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Mechanism and Kinetics of Dissolution of Asphaltene Resinous Substances in Organic Solvents

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ABSTRACT: *The results of an experimental study of the process of dissolution of asphalt-resinous substances in toluene are presented. A mechanism based on three stages is proposed, including the stage of diffusion transfer of dissolution products into the volume through the boundary layer, and the derivation of the kinetic equation from the condition of equality of diffusion and convective fluxes on the particle surface is described. Solutions for calculating the kinetics of dissolution of a single particle and the "collective" dissolution of many particles are presented. The dissolution coefficients were determined depending on the temperature.*

Keywords: *asphalt-resinous substances, aromatic solvents, boundary layer, convective diffusion, mass transfer, toluene.*

I. Introduction

Asphaltene–resinous and paraffinic deposits remain a major problem in the industry. The plugging ability of asphaltenes also manifests itself during production and at the stages following oil production, creating complications in oil refining, since asphaltenes constitute a significant part of heavy oils, which are increasingly being processed. This leads to a decrease in the profitability of production and is fraught with technical problems. Mechanical, physical, biological, and chemical combined methods with a combination of different methods are used to remove ARPD. More effective are chemical methods, i.e. treatment of equipment with solvents and technical detergents.

As such solvents for asphaltenes, products of oil refining and petrochemical production are usually used, for example, hexane, butylbenzene and xylene fractions, lighting kerosene, etc. [1]. These products contain hydrocarbons of the homologous series of methane and benzene. Hotier and numerous scientists [2-4] have proposed precipitators and solvents for asphaltenes. According to this scale, solvents for increasing the solubility of asphaltenes have the series: <xylene <toluene <benzene <chloroform <pyridine.

Even though a significant number of works [1, 5-6] are devoted to the development of methodological foundations for the targeted selection of solvents for the effective removal of ARPD, the results obtained using these techniques do not always coincide with the results of oil field tests. This can be explained by the fact that these solvent selection procedures do not fully take into account the kinetic aspects of the dissolution process.

When ARPD is immersed in a hydrocarbon solvent, the probability of penetration of solvent molecules deep into the ARPD is small. Therefore, the process of dissolution of ARPD components occurs mainly at the interface between the ARPD - solvent phases. The total dissolution rate of ARPD, as a type of heterogeneous reactions, consists of the rates of two successive stages: I) the physicochemical interaction of ARPD components with the solvent and II) the diffusion of products from the surface of the deposits into the solution. This approach justly admits the impossibility or low probability of the penetration of solvent

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molecules deep into the ARPD and assumes that the ARPD dissolution process occurs mainly at the ARPD - solvent interface. [7].

The rate of dissolution of ARPO is limited by the rate of the slowest of the above stages, which determines the area of the dissolution process (kinetic or diffusion mode). In [8], the dissolving ability of the surfactant, dodecylbenzene sulfonic acid (DBSA), is considered in detail, and it is reported that (DBSA) completely dissolves asphaltenes through acid-base chemical reactions in the heteroatomic centers of asphaltene molecules. And in [9], the results of treatment of asphaltenes with 16 different ionic liquids are presented, and it is reported that ionic liquids (trihexyl (tetradecyl) phosphonium bis (2,4,4-trimethylphenyl) phosphinate and trihexyl (tetradecyl) phosphonium bis (2-ethylhexyl) phosphate), solubilized or suspended a significant portion of the crude asphaltenes.

In [10], a model of the kinetics of dissolution of asphaltene–resinous substances in hexane and a mixture of hexane and benzene (1: 1) was proposed. Although the proposed model is empirical, it satisfactorily describes the experimental data. In this work, the kinetics of the process is not built on the phenomena of mass transfer under certain flow conditions but is considered simply as a heterogeneous process. In [11], for the convenience of determining the kinetic parameters, the expansion of the exponential model in the Maclaurin series is used, as a result of which the nonlinear model is reduced to a two-parameter Langmuir model. Evaluations of the effectiveness of the solvent used must be made based on the kinetic studies carried out, taking into account the concepts of the nature, sequence, and rates of the stages of the dissolution process. This study aims is to construct a kinetic model for the dissolution of asphaltene–resinous substances in an aromatic solvent-based on the phenomena of convective-diffusion mass transfer.

II. Experimental part

In this work, five dissolution methods of asphaltene–resinous substances were investigated to investigate their dissolution in organic solvents. Three of the approaches were based on common laboratory equipment designed for temperature control and stirring. The fourth was suitable for work at high pressures and temperatures, which allowed us to investigate the influence of these parameters on the dissolution process. The latter approach was suitable for conducting kinetic dissolution studies using gravimetric and spectrophotometric quantification methods. A practical dissolution technique was selected from among the five described above for detailed analysis.

To study the kinetics of the process of dissolution of asphaltene–resinous substances in toluene, which has a fractional character, experimental studies were carried out in mixing devices in the temperature range of 20–60^{0}C for 60 min. at the number of revolutions of the mixer equal to 1000–1200 min^{-1}. Asphaltene–resinous substances were released by additional evaporation of bitumen - tar fraction with a density of 1280 kg/m3, with an asphaltene content of 14.3% and paraffin - 7.2% from a mixture of Azerbaijani oils. A mixer with a volume of 5 liters was loaded with 1.6 kg of bitumen-tar fraction and 1.2 liters of toluene, and experiments were carried out under the indicated conditions.

III. Results and their discussion

It has been found that temperature is the physical parameter that most affects the dissolution phenomenon. Aromatic hydrocarbon content is a key chemical property of solvent mixtures that increases their solvency when applied to highly insoluble materials. It was observed that the high aromaticity of the asphaltene fraction worsens their solubility, since the determined kinetics of dissolution is inversely proportional to this property. It was also found that high aromaticity values of asphaltenes correlate with high density and low H / C ratio [12-13].

IV. Mass transfer processes in the dissolution of asphaltenes

Dissolution of asphaltene particles is a mass transfer process and, depending on the hydrodynamic flow regime, is characterized by different mechanisms. The process of dissolution of asphaltene–resinous substances in aromatic hydrocarbons is characterized by unsteady behavior, and therefore, the mass transfer models differ significantly depending on the nature of the hydrodynamic flow around a particle. In particular, in a laminar flow around a particle, the diffusion flux of a dissolved substance per unit time from the surface of asphaltene particles can be determined by the following expression [14].

$$J = \sqrt{\frac{3}{\pi}}\left(\frac{3D_M U}{2R}\right)^{1/2} \Delta C \tag{1}$$

With isotropic turbulent flow, with some assumptions, the same flow is defined as [7,15]

$$J = \sqrt{\frac{3\alpha}{\pi}}\left(\frac{\varepsilon_R}{\nu_c}\right)^{1/4} (UR)^{1/2} \Delta C \tag{2}$$

Here $\Delta C=C_0-C_1$ –is the driving force of the dissolution process, C_0, C_1 – is the concentration of the solute far from the particle surface and on the surface, D_M – is the molecular diffusion coefficient, U –is the flow rate, ε_R – is the dissipation of the turbulent flow energy per unit mass, R –is the particle radius, ν_c – is the viscosity of the medium, α – is the coefficient. Both solutions are obtained in cross-border conditions.

$$r \to \infty, \quad C = C_0; \qquad r = R, \quad C = C_1$$

As follows from equation (2), the flow of the asphaltenes mass from the surface of the particle is directly proportional to the dissipation of the energy of the turbulent flow and is inversely proportional to the toluene viscosity (ε_R/ν_c), i.e. at high values of viscosity, corresponding to low temperatures, the dissolution rate decreases and, similarly, at high rotational frequencies, corresponding to large values of energy dissipation, the dissolution rate increases.

It should be noted that the main condition for the dissolution of particles is the condition of equality on the surface of the boundary layer of diffusion and convective flows

$$-D_E \left.\frac{\partial C}{\partial r}\right|_{r=\delta} = \beta\left(C - C^*\right) \tag{3}$$

where *r*–is the coordinate along the thickness of the interphase layer, *C*–the concentration of the absorbed substance, $\delta -$ the thickness of the interfacial layer, which is proportional $\delta \sim \left(aD/V_0\right)^{1/2}$, V_0–where is the ambient velocity on the particle surface, β –is the mass transfer coefficient, and D_E - is the effective diffusion coefficient. The effective diffusion coefficient is defined as the sum of molecular DM and turbulent diffusion DT, and De=DM+DT as the dissolving particle approaches the surface, molecular diffusion dominates in the viscous sublayer, at a sufficient distance $D_T >> D_M$ from the surface. The turbulent diffusion coefficient is a function of the turbulent characteristics of the flow and the transverse coordinate, and not only of the physical characteristics of the medium. According to the statistical theory of turbulent diffusion, the value of the root-mean-square displacement of the particles of the dissolved medium from the initial position in the radial direction is determined by the dependence

$$\overline{r}^2 = 2D_T \Delta t \tag{4}$$

The distribution of the turbulent diffusion coefficient within the boundary layer is very complex (Fig. 1).

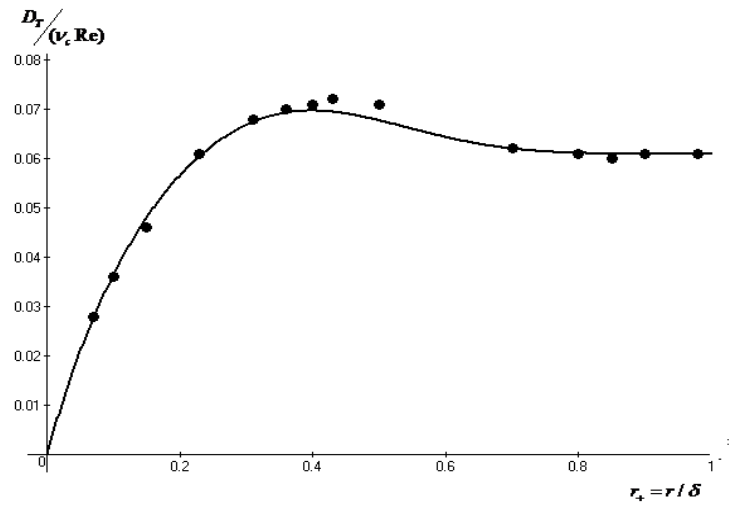

Fig. 1. Distribution of the turbulent diffusion coefficient over the thickness of the boundary layer (points - experiment [16], is the Reynolds number).

V. Mechanism and kinetics of solubility of asphaltenes in toluene.

The course of the processes of dissolution of asphaltene–resinous substances in toluene depends on the nature and properties of the particle and the solvent. The dissolution mechanism has three stages: the dissolving component (asphaltenes) is transported to the particle – solvent interface; the dissolving substance is transported by convective diffusion to the surface of the interphase boundary layer; the substance from the surface of the boundary layer must flow deep into the solution. All these stages are associated with the content of asphaltene–resinous substances in toluene, and upon reaching an equilibrium state, the dissolution process stops. The total dissolution rate is limited by the slowest second stage, i.e. removal of the dissolving substance from the surface of the particle, since the solvent diffuses only into the upper layers of asphaltene particles, gradually penetrating deep into the particle.

It can be assumed that the dissolution process is determined by the softening of the upper layers of asphaltene particles as a result of diffusion penetration of the solvent into the subsurface layers. In this aspect, expression (2) is the main condition for the surface dissolution of asphaltene particles. It should be noted that in mixing devices the degree of flow turbulence in the apparatus is determined by the rotation frequency of the mixer. Usually, at sufficiently high rotation frequencies, isotropic turbulence is achieved, which decays as it approaches the particle surface. The mass flow from a unit surface area of asphaltene particles is determined by equation (2), where the specific energy dissipation is proportional $\varepsilon_R \sim n_0^3 d^2$, n_0, d –nis the rotation frequency and the diameter of the mixer. Thus, with an increase in the rotation frequency, the dissolution process intensifies. In an isotropic turbulent flow, the turbulent diffusion coefficient entering into Eq. (3) depends on the energy dissipation and viscosity of the medium $D_T \sim \left(\varepsilon_R/\nu_c\right)^{1/2} \sim \left(n_0^{3/2} d\right)/\nu_c$.

The mechanism of dissolution of asphaltene–resinous substances in aromatic solvents is based on three stages: a) diffusion transfer of the solvent to the surface of asphaltene particles; b) physical dissolution of surface layers at certain temperatures; b) diffusion transfer of dissolution products into the volume through the boundary layer. Experimental studies on the dissolution of asphaltene–resinous substances in toluene are presented in Table 1. It should be noted that with an increase in the mixer rotation frequency, the process of dissolution of asphaltene–resinous substances in toluene intensifies to a certain limit and improves due to an increase in the intensity of flow turbulence, coefficients of turbulent diffusion, and mass transfer. On the other hand, an increase in the intensity of turbulence leads to an increase in the number of collisions and turbulent diffusion of asphaltene particles, which can facilitate the development of their coagulation processes. At low turbulence intensity, the dispersed system is prone to structure formation, with the manifestation of viscoelastic rheological properties.

Table 1. Dependence of the dissolution of asphaltene–resinous substances on time at different temperatures.

t, min	$T=20^0C$	$T=40^0C$	$T=60^0C$
	C, mass fraction	C, mass fraction	C, mass fraction
2.5	0.044	0.085	0.125
10	0.27	0.38	0.47
15	0.43	0.60	0.70
20	0.60	0.73	0.83
25	0.61	0.75	0.91
30	0.68	0.80	0.96
35	0.69	0.83	0.97
40	0.69	0.84	0.96
50	0.72	0.84	0.99
60	0.72	0.84	0.98

Experimental studies show that at low temperatures, the dissolution of asphaltene–resinous substances does not occur completely – at T=20^{0}C –72% and at T=40^{0}C –84%.

Using condition (3), introducing the change of variables from expression (4) $dr=(2D_E)^{1/2}t^{-1/2}dt$ we write the expression (3) in the form

$$\frac{\partial C}{\partial t}=-K\left(C-C^*\right) \qquad C(t)\Big|_{t=0}=C_0 \tag{5}$$

Here $K=\left(\frac{2}{D_E t}\right)^{1/2}\beta$ - is the mass transfer coefficient for the dissolution process, C0is the initial concentration of asphaltenes in toluene, and is the concentration of dissolved asphaltene–resinous substances in toluene. Expression (5) is the equation of the kinetics of the mass transfer diffusion process of dissolution. For a non-stationary dissolution process, if the value of the coefficient depends on time, then the solution to equation (5) will be presented in the form

$$C(t)=C^*-\left(C^*-C_0\right)\exp(-\int_0^t K(t)dt) \tag{6}$$

For a pure solvent $C_0=0$, this equation is simplified to the form

$$C(t)=C^*\left(1-\exp\left(-\int_0^t K(t)\,dt\right)\right) \tag{7}$$

Using experimental studies and expression (7), we can put: $K(t)=K_0t^{-1/2}$, $K_0=\left(2/D_E\right)^{1/2}\beta$ and $C^*(T)=57.33+0.7T^0C$. To dissolve a single particle, using these expressions from expression (7), we obtain the dependences; finally, the equation for the dissolution of asphaltene–resinous substances in toluene is represented in the form

$$C(t)=C^*\left(1-\exp\left(-\alpha t^{1/2}\right)\right) \tag{8}$$

where. For the "collective" dissolution of many particles, the effective time-average value of the mass transfer coefficient should be used

$$\beta_E = \frac{\int_0^{T_P} \beta dt}{T_P} = \beta \frac{t}{T_P}$$

where TP–is the time of complete dissolution of particles. As follows from Table 1, the time for the complete dissolution of asphaltene particles is 50–60 minutes. Taking this expression into account, solution (7) will be represented as

$$C(t) = C^*\left(1 - \exp\left(-\alpha t^{3/2}\right)\right) \qquad (9)$$

Where $\alpha = {}^{2K_0}\!/_{3T_P}$. The results of experimental studies and calculated values according to formula (9) for different temperatures are shown in Fig. 2. Practical calculations show that the temperature change varies insignificantly within the specified limit. Equation (8) satisfactorily describes the experimental data on the dissolution of asphaltene–resinous substances in toluene. Figure 2 shows the regions corresponding to the approximate direct dependence of the kinetics of dissolution of asphaltene–resinous substances in the form of an equation $C(t) = K(T)t$.

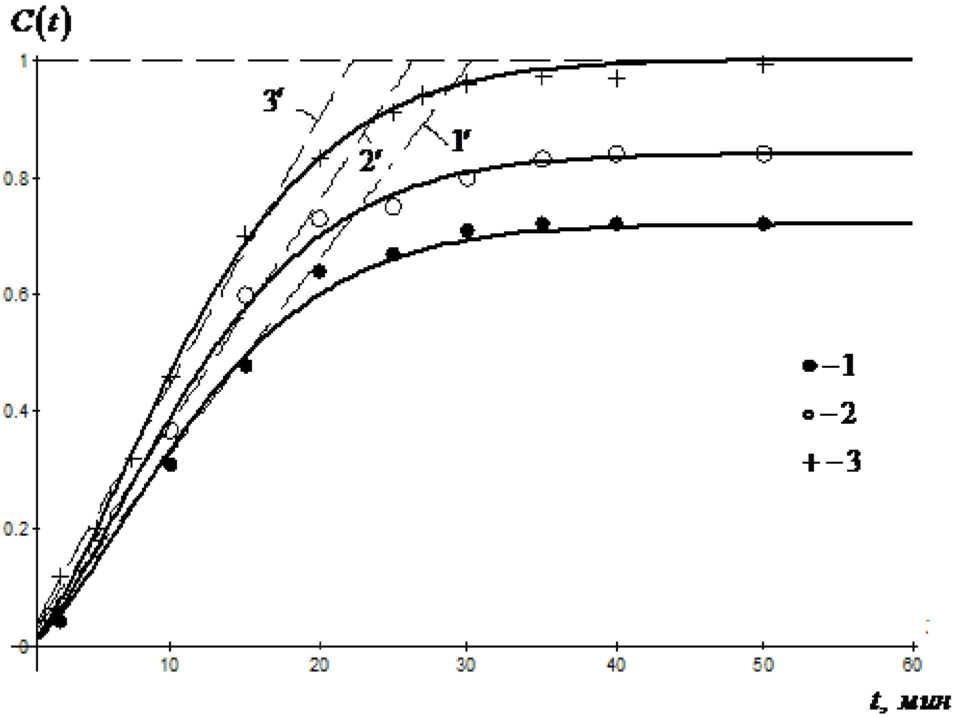

Fig. 2. Kinetic curves of dissolution of asphaltene–resinous substances in toluene at temperatures equal to: 1–20 ^0C ; 2–40 ^0C ; 3–60 ^0C . The straight lines correspond to the linear kinetics of dissolution of asphaltenes in toluene at temperatures equal to:1 -20 ^0C ; 2-40 ^0C ;3 -60 ^0C .

For a straight-line dependence, the dissolution constants can be approximated by an expression depending on temperature

$$\ln K = -\frac{752.087}{T} - 0.8507$$

with a correlation coefficient equal to $r^2 = 0.992$. In this dependence *T*–is the absolute temperature. As follows from Fig. 2, the linear correlation of the direct solubility is observed only at $t \leq 20$ min. and is observed within the viscous sublayer of the entire volume of the boundary layer.

VI. Conclusion

Based on the theory of mass transfer under conditions of isotropic turbulence, theoretical and experimental studies of the kinetics model of dissolution of asphaltene–resinous substances in toluene depending on temperature are proposed. Experimental studies were carried out at temperatures of 20, 40, 60 ^0C. The stage of convective diffusion of the solute in the boundary layer is considered as the dissolution mechanism. Solutions for calculating the kinetics of dissolution of a single particle and the "collective" dissolution of many particles are presented. The dissolution coefficients have been determined for both linear and nonlinear distribution of the concentration of the dissolved substance in the boundary layer.

VII. Acknowledgments

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