Study of the optical properties of asphaltenes of wax deposits of oil-water emulsions

A V Savelyeva1,2, N A Nebogina1, I V Prozorova1 and N V Yudina1

1Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, 4, Akademichesky Ave., 634055, Tomsk, Russia
2National Research Tomsk State University, 36, Lenin Ave. 634050, Tomsk, Russia

E-mail: hadejka@rambler.ru

Abstract. In this work, based on a comprehensive analysis of the optical absorption spectra obtained by spectrophotometry in the visible region, the change in the stability of asphaltenes isolated from wax deposits of emulsions with different water contents were studied. Asphaltenes of oil-water emulsion wax deposit with a small water content are characterized by maximum values of the light absorption coefficient. Asphaltenes which characterized by maximum values of the coefficient of light absorption and more capable of aggregation form wax deposit of 10 and 30 % of water-oil emulsions. A further increase in the water content in the emulsion to 50 and 70 % leads to the fact that the values of the light absorption coefficient are reduced, i.e. wax deposit form more stable asphaltenes. The least stable asphaltenes contain a highly aromatic polar fraction, are characterized by high molecular weights and precipitate from emulsions with a small water content and minimal average droplet sizes.

1. Introduction
The formation of oil-water emulsions at oil fields significantly complicates the extraction, gathering and treatment of stock tank oil and creates additional problems for its transportation and storage. This interfacial shell consists from resins and asphaltenes which also contribute to the intensive formation of wax deposits on the surface of oilfield equipment, thereby reducing well productivity and throughput of oil pipelines [1, 2]. To optimize the processes of extraction and transportation of oil and oil products, it is necessary to know the conditions under which the asphaltenes contained in the oil disperse system will not fall out of solution. There are practically no works dealing with the investigation of the effect of the water content of emulsions on the aggregation properties of asphaltenes. Optical studies of water-oil emulsions and their components make it possible to characterize their aggregation properties by establishing the dependence of the light absorption coefficient on the properties of high molecular weight compounds [3, 4].

The aim of this work was to investigate the aggregation properties of asphaltene of paraffin water-oil emulsions depending on the water content and to determine the relationship between the light absorption coefficient of asphaltenes and the structural-group properties of dispersed oil systems.

2. Experimental
In previous studies [5, 6], we investigated the structural and rheological characteristics of oil-water emulsions and their wax deposits depending on the water content. The objects of this study were asphaltenes of wax deposits of water-oil emulsions based on high-paraffin resinous oil (the content of paraffin hydrocarbons, resins, and asphaltenes was 18.2; 9.9, and 2.8 wt%, respectively). Water-oil
emulsions were prepared artificially on the basis of high-paraffin resinous oil (the content of paraffin hydrocarbons, resins, and asphaltenes was 18.2; 9.9, and 2.8 wt%, respectively) using a PE-0118 mixing device with a power of 150 W and a blade rotation speed of 2000 rpm for 10 min. A distilled water (DW) was used as a dispersed phase, the content of which varied from 10 to 70%.

Photometric studies of asphaltenes were carried out using a UVIKON 943 spectrophotometer at a wavelength of 500 nm in a quartz cell with a film thickness of 1 cm. The light absorption coefficient \( k \) was calculated by the formula:

\[
k = D(0.4343C)^{-1},
\]

where D is the optical density of solutions, C is the concentration of asphaltenes in a solvent, and l is the width of the cell.

3. Results and discussion

Optical studies of asphaltenes of oil-water emulsions wax deposit made it possible to calculate the light absorption coefficient \( k \). The maximum values of \( k \) are characteristic of asphaltenes isolated from wax deposit of 10% emulsion. The values of \( k \) of asphaltenes in the wax deposit of oil are lower than those of \( k \) of asphaltenes of deposits of 10% and 30% of emulsions. With an increase in the water content in the emulsion from 10% to 70%, \( k \) for solutions of asphaltenes decreases by 1.4 times (figure 1).

![Graph](image1.png)

**Figure 1.** Dependence of the light absorption coefficient of asphaltenes in wax deposit of oil-water emulsions on the water content (a).

![Graph](image2.png)

**Figure 2.** Dependence of the light absorption coefficient of asphaltenes in wax deposit of oil-water emulsions on size of droplets.

An inverse dependence with a high degree of correlation between the values of \( k \) of asphaltenes of emulsion deposits and one of the important characteristics of oil-water emulsions – droplet sizes was revealed (figure 2). Asphaltenes in the wax deposit of a 10% emulsion with a minimum average droplet diameter (4.4 μm) have maximum values of \( k \) (2856 cm\(^{-1}\)).

It is known that the polar natural surface-active substances of oil are concentrated in wax deposit. In addition, natural surfactants are natural stabilizers of oil-water emulsions. Petroleum acids are of greatest importance among anionic surfactants of oil, while nitrogenous bases are those among cationic surfactants. The main structural fragments of asphaltenes are condensed polyaromatic blocks, including heteroatoms of nitrogen, oxygen, sulfur, and metal complexes. The values of light absorption coefficient of asphaltenes in the wax deposits of emulsions are directly proportional to the content of carboxyl groups and strongly basic and weakly basic nitrogen in them: the higher \( k \), the more surface-active components are contained in the wax deposits (figures 3, 4).
The high correlation coefficient shows the relationship of the spectral characteristics of asphaltenes in the wax deposit of emulsions with the content of carboxyl groups and strongly and weakly basic nitrogen contained in the wax deposit. Thus, the introduction of water into the oil system results in the increased content of heteroatomic components in the asphaltenes involved in the formation of wax deposit of 10% emulsions which leads to an increase in the ability of asphaltenes to aggregate in the volume of a dispersion medium.

In this paper it is shown that an increase in the molecular mass values of asphaltenes of wax deposit of oil emulsions is accompanied by an increase in the light absorption coefficient (table 1). That is, asphaltenes of wax deposit of 10% emulsions are characterized by maximum values of molecular mass and light absorption coefficient. An increase in the water content in the emulsion is accompanied by a symbatic decrease in the molecular mass of asphaltenes and light absorption coefficient.

**Table 1.** Structural-group composition of asphaltenes of oil and asphaltenes of wax deposit of oil and emulsions with various contents of the aqueous phase.

| Parameters                        | Asphaltenes |
|-----------------------------------|-------------|
|                                   | Oil         | Wax deposit of oil | Wax deposit 10% emulsion | Wax deposit 30% emulsion | Wax deposit 50% emulsion | Wax deposit 70% emulsion |
| Molecular mass                    | 1045        | 1748              | 2612                     | 2532                      | 1549                       | 1214                       |
| Number of aromatic rings          | Rₐ          | 7.7               | 13.5                     | 19.0                      | 18.7                       | 9.4                        | 6.4                        |
| Distribution of carbon atoms [%]  | Fₐ          | 44.9              | 46.8                     | 47.7                      | 46.4                       | 43.1                       | 38.8                       |
| Number of carbon atoms of different types in a mean molecule | Cₐ | 34.2 | 58.6 | 90.2 | 85.0 | 48.0 | 33.9 |
|                                   | Cₚ          | 29.2              | 55.7                     | 99.0                      | 98.1                       | 63.5                       | 51.6                       |
|                                   | Cₐ          | 10.6              | 16.9                     | 22.4                      | 21.6                       | 16.7                       | 11.9                       |
|                                   | C₇          | 2.8               | 4.3                      | 7.8                       | 7.5                        | 3.7                        | 4.1                        |

Cₐ – aromatic carbon.  
Cₚ – carbon in aliphatic substituents.  
Cₐ – carbon in α-position to the cycle.  
C₇ – carbon in terminal methyl groups

According to the results of the structural-group analysis presented in Table 1, the number of aromatic rings Rₐ increases by a factor of 1.8 in the asphaltenes isolated from the oil wax deposit as
compared with the asphaltenes of the original oil. In the ‘mean’ molecule of asphaltenes from oil wax deposit, the content of aromatic carbon increases as compared to the asphaltenes of the oil.

Asphaltenes isolated from a wax deposit of 10% emulsion are characterized by an increase in the number of carbon atoms of the aromatic type Cₐ and carbon in the aliphatic substituents Cₚ by 1.5 and 1.8 times, respectively. With an increase in the content of aqueous phase in the emulsion to 70%, a 2-fold decrease in the number of Rₐ aromatic cores is observed. The proportion of aromatic carbon decreases by 1.2 times, and that of saturated carbon increases.

That is, asphaltenes, which are characterized by high molecular masses and also contain an increased amount of aromatic structures with a high degree of their condensation (table 1 and figure 5) have the maximum values of light absorption coefficient. At the same time, an increase in the water content in the emulsion from 10 to 70% leads to the fact that the asphaltenes that form the wax deposit become more aggregatively stable.

![Figure 5](image-url)  
**Figure 5.** Dependence of the light absorption coefficient of asphaltenes of wax deposit of emulsions on Rₐ and Cₐ.

4. Conclusion

Thus, in this paper the relationship of structural-group characteristics and the light-absorbing ability of asphaltene components of wax deposit of oil-water emulsions was considered. This relationship allowed us to characterize the degree of stability of asphaltenes, in particular, their aggregation properties. Wax deposit of 10 and 30% water-oil emulsions has been formed by asphaltenes, which are more capable of aggregation. A further increase in the water content in the emulsion to 50 and 70% has resulted in the formation of the wax deposit by more stable asphaltenes. The least stable asphaltenes contain a highly aromatic polar fraction. They are characterized by high values of molecular weights and settle out of emulsions with a low water content and the smallest average droplet size.

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