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# Kinetic Parameters of Dissolution of Asphalt-Tar-Paraffin Deposits in Some Hydrocarbon Solvents

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## Abstract

The process of dissolution of asphalt-tar-paraffin deposits of paraffinaceous type in the gas condensate of alkane basis and a mixture of hexane with benzene at a temperature of 10 and 25 °C was investigated. The kinetic description of the process was made with the help of Erofeev–Kolmogorov equation. Kinetic parameters were calculated: rate constants, activation energies and orders of the reactions of dissolution of asphalt-tar-paraffin deposits in the solvents under investigation.

**Key words:** asphalt-tar-paraffin deposits, gas condensate, aliphatic-aromatic solvent, reaction order, rate constant

## INTRODUCTION

One of the basic methods for fighting against the sediments of solid hydrocarbons (HC) and asphalt resinous substances formed on the walls of oil field equipment in oil extraction, gathering and transport of oil is the use of different reagents as removers. The products of refining and petrochemical production are used as removers, for example, hexane, butyl benzene and xylene fractions, illuminating oil, *etc.* [1]. In general, these products contain hydrocarbons of the homologous series of methane and benzene.

Despite the fact that a significant amount of work is dealing with the development of the methodological foundations for directed selection of solvents for efficient removal of asphalt-tar-paraffin deposits (ATPD), and the evaluation of solvents is performed by means of sufficiently reliable methods, often results obtained through these methods do not match with those of oil-field tests. This can be explained by the fact that the choice of solvent is made without taking into account physicochemical phenomena occurring in the system solvent–ATPD. This is mainly due to the lack of information on the mechanism of sediment interaction with solvents. Therefore, it is important and urgent to search for a new approach to determine the effectiveness of ATPD solvents: the choice of solvent for the efficient removal should take into account the kinetic aspects of dissolution. Kinetic studies will allow us to understand the mechanism of dissolution, to identify simple stages of the process and reveal possible interconnections between these stages. The value of the kinetic information, in particular for the process under study, is the possibility to optimize the chemical process.

In this paper we make an attempt to establish the basic kinetic regularities of the dissolution of ATPD in gas condensate, which is currently used as a reagent to remove deposits at the Irelyakh gas and oil field (GOD), and in the model of aliphatic-aromatic solvent, in order to assess their effectiveness in removing the deposits.

## EXPERIMENTAL

With the immersion of ATPD into a hydrocarbon solvent, the probability for solvent molecules to penetrate deep into ATPD is small, so the dissolution of the components of ATPD takes place mainly at the interface ATPD solvent. Thereforeë the total rate of ATPD dissolution as a form of heterogeneous reactions is the sum of the rates of two successive micro stages: the physicochemical interaction of ATPD components with the solvent and the diffusion of products from the surface of the sediments into the solution [12, 13]. Thus, the rate of ATPD dissolution is formed as a result of the relations between the rates of these micro-stages and is limited by the slowest reaction, which determines the kinetic or diffusion mode (region) of the dissolution process. However, there is no strict boundary between these regions: they are overlapped by so-called transition region, in which the rates of these stages are comparable.

We used the ATPD of paraffinaceous type (type $P_3$) [14] formed on the surfaces of oil well tubing during oil production at the Irelyakh GOF (Yakutia). The temperature of oil pool does not exceed 10–16 °C.

Investigation of the kinetics of ATDP dissolution was carried out by means of gravimetry at a temperature of 10 and 25 °C. Gas condensate [14] and a composite mixture of hexane and benzene (HBM) in the ratio of 1 : 1 were used as solvents for ATPD.

Statistical calculation of the parameters of kinetic models, expressed in the linear form, was performed by least squares using the $t$-distribution at $P = 0.95$.

The degree of dissolution was calculated as the ratio of dissolved ATPD to its total mass in the sample.

## RESULTS AND DISCUSSION

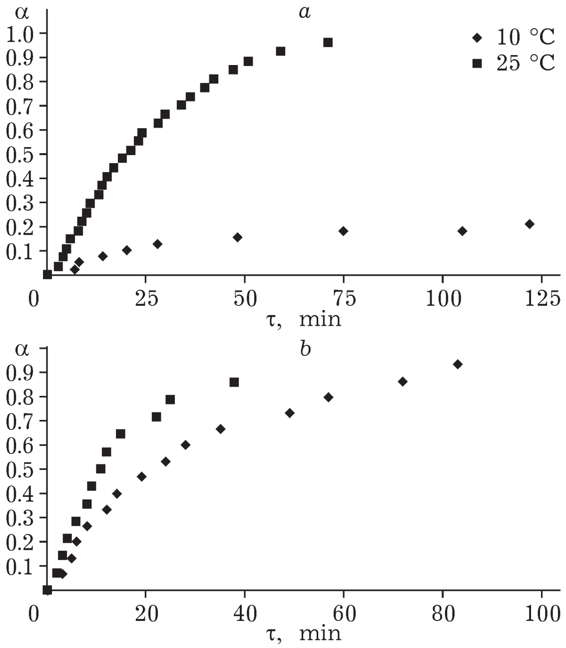

Fig. 1. Kinetic curves of ATPD dissolving in gas condensate (*a*) and HBM (*b*) in different temperatures.

The kinetic curves obtained for ATPD dissolution in HC solvents at different temperatures are shown in Fig. 1 as a dependence of dissolution rate (α) on time (τ). One can see that, compared to the rate of ATPD dissolution in HBM, the dissolution of ATPD in gas condensate is strongly dependent on temperature. Analysis of the shape the obtained curves showed that the dissolution of ATPD in the studied solvents refers to the class of reactions with the maximum initial rate. In the case of HBM, this can be explained by rather high chemical activity of the solvent, while in the case of gas condensate – by the influence of temperature. However, with an increase in the degree of dissolution, reaction rate gradually decreases. Such reactions are described by the well-known equation of Erofeev–Kolmogorov [15]:

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

Here α is the rate of ATPD dissolution; $k$ is a constant that determines the rate constant of the reaction; $n$ is a constant defining the type of the process: for $n < 1$ we have a diffusion process; for $n > 1$ we have a kinetic process; for $n = 1$ we have the first-order reaction, the rate of the chemical reaction is comparable to the rate of diffusion.

Reaction rate constants were determined using Sakovich's equation:

$$K = nk^{1/n} \qquad (2)$$

Kinetic parameters of ATPD dissolution in the studied solvents determined using equation (1) and the values of approximation reliability are presented in Table 1.

TABLE 1

Constants of ATPD dissolution process and the value of approximation reliability ($r^2$)

| Process temperature, °C | $n$ | $k$, $\text{min}^{-1}$ | $r^2$ |
|---|---|---|---|
| | **ATPD + gas condensate** | | |
| 10 | 0.50±0.04 | 0.0130 | 0.943 |
| 25 | 1.25±0.08 | 0.0160 | 0.996 |
| | **ATPD + HBM (1 : 1)** | | |
| 10 | 1.00±0.07 | 0.0320 | 0.981 |
| 25 | 1.05±0.13 | 0.0500 | 0.975 |

The data shown in Fig. 2 and the values obtained for reliability of approximation confirm the validity of the choice of the equation, because the experimental curves straighten in the coordinates log [−log (1 − α)] − log τ within a wide time range.

Parameter $n$, defined as the tangent of slope angle of the trend line, allows one to determine reaction order and the limiting step of ATPD dissolution in the studied solvents. Thus, the values obtained for n (Table 1) indicate that the reaction order of ATPD dissolution in gas condensate at 10 °C is less than unity ($n = 0.5$), so the process is limited by diffusion, but when the solvent is heated to 25 °C, the reaction becomes first-order. Therefore, with temperature rise, diffusion processes are intensified, and the rate of the physicochemical interaction between ATPD components and the solvent becomes comparable with the rate of their diffusion. In HBM, the reaction of ATPD dissolution is the first-order process at different temperatures.

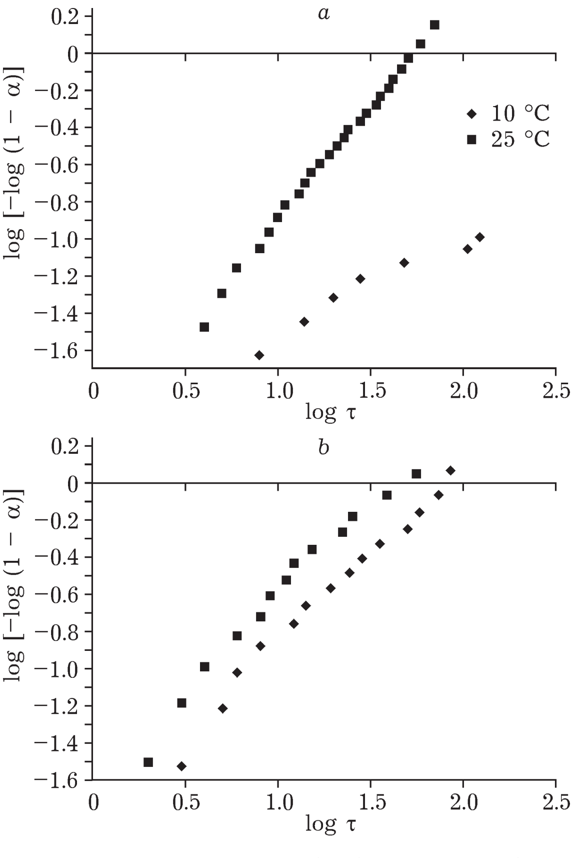

Fig. 2. Kinetic curves of ATPD dissolving in gas condensate (*a*) and HBM (*b*) in different temperatures.

We think that the effectiveness of a solvent in removing deposits will be high in the case if the rate of ATPD dissolution is not limited either by the rate of chemical reaction at the interface or by diffusion, so the dissolution must be a first-order reaction. In our case, this is achieved under two conditions: 1) heating of gas condensate, and 2) the use of aliphatic-aromatic solvent.

Along with the rate constant, the half-life ($\tau_{1/2}$) value is also used to characterize the rates of the first-order reactions. This value is independent of the starting concentration of the initial substance and is described by the equation [15]

$$\tau_{1/2} = \ln 2/K \quad (3)$$

Using this expression, we can determine the time within which a half of ATPD amount will be dissolved in gas condensate and HBM in the cases if ATPD dissolution in these HC proceeds as a first-order reaction. The data on rate constants determined using eq. (2), $\tau_{1/2}$ and the effective activation energy of ATPD destruction in solvents are presented in Table 2.

One can see that the rate constant of ATPD dissolution in gas condensate at a temperature increased by 15 °C increases by three orders of magnitude, and the rate of ATPD dissolution in HBM increases only slightly (within the order of the reaction). The rate constants of ATPD dissolution in HBM at 10 °C and in hot condensate practically coincide. The low value of $\tau_{1/2}$ of ATPD dissolution in HBM at 10 °C also points to the possibility of efficient use of HBM to remove ATPD at low temperatures. The dissolution of ATPD in HBM is characterized by a lower effective activation energy compared with gas condensate. This is the evidence that ATPD is easily destroyed in the binary solvent.

TABLE 2

Rate constants, the value of $\tau_{1/2}$, the activation energy of dissolution of ATPD in gas condensate and HBM

| Process temperature, °C | $K$, min$^{-1}$ | $\tau_{1/2}$, min | $E_a$, kJ/mol |
|---|---|---|---|
| | *ATPD + gas condensate* | | |
| 10 | $8.45 \cdot 10^{-5}$ | – | 292.60 |
| 25 | $4.42 \cdot 10^{-2}$ | 15.68 | |
| | *ATPD + HBM (1 : 1)* | | |
| 10 | $3.10 \cdot 10^{-2}$ | 22.36 | 31.64 |
| 25 | $6.10 \cdot 10^{-2}$ | 11.36 | |

Thus, it is inefficient to use gas condensate to remove deposits at the oil fields of the Nepa-Botuoba anteclise located in the zone of continuous permafrost because the dissolution of ATPD in the gas condensate is limited by diffusion. In this connection, it is impossible to achieve complete removal of the deposits from the surface of oil-field equipment. Treatment with hot condensate is also unreasonable because such procedures lead to recrystallization of paraffin and, consequently, to the formation of even more difficultly soluble deposits; it would be a much more complicated problem to remove them. The reaction of ATPD dissolution in the aliphatic-aromatic solvent at low temperatures is the first-order reaction with a small $\tau_{1/2}$ value, and it is characterized by the low effective activation energy. The listed factors provide evidence that composite solvents are promising for the removal of paraffinaceous type ATPD at low temperatures.

## CONCLUSION

It is shown in the investigation of the processes of ATPD dissolution in gas condensate and in the mixture of hexane with benzene at different temperatures as example that the results of kinetic studies can serve to evaluate the efficiency of solvents in removing the deposits. It is established that in the case if the process of ATPD dissolution in a reagent has the following kinetic parameters: the order of dissolution reaction is equal to unity; low values of $\tau_{1/2}$ and activation energy, – the use of this solvent to remove ATPD will be the most efficient. The proposed kinetic approach can be used as an additional tool to choose and evaluate the efficiency of the use of solvents.

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