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Nanofluid for enhanced oil recovery

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1. Introduction

New type of fluids usually called "smart fluids" has become more accessible for the oil and gas industry (Amanullah and Al-Tahini, 2009; Zitha, 2005). The nano-fluids are created by the addition of nanoparticles to fluids for intensification and improvement of some properties at low volume concentrations of the dispersing medium. Then the main feature of nanofluids is that their properties greatly depend on the dimensions of nanoparticles that are their components (Romanovsky and Makshina, 2004). Suspensions of nanodimensional particles have the following advantages; increase in sedimentation stability because surface forces easily counterbalance the force of gravity: thermal, optical, stress-strain, electrical, rheological and magnetic properties that strongly depend on size and shape of the nanoparticles can be created during production. It is for this reason that nanofluid properties often exceed the properties of conventional fluids (Kostic and Choi, 2006; Suleimanov, 2006; Wasan and Nikolov, 2003). The results of this experimental work show how dispersed nanoparticles in an aqueous phase can modify the interfacial properties of the liquid/liquid systems if their surface is modified by the presence of an ionic surfactant. Mixed particle/surfactant interfacial layers have been characterized through measurements of the effective interfacial tension and wettability.

It is obvious that the development of nanofluids for oil and gas production has a great practical importance (Fletcher and Davis, 2010; Zhang et al., 2010). In this connection, the experimental study of nanofluids intended for Enhanced Oil Recovery (EOR) is presented in this work.

ABSTRACT

An experimental study of nanofluids intended for enhanced oil recovery is presented in this work. An aqueous solution of anionic surface-active agents with addition of light non-ferrous metal nanoparticles was used as the focus of the study. It is shown that the use of the nanofluid permitted a 70–90% reduction of surface tension on an oil boundary in comparison with surface-active agent aqueous solution and is characterized by a shift in dilution. Use the developed nano-suspension results in a considerably increase EOR.

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2. Experiments, results and discussions

All the results reported here concern the interface with oil of diluted dispersions of non-ferrous metal nanoparticles in a anionic surfactant (sulphanole – alkyl aryl sodium sulphonate) aqueous solution.

While testing we used:

- 1. Nanopartciles supplied by Advanced Powder Technologies LLC Russian Federation, Tomsk. Light non-ferrous metal. The average particle size is approx. 90–110 nm. Single particles have the average size of 70–150 nm and form microagglomerates. The bulk density is about 0.32–0.37 g/cm³. BET surface area – $12 \text{ m}^2/\text{g}$.
- The anionic surfactant supplied by OilGasChemCo Ltd Moscow, Russian Federation. Chemical name: Sodium 4-alkyl-2ylbenzenesulfonate. Formula: CnH2n + 1–C6H4–S02ONa. Bleached powder 80% mass alkyl-2ylbenzenesulfonate sodium. Sodium sulfate 17% mass, apparent density: 110–170 κg/м³.

3. Nanoparticle influence on surface tension in surfactant solution

Presence of nanoparticles changes rheological properties and increase effect of surfactant solution on oil recovery processes. First of all it is change interfacial tension value of surfactant/oil interface more effectively (Munshi et al., 2008). Observed reduction of interfacial tension is the result of nanoparticles presence at the interfacial layers. In lower concentration of nanoparticle they are attached to the liquid surface and due to absorption process decrease surface tension. However in concentration larger than 0.4 wt.%, the nanoparticles nearly completely remove the surfactant from the bulk aqueous phase and there is no free surfactant available in the bulk. Thus, for nanoparticles concentrations below 0.4 wt.%, the interfacial tension of the dispersion

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is determined by a mixed layer composed by attached nanoparticles and surfactant adsorbed at the liquid interface (Ravera et al., 2006).

In the first series of experiments the interfacial (surface) tension, adsorption and wettability of investigated solutions were determined. Hereafter each performed and calculated values were shown according to 300 experiments conducted before. All reported interfacial tension values have been measured by a drop shape tensiometer DSA30 of Kruss company. Following methods of measurement were selected for our purposes:

- 1. Pendant Drop-method based on Laplace equation which describes relationship between the difference in pressure and interfacial tension.
- Sessile drop method is an optical contact angle method method is used to estimate wetting properties of a localized region on a solid surface.

All glassware and parts of the instrument in contact with the samples were carefully cleaned with different standard procedures, depending on the materials, to avoid any contamination. Before each measurement the absence of contaminants was checked by dynamic interfacial tension measurements on the pure water/oil or water/air interfaces.

The results of wetting angle and the interfacial tensions of aqueous solution–oil interface are produced by using the drop shape analysis method at 298 K. The results obtained are shown in Table 1.

Nanoparticles decreases surface tension 70–79% while using 0.004–0.0078% mass of sulphanole solution, but if sulphanole concentration is more than 0.0156% mass it becomes less (88–90%).

4. Nanoparticles influence on surfactant adsorption process

The adsorption process of surface-active agent was studied under static conditions on silica sand specimens of 0.315–0.2 mm diameter. 10 g silica sand, 100 ml surfactant aqueous solution and nano-fluid were taken. Two different surfactant concentrations in solution were used 0.0078%–0.05% mass, nanoparticles concentration was 0.001% mass. The experiments were conducted at a temperature of 298 K. Surface-active agent solution concentration was determined by the change of interfacial tension value determined every 24 h during 3 days from the time of specimen preparation. Values shown in Table 2 are performed and calculated experiments results of limiting surfactant absorption.

In the experiment with sulphanole after the first 24 h, desorption of some surface-active agent was observed, then the process was stabilized. In the presence of nanoparticles the sulphanole adsorption process is more stable and surfactant adsorption values went up 14.5 and 18.5 times, respectively.

5. Nanoparticles influence on oil wettability

Further oil wettability in the presence of surface-active agents and nanoparticles was determined. Sulphanole concentration was 0.05% mass, and nanoparticles concentration -0.001% mass. The experi-

| Table 1 |
|-----------------------------------------------------------------------------|
| Nanoparticle influence on change of surface tension in surfactant solution. |

| Concentration, % mass | | Surface tension (10 ⁻³ N/m) | | |
|-----------------------|---------------|----------------------------------------|----------------------------------------------------|--|
| Sulphanole | Nanoparticles | Surfactant solution | Surfactant solution with nanoparticles addition | |
| 0.004 | 0.001 | 31.4 | 9.2 | |
| 0.0078 | 0.001 | 18.4 | 5.5 | |
| 0.0156 | 0.001 | 16.6 | 3.6 | |
| 0.0312 | 0.001 | 14.7 | 1.8 | |
| 0.05 | 0.001 | 10.9 | 1.09 | |

Table 2

Nanoparticles influence on surfactant adsorption process.

| Concentration, (% mass) | | Surface tension while the time (10^{-3} N/m) | | | | Adsorption limit (mg/g) |
|-------------------------|---------------|--------------------------------------------------------|-----------|-----------|-----------|----------------------------|
| Sulphanole | Nanoparticles | Initial | 24 (h) | 48 (h) | 72 (h) | |
| 0.0078 | 0 | 18.4 | 20 | 19 | 19 | 0.04 |
| 0.0078 | 0.001 | 5.5 | 11 | 11 | 11 | 0.58 |
| 0.05 | 0 | 10.9 | 12.1 | 11.8 | 11.8 | 0.04 |
| 0.05 | 0.001 | 1.09 | 3.2 | 3 | 3 | 0.74 |

ments were performed at a temperature of 298 K. Results are presented in Table 3. As is shown in the table, oil wettability practically remains unchanged with nanofluid addition.

6. Nanoparticles influence on optical spectroscopy results

Spectra were obtained with use of Lambda-40 spectrophotometer, manufactured by Perkin Elmer, USA, over the range 190–1100 nm, UK-spectrophotometer of UR-20, Carl Zeiss, Germany, over the range 40–4000 sm⁻¹. Specimens of "Merk" company (purity is more than 98%) were employed. For optical spectroscopy results we intentionally used less effective nanofluid composition in order to show clearly differences in absorption process due to nanoparticles presence even in that case. All experiments run with different standard procedures.

To reveal the mechanism of the observed phenomena in the second series of experiments, optical spectroscopy of the solutions was carried out. Aquaeos surfactant solution with 0.0078% mass of sulphanole was used for that series of experiments.

The infra red (IR) spectra of sulphanole powder and sulphanole with nanostructurized component, isolated from aqueous solutions are shown on Fig. 1(a,b).

On Fig. 1(a), in the IR sulphanole spectrum absorption bands (AB) at 1166 and 1049 sm⁻¹ ascribed to S–O bond vibrations, 650 sm⁻¹ (C–S bond vibrations), 735 and 695 sm⁻¹ (substituted aromatics C–H bonds of benzene ring). For sulphanole powder with nanostructurized component, isolated from aqueous solutions, no significant changes of bands belonging to sulphanole are revealed.

Ultra violet (UV) and visible (VIS) spectra of surfactant aguoues solution at sulphanole concentration 0.0078% mass and the same solution with nanostructurized powder in $2.5 \, 10^{-4}$ % mass concentration are shown on Fig. 2(a,b). It is seen that the UV/VIS spectra of sulphanole aqueous solution are characterized by absorption bands at 262 and 233 nm. The first band belongs to sulphanole, the second is mostly like to an admixture of organic structures. Introduction of only $2.5 \, 10^{-4}$ % mass of nanostructurized powder into sulphanole aqueous solution causes noticeable changes in the absorption spectrum. Bands belonging to sulphanole aqueous solution practically disappear and instead two intensive bands have appeared at 223.0 (1.00) and 200 (1.09) nm the intensity of which is 2-fold higher. The experiments showed that an increase of nanostructurized component in solution from $2.5 \, 10^{-4}$ up to 5.010⁻³% mass did not materially affect absorption intensity. For sulphanole aqueous solution containing 0.01% mass of nanostructurized powder noticeable increase of absorption bands is observed at 200 nm

| Table 3 | |
|---------------------------------------------|--|
| Nanoparticles influence on oil wettability. | |

| Concentrati | Wettability | | |
|-------------|-------------|-----------|---------|
| Oil | Sulphanole | Nanofluid | (cos θ) |
| 100 | 0 | 0 | 0.7604 |
| 100 | 0.05 | 0 | 0.918 |
| 100 | 0.05 | 0.001 | 0.945 |

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