents these reagents is almost impossible. But when these solvents are heated to 25 °C the process begins to flow as a first-order reaction. That is, at higher temperatures there is an intensification of diffusion processes, and the rate of physic-chemical interaction with the solvent components of the ARPD becomes comparable with the rate of diffusion. Therefore, in the spring and summer to remove sediments it requires a smaller volume of condensate over the fall and winter. The ARPD dissolution in HBM at different temperatures occurs as a first-order reaction.

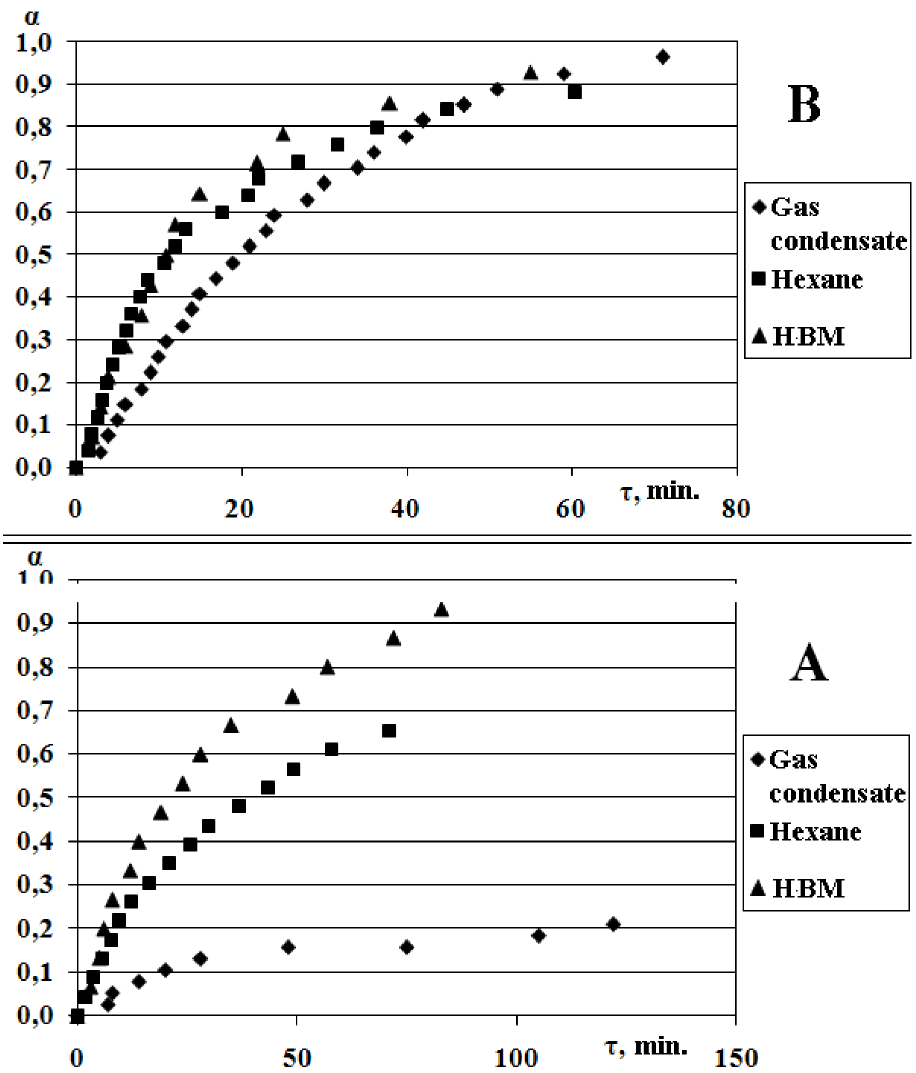

Fig. 1 Kinetic curves of the ARPD dissolving in the gas condensate, hexane, and HBM at 10 (A) and 25 °C (B)

Table 2. The constants of the ARPD dissolution process and the magnitude of the reliability of the approximation (r^2)

Model systems:		*n*	*k*	r^2
Sample	*t*, °C			
ARPD + Gas condensate	10	0.50 ± 0.04	$1.30*10^{-2}$	0.943
	25	1.25 ± 0.08	$1.60*10^{-2}$	0.996
ARPD + HBM	10	1.00 ± 0.07	$3.20*10^{-2}$	0.981
	25	1.05 ± 0.13	$5.00*10^{-2}$	0.975
ARPD + Hexane	10	0.84 ± 0.04	$3.60*10^{-2}$	0.991
	25	0.97 ± 0.03	$5.50*10^{-2}$	0.952

In our view, the effectiveness of the solvent will be high if the rate of the ARPD dissolution will not be limited either the rate of chemical reactions at the interface, or diffusion. In this case, this condition is fulfilled: 1) during the heating of the gas condensate and its light fraction, and 2) using the solvent composition.

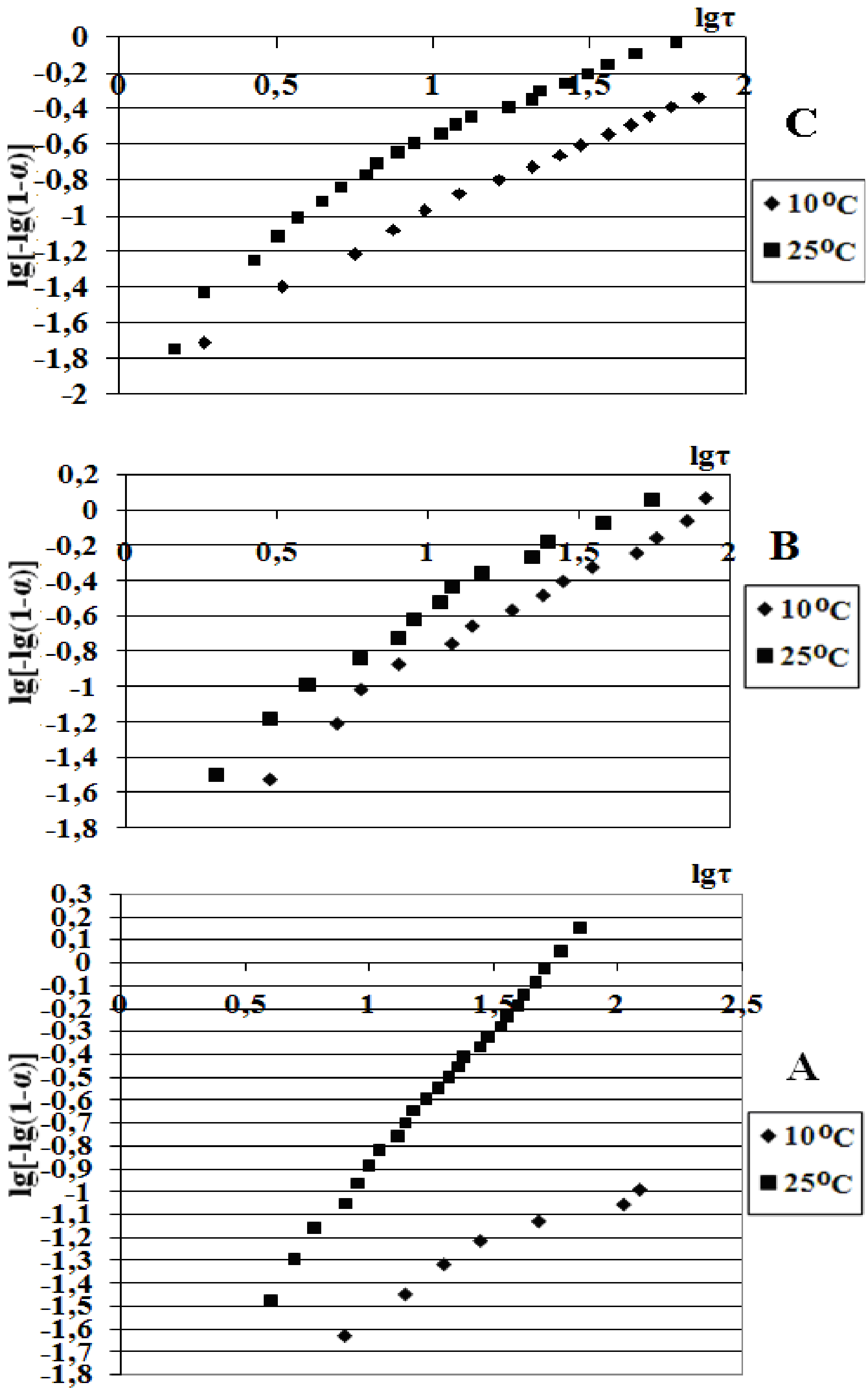

Fig. 2. Logarithmic anamorphosis of the kinetic curves of the ARPD dissolution in the gas condensate (A), HBM (B) and hexane (C) at 10 and 25 °C

To characterize the reaction rate of first-order rate constant, along with use value, called the half-period. This value does not depend on the initial concentration of starting material and is described by the formula [6]:

$$\tau_1/2 = \ln 2/K \quad (3).$$

Equation (3) makes it possible to calculate the time at which half of the ARPD amount will be dissolved in the gas condensate, HBM, and hexane, and when the ARPD dissolution in these hydrocarbons proceeds as a first-order reaction. In Table 3 is shown the rate constants found by the formula (2), values of $\tau_1/2$, and the effective activation energy of the ARPD destruction in solvents.

Table 3. The rate constants, $\tau_1/2$ and activation energy of the ARPD dissolution in the condensate, HBM and hexane

Model systems:		K, min^{-1}	$\tau_1/2$, min	Ea, kJ/mol
Sample	t, °C			
ARPD + Gas condensate	10	8.45*10^{-5}	-	292.60
	25	4.42*10^{-2}	15.68	
ARPD + HBM	10	3.10*10^{-2}	22.36	31.64
	25	6.10*10^{-2}	11.36	
ARPD + Hexane	10	1.61*10^{-2}	0.00	51.93
	25	4.89*10^{-2}	12.60	

It is seen that the rate constant of the ARPD dissolution in the gas condensate when heated increases by three orders of magnitude and the dissolution rate of the ARPD in HBM and hexane also increased, but only slightly, within the same order. The rate constants of the ARPD dissolution in HBM at 10 °C and in the heated condensate and hexane are practically identical. Low value of $\tau_1/2$ of the ARPD dissolution in HBM, also points to the possibility of effective use of HBM for the removal of the ARPD at low temperatures. In addition, the process of the ARPD paraffin type dissolving in HBM is characterized by a lower value of effective activation energy in comparison with other solvents.

Thus, the use of gas condensate or its light fraction to remove deposits from the surface of oilfield equipment in the autumn-winter period from the wells in the Irelyakh field is ineffective because the ARPD dissolution process in these reagents is limited by diffusion. But the hot solvent treatment during the cold season should be avoided, since such procedures lead to the recrystallization of wax and as a consequence of the formation of more insoluble deposits. In addition, the heating of low-boiling fractions of fire and explosion hazard. Therefore, condensate and its light fraction to remove the deposits do not fit. The process of the ARPD dissolving in aliphatic-aromatic solvent proceeds as a first-order reaction, has a small value of $\tau_1/2$ and is characterized by a low effective activation energy. These factors are favoring for composite solvents using to remove the paraffin-type deposits in the wells of the Irelyakh GOF, as in the cold and in warm weather.

Conclusions

It is established that the results of the solvent effectiveness evaluating derived "by the baskets," and from the standpoint of the formal-kinetic approach is almost the same, but based on the results of kinetic studies, it is possible to conduct a more complete assessment of the solvents effectiveness to remove deposits compared to the "method of baskets." Established, if the process of the ARPD dissolving in the reagent has the following kinetic characteristics: the order of dissolution reaction is unity, and the low values of $\tau_1/2$ and activation energy, the use of a solvent to remove the deposits is the most technologically. It is possible that the results of kinetic studies will be used as an additional tool in technological solutions in the choice of solvents.

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