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Changes in the Composition and Colloidal Stability of Heavy Oil in the Presence of Quinoline

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Abstract

The influence of low molecular weight nitrogenous bases (by the example of quinoline) on the composition and colloidal stability of asphaltenes in solutions and oil dispersed systems is investigated. The objects of study were model oil systems with the basic nitrogen content of 1.0–3.0 wt. %, obtained by mixing the original oil and quinoline. The content of basic nitrogen (N_{bas}) was determined using the method of non-aqueous potentiometric titration. Analysis of the colloidal stability of asphaltenes in solutions and oil systems was carried out by spectrophotometry. It is shown that the content of asphaltenes in oil systems is reduced by 0.22 wt. % with an increase in the content of basic nitrogen (quinoline) up to 3 wt. %. At the same time, the content of resins increases by almost 8 wt. %. With an increase in the content of quinoline in oil systems, the proportion of basic nitrogen in the asphaltenes isolated from them increases from 1.71 to 3.60 wt. %, which indicates the active participation of quinoline in the formation of supramolecular structures of asphaltenes during their precipitation with n-hexane. The presence of low molecular weight nitrogenous bases (quinoline) in oil contributes to a significant increase in the growth rate of aggregates and a decrease in the colloidal stability of oil systems.

Keywords: heavy oil, asphaltenes, quinoline, composition, colloidal stability

INTRODUCTION

The fraction of oil dispersed systems (ODS), characterized by the high asphaltene content, is annually increasing during the recent years in the resource basis of raw hydrocarbons [1]. Most heteroatoms and metals are concentrated in asphaltenes, which promotes the problems at the stages of heavy oil mining, transportation and processing [2]. Resource-efficient involvement of heavy oil feedstock into economic turnover requires the development of new technologies and optimisation of the existing ones to extract this feedstock and transform it into valuable petroleum products [3].

Asphaltenes are the most complicated oil components, their molecules are various combinations of polycyclic naphthenoaromatic fragments with alkyl substituents, bound with each other through aliphatic chains, in particular sulphur- and oxygen-containing bridges [4–7]. Under the changing external conditions (temperature, pressure, dispersion medium), asphaltenes are prone to self-association and to the formation of supramolecular structures: di-, trimers, nanoaggregates, clusters [4, 8–10]. Coarse supramolecular formations

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serve as the basis for the formation of various deposits in ODS, which causes worsening of the performance and commercial characteristics of the latter [8]. In spite of numerous attempts to solve the problems of the formation of asphaltene-containing deposits, the accuracy of predicting colloidal stability of ODS and the behaviour of supramolecular asphaltene particles under different conditions remains low. The reason is in the poorly investigated mechanism of asphaltene aggregation and the formation of asphaltene-containing deposits [11–13]. It is generally accepted that the formation of supramolecular asphaltene structures is mainly due to the stacking interactions of the aromatic structures of their molecules, as well as due to the presence of acid-base interactions, hydrogen bonds, coordination complexes of metals [9, 10, 14, 15]. It has been demonstrated that the formation of asphaltene aggregates in the solutions involves the molecules that contain not only aromatic fragments but also sulphoxide and ester groups, pyridine and pyrrole cycles [16]. However, the role of various functional groups in the molecules of dispersion medium and asphaltenes in the formation of supramolecular structures has not yet been determined in detail.

A subject of special significance is assessment of the influence of nitrogenous bases, represented in ODS by a mixture of the derivatives of pyridine, quinoline, benzo- and dibenzoquinolines, azapyrenes [17–19], on the processes of aggregation in asphaltenes in view of their attitude for intermolecular interactions due to the presence of conjugated aromatic systems and unshared electron pairs of nitrogen atoms. It is known from few works in this area that nitrogen-containing polar bases isolated from the resinous components of oil affect the ODS composition and the structure of asphaltene aggregates. For instance, the introduction of nitrogenous bases in excess into ODS causes a substantial increase in the yield of asphaltenes with a change of their primary and secondary supramolecular structures towards looser disordered structure [20, 21]. However, nitrogenous bases of resins under investigation also contain S- and O-containing functional groups, which can also participate in aggregation processes, so it is rather difficult to make a conclusion on the role of pyridine fragments alone. Thus, evaluation of the effect of "pure" nitrogenous bases on the formation and behaviour of supramolecular structures of asphaltenes deserves special attention.

The goal of the work is to study the influence of quinoline on the composition and colloidal stability of heavy oil and its asphaltene components.

EXPERIMENTAL

The objects of investigation were initial (native) and model oil systems with nitrogen content 0.1 to 3.0 wt. % (Table 1). Model oil systems were prepared by mixing initial oil (density at 20 °C is 911.0 kg/m^3, viscosity at 20 °C is 694.2 mm^2/s) and quinoline (Sigma-Aldrich, purity 98.9 %). Native oil usually does not contain nitrogen more than 3 wt. %, so it was unreasonable to prepare model mixtures with higher nitrogen content.

The characteristics of initial oil are presented in Table 2. With regard to density, this oil is related to heavy oils and is characterised by high resin content but relatively low asphaltene content. The total content of heteroatoms in initial oil is high (4.98 wt. %), but nitrogen content is only 0.1 wt. %. For this reason, we chose this oil as the initial feedstock to prepare model oil systems.

The elemental composition of initial oil was determined using a CHNS-analyser Elementar Vario EL Cube (Germany) by direct combustion at a temperature of 1200 °C, followed by the separation of gases and combustion products in three adsorption columns (with helium as carrier gas) and identification with a thermal conductivity detector. The element detection limit is 0.01 wt. %.

The material (group composition of oil systems was determined using a standard procedure. To

TABLE 1

Objects of investigation

Object of investigation	Nitrogen content, wt. %
Initial oil (H_0)	0.1
Model oil system (H_1)	1.0
Model oil system (H_2)	2.0
Model oil system (H_3)	3.0

TABLE 2

Composition of initial oil

Elemental composition, wt. %					Material composition, wt. %		
C	H	N	S	O	Oils	Resins	Asphaltenes
82.11	12.91	0.10	3.85	1.03	69.17	29.82	1.01

determine asphaltene content, oil systems were dissolved in a 40-fold excess of *n*-hexane, the solution was kept in the dark for 24 h. Then the solution was filtered through a blue ribbon paper filter, and asphaltene precipitate remained on the filter. Asphaltenes in the filter were placed in Soxhlet apparatus and purified from co-precipitated maltenes with *n*-hexane for 18 h until the solvent in the apparatus was colourless. Then, asphaltenes were quantitatively recovered from the filter and dried to the constant weight at a temperature of 50 °C. Maltenes that were obtained through filtration and purification of asphaltenes were brought together, *n*-hexane was evaporated in a rotary evaporator. Separation of maltenes into oils and resins was carried out by means of liquid adsorption chromatography. Silica gel of ASKG grade (particle diameter 0.1–0.5 mm) was used as the immobile phase. The sorbent/maltenes mass ratio was 40 : 1. Before applying maltenes, the sorbent in the column was treated with *n*-hexane to eliminate wetting heat. Hydrocarbons were eluted with *n*-hexane. Resinous substances were eluted with a mixture of ethanol and benzene at the volume ratio of 1 : 1.

The content of basic nitrogen (N_{bas}) in resins and asphaltenes was determined by potentiometric titration with a Mettler Toledo S80-K potentiometer (Switzerland). Asphaltene portion was 0.05 g. The portion was dissolved in 5 mL of toluene (benzene), and acetic acid was added in the amount of 20–25 mL. The solution of chloric acid in acetic acid was used as the standard solution for titration. The concentration of this solution was determined from the titration of quinoline solution in toluene. Titration proceeded by adding titrant portions of 0.1 mL and recording the readings after the addition of every portion of the acid, while the time between the moments of titrant addition within 30–60 s was followed with a seconds counter. The content of N_{bas} (wt. %) in resins and asphaltenes was calculated using equation:

$$N_{bas} = \frac{14 \cdot 100 \cdot C_t \cdot V_t}{1000 \cdot m}$$

where C_t is titrant concentration, mol/L; V_t is titrant volume consumed for titration, mL; m is the mass of petroleum product, g.

The aggregative stability of asphaltenes in oil systems and solutions was studied by spectrophotometry using a Perkin Elmer Lambda 950 instrument (USA). Analysis was carried out for 3600 s (with a step of 5 s). Cell thickness was 10 mm, wavelength 620 nm. To investigate asphaltene deposition in oil systems, a solution of oil system in *n*-hexane at a ratio of 1 : 40 was prepared in the cell, and the changes in the optical density were immediately followed according to the mode described above. The reference solution was *n*-hexane. To study the aggregative stability of asphaltenes without any influence of oil components, the solutions of asphaltenes in chloroform were prepared, with the concentration 0.1 wt. %. These solutions were mixed in the cell with *n*-hexane at a ratio of 1 : 3, and then analysis was carried out according to the mode described above.

TABLE 3

Material composition of oil systems under investigation

Object	Component content, wt. %		
	Asphaltenes	Resins	Oils
H_0	1.01	29.82	69.17
H_1	0.97	29.69	69.34
H_2	0.79	34.25	64.96
H_3	0.79	37.36	61.85

RESULTS AND DISCUSSION

The data on the group composition of oil systems under investigation are presented in Table 3. With an increase in the content of basic nitrogen (quinoline) in oil systems up to 2 wt. %, the content of asphaltenes decreases by 0.22 wt. %. However, a further increase in nitrogen concentration in oil systems from 2 to 3 wt. % does not lead to any further decrease in asphaltene content. This may point to the participation of quinoline in the formation of supramolecular structures of asphaltenes. The experimental data show that an increase in the content of basic nitrogen (quinoline) in oil systems is accompanied by an increase in the content of resins from 29.82 to 37.36 wt. %. A possible reason may be quinoline accumulation in the resin fraction because of their similar adsorption ability with respect to silica gel.

The primary evaluation of N_{bas} content in resin-asphaltene substances according to the data of potentiometric titration shows that N_{bas} content in resins varies more substantially than in asphaltenes (Fig. 1).

The quantitative data on N_{bas} content in asphaltenes, calculated from the curves of potentiometric titration, are presented in Table 4. It has been determined that the fraction of N_{bas} in asphaltenes increases from 1.71 to 3.60 wt. % with an increase in the content of basic nitrogen (quinoline) in the oil system, which points to the ac-

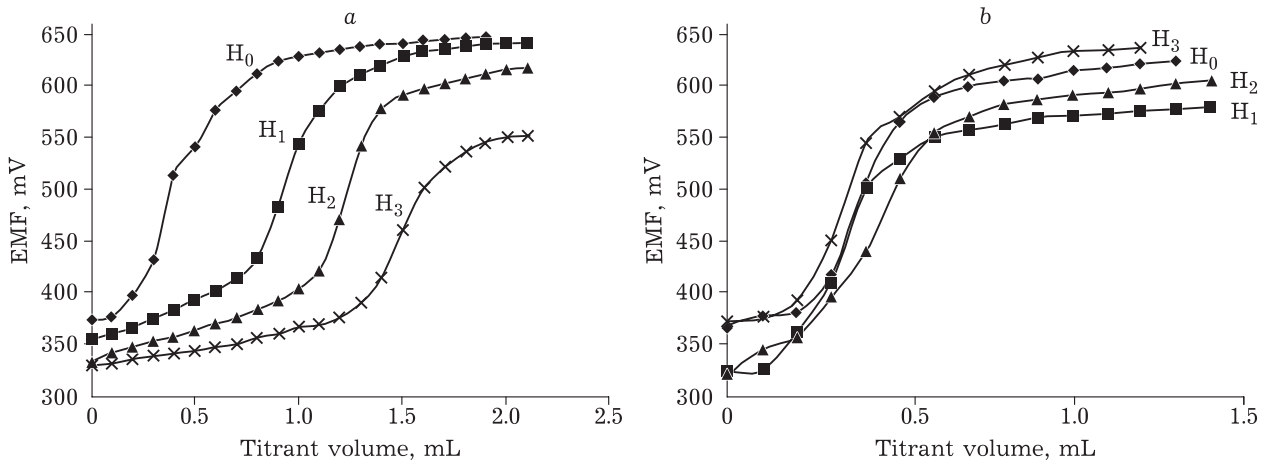

Fig. 1. Curves of non-aqueous potentiometric titration of resins (*a*) and asphaltenes (*b*). EMF – electromotive force.

tive participation of quinoline in the formation of supramolecular structures of asphaltenes during their precipitation with *n*-hexane. The fraction of N_{bas} in resins increases from 3.03 to 9.92 wt. %, which confirms the fact that quinoline is concentrated in resinous substances. So, the larger amount of basic nitrogen (quinoline) is present in the oil system, the larger is its amount accumulated in resinous-asphaltenic substances, which causes changes in their composition and supramolecular structure.

To provide quantitative evaluation of the effect of N_{bas} on the dynamics of asphaltene aggregation and sedimentation in oil systems, spectrophotometric analysis of this process was carried out. It is shown that quinoline concentration does not have a critical effect on the aggregative stability of asphaltenes in the presence of other oil components, which stabilise oil as a rule (resins, polycyclic aromatic hydrocarbons). However, an increase in optical density at the initial stage of aggregation within the time interval of 0–200 s is smoothed over with an increase in quinoline content in the system (Fig. 2). Primary increase in optical density is usually connected with an increase in the number of sizes of aggregates, then they reach a critical size and precipitate, which is accompanied by a decrease in the optical density of the solution. So, the addition of basic nitrogen (quinoline) into the oil system causes a decrease in the duration of the stage of asphaltene aggregate growth due to an increase in aggregation rate. This leads to faster asphaltene sedimentation.

To study the dynamics of asphaltene deposition without the influence of ODS components, we used asphaltenes isolated from initial oil and model mixtures, designated as A_0, A_1, A_2, A_3 according to the numbering of oil systems (Fig. 3). It has been established on the basis of the obtained data that the highest stability is exhibited by asphaltenes with N_{bas} content 1.71 wt. % (A_0), while the lowest one – by asphaltenes with N_{bas} content 3.60 wt. % (A_3). So, with an increase in the content of basic nitrogen (quinoline) in asphaltenes, their aggregative stability decreases. Results obtained in the study provide evidence that pyridine, quinoline and their derivatives, present in the dispersion medium, have a substantial influence on the processes of aggregate formation and on the colloidal stability of oil systems.

CONCLUSION

The influence of nitrogenous base (quinoline) on the composition and aggregation of asphaltenes in oil and in solution has been revealed. With an increase in the content of basic nitrogen (quinoline) to 3 wt. % in oil systems, asphaltene content decreases by 0.22 wt. %. At the same time, resin content increases by almost 8 wt. % due to quinoline accumulation in resinous substances. With an increase in quinoline concentration in the oil system, the concentration of N_{bas} also increases in propor-

TABLE 4

Basic nitrogen (N_{bas}) content in resins and asphaltenes

Object	N_{bas} content, wt. %	
	Asphaltenes	Resins
H_0	1.71	3.03
H_1	1.98	4.67
H_2	2.56	6.98
H_3	3.60	9.92

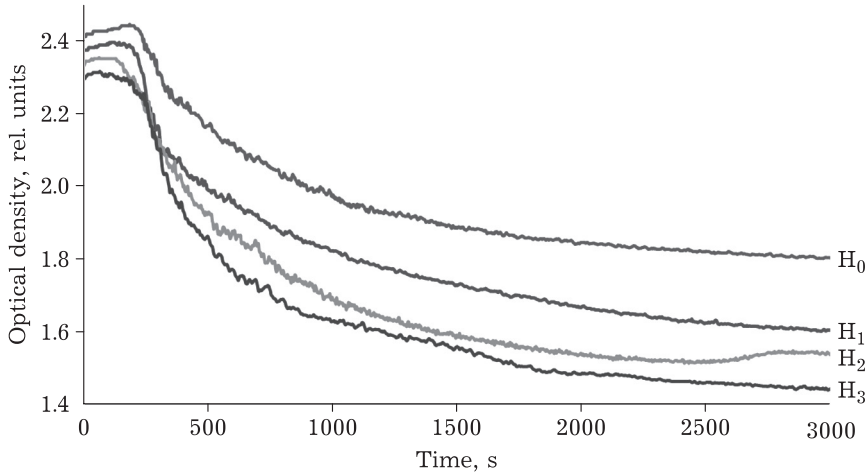

Fig. 2. Effect of the concentration of basic nitrogen (quinoline) on the colloidal stability of oil systems after the addition of *n*-hexane.

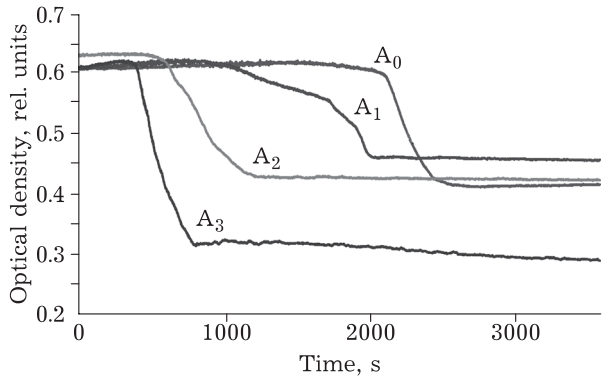

Fig. 3. Effect of the concentration of basic nitrogen (quinoline) on the colloidal stability of the solutions of asphaltenes in $CHCl_3$ (0.1 %) after the addition of *n*-hexane.

tion, by a factor of 3 for resins and 2 for asphaltenes. It has been established that the aggregative stability of asphaltenes decreases with an increase in N_{bas} content in them. Low-molecular nitrogenous bases in ODS act as promoters of the aggregation of asphaltene molecules, providing a substantial increase in the rate of aggregate growth and decrease in the colloidal stability of oil.

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