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The Study Of Solid High-Molecular Paraffin Hydrocarbons In Crude Oils

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Abstract- Information about the composition, structure and properties of high-molecular paraffin hydrocarbons is of great importance for understanding the phenomena of structuring oil disperse systems, changing their viscosity properties, as well as practical problems associated with the extraction and transportation of paraffin oils, for the development of physico-chemical and chemical methods of controlling asphaltene tar-paraffine deposits. In this connection, advanced study of their influence on the properties of oil disperse systems is essential.

The article studies the high-molecular compounds of paraffin hydrocarbons in the crude oils and their components, assesses their quantitative content and impact on the physical and chemical properties of crude oils, reveals the features of the composition of asphaltene resin-paraffine deposits conditioned by different content of high-molecular paraffin hydrocarbons in them. It has been determined by the method of differential scanning calorimetry the presence of alkanes in asphaltenes of oils. It has been found that high-molecular alkanes in oils structure dispersion medium or concentrate in the resin-asphaltene components, which defines different mechanisms of formation of the viscous properties of crude oils.

Keywords: crude oil, asphaltene resin-paraffin deposits, paraffin waxes, oil disperse system, asphaltenes.

1. INTRODUCTION

High content of solid paraffin hydrocarbons in the oil deteriorates its quality and causes troubles when producing and transporting it [1, 2]. Undeservedly little attention was paid to the study of high-paraffinic hydrocarbons in crude oils compared to the relatively low-molecular weight paraffin hydrocarbons. This is connected with difficulties in isolating of high molecular weight hydrocarbons, as well as lack of reliable methods for their detection and investigation. In the last decade, the interest in these compounds in the crude oils has been heightened again due to the development of high-temperature gas-liquid chromatography method[3]. The current state of research of crude oil in the field of chemistry shows [4-6] that the information on the composition, structure and properties of high-paraffin is of paramount importance for solving the problems concerning the structuring of oil disperse systems, change of their viscosity properties, as well as for practical tasks related to the recovery and transporting paraffin oils, for development of physico-chemical and chemical methods of controlling asphaltene resin-paraffine deposits. In this connection, fundamental investigation of their influence on the properties of oil disperse systems is undoubtedly urgently needed.

The article studies the structure, content and crystallization of high-molecular paraffin hydrocarbons in crude oils, their influence on the properties of oils and asphaltene resin-paraffin deposits.

2. RESEARCH METHODS

The chemical nature of solid paraffin petroleum hydrocarbon has not been fully elucidated yet[2, 7], but it is assumed that they consist mainly of methane hydrocarbons to which to a greater or lesser extent, naphthenic and aromatic hydrocarbons are admixed. Insufficient examination of high-molecular paraffin hydrocarbons is conditioned by the difficulty of their isolation from the oil and the lack of methods for studying them. Isolation of hard block paraffin oils has been performed as follows. Oils fraction is dissolved in a mixture of acetone and benzene (1: 1) at a rate of 10 ml per 1 g of the sample and placed in isopropyl bath, cooled to a temperature of minus 20 ± 1 ° C. Hard paraffin, filtered and washed off the filter with hot benzene, settles down from the cooled solution. Today, the method of high-temperature gas chromatography is probably the only method for their research. Hydrocarbon composition of oils and waxes was studied by the method of gas-liquid chromatography using a chromatograph "Chromium-5 'with a flame ionization detector to temperature programming from 80 to 300 ° C. The capillary column of 25 m long, filled with Apiezon L, carrier gas – hydrogen were used. On the basis of the data of gas-liquid chromatography, using the method of internal normalization, the individual hydrocarbon composition of crude oils and paraffin waxes isolated from oils and asphaltene resin-paraffin deposits is determined. The ability of high-molecular paraffin hydrocarbons to be crystallized under certain conditions allows to apply the method of differential scanning calorimetry for their detection and study [8-11]. Calorimetric study of crude oils was carried out using the calorimeter of the company SETARAM. We used the standard cells, scanning interval 20-150 ° C, scanning velocity 0.2 ° C / min. Calibration on the thermal effect was carried by Joule-effect, adjustment of temperature - on the melting point of pure indium. Each experiment had been carried out 2-3 times. Temperature measurement error was 0.2oS±, thermal effects - 4%.

3. RESEARCH RESULTS AND THEIR DISCUSSIONS

Crude oil 1 has a high content of oily fractions and refer to paraffin type, crude oil 2 is high-paraffin with low content of gasoline fractions boiling away up to 200 ° C, is characterized by a high content of resin and low asphaltene content, and crude oil 3 – by high content of gasoline fractions, both latter oils refer to high-paraffin oils (Table 1). Crude oil 2 was determined for by pour point -15 ° C. Samples of oil 3 are viscous mass with high density, high viscosity.

Table 1. Physico-Chemical Properties and Composition of Crude Oils

Crude oil	1	2	3
Density at 20°C, kg/m^3	732.0	903.0	812.0
Kinematic viscosity at 20°C, mm^2/s	2.3	51.3	39.1
Gasoline fraction up to 200^{0}C	19.8	12.0	29.2
Type content of, % wt.:			
oil	66.2	52.6	40.6
resin	8.6	22.6	14.9
asphaltenes	1.6	4.4	1.6
Paraffin waxes	4.2	7.5	12.2

When analyzing the crude oils by the methods of gas-liquid chromatography (GLC), it was revealed therein the presence of solid n-alkanes from C_{16} to C_{36}. The molecular weight distribution of n-alkanes in paraffin oils is shifted towards low molecular weight, in high paraffin oils - towards high-molecular n-alkanes. A special feature of crude oil *3* is the presence of bimodal molecular weight distribution of n-alkanes with maxima of C16 to C18 and C26-C28 (**Figure 1**).

When outputting crude oil in oil-field equipment with change of thermodynamic conditions, it was formed asphaltene resin-paraffin deposits (ARPD) which were selected for analysis in parallel with sampling of oil. The samples of asphaltene resin-paraffin deposits are hard dark brown substances with a sharp smell of oil. From the samples of ARPD there were extracted organic part with a mixture of three solvents (2: 1: 1, chloroform, benzene, isopropanol-1). Type content of ARPD was determined by the method which is in current use by oilmen.

Table 2. Type Content of Asphaltene Resin-Paraffin Deposits

Asphaltene resin-paraffin deposits isolated from crude oil:	1	2	3
Type Content of, % wt.:			
oil	39.1	38.2	37.,5
resin	11.1	13.2	10.3
asphaltenes	13.8	6.2	2.0
Paraffin waxes	35.7	42.0	50.5

The maximum content of asphaltenes is isolated from the asphaltene resin-paraffin deposits of crude oil *1* - 13.8%. It is also characterized by a low content of paraffin wax. Two samples of oil asphaltene resin-paraffin deposits *2* and *3* differ by about the same oil content but different amounts of paraffin and asphaltenes. By high content of paraffin waxes ARPD of oil *3* and of oil *2* is isolated, the obtained samples (of paraffin waxes) have solid consistence, and the most refractory and high molecular weight waxes are contained, by melting point and crystallization, in the samples *2* and *3*.

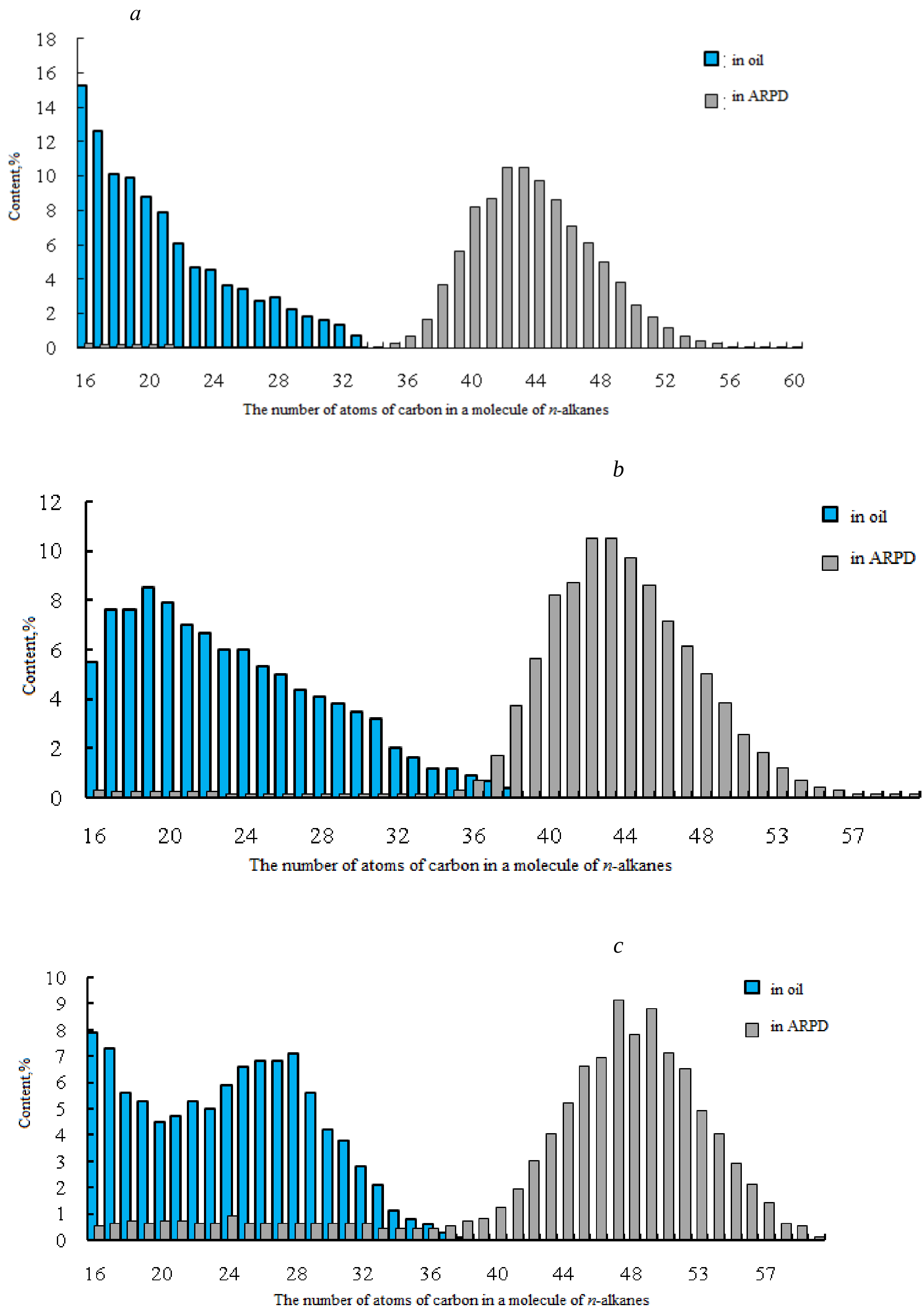

Figure. 1. The molecular weight distribution of n-alkanes of oil and asphaltene resin-paraffin deposits: *a* - 1, *b* - 2, *c* – 3

The n-alkanes of oil *2* contain alkanes from C_{16} to C_{38} with a broad maximum of the molecular-weight distribution, attributable to C_{16}-C_{28}. Oil *3* contain *n*-alkanes from C_{16} to C_{36}, it is characterized by a bimodal distribution of *n*-alkanes with maxima of C_{14}-C_{18} and C_{26}-C_{28}.

It has been found coprecipitation of high-molecular *n*-alkanes with asphaltene of oil, it has been revealed that a maximum of the molecular-weight distribution is shifted toward higher molecular *n*-alkanes in the line oil→ paraffin→ asphaltenes. By the method of high-temperature gas chromatography, we have succeeded in detecting the presence of oil in high-molecular *n*-alkanes C_{40}-C_{59}, the content of which in oil is likely to be very small. It has been found that the concentrate of high molecular weight alkane hydrocarbons precipitates with asphaltenes in their isolation from oil. It has been revealed the presence of high-molecular solid *n*-alkanes up to C_{59} and higher in all of oil asphaltenes.

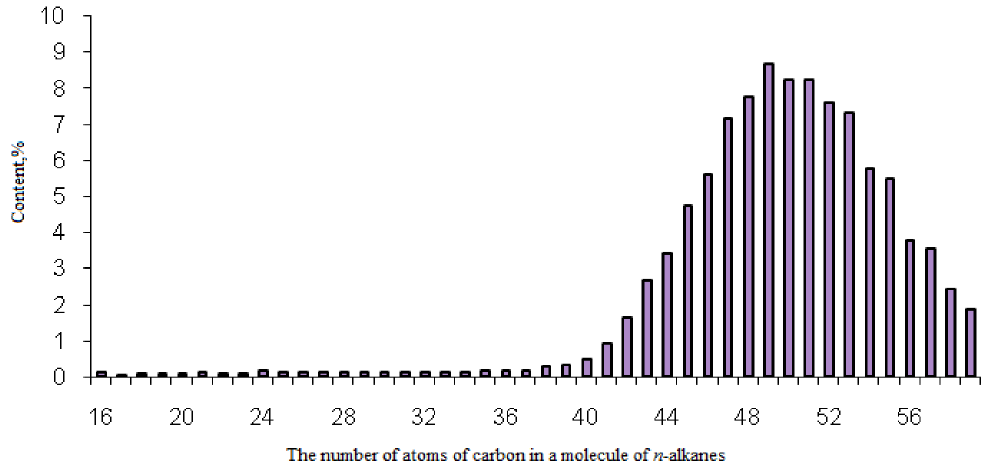

Figure 2. Molecular-weight distribution of *n*-alkanes contained on asphaltenes of oil *2*

The presence of refractory alkanes C_{40}-C_{60} in asphaltenes can be explained by their increased adhesion to the particles of asphaltenes. It is known [12] that the low-molecular *n*-alkanes C_{16}-C_{32} do not have high adsorption properties and cannot stay on the surface of the asphaltenes by washing the latter with hot petroleum ether.

The extracted samples of asphaltene resin-paraffin deposits from oils have been studied using the method of differential scanning calorimetry. The content of the crystalline phase in the samples of ARPD and crystallization temperature of paraffin hydrocarbon are shown in **Table 4**, the curves characteristic of DSC **-** in **Figure 3**.

The sample of asphaltene resin-paraffin sediments of oil *1* is characterized by a high content of crystalline phase and distinguished by the lowest crystallization temperature. High temperature of crystallization is possessed by the ARPD sample of oil *3*, according to high crystallization temperature of 80 ° C, the crystalline phase appears to consist of higher molecular weight paraffin hydrocarbons than of oil deposits *1* and *2*.

Table 4. Data of Differential-Scanning Calorimetry

Asphaltene resin-paraffin deposits isolated from crude oil:	1	2	3
Melting point, °C	68	75	80
Content of crystalline phase, %	53	26	71

The ARPD of crude oil *1* although contains more crystalline phase, one can note that it is composed of less refractory paraffin hydrocarbons than the composition of sample *2* and *3* has. Fig. 3 shows DSC curves of heating samples of ARPD from oils *1*, *2* and *3*, which one can graphically compare the uniformity of the composition of the various ARPD (by width of endo effect on the DSC curve) and see that the difference is conditioned by different composition of the original oils.

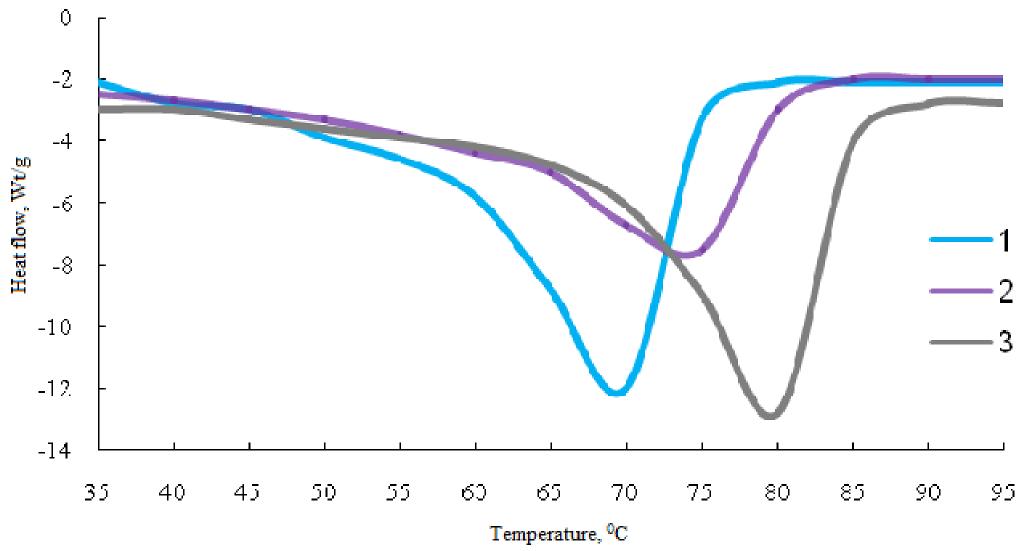

Fig. 3. The curves obtained by differential scanning calorimetry of asphaltene resin-paraffin deposits of oil *1*, *2*, *3*, respectively

On the basis of colorimetric analysis one can say that waxes in oils have a great affinity with the dispersion medium. When paraffin being isolated from oils by standard procedures (freezing), paraffin holds part of the dispersion medium, which causes a lower fraction of the crystalline phase therein, as well as amorphous-crystalline structure. High temperatures of crystallization of waxes in asphaltenes and extracted ones from maltenes, a high proportion of the crystalline phase in them and relatively narrow ranges of melting (crystallization) indicate the presence more refractory and more uniform molecular weight and structure paraffin hydrocarbons in them.

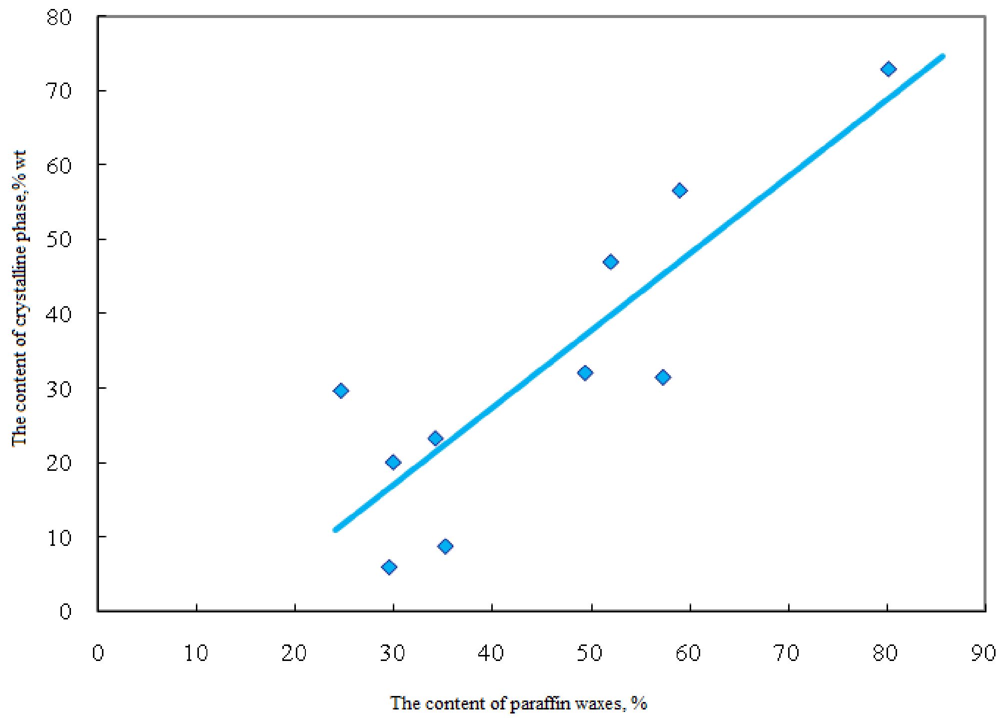

Figure 4. Dependence of the content of crystalline phase in asphaltene resin-paraffine deposits on the content of paraffin waxes in them

4. SUMMARY

According to the content of paraffin hydrocarbons, crude oils refer to highly paraffin oils with a predominance of *n*-alkanes of C_{16}-C_{38} composition. The molecular-weight distribution of *n*-alkanes in the oils is shifted towards low molecular weight, in high paraffin oils – towards high molecular *n*-alkanes. Most high molecular paraffin hydrocarbons present in oil *3*. The relatively low proportion of crystalline phase in the oils and low temperature of crystallization indicate that the crystal phase consists of molecules different in weight and structure, intensively interacting with each other and with the particles of the dispersion medium of oils. As a result, during the crystallization, waxes retain a significant portion of low melting components of the dispersion medium. Virtually identical low solubility of the asphaltenes proper and high molecular paraffin hydrocarbons in low-molecular *n*-alkanes leads to the fact that by a standard procedure of precipitation of asphaltenes, high molecular paraffin hydrocarbons coprecipitate with them. The presence of refractory paraffin hydrocarbon in oils can be determined by the content and the melting point of the crystalline phase in the asphaltenes. The analysis of correlation coefficient indicates that the content of the crystalline phase in the samples of asphaltene deposits in oil is determined primarily by the content of paraffin waxes, sufficiently expressed is also the dependence of the content of the crystalline phase in asphaltene resin-paraffin deposits and the melting point. The asphaltenes ARPD have high molecular paraffin waxes, the composition of which depends on the origin of asphalt and paraffin units. For a more precise determination of the composition and content of high molecular paraffin waxes in the samples of ARPD the most informative are the methods of calorimetry and high-temperature gas-liquid chromatography. Three samples of ARPD have been studied: the first is characterized by a high content of oils and asphaltenes, the lowest content of high-molecular refractory waxes; the second sample is medium oil content, high content of high-refractory paraffin and more amorphism of the crystalline phase; the third type of samples is characterized by low oil content and a high content of high molecular paraffin hydrocarbons and high content of the crystalline phase.

5. CONCLUSION

The understanding of nature and mechanisms of formation of the composition of asphaltene resin-paraffin deposits in the exploitation of oil fields will allow more reasonably approach to choosing the most effective agents for preventing their formation. At the same time, the most important task is to develop scientific and applied aspects to characterize the patterns of asphaltene resin-paraffin deposits of oils in order to identify their composition. In this study, an in-depth study of the crystalline phase of high-paraffin, content of which in the samples of asphaltene resin-paraffin deposits sometimes reaches 80% and higher, which is the beginning of the structuring of asphaltene resin-paraffin deposits of various types has been carried out. A systematic study of the high-molecular paraffin hydrocarbons in crude oils and asphaltene resin-paraffin deposits has been conducted. Differential scanning calorimetry method is an informative and prospective in the study of paraffinic hydrocarbons. With it, it has been established the presence of a crystalline phase alkanes in oil asphaltenes.

THE CONFLICT OF INTERESTS

The author confirms that the present data do not contain any conflict of interests.

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