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Use of the Technique of Spectrophotometry to Study the Stability of Crude Oil from the Usinsk Field

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Abstract

The effect of heavy high molecular mass components of crude oil (asphaltenes, resins, and aromatic hydrocarbons) on its aggregative stability was studied on the example of heavy oils from the Usinsk field. The componential composition of oil samples was determined by precipitation and chromatography methods. Different spectral characteristics in the visible region that allow operatively comparing the resistance of crude oil against precipitation of asphaltenes were determined by the method of electron spectroscopy. For this purpose, dynamic curves of a change in the optical density were removed in solvent/precipitator (toluene/hexane) system and light absorption (K_{500}) and colour (K_c) coefficients were computed. The stability of crude oil was determined by not only the ratio of resin and asphaltene components, as demonstrated. Oil aggregative stability versus the degree of condensation and a network of aromatic compounds was revealed using colour coefficient.

Keywords: heavy oil, composition, resins, asphaltenes, stability, spectral coefficients

INTRODUCTION

One of the most common problems in the oil industry is related to oil precipitation. Crude oil movement along the bed, and also along processing equipment during extraction and transportation leads to phase transformations and a change in system stability. Whereupon asphalt-resin-paraffin deposits (ARPD) are generated in the equipment surface. Precipitate formations reduce the permeability of reservoirs and wettability of the pore space of rocks, well production and productivity [1].

Currently, the extraction of highly watered and heavy oils, especially sensible to the complex behaviour of the asphaltene phase, is growing. Crude oil is regarded as oil disperse system (ODS). Asphaltenes and resins are two groups that comprise colloidal dispersion part of crude oil. One of the important properties of ODS is its aggregative stability, the study of which numerous papers are devoted to [2–4]. The development of criteria of oil stability represents an important scientific and applied task. High stability of oil systems is required in some cases: during extraction, transportation, storage, and heating in tube furnaces. On the contrary, in deparaffinization, deasphaltation, and crystallization processes *etc*. [5], it is advisable to accelerate system delamination process.

Asphaltenes are the heaviest components of crude oil; their main structural fragments are presented by condensed polycyclic (mainly, polyaromatic) systems that include heterocyclic and non-heterocyclic nitrogen, oxygen, and sulphur compounds, and also traces of metals (nickel, vanadium, *etc*.). Normal paraffin chains mainly C_1–C_4 are present in asphaltenes. However, long chains, up to C_{16}–C_{20}, are also present. Asphaltenes play the primary role in the structuring of ODS and determine the stability of the colloidal structure of crude oil. The resistance of crude oil to flocculation and the precipitation of asphaltenes is mainly ensured by the steric effect of resins adsorbed onto asphaltenes. To monitor the deposition of asphaltenes from oil systems, various methods are used. Viscosity measurement [5], microscopy [6], electric conductivity [7] and spectrophotometric [2] methods are among them.

The present work explored a change in the resistance of crude oil on the ground of complex analysis of optical absorption spectra acquired using electron spectrophotometry in the visible region.

EXPERIMENTAL

Samples of crude oil from the Usinsk field (Komi Republic), produced from wells jointly operating the upper, middle, and lower (UO + MO + LO, well No. 1248), the upper and middle (UO + MO, wells No. 2752, 2805), and also the middle and lower (MO + LO) objects (wells No. 3418 and 429) of the Permo-Carboniferous strata were selected as research targets. Mechanical impurities and water were removed from oil samples by the sequential centrifugation and settling over calcined calcium chloride. It was found in [8] that crude oil samples selected from the upper, middle and lower objects of the bed tended a certain change in the componential composition.

Physicochemical properties and composition of selected oils were determined. Oil viscosity was determined by oscillatory viscometry using Rheokinetic tuning fork viscometer; the density was determined by the picnometric method.

The componential composition (oils, resins, and asphaltenes) of crude oil samples were explored by precipitation and chromatography methods. Asphaltenes were preliminarily isolated from oil samples by the Golde method and their content was determined. Maltenes (deasphaltenizates) obtained after separation of asphaltenes were applied onto ASKG silica gel in a Soxhlet apparatus, oils were primarily desorbed of the sorbent by multiple hot extraction with hexane, then, resins – with a mixture of alcohol and chloroform (7 : 93).

The stability of crude oil towards the precipitation of asphaltenes was explored using electron spectrophotometry. This is a facile, convenient, and the most optimum procedure due to the availability of available and small-sized spectrophotometers that laboratories of oil fields and refineries are equipped with. The spectrometric study was carried out using UVIKON-943 spectrophotometer (λ = 650 nm) that allows automatically recording in dynamic mode optical density changes in the solvent/precipitator medium, registering flocculation process according to an increase in visible adsorption over time, while the precipitation process of asphaltenes – by adsorption decrease. The maximum optical density attests to growth process termination of asphaltene particles. Since it is hard to determine points of the beginning of flocculation and the precipitation of asphaltenes because of a darker shade of oil systems, then their solutions were analysed in toluene (1 mass %). The dynamics change in the optical density (D) versus time depending on the solvent/precipitator ratio becomes most apparent with greater amounts of the precipitator in the system, as which n-hexane was used [9]. In all experiments, the toluene to n-hexane ratio was 1 : 3. The curve of changes in the optical density was recorded for 240 min. All measurements were performed under similar conditions.

Specific absorbance values of solutions of oil samples under study in toluene (K_{500}) were computed on the grounds of the Bouguer–Lambert–Beer law, recording their spectra in a 1 cm cuvette using UVIKON-943 spectrophotometer near a wavelength of 500 nm.

RESULTS AND DISCUSSION

Table 1 presents the data of physicochemical properties (density and dynamic viscosity), and also the contents of oils and resinous-asphaltenic materials in crude oil samples under study. It can be seen that all samples are characterized by a high content of resins and asphaltenes. Significant indicators of density and viscosity allow relating crude oil samples to heavy, bituminous, and highly viscous types (GOST P 51858–2002).

TABLE 1

Physicochemical characteristics of crude oil

Well number	Content, mass %			Density, g/cm^3	Viscosity, mPa·s (20 °C)
	Oils	Resins	Asphaltenes		
429	73.9	16.1	10.0	0.973	7425
1248	71.5	21.0	7.5	0.980	5487
3418	68.6	22.3	9.1	0.964	9500
2805	74.4	16.2	9.4	0.998	14364
2752	72.2	13.8	14.0	0.978	11673

Figure 1 gives dynamic curves of changes in the optical density of samples produced during the addition of n-hexane to a solution of crude oil in toluene. It is worth noting that compared to samples from other wells, a solution of crude oil from well No. 3418 (curve *4*) is characterised by a less dramatic increase in the optical density over time but its higher value after curve exit onto the plateau.

This attests to slower flocculation of asphaltenes and smaller amounts the laid down unstable particles from this crude oil. Furthermore, asphaltene precipitation time determined according to the beginning of a decrease of the optical density in the dynamic curve is 30 min for crude oil from well No. 3418, which 3 times exceeds precipitation time for crude oil from well No. 429 (10 min) and almost 6 times – from wells No. 1248 and 2752 (for them, precipitation begins already in 5 min after the addition of n-hexane).

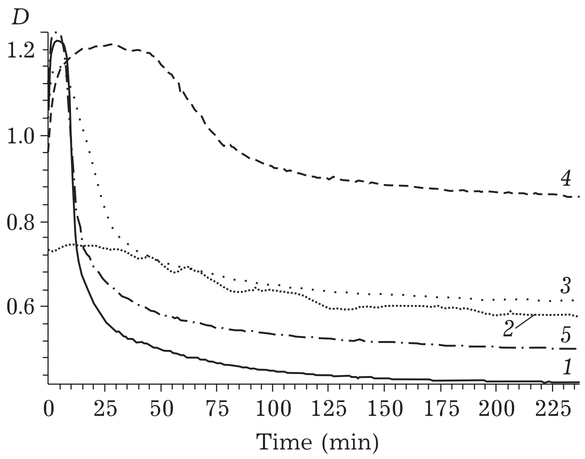

Fig. 1. Dynamic curves of changes in the optical density of crude oil solutions from different wells: No. 2805 (*1*), No. 429 (*2*), No. 1248 (*3*), No. 3418 (*4*), No. 2752 (*5*).

Judging by the nature of dynamic curve *2* referring to crude oil from well No. 429, the flocculation process for it is almost absent; a minor change in the optical density corresponds to the precipitation of asphaltenes. A stepwise decrease of the optical density over time for this sample is related to content reduction of initially least stable asphaltene particles, and then – more resistant ones that have higher aromaticity [2].

The most dramatic decrease in the optical density after curve exit onto the plateau corresponding to asphaltene precipitation stage is observed for crude oil from wells No. 2752 and 2805, moreover, the value D for the latter reaches the maximum, which speaks of the maximum amount of the laid down unstable particles. Hence, crude oil from well No. 2805 (curve *1*) is least resistant compared to samples from other wells.

As already noted above, the studied crude oils are different by the content of resinous-asphaltenic components (see Table 1). It is known that not only external factors but primarily the composition of crude oil itself [10] affect the resistance of oils towards asphaltenes, moreover, resins act as asphaltene dispersants and prevent their aggregation [11]. To assess the stability of crude oil, the authors of [12, 13] propose using the stability index that is determined as the resin/asphaltene ratio (R/A). As can be seen from the data of Table 2, the minimum R/A value (0.98) is observed for oil from well No. 2752, while the maximum one (2.79) – for oil from well No. 1248. Judging from this, one may assume that crude oil from well No. 2752 is least resistant, while that from well No. 1248 has the maximum stability. However, this does not correspond to spectrophotometric study results. Crude oil from well No. 1248 is less stable compared to oil from well No. 3418, as evidenced by the less

TABLE 2

Spectral coefficients

Well number	R/A	K_{500}	K^1_{500}/K^2_{500}	K_c
429	1.62	9.02	1.39	4.43
1248	2.79	8.98	1.70	4.18
3418	2.47	9.80	1.36	4.71
2805	1.71	9.83	2.00	4.08
2752	0.98	9.86	1.96	2.89

Note. K_c is colour coefficient.

wide maximum optical density, as well as by its sharper change according to Figure 1.

This is also true with the sample from well No. 429: in relation to the R/A ratio (1.62); it can be attributed to unstable crude oil, but the opposite follows from the comparison of dynamic curves. Thus, the findings confirm the conclusion made in [2] that R/A is not the only indicator that determines the stability of oil disperse systems towards the precipitation of asphaltenes. Other factors also affect the asphaltene precipitation process. For example, the presence of aromatic hydrocarbons in a dispersion medium has a positive impact on the resistance of asphaltenes due to their chemical affinity [14].

To comparatively assess the stability of crude oil, our studies used the values of the specific indicator of light absorption of oils near a wavelength of 500 nm (K_{500}). Paper [15] revealed the direct correlation between the K_{500} indicator and IR and ^1H NMR spectroscopy data, which reflect the relative content of in samples of aromatic structural fragments.

As can be seen from Table 2 data, the specific indicators of light absorption near 500 nm for the crude oil sample from well No. 3418 (9.8) are higher than that for the probe from well No. 1248 (8.98). This may attest to a higher content of aromatic hydrocarbons therein and consequently, its higher stability compared to the sample from well No. 1248, which is in agreement with the data in Fig. 1. At the same time, crude oils from wells No. 2752 and 2805, characterised by the highest K_{500} values (9.86 and 9.83, correspondingly) turned out to be least resistant.

As it follows from the data of Fig. 1, the optical density of solutions also decreases after the precipitation of asphaltenes therefrom. Therefore according to the ratio of this indicator computed before and after the precipitation of asphaltenes (K^1_{500} and K^2_{500}, respectively), one may assess the amount of the laid down asphaltenes, and consequently the stability of crude oils. Specific absorption coefficients were calculated by us and K^1_{500}/K^2_{500} value was determined according to the results of the analysis of adsorption spectra for solutions of initial crude oil and samples selected from the upper layers of crude oil solutions after the precipitation of asphaltenes. As can be seen from Table 2, the maximum ratio (2.00) is typical for oil from well No. 2805 that has the minimum stability, according to the data of Fig. 1. The ratio of specific absorption coefficients (K^1_{500}/K^2_{500}) increases in the following series of wells: No. 3418 < 429 < 1248 < 2752 < 2805. This corresponds to stability reduction of the considered crude oils according to the nature of dynamic curves (see Fig. 1).

To comparatively characterize crude oils, paper [16] used the parameter K_c = E4/E6 (colour coefficient) that is the ratio of optical densities of a solution of oil near wavelengths of 465 and 665 nm. It characterizes the degree of condensation of the aromatic carbon grid. The smaller K_c is, the higher is the degree of condensation. It is worth considering the interrelation of this parameter and the stability of crude oil. According to the findings (see Table 2), colour coefficient decreases in the following series of well samples: No. 3418 > 429 > 1248 > 2805 > 2752. This attests to an increase in the degree of condensation of the aromatic carbon grid and most likely corresponds to a decrease in the resistance of these samples, which is in good agreement with the data of Fig. 1. The minimum value of colour coefficient (2.89) for the sample from well No. 2752 pointing out at the highest condensation of components therein compared to other samples should be noted. Apparently, this is what explains the earliest time (5 min) of the beginning of the precipitation of asphaltenes observed for this sample (see Fig. 1).

CONCLUSION

Thus, it has been proven that comparative analysis of the stability of crude oils towards the precipitation of asphaltenes based only on the ratio of resins to asphaltenes or the specific coefficient of absorption (K_{500}) does not produce objective results. It is worth considering the totality of various factors that determine oil aggregative resistance including colour coefficient.

The findings demonstrate an opportunity for comparative assessment of the stability of crude oil *via* the trend towards the precipitation of asphaltenes on the ground of spectrophotometric method data: according to optical density change dynamics over time, the ratio of coefficients of light absorption of crude oil and deasphalter, an also by colour coefficient. The preliminary projected change in the stability of crude oil under certain conditions may be made using this method. Furthermore, its recovery, transportation, and recycling processes may be optimized.

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