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The integrated effect on properties and composition of high-paraffin oil sludge

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Abstract

The study is devoted to the integrated effect of acoustic treatment and addition of an inhibitor on viscosity-temperature properties and n-alkane composition in high-paraffin oil sludge. Ultrasonic treatment for 1 minute and addition of the inhibitor at the concentration of 0.05 % wt. decrease viscosity by 10 times and pour point by 8 °C.

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1. Introduction

Due to depletion of light hydrocarbon reserves, oil companies have to develop deposits of high-paraffin oils with a positive pour point. A decrease in temperature of such oils is accompanied by formation of a dispersed phase with high-molecular n-alkanes of C₁₈H₃₈-C₆₅H₁₃₂ composition. A spontaneous increase in viscosity of high-paraffin oil, up to loss of fluidity, is observed in the sol-gel temperature transition region. The resulting gel is of a solid structure formed by a three-dimensional grid of interconnected paraffin crystals and an occluded dispersion medium¹.

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Pumping of such high-paraffin oils is associated with high rates of paraffin deposition in pipelines and some parts of oil equipment, which make their operation much more difficult and result in higher labour and material costs.

Deposition can be avoided or inhibited by using smooth (protective) coatings, insulating pipelines, heating oil, increasing solving power of oil by means of petroleum solvents. The traditional method for sludge formation in oil equipment is to apply chemical reagents that prevent or inhibit paraffin deposition during oil production and transportation². The chemical method is highly effective and easy to implement. Reagents have the prolonged effect³.

Over the recent decade, the physical treatment methods have been under development⁴⁻⁶. They allow one to significantly improve structural and mechanical properties of "difficult" oils. One of such methods is ultrasound treatment in a frequency band of 22 – 44 kHz^{7,8}. The primary physico-chemical and chemical effects induced by acoustic fields in the oil system are mainly nonlinear effects, the most important of which is cavitation⁹. Ultrasonic cavitation is noted to be a unique and effective mechanism that locally concentrates a relatively low medium energy of an acoustic field in very small quantities. Ultrasound waves pass through a liquid medium in consecutive compression and expansion steps, with formation of cavitation bubbles, the centers of which are dissolved gas molecules. The complex structural units of the oil dispersion system at or even near the surface of cavitation bubbles are exposed to strong deformations which break intermolecular bonds^{10,11}.

Purpose of this paper is to study the integrated effect of the inhibitor based on alkyl acrylate copolymers and ultrasound treatment on structural and rheological properties, as well as on composition of high-paraffin oil sludge.

2. Subjects and methods

High-paraffin oil with pour temperature of 4.4 °C, containing 98.6 % wt. of oils (including 6.9 % wt. of n-alkanes), 1.4 % wt. of silica-gel resins, without asphaltenes, was taken as a test subject.

Ultrasound treatment of the samples was performed by sonifier UD-20 at the frequency of 22 kHz and the rate of 6.2 W/cm². The sample was treated in a thermostatically controlled cell for 0.5-10 minutes. Then 0.01-0.1 % of the inhibitor was added to oil. Rheological properties of oil samples were studied using the rotation viscometer Brookfield DV-III ULTRA. Forward and backward isotherm curves were recorded in the shear velocity range of 0–85 s⁻¹ at 5 °C. Pour point was measured by INPN device (KRISTALL).

The deposition process was quantitatively estimated by the device designed on the basis of the "cold finger" test method¹². The experiment was conducted for 1 hour at the oil temperature of +30 °C and the finger temperature of +5 °C. The resulting oil deposits were analyzed using chromatato-mass-spectrometry quadrupole system GSMS-DFS "Termo Scientific" by MIM (multiple ion monitoring) method. Mass chromatograms were scanned on the basis of characteristic ions in the temperature programming mode: initial temperature 80 °C, final temperature 300 °C, rate 4 °/min. The capillary quartz column of 30 m in length and the inner diameter of 0.25 mm was used with the stationary phase DB-5MS (0.35 µm film). Deutero-acenaphthene was used as standard. The acquired results were processed using Xcalibur software.

IR spectra of oil and its deposits in CHCl₃ solution were recorded in FTIR spectrometer NICOLET 5700 in the range of 400-4000 cm⁻¹. The samples from the CHCl₃ solution were applied in the form of film to KBr plates. OMNIC 7.2 Thermo Nicolet Corporation was used to process IR spectra and to determine optical density. Content of aliphatic compounds in the samples was calculated as the ratio of total absorption band intensity of methylene groups in paraffin chains (720 cm⁻¹) and methyl groups (1370 cm⁻¹) to aromatic C=C_{aroma}-bonds (1600 cm⁻¹) ($\sum \text{CH}_2 + \text{CH}_3 / \text{C} = \text{C}_{\text{aroma}}$). Content of alkyl links with a chain of more than four carbon atoms was calculated as 720/1465 cm⁻¹. Branching coefficient was calculated as 1380/1465 cm⁻¹.

3. Results and discussion

The previous studies have shown that ultrasound treatment of high-paraffin systems adversely affects their structural and mechanical characteristics. In particular, viscosity and pour point tend to increase^{13,14}. This paper determines structural and rheological characteristics of high-paraffin oil under the integrated effect of ultrasound treatment and the inhibitor, a polymer component of which is represented by dodecylamine-modified poly(methyl methacrylate)¹⁵.

The target oil was treated in an acoustic field for 0.5-10 minutes. Ultrasound treatment for 1 minute without

inhibitor decreases oil viscosity in the low shear velocity range. At a higher mechanical load, rheological parameters increase as compared to the initial sample (Fig. 1). Pour point of processed oil gradually increases with growing exposure time and reach +0.3, 2 and 4 °C after 1, 5 and 10 minutes, respectively.

The inhibitor added to oil at the concentration of 0.01-0.1 % wt. significantly decreases dynamic viscosity in the wide shear velocity range (Fig. 1). At the optimal concentration of the inhibitor (0.05 %) to the oil mass, the effective viscosity at shear velocity of 10 s^{-1} decreases by 12 times. The depression effect is strengthened after addition of the inhibitor at the concentration of 0.05 % wt. to oil treated by ultrasound throughout the shear velocity range.

Forward and backward isotherm curves were recorded at 5 °C for estimating stability of the structures generated in the test samples. As shown in Fig. 2, forward and backward curves provide a hysteresis loop. Hysteresis phenomena in shear thinning fluids (thixotropic systems) are attributed to delay of restorative processes of the structure or insufficient destruction of the original structure¹⁶. High shearing stresses of the forward isotherm curve in the low shear velocity range suggest that the initial oil is highly structured. Increase in a mechanical load causes destruction of the structure which cannot be restored after unloading (Fig. 2). The loop area slightly decreases after ultrasound treatment. After the integrated treatment, forward and backward curves almost coincide with each other. Hysteresis loops allow one to estimate strength of intermolecular bonds which are broken under the effect of shear strength and then relax in time. The internal energy to break the dispersed system (W) was calculated by loop area¹⁷. As shown from Table 1, after the integrated effect of ultrasound and the inhibitor, the internal energy to break the dispersed system reduces by 58 times. This suggests that the n-alkanes crystallization process is inhibited, and crystalline structures cannot generate a continuous structural network.

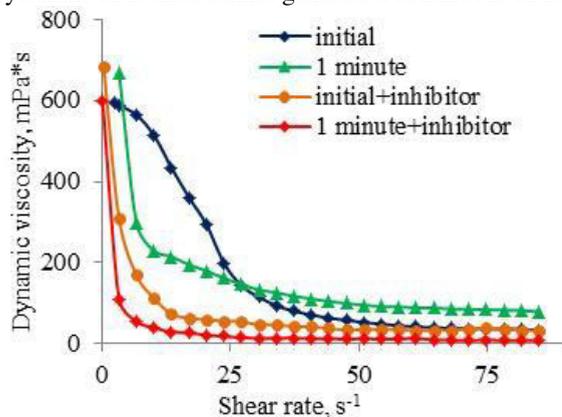


Fig. 1. Effect of treatment conditions on dynamic viscosity of oil at 20 °C

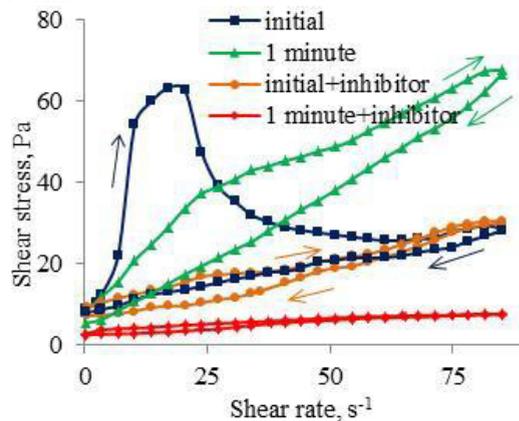


Fig. 2. Forward and backward isotherm curves for oil samples at 5 °C

Pour point of oil decreases simultaneously with change in viscosity. The integrated effect provides the maximum depression of pour temperature: 8 °C (Table 1).

Change in viscosity and temperature parameters of treated oil certainly affects formation of a dispersed phase. The deposition process was studied at the oil temperature of 30 °C and the finger temperature of 5 °C. Table 1 shows that ultrasound treatment for 1 minute causes a two-fold increase in mass of the deposit, while application of the inhibitor significantly reduces it. The integrated effect strengthens the inhibitory effect of the inhibitor.

Table 1. Effect of treatment on pour point, internal energy to break the oil structure and amount of the deposit

| Sample | T ₃₀ , °C | W, J | Mass of deposit / 100 g of oil |
|----------------------|----------------------|------|--------------------------------|
| initial | -4.4 | 580 | 3.25 |
| 1 minute | +0.3 | 510 | 7.48 |
| inhibitor | -11.0 | 90 | 1.31 |
| 1 minute + inhibitor | -12.4 | 10 | 0.95 |

Chromato-mass-spectrometry was used to determine composition of n-alkanes in the oil fraction of the deposits isolated from oil samples. The molecular weight distribution of n-alkanes in the deposits of both initial and treated

samples is of the bimodal nature. The peaks of the n-alkane distribution in the initial oil deposit fall on $C_{13}H_{28}$ and $C_{18}H_{38}$ (Fig. 3). Ultrasound treatment has almost no effect on the composition and distribution of n-alkanes in the

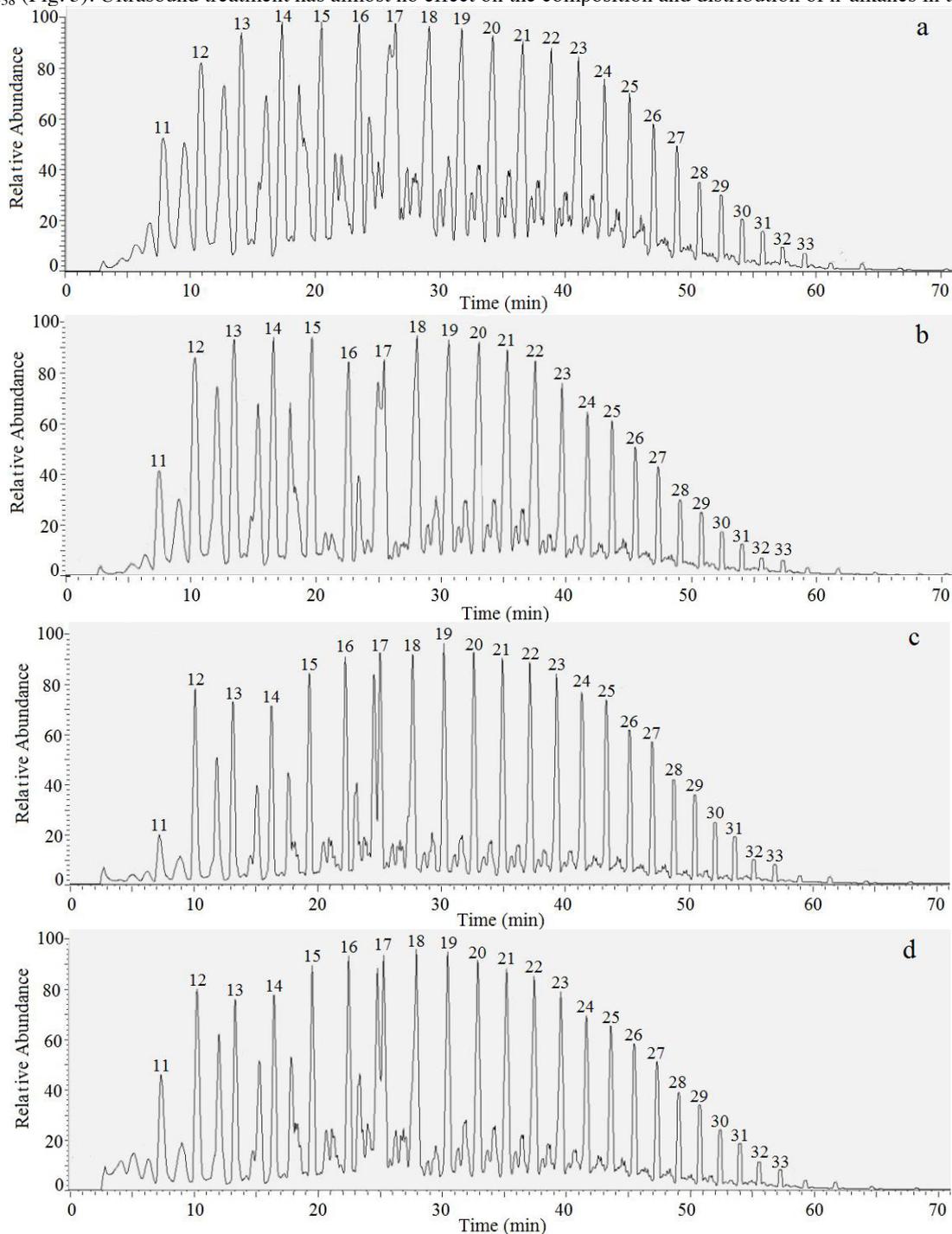


Fig. 3. Mass fragmentograms of the oil fraction after ion exposure with m/z 57 (alkanes): (a) initial; (b) 1 minute; (c) inhibitor; (d) 1 minute+inhibitor.

deposit. Addition of the inhibitor increases the content of C₁₈-C₃₃ fraction in oil deposits by 8 % as compared to the initial sample. The integrated effect causes the redistribution of n-alkanes in the oil deposits: the position of the second maximum is shifted to the region of hydrocarbons with higher molecular weight (C₂₃H₄₈) (Fig.4).

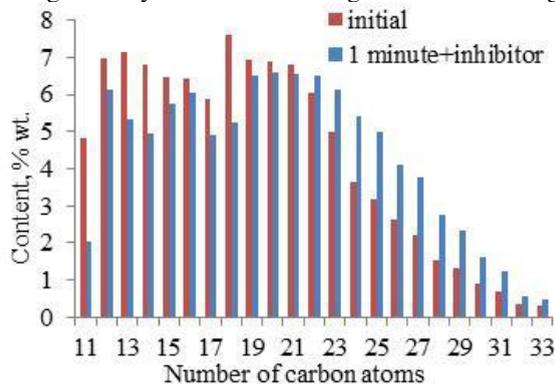


Fig. 4. The molecular weight distribution of n-alkanes in the oil fraction of oil deposits

The coefficient $K = H-(C_{11}-C_{17})/H-(C_{18}-C_{33})$ defining the ratio of paraffin hydrocarbons of the normal structure shows that the share of high-molecular homologues in the oil fraction of treated oil deposits has increased (Table 2).

Table 2. – Effect of treatment on n-alkane content in the oil fraction of oil deposits

| Sample | Content, wt. % | | K |
|----------------------|----------------------------------|----------------------------------|------|
| | C ₁₁ -C ₁₇ | C ₁₈ -C ₃₃ | |
| initial | 44.6 | 55.4 | 0.80 |
| 1 minute | 44.2 | 55.8 | 0.79 |
| inhibitor | 36.9 | 63.1 | 0.58 |
| 1 minute + inhibitor | 35.2 | 64.8 | 0.54 |

According to IR spectral ratios, no noticeable changes are observed in oil samples isolated from the oil deposits after 1 minute of ultrasound treatment (Table 3, Fig. 5). After addition of the inhibitor, branching coefficient of alkanes (D_{1380}/D_{1465}) in oil deposits decreases, while the content of alkyl links with a chain of more than four atoms increases (D_{725}/D_{1465}).

Table 3. Normalized optical density of absorption bands in IR spectra of the oil fraction in deposits

| Sample | Position of the absorption band, cm ⁻¹ | |
|----------------------|---|--------------------|
| | D_{1380}/D_{1465} | D_{725}/D_{1465} |
| Initial | 0.42 | 0.27 |
| 1 minute | 0.44 | 0.28 |
| inhibitor | 0.39 | 0.35 |
| 1 minute + inhibitor | 0.48 | 0.39 |

The oil fraction of the deposits isolated from oil exposed to the integrated effect shows an increase both in branching coefficient and content of polymethylene chains.

Content of aliphatic compounds in the samples increases to reach 13.5 (initial), 15.4 (1 minute of ultrasound treatment), 16.5 (with inhibitor), and 16.7 (ultrasound treatment + inhibitor). These findings are consistent with available chromatography–mass spectrometry data.

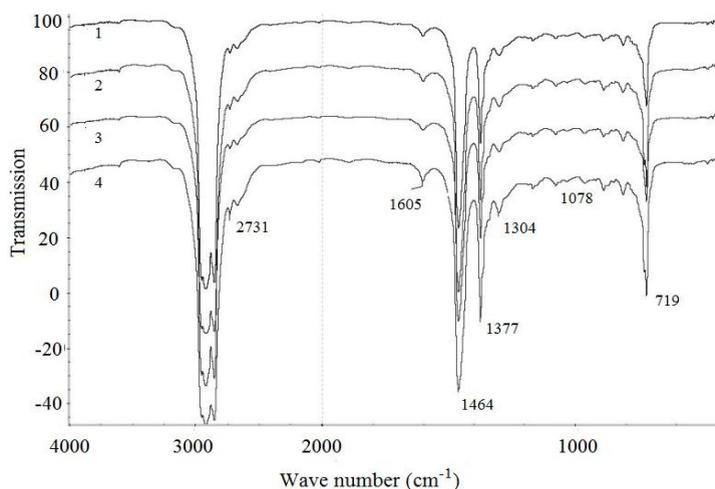


Fig. 5. IR spectra of oil deposits: 1 – initial; 2 – inhibitor; 3 – 1 minute; 4 – 1 minute + inhibitor

Conclusion

Thus, the completed studies show that the integrated effect of ultrasound treatment for 1 minute and the subsequent addition of the inhibitor at the concentration of 0.05 % wt. improve the structural and mechanical oil parameters. Treatment in an acoustic field strengthens the depression and inhibitory effects of the inhibitor. Short-term ultrasound treatment does not affect distribution of n-alkanes in the oil fraction of the deposits isolated from oil. Due to addition of the inhibitor and the integrated effect, the second peak of the n-alkane distribution is shifted to components with higher molecular weight; n-alkane content of C_{18} – C_{33} fraction in the deposits increases. These findings are consistent with available infrared spectroscopy data.

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