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Changes in the Structural Parameters of Resins and Asphaltenes during Oil Dewaxing with Liquefied Gas

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Abstract

Changes in the structural parameters of tar and asphaltene molecules of sediments obtained after oil dewaxing with liquefied petroleum gas at temperatures of 0, −5, −15 and −25 °C were studied. It is shown that with a decrease in process temperature the amount of precipitate formed in the process increases from 10.9 to 13.4 mass %; deeper dewaxing, complete deasphalting and partial detarring also take place. It was established that a decrease in precipitation temperature from 0 to −25 °C causes changes in the structural-group characteristics of asphaltene and resin molecules: molecular mass, the number of aromatic and naphthenic cycles, alkyl substituents and structural blocks in the molecule.

Keywords: asphaltenes, resins, liquefied gas dewaxing

INTRODUCTION

Formation intensity and the composition of asphaltenes-resin-paraffin sediments (ARPS) during oil production and transportation are determined mainly by the content of solid hydrocarbons, resins, asphaltenes and their ratio [1–3]. The effect of external factors (temperature, pressure) leads to changes in the physicochemical properties of oil systems. As a result of a decrease in temperature and pressure, the potential capacity of oil systems to dissolve high-molecular compounds decreases, which causes the formation of ARPS [4, 5].

Asphaltenes are high-molecular oil components with the largest molecular mass. Their molecules are complicated polycyclic formation containing aromatic, naphthene and heteroaromatic cycles with aliphatic side substituents. These features of asphaltenes structure determine their ability to form associates [5–7]. Asphaltenes are usually present in oil in the form of colloid particles, while resins are present as compounds dissolved in the hydrocarbon medium or sorbed on the surface of asphaltenes colloids [8]. Changes in the composition of the dispersing medium, pressure and temperature promote structural transformations not only in asphaltenes aggregates but also in resinous components [9, 10].

At present, many methods are proposed are used to prevent or remove sediments from the surfaces of oil equipment, however, all these methods are either expensive or insufficiently efficient [1, 2, 11–13]. One of the most attractive methods from the economical point of view for preventing the formation of ARPS may be low-temperature purification (dewaxing) of oil using liquefied natural gas directly at the field [2, 11, 13]. This method allows a substantial decrease in the content of solid paraffins and asphaltenes in crude oil and improvement of the physicochemical characteristics of the oil.

Efforts aimed at solving the fundamental and applied problems connected with ARPS, the development of a rational technology preventing their formation require substantial enhancement of the amount and profoundness of the information on the composition of the components of these deposits (solid paraffins, resins, asphaltenes). This aspect provides the relevance of the works aimed at the integrated investigation of the composition and structure of high-molecular compounds in the oil.

The goal of the present study was to investigate the structural characteristics of resin and asphaltenes molecules during oil dewaxing with liquefied gas depending on process temperature.

EXPERIMENTAL

The subject of the investigation was oil from the Kharyaginskoe deposit with a high content of paraffins (10.2 mass %), resins (5.4 mass %) and asphaltenes (1.6 mass %). With respect to [physicochemical characteristics, this kind of oil is distinguished by the high solidification temperature, (16.0 °C), its density is 844 kg/m^3, and its viscosity (at 25 °C) is 16.2 mm^2/s. Liquefied gas (a mixture of propane and butane) was used as a dewaxing agent.

The treatment of oil with liquefied gas was carried out at the ratio of oil/liquefied gas equal to 1 : 3 at different negative temperatures (0, −5, −15, −25 °C) obtaining a precipitate (a mixture of solid paraffins, resins and asphaltenes) and purified oil (raffinate).

The procedure of oil dewaxing with liquefied gas was described in [11]. Experiments were carried out with a laboratory set-up consisting of a pressure cylinder with liquefied gas, a steel extractor 280 cm^3 in volume, equipped with temperature and pressure sensors, a filter for the separation of the formed sediments, a thermostat for cooling the mixture. About 50 cm^3 of oil was placed into the extractor, and then the calculated amount of liquefied gas was allowed to enter by self-flowing from the cylinder. The amount of the introduced mixture was controlled by weighing. Cooling rate within a temperature range from +20 to −20 °C was 5 °C/min, and within the range from −20 to −25 °C – about 4 °C/min. The time within which the extractor was kept at given temperature points was 10 min. Process temperature was controlled with the help of a thermometer inserted into the inlet fitting of the filter.

The composition of n-alkanes in the deposit was analyzed using a high-temperature gas chromatograph Khromos 1000 (Russia) with the flame ionization detector and an NT-5 capillary column 15 m long, with the inner diameter 0.22 mm. Chromatograms were recorded in the mode of linear temperature programming from 80 to 390 °C with a heating rate of 15 °C/min.

The material composition of the oil, namely the content of asphaltenes, resins and oils, was determined according to the procedure described in [14]. Oil was diluted with hexane in a 40-fold excess, and the solution was kept for 24 h. Precipitated asphaltenes were separated by filtering, washed with hexane from oils and resins. Maltenes were applied onto a layer of activated silica gel ASK (1 : 15 by mass), and then successively petroleum oils were washed off in the Soxhlet's extractor with *n*-hexane, and resins were washed off with a mixture of ethanol and benzene (1 : 1 by volume).

The material composition of the sediments obtained by dewaxing was determined using the above-described procedure. The sediments were transformed into the liquid state by preliminary heating to 40–50 °C, then a 40-fold excess of *n*-hexane was added to get asphaltenes precipitated. Maltenes were separated into oils and resins.

The structural group analysis (SGA) of high-molecular compounds is based on the data of NMR ^{1}H spectroscopy, elemental composition and molecular mass [15]. The NMR ^{1}H spectra were recorded with the help of an AVANCE AV 300 Fourier spectrometer (Bruker, Germany, $CDCl_3$ as a solvent, hexamethyldisiloxane as the internal standard) with the sample concentration in $CDCl_3$ equal to 1 mass %. The average molecular masses (AMM) of asphaltenes were measured using the cryoscopic procedure in naphthalene. Elemental composition was determined with a Vario EL Cube CHNS-analyzer (Elementar Analysensysteme GmbH, Germany) [15].

The construction of average structures of asphaltenes and resin molecules, calculation of their minimal steric energy were carried out with the help of the software [16] developed at the Institute of Petroleum Chemistry SB RAS, based on the Monte Carlo approach proposed in [17]. The structures of average molecules of resins and asphaltenes were constructed using the data of SGA: the amount of aromatic and naphthene rings, paraffin fragments, the content of carbon, hydrogen, sulphur, nitrogen and oxygen, the number of structural units in the molecule.

RESULTS AND DISCUSSION

Oil dewaxing with liquefied gas followed by the isolation of precipitated ARPS was carried out at a temperature of 0, −5, −15 and −25 °C (Table 1). One can see that the amount of the formed precipitate increases from 10.9 to 13.4

mass % with a decrease in temperature from 0 to −25 °C due to an increase in the content of solid paraffins and resins in the precipitate. The amount of solid paraffins in the precipitate obtained at −25 °C is 2.4 times larger, and the amount of resins is 1.3 times larger than in the precipitate obtained at 0 °C. Asphaltenes completely pass into the precipitate at any temperature during dewaxing. Raffinates are deasphalted oil. With a decrease in the temperature of the dewaxing process, the physicochemical characteristics of purified oil improve: viscosity decreases by a factor of 2.5, oil chilling temperature decreases from +14 to −14 °C (see Table 1).

In the sediments obtained after dewaxing, n-alkanes are represented by the homologous series of compounds with up to 57 carbon atoms (Fig. 1). Along with solid *n*-alkanes C_{17+}, the sediments also contain low-molecular homologues C_{11}–C_{16}. The presence of the latter compounds is connected with process conduction at a negative temperature. For instance, low-molecular C_{11}–C_{16} homologues in the sediments obtained at a temperature of 0, −15 and −25 °C account for 3.9 – 6.7 rel. %. An exclusion is the sediment obtained at −5 °C, in which the fraction of *n*-alkanes C_{11}–

TABLE 1

Composition and physicochemical characteristics of dewaxing products

Process temperature, °C	Yield, mass %		Physicochemical characteristics of purified oil		Content in sediment, mass %		
	Sediment	Raffinate	Viscosity at 25 °C, mm^2/s	Solidification temperature, °C	Paraffins	Resins	Asphaltenes
0	10.9	89.1	14.9	+14	1.4	1.8	1.6
−5	12.2	87.8	13.8	+9	1.8	1.7	1.6
−15	12.9	87.1	5.7	0	2.4	1.8	1.6
−25	13.4	86.6	6.3	−14	3.4	2.3	1.6

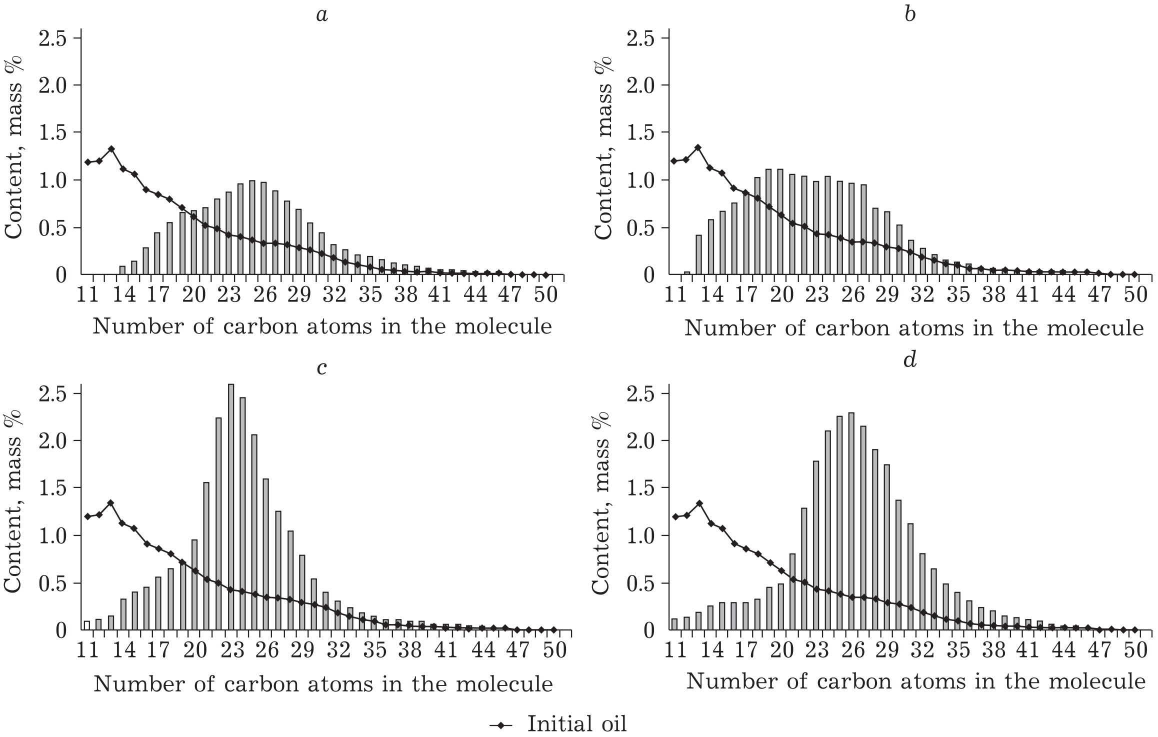


Fig. 1. Molecular mass distribution of *n*-alkanes in sediments obtained at different temperatures of oil dewaxing, °C: 0 (*a*), −5 (*b*), −15 (*c*), −25 (*d*).

TABLE 2

General characteristics and average structural parameters of asphaltene molecules in sediments

Parameter	Asphaltenes of sediments				
	Initial	Isolated at dewaxing temperature, °C			
		0	−5	−15	−25
Average molecular mass, a.m.u.	1132	1737	1771	1262	1520
Elemental composition, mass %:					
C	84.17	85.05	85.32	84.94	86.29
H	8.33	7.89	7.78	7.80	7.29
N	0.68	1.18	0.99	1.16	1.02
S	2.79	3.3	2.95	3.39	2.37
O	4.03	2.58	2.96	2.71	2.67
Number of atoms in molecule:					
C	79.40	123.11	125.9	89.33	109.3
C_a	31.55	54.28	52.5	36.36	45.26
C_n	39.65	63.18	66.7	47.84	59.28
C_p	8.20	5.65	6.7	5.13	4.76
C_α	11.28	16.60	16.5	12.03	15.14
C_γ	3.92	5.65	6.7	5.13	4.76
Distribution of carbon atoms, %:					
f_a	39.74	44.09	41.7	40.70	44.41
f_n	49.93	51.32	53.0	53.56	54.23
f_p	10.33	4.59	5.3	5.74	4.36
Ring composition:					
K_{total}	17.04	28.42	31.6	22.87	32.14
K_a	7.41	13.17	12.6	8.76	10.81
K_n	9.62	15.25	18.9	14.11	21.31
Number of structural blocks, m_a	2.47	3.62	3.6	2.74	3.19

Note. Here and in Table 3: $С_а$, $С_н$, $С_п$, $С_\alpha$, $С_\gamma$ stand for the amount of carbon atoms in aromatic, naphthene and paraffin structures of molecules, in the α-positions to heteroatomic functional groups and aromatic cores, and in terminal methyl groups not bound with the latter, respectively; f_a, f_n and f_p are the fractions of carbon atoms in the corresponding structural fragments; K_{total} is the total number of rings, K_a and K_n are the amounts of aromatic and naphthene cycles in the average molecule, respectively.

C_{16} is 14.1 rel. %. At this temperature, a fine suspension is formed during dewaxing at this temperature, which causes co-precipitation of a large amount of low-molecular hydrocarbons.

Resins and asphaltenes isolated from the sediments were analyzed by means of SGA, which allows calculating the average distribution of atoms over structural elements of the molecules of resins and asphaltenes [14].

Analysis of the data on the changes in the structural group composition of average asphaltenes molecules from the sediments formed during dewaxing at different temperatures showed that their AMM is substantially higher than that of initial asphaltenes (Table 2). This happens due to an increase in the amount of naphthene and aromatic rings in asphaltenes molecules. However, no clear regularity could be detected in the changes of asphaltenes AMM depending on dewaxing temperature. For example, with a decrease in temperature from 0 to −15 °C the AMM of asphaltenes in the deposits decreases from 1771 to 1262 a.m.u., then with a decrease in temperature to −25 °C it increases to 1520 a.m.u. It was established that the molecules of asphaltenes in the deposits formed at a temperature from 0 to −15 °C are composed of four blocks, while the molecules of initial asphaltenes and those isolated at −25 °C are composed of three structural blocks. The aliphatic framing of asphaltenes molecules (C_p) obtained by means of dewaxing decreases with a decrease in temperature in comparison with initial asphaltenes, while the amount of aromatic (K_a) and naphthene rings (K_n) increases (see Table 2). This may be connected with the changes in the forces of intermo-

TABLE 3

General characteristics and average structural parameters of the molecules of resins in the sediments

Parameter	Resins of sediments				
	Initial	Isolated at dewaxing temperature, °C			
		0	−5	−15	−25
Average molecular mass, a.m.u.	652	848	861	852	719
Elemental composition, mass %:					
C	84.44	83.86	85.41	84.87	84.85
H	7.86	9.22	8.29	9.49	8.29
N	1.12	1.21	0.74	1.49	1.04
S	2.40	3.53	2.37	2.44	2.44
O	4.18	2.18	3.19	1.71	3.38
Number of atoms in the molecule:					
C	45.88	59.26	61.28	60.26	50.84
C_a	13.94	20.88	17.77	19.28	14.61
C_n	29.21	24.05	40.05	28.38	33.52
C_p	2.73	14.33	13.45	12.60	2.71
C_α	6.39	7.42	7.65	6.78	6.07
C_γ	2.73	3.67	3.45	3.72	2.71
Distribution of carbon atoms, %:					
f_a	30.37	35.24	29.01	32.00	28.74
f_n	63.67	40.59	65.36	47.09	65.93
f_p	5.96	24.17	5.63	20.90	5.33
Ring composition:					
K_{total}	14.05	10.83	17.53	11.43	14.59
K_a	3.23	3.39	3.50	4.59	4.05
K_n	10.82	5.88	13.44	6.84	10.54
Number of structural blocks, m_a	1.55	1.93	1.76	1.95	1.59

Note. For designations, see Table 2.

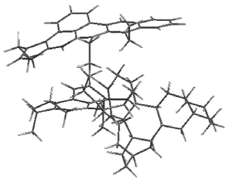
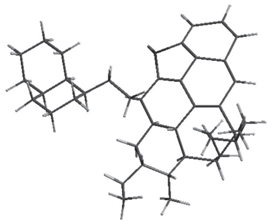
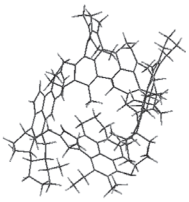
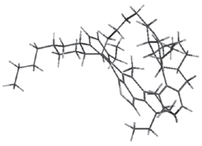
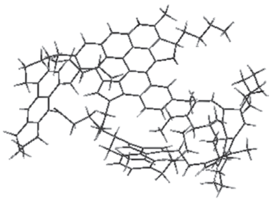
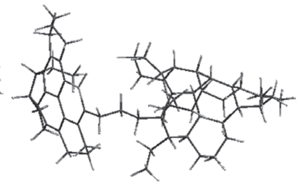
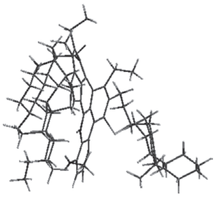
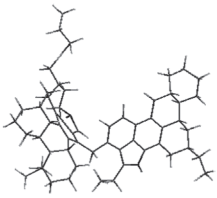
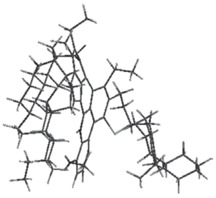
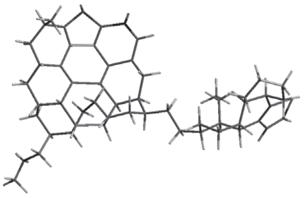
lecular interactions of asphaltenes molecules with each other and with other oil components during the changes in the composition of dispersion medium due to dilution with liquefied gas and due to the negative process temperature. Among possible examples, it is necessary to mention π-interaction between the aromatic fragments of asphaltenes and resin molecules that form the block structure together; the interaction between two unpaired electrons, as well as between the radicals and the system of π-electrons of the neighbouring asphaltene molecules; interactions due to hydrogen bonds participated by heteroatoms [18].

No clear regularity is observed in the changes of the structural parameters of average molecules of the resins in sediments depending on process temperature, similarly to the case of asphaltenes. The average molecular mass of the resins in sediments increases with a decrease in dewaxing temperature (Table 3), which is due to an increase in the number of aromatic cycles. However, the number of naphthene cycles changes jumpwise with a decrease in temperature. Resin molecules, both initial and those isolated from sediments, are the structures composed of two blocks. Unlike for asphaltenes, resins do not possess the ability to get self-associated and to form coarse aggregates. The aliphatic framing of the average molecules of initial resins is insignificant ($C_p \approx 3$), while an increase in the number of alkyl carbon atoms to 13-14 is observed in the molecules of resins in the sediments with a decrease in temperature from 0 to −15 °C, and at −25 °C the content of peripheral carbon chains in the molecules of resins again decreases sharply to the initial value (see Table 3).

On the basis of SGA data, hypothetical structures of the average asphaltenes and resin molecules were constructed. Their full steric energies were calculated by means of molecular dynamics. Among thus drawn structures, those exhibiting the least deviation from the parameters

TABLE 4

Hypothetic structures of the molecules of resins and asphaltenes

Temperature of dewaxing process, °C	Asphaltenes	Resins
Initial		
0		
−5		
−15		
−25		

calculated according to SGA data were selected (Table 4). The changes in the structural parameters of asphaltene and resin molecules during dewaxing may be clearly followed in the spatial structures. In comparison with initial molecules, the number of their structural blocks, aromatic rings, alkyl fragments changes along with the possible positions of heteroatoms. Voluminous four-block asphaltene molecules occupying large space tending to the most stable state from the viewpoint of thermodynamics get packed into denser 'clews' than the molecules composed of a smaller number of blocks (see Table 4).

CONCLUSION

The results obtained in the investigation showed that oil dewaxing with liquefied gas causes a substantial decrease in the content of solid paraffins, deasphalting and partial deresinification, thus physicochemical characteristics improve substantially.

It was established that the change of the chemical composition of dispersion medium due to the dilution with liquefied gas and due to oil dewaxing at different negative temperatures affects the structures of nano- and micro-aggregates of asphaltenes, their spontaneous assembling and precipitation. It is demonstrated that a decrease in dewaxing temperature leads to the change in the structural parameters of the molecules of asphaltenes and resins isolated from the precipitated sediments: the average molecular mass, the fraction of aromatic and naphthene fragments, the total amount of alkyl substituents and the degree of their branching.

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