Abstract. The aggregative stability of oil produced from oil-saturated reservoirs in various oilfields is studied. The results show that the composition of oil components has a substantial influence on the stability of oil. The composition of oil is investigated by the methods of extraction, liquid adsorption chromatography, and IR spectrometry, which allow to determine the content of resins, asphaltenes, and saturated and aromatic hydrocarbons. The resistance of oil to asphaltene precipitation is studied by electron spectrophotometry. It is shown that stability increases in oil samples containing a higher amount of aromatic structures and resins compared to asphaltenes. The obtained patterns of changes in the resistance of the oils under study to asphaltene precipitation may also hold true for oils produced in other oilfields. These oils may differ in composition and properties due to the peculiarities of their genesis.

Keywords: oil composition, asphaltene precipitation, oil resistance.

Acknowledgments. The work was carried out within the framework of the state task of the Institute of Petroleum Chemistry SB RAS, funded by the Ministry of Science and Higher Education of the Russian Federation (NIOKTR no. 121031500046–7).
Влияние состава нефти на ее устойчивость к осаждению асфальтенов

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Аннотация. В работе изучена агрегативная устойчивость нефти, добытой из нефтенасыщенных пластов на различных месторождениях. Результаты показали, что важное влияние на устойчивость нефти оказывает состав ее компонентов. Для исследования состава нефти были использованы методы экстракции, жидкостной адсорбционной хроматографии и ИК-спектрометрии, позволяющие определять содержания смол, асфальтенов, насыщенных и ароматических углеводородов. Устойчивость нефти к выпадению асфальтенов была изучена методом электронной спектрофотометрии. Показано, что устойчивость возрастает в образцах нефти, содержащих более высокое количество ароматических структур, а также смол по сравнению с асфальтенами. Полученные закономерности изменения устойчивости изученных нефтей к выпадению асфальтенов могут распространяться и на нефти, добываемые на других месторождениях, отличающихся составом и свойствами, обусловленными особенностями генезиса.

Ключевые слова: состав нефти, осаждение асфальтенов, устойчивость нефти.

Благодарности. Работа выполнена в рамках государственного задания для Института химии нефти СО РАН, финансируемого Министерством науки и высшего образования Российской Федерации (НИОКТР № 121031500046–7).

Цитирование: Стахина, Л.Д., Петренко, Т.В., Русских, И. В. Влияние состава нефти на ее устойчивость к осаждению асфальтенов. Журн. Сиб. федер. ун-та. Химия, 2023, 16(1). С. 47–58. EDN: SXYNRG

Introduction

The incompatibility and instability of oils are often responsible for the precipitation of asphaltenes in crude oil and its blends. Generally, for heavy oils having similar aromatic and saturated content, stability increases with decreasing asphaltene content. However, light crude oil with a relatively low asphaltene content may be less stable than heavy oil with a higher asphaltene content due to the influence of other components. This may be due to the low concentration of aromatic compounds and the high content of saturated compounds in the oil. This correlation is mainly applicable for comparison of light oils [1–4].

It is known that resins (R) are considered natural asphaltene peptizers keeping them in solution [5]. To test oil for asphaltene (A) stability, the asphaltene/resin (A/R) or resin/asphaltene (R/A) ratios are widely used [6, 7]. Both components are heavy and non-volatile, and both can be precisely quantified. In some cases, these ratios can provide a preliminary prediction of the resistance of oil to asphaltene
precipitation under certain conditions and help optimize the processes of oil production and refining. A simplified method is known for selecting wells for exposure to a solvent according to the quantitative ratio of asphaltenes and resins in the produced product [8]. If the A/R value is below 0.35, then the oil is considered stable; if it exceeds 0.35, then the oil is classified as unstable. To compare oils by their stability, Sepúlveda Gaona J. A. has proposed the SARA fractionation method. According to this method, on the basis of a number of interrelations of the component composition, we can distinguish between three following zones: stable, metastable, and unstable [9].

The purpose of this work is to study the stability of oils with different physical and chemical properties and composition of components, and to establish possible relationships between the electronic absorption spectra of oil and IR spectrometric characteristics.

**Experimental part**

The objects of study were oils sampled in the oilfields of various regions: Usinskoye (Timan-Pechora province), Tazovskoye, Russkoye, Nurminskoye, Novoportovskoye, Tagrinskoye, Arkhiteshskoye, Urengoyskoye, Vyngayakhinskoye, Yuzhno-Vyngapurskoye, Zapolyarnoye, Samburgskoye, Yamsoveyskoye, Festivalnaya (Northern part of Western Siberia), Borovskoye (Volga-Ural province), Kokaity (Republic of Tajikistan, Central Asia), Naftalan (Eastern Transcaucasia, Republic of Azerbaijan), Emlichheim (Germany). The oils under study differ both in physicochemical properties and composition of components (Table 1).

IR spectra of oil were recorded in the range of 400–4000 cm⁻¹ using a NICOLET 5700 FTIR spectrophotometer (Thermo Electron Corporation, USA). Based on the obtained optical densities, the parameters characterizing the conditional content of structural fragments in oils were calculated [10]:

\[
C_1 = \frac{D_{1605}}{D_{722}} \quad \text{— the ratio of aromatic to aliphatic structures;}
\]

\[
C_2 = \frac{D_{1605}}{D_{722}} \quad \text{— the conditional content of aromatic structures;}
\]

\[
C_3 = \frac{D_{874}}{D_{1605}} \quad \text{— the ratio of substituted bi- and tricyclic aromatic structures to the total content of aromatic fragments;}
\]

\[
C_4 = \frac{D_{742}}{D_{722}} \quad \text{— ratio between polycyclic aromatic and aliphatic structural fragments or the content of condensed aromatic compounds;}
\]

\[
C_5 = \frac{D_{1377}}{D_{1465}} \quad \text{is the ratio of the content of iso-alkanes and branched alkyl substituents in cyclic compounds to n-alkanes or the degree of branching.}
\]

Determination of the group composition – the content of hydrocarbons (HC), resins and asphaltenes of oil – was carried out according to the standard method [11].

The aggregative stability of oil samples was investigated by electron spectrophotometry using a UVIKON 943 device programmed to automatic registration of changes in optical density over time in a precipitant/solvent medium. We used hexane/toluene in a ratio of 3:1, the concentration of oils was 1 wt.%. The curve of changes in optical density was recorded for 200 min at a wavelength of 650 nm in a 1-cm-thick sealed cell [12].

The values of specific absorption coefficients \( (K_{500}, \text{dm}^3/\text{g} \cdot \text{cm}) \) of oil solutions in toluene were calculated based on the Bouguer-Lambert-Beer law by measuring the optical density at a wavelength of 500 nm [13].

The Color Index (C.I.) of the oil solution, which characterizes the degree of condensation of aromatic cores [14], was determined by the formula:
C.I. = $D_{465}/D_{665}$,

where $D_{465}$ and $D_{665}$ are the optical densities of the oil solution in toluene at 465 and 665 nm.

**Results and discussion**

In density, the oils under study can be classified into four types [15]:

1 – light oils (830–850 kg/m$^3$): Urengoyskaya-1, -2, Yamsoveyskaya;

2 – medium oils (850–870 kg/m$^3$): Nurminskaya, Arkticheskaya, Urengoyskaya-3, Zapolyarnaya, Vyngayakhinskaya, Yuzhno-Vyngapurskaya, Samburgskaya;

3 – heavy oils (870–895 kg/m$^3$): Tagrinskaya, Festivalnaya;

4 – bituminous oils (more than 895 kg/m$^3$): Emlichheim, Tazovskaya, Russkaya, Naftalan, Kokaity, Novoportovskaya, Borovskaya, Usinskaya-1,-2,-3 (boreholes Nos. 3418, 5339, 2956, respectively).

Based on the content of resin-asphaltene substances (RAS), the oils under study are divided into three groups in their component composition (Table 1) [15]. The first group of low resinous oils includes oil samples 4, 7–9, 15, 16, and 18, where the RAS content is less than 5 wt%. Samples 1–3, 5, 6, and 10–14 with RAS content from 5 to 15 wt% are included in the second group of resinous...
oils. The third group of highly resinous oils includes oil samples 17, 19, and 20–22 whose total RAS content is above 15 wt%. It follows from the data in Table 1 that as the RAS content increases with a decrease in the percentage of resins compared with that of asphaltenes (R/A) the density of the oils under study increases.

To conduct a comparative analysis of oils for their resistance to asphaltene precipitation, we used the technique proposed by Sepúlveda J. A. et al. [9]. The oil samples under study (Table 1) were divided into three zones according to the ratios of resins and asphaltenes (R/A). The values A/R of the R/A ratios for these oils ranged from 40.1 (Emlichheim) to 2.3–2.6 (Borovskaya, Usinskaya –1, –2, –3) (Fig.1).

As can be seen from Fig. 1, oils with a R/A ratio higher than 20 (samples 1–3) belong to the stable zone. The metastable (intermediate) zone includes oils whose R/A ratio ranges from 10 to 20 (samples 4–7), while the rest of the oils (samples 8–22) are unstable. It should be noted that, according to this method, despite the relatively high content of RAS (9.1–12.5 wt%), samples 1–3 fall into the stable zone due to the percentage of resins (21.8–40.1 wt%), which is higher than that of asphaltenes (Table 1).

To solve various problems of the production, transportation, and refining of oils, the potential for use of their electronic absorption spectra were shown [16–18]. In this work, a comparative analysis of the resistance of the oil samples under study to the precipitation of asphaltenes was carried out using the method of electronic spectrophotometry. Examples of dynamic curves of changes in the optical density D for solutions of oil in toluene after addition of hexane as a precipitant are shown in Fig. 2.

At the initial stage, after the addition of hexane to the toluene solution of oil, the system undergoes a structural rearrangement and asphaltene flocculation begins. The least stable particles precipitate first, as evidenced by the stepwise change in D. The graphical point of maximum of optical density corresponds to the completion of the growth of asphaltene particles, and its further decrease in time corresponds to a decrease in the content of asphaltenes in the solution resulted from their precipitation.

Under the conditions of this study noteworthy is the absence of the stage of asphaltene flocculation for oils from such fields as Naftalan, Vyngayakhinskoye, Russkoye, and Emlichheim (Fig. 2). A similar pattern is also observed for oils from the Festivalnoye and Yuzhno-Vyngapurskoye fields, i.e. dynamic curves are not shown. Practically no changes in optical density over time are observed for these oils,
except for Emlichheim, which may suggest their higher resistance to asphaltene precipitation compared to other samples under study.

It also follows from the results of comparing the dynamic curves that the oils of the Urengoyskoye, Usinskoye, Zapolyarnoye, and Borovskoye fields are the least stable. For these samples, a less broad maximum corresponding to the stage of asphaltene flocculation, and a shift towards an earlier onset of precipitation are observed (Fig. 2). In addition, an increase in the rate of asphaltene precipitation is observed, as evidenced by a sharper change in optical density during this period compared to other oils. The oils of the Kokayty and Tazovskoye fields occupy an intermediate place, since in their case the presence of flocculation stage is observed and an asphaltene precipitation begins later. Hence, they can be characterized as metastable oils among the oils under study. It should be noted that the agreement of results characterizing the stability of oils based on dynamic curves of changes in optical density with those obtained by taking into account the ratio of resins and asphaltenes (R/A) is not the case for all the oils under study. As follows from Fig. 2, according to this method, the oils of the Vyngayakhinskoye and Kokayty fields can be considered as fairly stable, while according to Fig. 1 they may be classified as unstable oils. This indicates that, in addition to the R/A ratio, other factors also influence the process of asphaltene precipitation.

For a comparative characterization of stability based on the data of optical densities of oil solutions, we calculated the color index (C.I.), which characterizes the degree of condensation of aromatic cores (Table

Fig. 2. Dynamic curves of changes in the optical density of solutions of oil sampled in following oilfields: Naftalan (1), Vyngayakhinskoye (2), Kokayty (3), Tazovskoye (4), Russkoye (5), Samburgskoye (6), Urengoyskoye-2 (7), Usinskoye-1 (8), Emlichheim (9), Zapolyarnoye (10), Urengoyskoye (11), Borovskoye (12)
It is known that the lower C.I., the greater the degree of condensation of aromatic cores and the harder it is for the particles to approach each other [14]. It is evident from the data in Table 2 and Fig. 2 that the value of color index is ≤ 8 for more stable oils, which are characterized by the absence a flocculation stage under the conditions of study. The stepwise precipitation of asphaltenes is most pronounced for the oil from the Samburgskoye field, whose color index is 8. As a rule, the value of the color index for less stable oils is higher than 8. An exception is the oils of the Usinskooye and Borovskoye fields, which, according to the results of our studies, are classified as the least stable, while for them C.I. ≤ 5.

This is may be due to a rather low content of resins (Table 1) at high RAS content (23.2–31.4 wt%), since resins are asphaltene peptizers. Thus, when considering the stability of oil, it is necessary to take into account the content of RAS, the ratio of resins and asphaltenes (R/A), and the degree of condensation of aromatic cores (C.I.).

It is known that an increase in the stability of asphaltenes is promoted by the presence of aromatic hydrocarbons in the dispersion medium due to their chemical affinity. As already reported, the high value of the specific absorption coefficient \( K_{500} \) suggests the high content of aromatic structures in oil [13]. This coefficient is a fairly informative parameter in the study of the optical properties of natural compounds.

Fig. 3 shows that the \( K_{500} \) values of some oils are lower than those of the asphaltenes isolated from them. The \( K_{500} \) values depend on the R/A ratio in the oil. Thus, the R/A ratios for oils from the Russkoye and Naftalan fields are 15.9 and 21.8, respectively. The \( K_{500} \) values for these oils are 2.2 and 1.9, respectively. They are significantly less than the \( K_{500} \) values for the oil samples from the Usinskoye field, where R/A ratio is 2.5 and 2.6, and \( K_{500} \) is 10.4 and 10.6, respectively. As is known, oil asphaltenes contain more aromatic structural fragments than resins [19, 20].

Additional information about the composition of all the oils analyzed can be obtained from the results of studies of aromatic structures using IR spectrometry data (coefficients \( C_1 \) and \( C_4 \)).

<table>
<thead>
<tr>
<th>Oil code</th>
<th>Color index</th>
<th>( C_1 )</th>
<th>( C_4 )</th>
<th>( K_{500} )</th>
<th>Oil code</th>
<th>Color index</th>
<th>( C_1 )</th>
<th>( C_4 )</th>
<th>( K_{500} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>3.0</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>19</td>
<td>4.7</td>
<td>1.5</td>
<td>1.3</td>
<td>9.8</td>
</tr>
<tr>
<td>13</td>
<td>4.2</td>
<td>0.6</td>
<td>0.9</td>
<td>2.4</td>
<td>20</td>
<td>4.7</td>
<td>1.7</td>
<td>1.4</td>
<td>10.4</td>
</tr>
<tr>
<td>1</td>
<td>4.4</td>
<td>0.4</td>
<td>0.5</td>
<td>6.6</td>
<td>21</td>
<td>4.8</td>
<td>1.6</td>
<td>1.3</td>
<td>10.6</td>
</tr>
<tr>
<td>12</td>
<td>4.5</td>
<td>0.6</td>
<td>1.0</td>
<td>1.0</td>
<td>22</td>
<td>5.0</td>
<td>0.8</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>17</td>
<td>5.3</td>
<td>1.4</td>
<td>1.5</td>
<td>2.0</td>
<td>11</td>
<td>8.4</td>
<td>0.5</td>
<td>0.9</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>6.2</td>
<td>1.3</td>
<td>1.5</td>
<td>2.2</td>
<td>6</td>
<td>9.4</td>
<td>0.6</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>7.1</td>
<td>1.4</td>
<td>1.7</td>
<td>1.9</td>
<td>4</td>
<td>10.0</td>
<td>0.9</td>
<td>1.4</td>
<td>0.2</td>
</tr>
<tr>
<td>8</td>
<td>7.4</td>
<td>0.6</td>
<td>0.9</td>
<td>0.3</td>
<td>7</td>
<td>11.3</td>
<td>0.6</td>
<td>0.9</td>
<td>1.8</td>
</tr>
<tr>
<td>9</td>
<td>7.6</td>
<td>1.2</td>
<td>1.5</td>
<td>1.1</td>
<td>2</td>
<td>11.6</td>
<td>0.6</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>16</td>
<td>8.0</td>
<td>0.4</td>
<td>0.7</td>
<td>0.6</td>
<td>10</td>
<td>12.8</td>
<td>0.5</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18</td>
<td>12.9</td>
<td>0.5</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td>17.5</td>
<td>0.5</td>
<td>0.9</td>
<td>0.1</td>
</tr>
</tbody>
</table>
be seen from Table 2, the highest values of aromaticity coefficients (C_1) are demonstrated by the group of more stable samples, namely by oils 17 (1.4), 5 (1.3), 3 (1.4), and 9 (1.2). They also have high relative content of C_4 condensed arenes (1.5, 1.5, 1.7, and 1.5, respectively). These results are consistent with data obtained with the use of K_500 and C.I. We tried to find a possible relationship between all obtained coefficients for the oils under study.

In Table 3 and in Fig. 4 shown are the results of determining the functional relationship between K_500 and IR spectral parameters reflecting the composition for all oil samples under study and separately for more stable oil samples, where the flocculation stage was practically not observed, as well as for less stable oil samples, where this stage was observed (Table 2). It should be noted that most of the revealed dependencies are approximated by a second order polynomial function (2OPF) and, with somewhat less reliability, by linear and power functions. It is evident from Table 3 that the value $R^2$ of approximation reliability (R-squared value) is the highest (from 0.6282 to 0.9334) in the case of the K_500 functional relationship with the C_1–C_4 parameters reflecting the content of aromatic structures (C_1, C_2, C_3, C_4) and with the C_5 parameter reflecting the content of aliphatic ($D_{1377}/D_{1461}$) groups for less stable oil samples. For more stable oil samples, the $R^2$ value (0.8276 and 0.6753) is the highest only in the case of a functional relationship between K_500 and C_1 and C_4 parameters. For these oils the relationship of K_500 with C_2, C_3 and C_5 parameters is insignificant and varies with reliability $R^2 = 0.4673$ and less.

For all oil samples, the highest $R^2$ values (0.7991 and 0.8230) are observed only in the case of the relationship between K_500 and C_1 and C_2 parameters.

The results of determining the relationship between C.I. and other spectral parameters of the oils under study are presented in Table 4 and in Fig. 5.

It follows from Table 4 and Fig. 5 that the value of the approximation reliability $R^2$ is highest (from 0.6691 to 0.8344) only in the case of a functional relationship between C.I. and IR parameters C_1, C_2, and C_4 reflecting the content of aromatic structural fragments for less stable oil samples. Lower $R^2$ values (from 0.5199 to 0.5689) were found for the relationship of C.I. with the IR parameter C_5, which reflects the ratio of the content of iso-alkanes and branched alkyl substituents in cyclic compounds to n-alkanes. The relationship between C.I. and K_500 (Table 4) was determined with
Table 3. Correlation indices between $K_{500}$ and IR spectral parameters of oil reflecting their composition

<table>
<thead>
<tr>
<th>Function $Y=f(K_{500})$</th>
<th>R-squared value ($R^2$) for the function approximating the trendline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All oils</td>
</tr>
<tr>
<td>$C_1 = f(K_{500})$</td>
<td>0.7991</td>
</tr>
<tr>
<td>$C_2 = f(K_{500})$</td>
<td>0.8230</td>
</tr>
<tr>
<td>$C_4 = f(K_{500})$</td>
<td>0.2633</td>
</tr>
<tr>
<td>$C_5 = f(K_{500})$</td>
<td>0.2987</td>
</tr>
<tr>
<td>$C_6 = f(K_{500})$</td>
<td>0.3574</td>
</tr>
</tbody>
</table>

Fig. 4. Functional relationship between $K_{500}$ and IR parameters reflecting the oil composition
Fig. 5. Functional relationship between color index (C.I.) and IR parameters reflecting the composition of oils

Table 4. Correlation indices between C.I. and other spectral parameters of the oils under study

<table>
<thead>
<tr>
<th>Function $Y = f(X)$</th>
<th>Oil samples</th>
<th>R-squared value ($R^2$) for the function approximating the trendline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2OPF</td>
</tr>
<tr>
<td>$C_1 = f(C.I._1)$</td>
<td>Less stable oils</td>
<td>0.6837</td>
</tr>
<tr>
<td></td>
<td>More stable oils</td>
<td>0.8344</td>
</tr>
<tr>
<td>$C_2 = f(C.I._2)$</td>
<td>Less stable oils</td>
<td>0.6691</td>
</tr>
<tr>
<td></td>
<td>More stable oils</td>
<td>0.6817</td>
</tr>
<tr>
<td>$C_3 = f(C.I._3)$</td>
<td>More stable oils</td>
<td>0.5689</td>
</tr>
<tr>
<td></td>
<td>Less stable oils</td>
<td>0.5199</td>
</tr>
<tr>
<td>$C.I. = f(K_{500})$</td>
<td>All oils</td>
<td>0.1993</td>
</tr>
<tr>
<td></td>
<td>More stable oils</td>
<td>0.4500</td>
</tr>
<tr>
<td></td>
<td>Less stable oils</td>
<td>0.6990</td>
</tr>
</tbody>
</table>
noticeable reliability by polynomial ($R^2 = 0.6990$) and power ($R^2 = 0.7441$) functions only for less stable oil samples.

**Conclusions**

The results of the study show that not only the ratio of resins to asphaltenes must be taken into account in the case of a comparative analysis of oils for their resistance to asphaltene precipitation. For a rapid comparative assessment, the method of electronic spectrophotometry can be used. This method is based on recording a dynamic curve of changes in optical density over time and determining the specific absorption coefficient $K_{500}$ and the color index C.I.

For all oil samples under study, a functional relationship between the specific absorption coefficient $K_{500}$ and IR parameters, reflecting the content of aromatic structures, was established with a high accuracy of approximation. This relationship was also observed for unstable oil samples, which are characterized by asphaltene flocculation.

**References**


