STUDY ON IMPACT OF THE SIZE OF COMPOUND MICELLES COMPRISED OF ANIONIC AND NONIONIC SURFACTANTS ON EFFICIENCY OF RESIDUAL OIL DISPLACEMENT AFTER FLOODING

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ABSTRACT
The main goal of the Russian O&G sector is to raise the oil recovery factor (ORF) through developing new and improving existing technologies of enhanced oil recovery. Among the latter, most efficient are physicochemical methods for the formation stimulation based on the use of different types of surfactants. Surfactants incorporated in chemical formulations bring about efficient residual oil displacement after flooding due to the ultra low oil/water interfacial tension and a change in the capillary number [1]. According to a few studies [2, 3, 4] the best effect in residual oil recovery was achieved with the formulations comprised of different types of surfactants. When mixed, such surfactants exert synergistic effects on the reagent’s surface activity, its rheology and behavior in the variable formation conditions. This paper discusses lab test results related to the impact of the size of compound micelles comprised of a mixture of anionic surfactants sourced from low quality hydrocarbon and nonionic surfactants on efficiency of residual oil displacement in high water cut wells. It has been proven that varying of the anionic/nonionic surfactant proportion in the mixture influences dramatically the size of the formed micelles, their interfacial activity, and efficiency of high viscosity oil displacement. 

Keywords: petroleum sulfonates, surfactants, mixed micelles, displacement efficiency, interfacial tension.

INTRODUCTION
Surfactants have been in common use for enhanced oil recovery [5]. Well-known technologies such as ASP flooding, surfactant flooding, micellar-polymer flooding (MFP) [5-7], etc., rely on different surfactant types and their mixtures. Such interest in the physicochemical properties of surfactant mixtures is associated with the observed synergistic effects and their high performance: combining of different surfactants greatly facilitates desirable changes in the system properties and allows avoiding a synthesis of new formulations. Synergy in mixing of surfactants from various series is expressed through the improved properties of the mixture against its individual components [8]. Mixed surfactants exhibit higher surficial activity and reduce the interfacial tension (IFT), change the critical micelle concentration, influence the micelle growth and type, including novel self-organization types in surfactant solutions, variate solution wettability and rheology, and affect dispersing, detersive and emulsifying properties of solutions [8-11].

Surfactant mixture solutions have been rather extensively researched over the past years. Many combinations of nonionic, anionic, cationic, and ampholytic surfactants have been studied and the method of different surfactant types combining has found wide applications in enhanced oil recovery processes [5,7], which allows the optimization of formulations in terms of geological and physical field conditions.

Among well-known commercial nonionic surfactants most popular are alkylphenol ethoxylates with a different number of hydroxyethyl moieties (nonylphenol ethoxylates, NPE, n=8, 10, 12) owing to their high surficial activity and saltwater tolerability. It is common knowledge that the addition of anionic surfactants results in a noticeable change of turbidity temperature and a change in the surface tension [8, 12]. Arpita Sahu et al. [13] examined the surficial properties and thermodynamic parameters of sodium dodecylbenzenesulfonate mixtures and nonionic surfactants (Tergitol 15-S-12, Tergitol 15-S-9, and Tergitol 15-S-7). Thermodynamic data makes it possible to control micellization, optimize the preparation of formulations with the preset properties and their application technologies as well as to reduce their cost. It has been reported ibid that both the surface tension and the critical micelle concentration depend on the nonionic surfactant concentration and ethoxylated fragment values (Tergitol 15-S-12, Tergitol 15-S-9, and Tergitol 15-S-7). Also, in place are changes in relative solution viscosity during mixing of anionic and nonionic surfactants. The maximum is achieved at the anionic surfactant’s molar concentration in the range from 0.4 to 0.6 unit fractions depending on the nonionic surfactant type in use. As shown by A. Bera et al. in [14], a combination of nonionic (Tergitol 15-S-7, Tergitol 15-S-9, and Tergitol 15-S-12), anionic (sodium lauryl sulfate – SDS) and cationic (hexadecyltrimethylammonium bromide – HTAB) surfactants with salts causes changes in IFT and their optimal compositions allow extra oil recovery up to 24%.

Surfactants’ impact on oil displacement efficiency is associated with a change in the capillary number because of low IFT achieved [15, 16], which is why surfactant mixtures that have lower IFT values, in many instances, appear more efficient for oil displacement than individual species [17].

This research was focused on the impact produced by the size of compound micelles, which consist...
of a mixture of anionic and nonionic surfactants, on the interfacial tension at the oil-saltwater interface and on efficiency of high viscosity oil displacement from heavily watered formations with intrinsic high formation and injected water salinity. The behavior of NPE-series nonionic surfactants with the different number of ethoxylated groups (n – 8,10,12) in a combination with anionic surfactants having a broad molecular mass distribution was examined. A hydrocarbon solution of ammonium petroleum sulfonate (PS, an oil-soluble surfactant), an intermediate in the production of sulfonate dopes, was utilized as a source of anionic surfactants. Such surfactants are attractive due to their low cost as compared to synthetic anionic surfactants. Apart from that, they incorporate anionic surfactants with different molecular characteristics such as sulfonated mono-, di- and polysubstituted alkyl benzenes, naphthalenes, and polycyclic aromatics, which, in porous media, are capable of generating micellar systems with various sizes and properties and thereby ensure higher performance under changeable geological and physical conditions in the formation, viz. oil viscosity, salinity, formation temperature, mineralogy of rocks, etc.

MATERIALS AND METHODS

An anionic surfactant was sourced from petroleum sulfonate (PS, an oil-soluble surfactant), an intermediate in the production of sulfonate dopes [20]. It contains 15 – 17 % mass of ammonium petroleum sulfonate with an average equivalent weight 600-630 and 30 – 32 mass % of hydrocarbon (a gasoline/non-sulfonated oil mixture) with density 830 kg/m³ and dynamic viscosity 6.8 mPa·s. Nonylphenol ethoxylates (NPE) were studied as a nonionic component, the number of ethoxylated groups – n= 8, 10, and 12 according to Technical Specifications 2483-077-05766801-98.

A study on the size of compound micelles and their size distribution was performed with a laser light scattering particle size analyzer Microtrac Nanotrac Ultra. The instrument determines the particle size and shape in aqueous and organic media using a dynamic light scattering technology.

IFT was measured by a spinning drop method with the use of a Spinning Drop Video Tensiometer (DataPhysics, SVT 15N). A 6.0-6.4 mL drop was injected with a chromatographic applicator. IFT measurement data for each sample was recorded at the system equilibrium point achieved with the constant rotation speed 7000 1/min and at 23 °C. The test temperature corresponded to that of the formation.

Oil with viscosity 93.33 mPa·s and density 902.0 kg/m³ and formation water with the total salt content 212 g/l and density 1148 kg/m³ were employed to measure IFT and oil displacement efficiency of the prepared solutions.

The solutions were prepared using injected water with the salt content 141.6 g/l, density 1158 kg/m³ and total surfactant concentration equal to 5% mass.

Displacement efficiency of the prepared solutions was measured using core samples in thermostat glass tubes 20 cm long and 1.6 cm in diameter as core holders (porosity – 30.5%, permeability – 0.05 mkm²). A sand packed tube with terrigenous rock was saturated with formation saltwater for porosity measurements. Next, the core was saturated with oil, saltwater was pumped through the sample several times until a complete water cut of the exhaust fluid (imitation of flooding), and residual oil saturation was determined. After that, a 5%-surfactant micellar solution (MS) and polyacrylamide buffer slug containing 0.05% polymer (FLOPAAM. 3630S by SNF Floerger, France) were injected. The MS slug volume was 20% of the pore volume and the buffer polymer solution accounted for 50% of the pore volume. MS efficiency was evaluated from the residual oil displacement rate after flooding.

RESULTS AND DISCUSSION

The size of the micelles formed in the solution depends on the NPE/PS ratio and the number of ethoxylated groups in the NPE molecule. Table 1 shows the micelle size changes with regard to the number of ethoxylated moieties (NPE – n where n = 8, 10, and 12 is the number of ethoxylated groups in the NPE molecule) and to the NPE/PS ratio. The nonionic surfactants have different affinity to the hydrocarbon phase and their compatibility diminishes as ethoxylated groups in the nonionic surfactant molecule grow in number. An increase in the number of ethoxylated groups in the NPE molecule results in a decreased size of the formed micelles at all NPE/PS ratios studied. A higher concentration of anionic surfactants in the mixture leads to micelle strengthening. Of note is that the micelle size is considerably higher in the case of NPE-8 than with NPE-10 and NPE-12. At some ratios, a bimodal distribution of differently sized micelles was observed, although no bimodal distribution was found for NPE-12. For NPE-10 it was merely detected at its concentration decrease to 30 % whereas for NPE-8 it was registered across the overall concentration range. Therefore it appears possible to influence the size of micelle aggregates by varying of the ratio of nonionic and anionic surfactants.

The next step was to study a relation between the interfacial tension, number of ethoxylated groups and NPE/PS ratio (see Table 2 and Figure 1). The data evidences that IFT values for all the studied formulations are rather close whereas the highest IFT activity is displayed by NPE-8 in the overall NPE/PS range.
Table-1. Relationship between the micelle size, NPE/PS ratio and the number of ethoxylated groups.

<table>
<thead>
<tr>
<th>NPE/PS ratio</th>
<th>Number of ethoxylated groups (n)</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>70/30</td>
<td>Average particle size: 82% - 62.53 nm, 18% - 1589 nm</td>
<td>Average particle size: 33.1 nm</td>
<td>Average particle size: 37.6 nm</td>
<td></td>
</tr>
<tr>
<td>50/50</td>
<td>Average particle size: 70.8% - 3181.1 nm, 29.2% - 182 nm</td>
<td>Average particle size: 28.18 nm</td>
<td>Average particle size: 85.0 nm</td>
<td></td>
</tr>
<tr>
<td>30/70</td>
<td>Average particle size: 70.8% - 4126 nm, 29.2% - 1265.5 nm</td>
<td>Average particle size: 1563.4 nm</td>
<td>Average particle size: 130.2 nm</td>
<td></td>
</tr>
</tbody>
</table>

Table-2. Relationship between the interfacial tension, NPE/PS ratio and the number of ethoxylated groups.

<table>
<thead>
<tr>
<th>Number of ethoxylated groups (n)</th>
<th>NPE/PS ratio (mass)</th>
<th>70/30</th>
<th>50/50</th>
<th>30/70</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.16</td>
<td>0.21</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.23</td>
<td>0.34</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.52</td>
<td>0.56</td>
<td>0.65</td>
<td></td>
</tr>
</tbody>
</table>

A nonionic surfactant concentration rise entails an IFT drop across the overall variety of the tested concentrations. The formulation comprised of NPE-8 and PS, 70% and 30% respectively, is of most interest in terms of the IFT value. Further studies were focused on the shift in the nonionic NPE-8/PS value toward the NPE-8 concentration increase. Figure-2 presents a relation between IFT and the NPE-8/PS content in the formulation. As seen from the data, mixing of anionic and nonionic surfactants results in a synergistic effect and IFT reduction. IFT at the ‘oil-formulation’ interface in the absence of PS (100% NPE-8) is 1.39 mN/m. A rise in the anionic surfactant concentration up to 20% brings about a drastic drop of the interfacial tension down to 0.16 mN/m with the optimum in the anionic surfactant concentration range from 50 to 80%. An attempt to measure IFT for the 100% PS formulation was failing due to a low solubility of the surfactant in saltwater. So, the nonionic surfactant addition to the formulation improves PS compatibility with saltwater and reduces the IFT value on the ‘oil-formulation’ interface against individual surfactants (NPE and PS). Among the tested nonionic surfactants, the best
effect is produced by NPE-8 that has higher affinity to the hydrocarbon phase than NPE-10 and 12.

\[
\text{IFT, mN/m:}
\]

Importantly, the bimodal micelle size distribution occurs at this ratio (Table 1) and particles with the average size 62 nm (~ 82%) along with larger aggregates sized on average 1589 nm (~ 18%) predominate in the solution.

**Inference**

The prepared solutions were studied in modelling of geological and physical parameters of a field characteristic of high oil viscosity, a high salt content of formation and injected water, and a low formation temperature.

The use of PS without a co-surfactant is constrained by its low solubility in saltwater. It is possible to improve compatibility through the addition of nonionic surfactants such as nonylphenol ethoxylates with the different number of ethoxylated moieties (8,10,12) as proposed herein.

The study on mixed surfactants has shown that the addition of the nonionic surfactant to the anionic one leads to a change in the size of the formed micelles and reduction of the interfacial tension as well as influences residual oil displacement efficiency. PS and NPE mixtures produce a broad scope of differently sized micelles whose size can be controlled by varying the PS/NPE ratio and the number of ethoxylated moieties in the NPE molecule. An increase in the number of ethoxylated groups in the NPE molecule causes micelle size reduction at all tested NPE/PS ratios. A higher PS concentration in the mixture also improves micelle strengthening and, noteworthy, the micelle size is considerably higher in the case of NPE-8 than where NPE-10 and NPE-12 are used. At some ratios, a bimodal distribution of differently sized micelles is observed. Although no bimodal distribution was found for NPE-12 and, as for NPE-10, it was merely detected at its concentration decrease to 30 % whereas for NPE-8 it was registered across the overall concentration range. The highest displacement efficiency was exhibited by the formulations prepared from PS and NPE-8, having higher affinity to the hydrocarbon phase. They are specific of the minimal interfacial tension (from 0.16 to 0.52 mN/m) and bimodal by-size micelle distribution.

**CONCLUSIONS**

The research has demonstrated that an intermediate in the production of sulfonate doping agents (an oil-soluble surfactant, PS) is applicable for oil recovery enhancing processes. PS is an oil-soluble anionic surfactant having a broad molecular mass distribution and average molar mass 600-630. Such surfactants show promise as they are relatively cheap and incorporate anionic surfactants with different molecular characteristics, such as sulfonated mono-, di- and polysubstituted alkyl benzenes, naphthalenes, and polycyclic aromatics, which are capable of generating micellar systems with various sizes and properties and thereby ensure higher performance of the formulation under changeable geological and physical conditions in the formation, viz. oil viscosity, salinity, formation temperature, mineralogy, etc.
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