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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/cm<sup>3</sup>. BET surface area – 12 m<sup>2</sup>/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/м<sup>3</sup>.

#### 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 <sup>-3</sup> 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	Surface tension while the time $(10^{-3} \text{ N/m})$				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<sup>-1</sup>. 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<sup>-1</sup> ascribed to S-O bond vibrations, 650 sm<sup>-1</sup> (C-S bond vibrations), 735 and 695 sm<sup>-1</sup> (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<sup>-3</sup>% 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.	

Concentratio	n, (% mass)		Wettability
Oil	Sulphanole	Nanofluid	$(\cos \theta)$
100	0	0	0.7604
100	0.05	0	0.918
100	0.05	0.001	0.945



Fig. 1. IR spectrum of powder separated from aqueous solution: a) sulphanole; b) sulphanole with nano-powder addition.

(1.25) whereas the intensity of absorption bands at 223.0 nm hardly changed. The experiments showed that the increasing of nanostructurized component in solution from  $2.5 \cdot 10^{-4}$  up to  $5.0 \cdot 10^{-3}$ % mass did not materially affect absorption intensity.

The results described here unambiguously show that the change of initial absorption bands belonging to sulphanole aqueous solution in the presence of a nanostructurized component is controlled by interaction of sulphanole anions ( $C_{12}H_{25}-C_6$  H<sub>4</sub>–SO<sub>3</sub>) with cations of nanopowder surface.

To find out the nature of this interaction and the structure of sulphanole anion complexes with surface hydroxyls of the nanostructurized component, first of all it is necessary to pay attention to the following circumstances. During introduction of nanostructurized powder into sulphanole aqueous solution a) absorption bands are moved towards the lower frequency (hypsochromic shift); b) absorption bands intensity significantly increases (hyperchromic effect).The mechanism of interaction, adsorption of surfactant molecules on solid surfaces, can be studied by detail research of electronic and oscillating spectra absorption bands behavior of these molecules and the adsorbent. Out of given UV/VIS and IR-spectra (Fig. 1) it is clearly shown that surface-active agent adsorption electronic spectra in comparison with the surface-active agent spectrum. In IR-spectra wide absorption band with maximal 3350 sm<sup>-1</sup> (Fig. 1(a,b)) is shown against a background of band intensity decrease at 3500–3400 sm<sup>-1</sup>. Washing of bands by



Fig. 2. Saturation spectrum UV/VIS of aqueous solution: a) sulphanole; b) sulphanole with nano-powder addition.

shaking during 1 h in water causes some changes in spectrum, i.e. band intensity is decreased in the region of 2800–3000 sm<sup>-1</sup>, and intensity of hydroxyl residual band remains practically unchanged. Holding specimens at a temperature of 303.15–313.15 K during 2 weeks did not materially change the spectrum shape. The experiments conducted show surfactant chemosorption at the initial stage of adsorption and physical adsorption at subsequent stages.

#### 7. Nanoparticles influence on rheological properties of the nanosuspension

Rheological properties of the nano-suspension were determined on rotational viscosimeter PVS of Brookfield engineering at a temperature of 298 K. The PVS is a dynamic coaxial cylinder, controlled shear rate rheometer. The outer cylinder (sample cup) is driven by a stepper motor at speeds from 0.05 rpm to 1000 rpm. The inner cylinder (bob) contains an RTD probe on the surface to provide temperature measurement where the shear stress is being measured. Several cup and bob designs with different geometries are available to suit various applications. We used TA5B5 rotor-bob combination which gave us a possibility to take measurement in a range from 0.5 to 1 million  $cP(mPa \cdot s)$ . All the measurements controlled and provided under the special software.

The dependence of shear stress on shear rate for aqueous solutions of anionic surfactant with and without addition of nano-particles is shown

on Fig. 3. As may be seen from the figure, nano-particle addition causes modification of the flow character from Newtonian to non-Newtonian (pseudoplastic), i.e. the obtained nano-fluid is characterized by shift dilution. The minimal Newtonian viscosity of the surfactant aqueous solution was 0.98 mPa·s, however with added nano-particles it became twice higher and was equal to 2 mPa·s. Surfactant aqueous solution was 0.05% mass sulphanole concentration.



Fig. 3. Rheological curve of anionic surfactant aqueous solution without addition and with addition of nanoparticles.

# 8. Nanoparticles influence on the processes of Newtonian oil displacement in homogeneous and heterogeneous porous medium were tested

Tests simulating the processes of Newtonian oil displacement in homogeneous and heterogeneous porous medium were carried out on the unit, a diagram of which is shown on Fig. 4.

Tests were carried out according to the following plan:

- the column of high pressure was filled with quartz sand of required fraction, the unit was connected in accordance to Fig. 4, permeability to air was determined and vacuum treatment of the whole unit was carried out at constant thermostat setting;
- the porous medium was saturated by water that was displaced by oil with viscosity of 7 mPas at 298 K up to complete saturation with simultaneous measurement of stratum pore volume;
- the required pressures were set on the inlet and outlet to the column and oil was filtered oil was passed through at constant flow rate. This enabled the permeability of porous medium to oil to be determined;
- the PVT chamber was filled by displacement fluid (tap water, water with sulphanole addition and nano-particles) depending on test purpose;
- oil was displaced by the displacement fluid at constant pressure drop and the quantity of displaced oil was determined.

Tests were carried out in the following porous media:

- homogeneous with permeability 1 D and porosity 26%;
- stratified and heterogeneous with contacting homogeneous layers (permeability of layers is 0.4 and 1.6 D; porosity 20 and 28%, accordingly), that was achieved by using the partition gradually removed in the process of column filling.

For comparison of results, the mean of the heterogeneous porous medium permeability was chosen to be equal to that of the homogeneous medium. Displacement was carried out at pressure drop 0.1 MPa and a temperature of 298 K.

We used 3 different displacement agents for that series of experiments: water, aqueous solution of surfactant (0.05% mass sulphanole



Fig. 5. Dependence of oil recovery, %OOIP from pore volume of the injected fluid in stratified heterogeneous medium at displacement by nanofluid slug.

solution) and nanofluid (0.05% mass sulphanole solution, 0.001% mass nanoparticles). The results were registered as of oil recovery, %OOIP dependent on pore volume of the injected fluid and shown in Figs. 5 and 6 and Table 4.

In homogeneous porous medium at water-free oil recovery nanofluid increased oil recovery (%OOIP) to 51% and 35% accordingly to water and surfactant solution. Finite oil recovery (%OOIP) increasing was 17% comparing with water and 12% comparing with surfactant solution.

In heterogeneous porous medium at water-free oil recovery nanofluid as displacement agent increased oil recovery (%OOIP) more than 66% accordingly to water, but finite oil recovery increase was 17% and 22% comparing with surfactant solution and water accordingly.

It should be noted that at oil recovery by nano-fluid slug (20% from pore volume), water-free and finite oil recovery the same as analogous parameters at constant recovery by nanofluid.

To determine the influence of the treatment of the porous medium and the nanosuspension using high-viscosity oil we used in our experiments 0.05%, mass surfactant solution as aqueous solution of surfactant and the same composition containing 0.001%, mass nanoparticles as nanofluid.



Fig. 4. Configuration of test unit. 1 - recorder; 2 - source of supply; 3 - standard (test) pressure gauge; 4 - column with porous medium (bed model); 5 - strain gauge "Saphir"; 6 - PVT chamber; 7 - compensator; 8 - ultrathermostat; 9 - distributing manifold and pressure controller; 10 - proportioning pump; 11 - closing valves; 12 - resistance box.



Fig. 6. Dependence of oil recovery, %OOIP from pore volume of the injected fluid: a) in homogeneous pore medium; b) in layered heterogeneous medium.

The tests conducted can be seen in Fig. 4. Oil with viscosity of 20 mPas at 298 K was utilized. The content of the oil heavy components was 17%. The porous medium was saturated by formation water that was displaced by crude oil. When only pure oil was produced at the outlet, residual water volume was 28–30% of the pore volume. Then crude oil was displaced by the nanofluid. For the purpose of comparison the same tests were conducted using water and an aqueous solution of anionic surfactant as a working agent. Test results are shown on Table 5.

As it is obvious from Table 5, the production rate of oil displaced by the nanofluid is increased almost 1.5 fold in comparison with the aqueous solution of anionic surface-acting agent and 4.7 fold in comparison with water. This despite that minimal nanofluid Newtonian viscosity is 2 fold higher than the viscosity of water and surfactant aqueous solution. It is obvious that the decrease of interfacial tension on the nanofluid–oil interface and improvement of pore wettability cause an energy reduction of oil in connection with the porous medium surface because of which the oil flow rate is increased.

#### Table 4

Water-free and finite factors of oil recovery, %OOIP for different displacement agents.

Displacement agent	Oil recovery, %OOIP in homogeneous porous medium		Oil recovery, %OOIP in heterogeneous porous medium	
	Water-free % OOIP	Finite % OOIP	Water-free % OOIP	Finite % OOIP
Water	35	51.3	26.4	45.8
Aqueous solution of surfactant	39	53.4	22.2	47.5
Nanofluid	53	60.3	44	56
Nanofluid slug	-	-	44	56

Гal	ble	5
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Working agent	Additives	Concentration	Oil flow rate (sm <sup>3</sup> /s)
Water Aqueous solution of surfactant Nanofluid	Water Surfactant Surfactant Nanoparticles	100 0.05 0.05 0.001	0.015 0.048 0.07

#### 9. Conclusions

- 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%).
- In the presence of nanoparticles the sulphanole adsorption process is more stable and surfactant adsorption values exceed those observed in surfactant solution by 14.5–18.5 times.
- Nanoparticles added to the sulphanole solution practically remain unchanged oil wettability.
- Nanoparticle attached to the liquid surface and due to absorption process decrease surface tension. The results of spectrographic measurements shows the change of initial absorption bands belonging to sulphanole aqueous solution in the presence of a nanostructurized component controlled by interaction of sulphanole anions (C<sub>12</sub>H<sub>25</sub>-C<sub>6</sub> H<sub>4</sub>-SO<sub>3</sub>) with cations of nanopowder surface.
- Nanoparticles added to the surface-active agent solution cause flow character modification from Newtonian to non-Newtonian (pseudoplastic), i.e. the nanofluid is characterized by shift dilution. The minimal Newtonian viscosity of the surfactant aqueous solution with added nano-particles is twice as high as without the nano-particles and is equal to 2 mPa·s.
- Finally we got following advantages of nanofluid as displacement agent: In homogeneous pore medium water-free oil recovery increasing was 51% and 35%, finite was 17% and 12% accordingly to water and surfactant solution. In heterogeneous pore medium water-free oil recovery increasing was 66% comparing with water, finite was 22% and 17% accordingly to water and surfactant solution. It should be noted that at oil recovery by nano-fluid slug (20% from pore volume), water-free and finite oil recovery the same as analogous parameters at constant recovery by nanofluid.
- Application of the nanosuspension developed here permitted significant increase in the efficiency of oil displacement flow rate. The production rate of oil displaced by the nanofluid is increased almost 1.5 fold in comparison with the aqueous solution of anionic surface-acting agent and 4.7 fold in comparison with water.

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