ASPHALTENE MOLECULES ASSOCIATION EFFECT
ON CRUDE OIL FLOW THROUGH POROUS MEDIUM

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Filamentary structures are forming of asphaltene molecules in crude oil when it is flowing through porous medium due to aggregation-disintegration equilibrium disturbance causing by adsorption. Asphaltic components adsorption was detected on the base of their content in oil measurements provided by Electron Paramagnetic Resonance. A shape of the structures (filaments) is determined by spatial properties of asphaltene micelle core (associate of asphaltene molecules). Filamentary structures explain observed experimentally characteristics of crude oil flow through porous medium (sandstone): (i) permeability of core by crude oil and its drastic difference from that by gas, (ii) permeability dependence on the flow direction and flow rate, (iii) the difference of dynamic equilibrium establishment time after increase (t_i) from that after decrease (t_d) of flow rate (t_d is considerably higher than t_i).

INTRODUCTION

Crude oil flow through porous medium depends significantly on the dispersive properties of oil, i.e. microstructure formation, its stability etc., the characteristics of flow in turn influence on the efficiency of oil recovery [1,2]. The disperse phase in crude oil is usually represented by the following microstructures: (i) asphaltene associates and micelles, (ii) microcrystalls of solid paraffins, (iii) microparticles of minerals torn off the reservoir pore walls, and (iv) complex agglomerates of the above listed particles. This work is restricted to the microstructures involving asphaltenes.

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A concept of the micellar structure of asphaltene bitumens was formulated in 1940 by Pfeiffer and Saal [3]. Subsequent investigations [4-6] showed the main type of structures in bitumens and in extracted from crude oil heavy fractions are asphaltene associates. These associates were found to be a structure comprising about 5 condensed aromatic discs (each of them is representing asphaltene molecule core) with approximately parallel planes, stacked one over other. On the periphery chains of aliphatic and/or naphthene-cyclic systems are attached to the discs in accordance with the known structure of asphaltene molecules [4]. The dimensions of the associates according to the results of various methods are from 14 to 30-50Å [6,7]. The average size of asphaltene microparticles in solutions (benzene) studied by electron microscopy was found to be 20-30Å [8].

Self-association propensity of asphaltenes and resins in low-molecular-weight solvents (pyridine and nitrobenzene) are studied by means of surface tension measurements [9]. Only if asphaltenes were self-associating, and resines were not, the classical model of asphaltene micelle in crude oil (asphaltenes coated by resins) based on [3] would be correct. Investigation [9] sowed, however, that either asphaltenes or resins are self-associating in the solvents used. Moreover, Taylor [10] pointed to some incorrectness in results interpretation in [9], and noted that the data mentioned indicate the absence of a critical micellization concentration in nitrobenzene and the existence of such critical concentrations for both asphaltenes and resins in pyridine. Hence, the classical asphaltene micelle structure does not accord completely to modern knowledge, besides a nature of medium influences significantly micelle structure and properties.

Accounting for the significance of the medium, in the subsequent investigations [11,12] asphaltene association was studied by means of Electron-Nuclear DOuble Resonance (ENDOR) in crude oil. It was shown that the main part of asphaltene molecules in crude oil at native conditions are associated with each other, and the associates structure in crude oil is similar than that observed previously in bitumens and in extracted from crude oil

heavy fractions (see, e.g. [4-6]). Asphaltene associates are the cores of micelles in crude oil, the micelles themselves exhibit spatially anisotropic properties [13]. This anisotropy is an axial one with axis perpendicular to the condensed aromatic fragments planes of asphaltene molecules. Spatial anisotropy lies primarily in the anisotropic micelle core environment. Near poles the core is surrounded mainly by resin molecules, whereas equatorial environment is represented mainly by molecules of heavy oily fraction [13].

This work was aimed at studying of asphaltene associates agglomeration influence on crude oil flow through porous medium.

EXPERIMENTAL

Crude oil flow was studied either through natural core or through synthetic porous media. The natural core was a cylindrical plug of 11.6 cm length and 3.8 cm diameter cut of Bentheimer quartz sandstone of 0.29 μm^2 permeability by gas. Experiments were performed with a multiphase filtration setup described in detail elsewhere [14]. The confining pressure was 14 MPa and the hydrostatic pressure of crude oil in pores was 8.0 MPa. The bulk flow rate of crude oil was controlled by the translational velocity of a press piston. This parameter was varied from 0.08 to 20 cm^3/h according to the experimental schedule. The pressure drop on the core was measured by a differential manometer.

Synthetic porous media were represented by cylindrical columns 50 cm in length and 6.6 cm^2 cross section area filled with ground quartz sand. Their permeability by gas were from 0.11 to 0.25 μm^2. Crude oil filtration was with an excess pressure from 0.3 to 0.6 MPa, and backpressure equal to atmospheric one. The experiments were performed at 21° C.

Crude oil samples were taken at the output of core or synthetic porous media and analyzed for the content of resin-asphaltene fraction (RAF). The concentration of RAF containing paramagnetic molecules was measured as some integral characteristics by means of Electron Paramagnetic Resonance (EPR). EPR spectra of crude oil were measured at room temperature with a

commercial Bruker ESP-300 X-band ($v \approx 9.5$ GHz) spectrometer. The spectra were a singlet signal near g-factor of free electron (2.0023) with a peak-to-peak linewidth 4.1 Oe. The RAF concentration C was measured by the line intensity and normalized to the RAF content C_o in the initial oil, in other words, relative RAF content C/C_o was measured.

The experiments were performed with dead crude oil from Kara-Chukhur field possessing the following characteristics: asphaltene content 0.1 wt%, resin content 3.7 wt%, paraffins 6 wt%, viscosity at 21°C 15.4 mPa·s, density 0.855 g/cm^3. Thus, the RAF content in initial crude oil was 3.8 wt%.

RESULTS AND DISCUSSION

A typical dependence of RAF content in probes of crude oil at the output of synthetic porous medium is depicted in Fig.1 versus the ratio V/V_1 of the output oil volume to the volume of pores. The RAF content at the initial filtration stage is much lower than that in an injected oil due to adsorption of RAF by the surface of pore channels. The adsorption-desorption equilibrium is established approximately at $V/V_1 = 1$. Basing on these data an amount of RAF adsorbed in porous medium can be readily evaluated. The specific (per unit surface area) mass of adsorbed RAF was determined in five experiments as $(1.6-2.6) \cdot 10^{-6}$ g/cm^2. The pore surface necessary here was estimated by semiempirical correlation [15]

$$S = m\sqrt{m / 2k}, \qquad (1)$$

where m is the porosity, k is the permeability of the medium (expressed in m^2), and S is the specific surface area (in m^2/m^3).

The same figure shows also the dependence on V/V_1 of the permeability of porous medium by oil. It can be seen that the permeability decreases from its initial value (close to the permeability by gas) to a significantly lower final value and remains constant after establishment of adsorption-desorption equilibrium. Such a behavior allows one to conclude that the permeability decrease is relevant to RAF adsorption. The following adsorption models are

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possible: (i) as a monolayer of associates, (ii) as a polyassociate layer, feasibly of nonuniform thickness, and (iii) as a filamentary structures comprising chains of associates and gel-like formations.

Only the third mechanism can explain the experimentally observed results. Indeed, if the adsorption were in a form of monolayer then, assuming an adlayer density $\rho = 1$ g/cm^3, the adlayer thickness would be in the range 160-270Å. This value exceeds significantly the dimensions of the condensed aromatic core of associate (14-20Å) determined previously [11,12]. With peripheral fragments the total size of associates can reach 30-40Å, which is still much lower in comparison with the above estimated adlayer thickness. If the adsorption were in the form of polyassociate layer with the mean thickness accordant to the above estimated value, it would be impossible to explain the observed decrease of permeability by oil. Such an adlayer thickness cannot account for any valuable decrease in the pore cross-section for the pore size exceeding 1 μm.

The third mechanism explains both a decrease in the permeability at the expense of RAF adsorption and the experimental values of the specific adsorbed mass of RAF. The asphaltene micelle in crude oil structure as studied previously [13] implies the preferential coagulation mechanism: a formation of asphaltene associate chains ("filaments") in which associates are attached to each other by their poles. Such a coagulation can be brought about by the decrease of resin molecules concentration in crude oil, which in turn is caused by adsorption (evidently, an adsorption process of light resin molecules is considerably faster and probable than that of asphaltene associates). Hence, it can be concluded that the filamentary structures formation most probably accompany RAF adsorption process. Let us consider the porous medium upon establishment of adsorption-desorption equilibrium as an initial system of pores with added filaments of coagulated RAF associates (for the sake of the simplicity we suppose the filaments to be attached with one end to the adsorption centres of the pore surface). Adopting this model, we estimate the surface area of filaments by formula (1) using the permeability value upon the

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establishment of the adsorption-desorption equilibrium. Assuming that the diameter of filaments d is much less than their length, we can neglect the edge faces and obtain d $=23-39$Å. This value is in a good agreement with aforementioned data on the dimensions of asphaltene associates, thus confirming accepted model of filamentary structures formation.

The influence of filamentary structures formation on crude oil flow was studied using quartz sandstone plug. The experimental adsorption curve for this system is similar to that depicted in Fig.1.

The specific surface area S $= 6.5 \cdot 10^4$ cm^2/cm^3 of plug was determined by low-temperature nitrogen adsorption technique in Brunauer, Emmett, and Teller (BET) [16] polymolecular adsorption approximation. The specific surface area of pores with diameters exceeding 100Å was estimated from the above value as $1.5 \cdot 10^4$ cm^2/cm^3. The estimation was made by subtracting from the total surface area S the value of surface area corresponding to pores below 100Å in diameter. The latter was evaluated by integrating through the pore size distribution function, the latter achieved from nitrogen desorption curve by BET method. The specific mass of RAF adsorbed by core was $1.1 \cdot 10^{-7}$ g/cm^2. In our opinion, this value indicates that the asphaltene adsorption centers occupy only a part of the core surface (which is a reasonable assumption if to take into account that the limiting flat surface of the order of 100Å^2 is necessary for asphaltene associate adsorption). Moreover, the adsorption of filamentary structures is possible only within pores whose sizes markedly exceed 100Å. These speculations agree with the accepted adsorption model.

Fig.2 shows the stationary pressure drop caused by crude oil flux versus the rate of flow for filtration in forward direction (curve 1), for filtration in the opposite direction upon reversal of flow (curve 2), and for forward filtration after the second direction reversal (curve 3). One can see that filtration in an opposite direction (curve 2) is characterized by the less pressure drop than that in forward direction (curves 1 and 3). This suggests that certain residual

orientation of filamentary structures formed upon RAF adsorption is retained after reversal of the flow.

The dependence of the pressure drop on the direction of the flow can be explained assuming that the filamentary structures, being attached with one end to the surface of pores, have a preferential tilt in the direction opposite to that of the flow existed during filament formation. Filaments are supposed to be somewhat resilient. A reason for preferential orientation of filaments can be the following. For filaments tilted in the direction of the flow the projection of hydrodynamic forces onto the filament axis favors their breakage, while for filaments tilted against the flow this projection contributes to higher bonding of elements represented by asphaltene associates. Hence, the filaments will be tilted preferentially against the flow, or, speaking more strictly, the mean equilibrium length of filaments tilted against the flow will be greater than of those tilted to the flow.

A pressure drop establishment time after increase of flow rate is different from that after decrease of flow rate. An establishment time $t_i \sim 120$ s after flow increase is small enough, and it can be deduced that experimental system response (including piezoconductivity of oil saturated plug, amplifier, plotter time constants etc.) is not longer than t_i. In case of flow decrease a time of new steady pressure drop establishment $t_d \sim (3-6) \cdot 10^3$ s. Such a behavior is clear if a model of filaments of asphaltene associates is accepted. Here we suppose that oil viscosity in a pore is determined by the filament mean equilibrium length. According to this model t_i is defined by comparably fast process of filaments breakage into smaller pieces (and according decrease of viscosity η). Dislikely, t_d is determined by a process of filament growth which is slower as its rate is controlled by the diffusion of filaments. A rate of this process $K = 1/t_d$ can be roughly estimated by the rate constant of bounding of two chains of $l/2$ length into a chain of l length:

$$K = 4\pi D \cdot (d_{ass} / 2) N_f \cdot f, \qquad (2)$$

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where $N_f = N_{ass}(d_{ass}/l)$ - filament concentration, N_{ass} - associate concentration, $f \sim (N_f/N_{ass})^2$ - steric factor accounting for the fact that only a part of collisions will lead to chains bonding. According to Stokes-Einstein formula diffusion coefficient

$$D = \frac{kT}{6\pi\eta(l/2)},\qquad(3)$$

where k - Boltzmann constant, T - temperature. From (2) and (3) it is easy to evaluate

$$N_f/N_{ass} = \left\{\frac{3}{4}\frac{K\eta}{kTN_{ass}}\right\}^{1/4},\qquad(4)$$

which yields with experimental values $N_{ass} = 1.9\cdot10^{26}$ m^{-3} (evaluated from asphaltene content), $K = 3.5\cdot10^{-4}$ s^{-1} a value of associates in a single filament $N_{ass}/N_f = 660$, hence the filament length is of the order of 1.3 μm. The filament length due to hydrodinamic forces (flow gradients inside pores) should be proportional to the reverse flow rate: $l \sim Q^{-1}$. Accounting for pressure drop $P \sim \eta Q$ and accepting the influence of filament length on the bulk viscosity to be similar than that for diluted polymers $\eta \sim l^{1/2}$ [17], we conclude that for our experiments $P \sim Q^{1/2}$. The solid lines (Fig. 2) obtained by least root squares method from experimental data for $P = A\cdot Q^n$ are characterized by n - values 0.58, 0.63, and 0.47 for cases 1, 2, and 3 accordingly. So, this rough consideration appears rather satisfactory description of the experimental results.

CONCLUSION

The character of crude oil flow in a porous medium is significantly affected by the adsorption of resin-asphaltene fraction on the surface of pores. The adsorption is accompanied by filamentary structures formation of asphaltene associates, the shape of structures being defined by the axial anisotropy of asphaltene micelle in crude oil [13]. The diameter of filaments is

20-40Å, which corresponds to the asphaltene associate size. The length of filaments is of the order of 1 μm. A part of filaments are attached to pore walls and predominantly tilted in the direction opposite to that of the flow during the filament formation. Upon reversal of the flow direction the filamentary structures retain a certain residual orientation.

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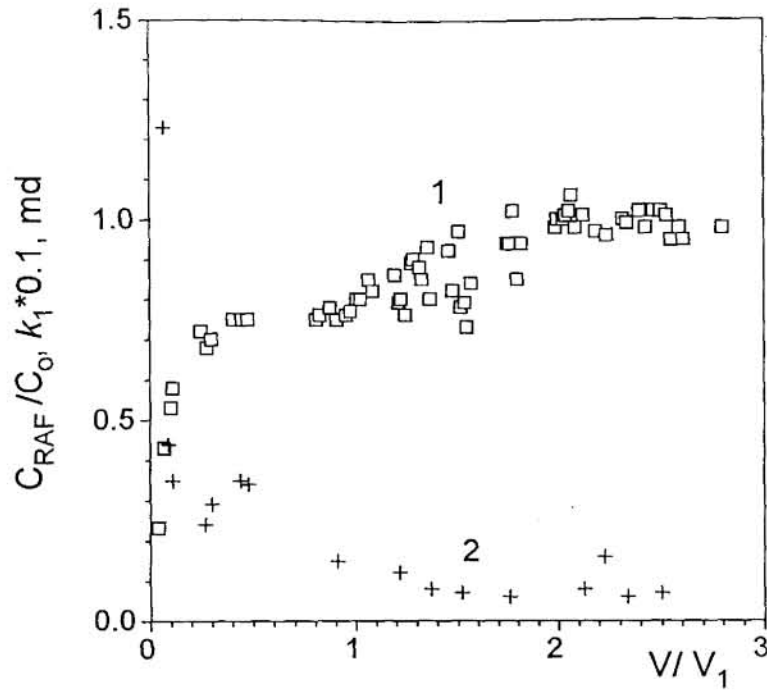
Fig. 1. A typical dependence on relative filtered oil volume of RAF content (1) in oil at the output synthetic porous medium and of permeability by oil (2).
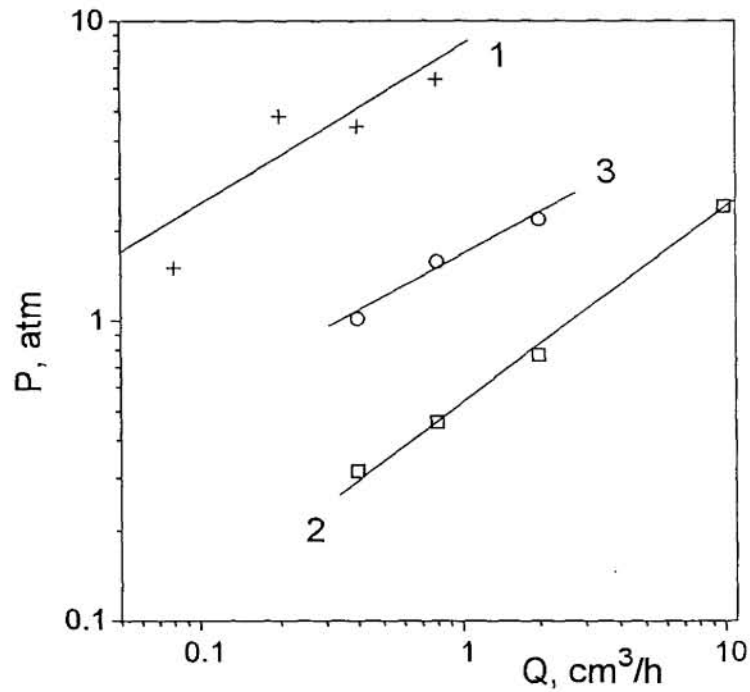

Fig. 2. Pressure drop on sandstone plug versus oil injection rate for forward direction (1), opposite direction after reversal of flow (2), and for forward direction after second reversal of flow (3).