Evaluation of the effect of new-synthesized heterocyclic compounds as inhibitors of ARP deposits

D Ibragimova\textsuperscript{1,2}, D Ivanov\textsuperscript{2}, Z Sharafieva\textsuperscript{2}, L Shamsutdinova\textsuperscript{2}, A Milovankin\textsuperscript{1}, S Petrov\textsuperscript{1,2}

\textsuperscript{1}Kazan Federal University, Kazan, Russia
\textsuperscript{2}Kazan National Research Technological University, Kazan, Russia

E-mail: khalidina@mail.ru

Abstract. This article is devoted to the studying of the problem of the resin and asphaltene deposits formation in the process of oil production and transportation using the example of high-viscosity oil from the Ashalchinskoe field. The chemical method for the prevention and removal of ARP, connected with the use of phosphorylated alkylphenols is considered in detail. Extraction of asphaltenes was carried out by selective dilution of the oil sample following by washing in Soxhlet apparatus. Hydrocarbon structure of asphaltenes was studied by the method of IR-spectroscopy on the spectrometer PerkinElmer. Paramagnetic characteristics of asphaltenes were analyzed by EPR method. Rheological properties of oil emulsion were studied by viscosimetry method using rotational viscometer One Touch Lamy Rheology. The graphs that indicate the dependence of the viscosity of oil emulsions on applied shear stress were plotted. The method of the "cold rod" was used to evaluate the inhibitory effect of the new organic compound.

1. Introduction

Modern petroleum industry is characterized by the intensification of the development of heavy oil fields concentrated with the content of high-molecular weight components which cause significant difficulties and problems in petroleum extraction and transportation. A serious issue among them are the high pour point, high oil viscosity and anomalous rheological behavior appearing in the variability of the dynamic viscosity, which depends on the applied shear stress and fluid velocity. It can be explained by the formation of spatial structural linear and cross-linked colloidal systems containing high-molecular substances, such as resins, asphaltenes and paraffins [1].

According to this theory oil can be described as multicomponent mixture of various organic compounds, among which the largest molecular-mass structural constituents are asphalt-resin substances. The main structure elements of resins and asphaltenes molecules are highly condensed polyaromatic molecules bearing long aliphatic chains and alicyclic substituents with a high content of heteroatoms (sulfur, nitrogen and oxygen) and trace metals (nickel and vanadium) [2]. The content of high-molecular-weight asphaltenes, resins and paraffines that tend to form high-structured systems – macroassociates - cause anomalous rheological properties and ARP deposits considerable difficulties in the transportation, oil storage, as well as a decrease of the efficiency of oil production and refining.
These depositions accumulate on the inner surface of production well tubing, strings and crude oil pipelines and cause a decrease in the internal diameter, and as a consequence, a decrease in the lifting capability and amount of fluid produced by the well. The process of ARP formation is caused generally by temperature and pressure changes, variability of oil fractional and chemical composition, dilution with other oils and acid fracturing of formation [3].

An effective and widely-used method of removal and prevention of the ARPD formation is a chemical method involving the use of organic solvents and inhibiting additives.

In the research [4] different aromatic hydrocarbons were selected and tested as ARPD inhibitors and deposits solubilizers. Non-commercial reagents were taken based on their structural content especially on functional groups. The highest inhibitory has compounds with -COOH group due to hydrogen bonding between asphaltenes and polar groups.

The article [5] presents the results of searching for new highly effective ways to protect the surface of wells and pipelines from asphalt-resin-paraffin deposits by introducing compounds that inhibit their formation. Also on the efficiency of inhibition were tested individual components: α-olefins (hexene-1 and octene-1), oleic acid, alkylaromatic hydrocarbons. Thus, as a result of the study, it was established that α-olefin C₈ in a mixture with paraffin has a high efficiency of inhibition with respect to ARPD, in comparison with other experimental samples. The inhibitory efficiency of α-olefins is explained by their increased adsorption ability to the surface of paraffin deposits due to the presence of a double bond.

Most studies to assess the efficiency of inhibitors compare the inhibition degree of substances with organic solvents [6-8]. However, the use of chemically pure paraffin solvents in industrial conditions is not economically feasible. Therefore, the most cost-effective and effective are inhibiting additives that prevent the formation of paraffin. At the same time, the safest and most stable operation of the equipment for oil production and processing is achieved, the costs of production and oil transportation are reduced. Since different additives have different inhibitory effects, it is necessary to determine the effectiveness of reagents for more rational use in industry. Therefore, study of the rheological properties of oil and ways to influence on them is an actual problem in modern petrochemistry.

2. Materials and Methods

For the research the high-viscosity oil of Ashalchinskoe field was taken. Spatially hindered phosphorylated alkylphenols are used as analyzed organic compounds. Proposed mechanism of their action is based on the adsorption process because of presence of polar groups in the molecule.

Extraction of asphaltenes is based on their selective solubility in different organic solvents. So asphaltenes were extracted from a heavy crude oil by dilution of the sample with petroleum ether in volumetric ratio 1:40 followed by washing with toluene in Soxhlet apparatus, distillation of extraction solution and drying.

The method of infrared (IR) spectroscopy is used to determine the structure of the hydrocarbon part of asphaltenes and the content of heteroatomic substituents. This analysis was carried out using spectrometer PerkinElmer Spectrum. Disintegrated asphaltenes were mixed with potassium bromide powder and pressed into tablet. To determine the main structural parameters of asphaltenes spectral coefficients are calculated based on their IR spectrum.
In addition to IR spectroscopy, for a comparative analysis of asphaltenes the electron paramagnetic resonance method is used. Using the EPR spectrum, the paramagnetic index of the oil sample is measured [9].

Rheological properties of oil were estimated by viscosimetry method using rotational viscometer First Touch (Lamy Rheology, France). Research was carried out at various quantities of shear rate in the interval from 40 to 250 rpm. Viscosity of the samples was evaluated systematically in 3 volumes containing crude oil (65 ml) and alkylphenols respectively. Mass ratio of mixtures oil-additive component is 100:1. The curves viscosity-shear rate of heavy oil are measured on the base of obtained data.

Evaluation of the efficiency of ARP inhibitors was carried out by the method of "cold rod". This method consists of determining the mass of asphalt-resin-paraffin deposits on cooled metal U-shaped tubes during their crystallization. The study of the effectiveness of reagents was carried out simultaneously in 4 tanks:

- the first sample was the control;
- the second sample contained the test oil and toluene as an organic solvent paraffin;
- the third and fourth samples contained oil and the studied organic substances as inhibiting reagents.

Metal containers were placed in a test block, into which cooled U-tubes were lowered. Over the next 20 minutes, the test specimens were being evenly mixed. The temperature of the thermostat was equal to 35 °C, the temperature of the cooling agent flowing through the U-shaped tubes was 0 °C.

3. Results and Discussions

3.1. Infrared spectroscopy

The IR-spectrum of investigated asphaltenes is shown on the Figure 1. Spectrum coefficients calculated on the base of spectrum are given in Table 1 [10-12].

![Figure 1. IR-spectrum of analyzed asphaltenes.](image-url)
Table 1. Spectral coefficients.

| Spectral coefficients                  |       |
|----------------------------------------|-------|
| Aliphatic coefficient (Al)             | 2.390 |
| Branching coefficient (Br)             | 0.950 |
| Condensation coefficient (Cn)          | 0.600 |
| Oxidation coefficient (Ox)             | 0.929 |
| Sulfurized coefficient 1 (Su1)         | 0.890 |
| Sulfurized coefficient 2 (Su2)         | 0.888 |

3.2. EPR-analysis

The EPR-spectrum of investigated asphaltenes is shown on the Figure 2 and Figure 3.

Figure 2. EPR-spectrum of investigated asphaltenes.

Figure 3. Oscillation amplitude of free radicals.
Paramagnetism of asphaltenes is mainly caused by the presence of free stable radicals (FSR) - unpaired electrons delocalized by polyconjugated systems - and vanadyl complexes. The figure 2 shows the EPR spectrum for a sample of asphaltenes, recorded in the stationary mode. The spectrum consists of a single line of stable radicals and the ultrathin structure of the VO$^{2+}$ vanadyl porphyrin complexes presented by 2 groups of lines. The number of lines in each group is equal to 8 and corresponds to the interaction of the unpaired 3d1-electron of tetravalent vanadium ion V$^{4+}$ with its nuclear spin $I = 7/2$.

Figure 3 presents us the part of EPR spectrum consisting of line of FSR and the low field line of vanadyl porphyrin complex. The ratio of stable free radicals’ amount to vanadyl porphyrin complex amount is equal to 4.1 and is called paramagnetic index.

3.3. Viscosimetry method

On the base of obtained data, the curves viscosity-shear rate are plotted and shown on the Figure 4.

![Figure 4](image_url)

**Figure 4.** Dependence of oil emulsions viscosity on applied shear stress.

Viscosity of crude oil decreases non-linearly with shear rate increase while samples containing oil and alkylphenols as organic compounds are characterized by presence of extremum in the interval 110-170 rpm. Addition of analyzed heterocyclic compounds increases the viscosity of oil emulsions in whole.

3.4. «Cold rod» method

The degree of inhibition of studied compounds is presented on the Figure 5. It is equal to the ratio of the difference between the masses of the deposits of the studied additives and the control sample to the mass of paraffin deposited during the experiment. After calculating, we determined that the second organic
compound has the most effective inhibitory effect. Toluene and the first inhibitor-reagent are less effective, so their use is impractical to remove ARPD formed from the studied oil.

![Inhibitory effect of analyzed compounds.](image)

**Figure 5.** Inhibitory effect of analyzed compounds.

4. Conclusion

We studied inhibitory properties of new-synthesized aromatic compounds as well as the influence of them on the rheological properties of high-viscosity oil. Also, high-molecular mass asphaltenes of the oil sample were estimated by different spectral methods. Asphaltenes of investigated oil possess a high oxidation and sulfurized state degree thus they contain significant amount of heteroatoms. At the same time asphaltenes have an increased content of free stable radicals. Thus, presence of heteroatoms and conjugated electron system of aromatic fragments cause the tendency of asphaltenes for association. Addition of investigated alkylphenols leads to the local increase of oil emulsions viscosity so it can be explained by formation of more stable colloidal structure consisting alkylphenols and asphaltene associates and paraffines. Results show that the second organic compound with 65.6% ARPD precipitation reduction has the best efficiency among the tested reagents.

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