Experimental investigation of the effect of volume concentration and average diameters of nanoparticles on the contact angle of wetting between nanofluids and different substrates

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Abstract. The influence of different volume concentrations and average diameters of Al₂O₃ nanoparticles on the contact angle of wetting between nanofluids and different substrates was experimentally investigated. The concentrations of aluminium oxide nanoparticles were varied from 0.0625 vol.% to 1 vol.%. The average diameters of aluminium oxide nanoparticles were varied from 43 nm to 150 nm. Andesite, diabase, gabbro-diabase and metabasalt were chosen as the substrates. The dependences of the value of the contact angle of wetting between nanofluids and different substrates were obtained as a result of the experiments. It was shown, that the contact angle of wetting nonlinearly depended on the nanoparticles volume concentration. In addition, it was found that the wetting angle also depends on the substrate material, on which the drop lies. It was also obtained that the contact angle of wetting between different substrates and nanofluids with average and huge nanoparticles (> 75 nm) increased 1.25-1.5 times even at the smallest concentration (0.0625 vol.%) and then achieved the plateau. In contrast, the contact angle of wetting between different substrates and nanofluids with small nanoparticles (< 50 nm) reached maximum at a concentration of 0.0625 vol.% and after that slowly decreased to the values lower than those for the pure water.

1. Introduction

Active interest in suspensions with nanoparticles (nanofluids) appeared a quarter of a century ago and has been growing ever since. The amount of publications devoted to the study of properties and applications of nanofluids increases exponentially. Interest in nanofluids is associated with two main factors. Nanoparticles due to their small size have unusual properties extrinsic to macroscopic disperse particles. Unusual properties of nanoparticles predetermine non-standard properties of nanofluids, being their components. As a result the range of nanofluids applications is wide. Studies of the use of nanofluids in the problems of heat transfer intensification are developing extremely rapidly. Investigations have shown a significant intensification of heat and mass transfer in various applications due to the addition of nanoparticles to the fluid. In particular, it was shown that the nanofluids allow intensifying forced convection by 20-40% and increasing the critical heat flow in boiling by 200%, which opens new prospects for increasing the efficiency of heat exchangers. The use of nanofluids in biomedical applications is developing very intensively. Nanofluids will provide local diagnostics and pinpoint the injury of the body, and perform target delivery of medications to the damaged organ. Nanofluids are used actively in the chemical industry to accelerate and control chemical reactions.
(nanocatalysis), to create new thermal energy transport and production systems, new medicinal and cosmetic preparations, to recognize various types of pollution and for air and water purification systems, in new lubricants, varnishes and paints, nanosensors and nanoactuators, etc. Relatively recently nanofluids have been applied mainly abroad in the technology of development and operation of oil and gas fields. At present, nanofluids are very actively used by foreign oil and gas companies. Nevertheless, a large number of new research papers in this field are published annually.

The oil exploration and production sector is one of the main and the most important sectors in the oil and gas industry, not only in the economy of the Russian Federation but also in many foreign countries. The oil fields are gradually depleted everywhere, therefore, the issues of developing and applying new oil production technologies are becoming topical in terms of a significant increase in oil recovery of already developed reservoirs, as well as used and mothballed fields, where traditional residual oil reserves can no longer be recovered. At present, oil from the porous rock is displaced by water, but the coefficient of oil recovery by water remains quite low.

The efficiency of oil recovery from oil-bearing strata by modern industrial development methods in all oil-producing countries is considered unsatisfactory. The average final oil recovery of strata for different countries and regions is from 25 to 40%. Residual (or non-recoverable by industrial development methods) oil reserves reach on the average 55-75% of the initial geological reserves of oil in the subsurface. Therefore, an increase in oil recovery, of course, is extremely important. Today, there are already a number of appropriate technologies. However, modern methods for increasing oil recovery are significantly more complex, expensive and environmentally harmful than traditional methods. During the application of these methods, complex processes occur in the strata: phase transitions, chemical reactions and transformations of substances, capillary and gravitational processes, etc. At the moment, the following methods of increasing the oil recovery of the stratum are known: steam-thermal effect on the stratum, intrastriatal burning, oil displacement by hot water, air and gas injection into the stratum, oil displacement by aqueous solutions of surfactants (including foam systems), by solutions of polymers, or by chemical reagent compositions, as well as ultrasound treatment [1-8].

In recent years, foreign studies have shown that the use of nanoscale emulsions and suspensions may significantly increase the oil recovery ratio from stratum [9-13]. It was shown in [9] that micro- and nanoemulsions are very effective injecting fluids for extracting residual oil from reservoir in chemical enhanced oil recovery. Oil displacement takes place due to attaining ultralow interfacial tensions and reduced fluid viscosity. Besides, nanoscale emulsions and suspensions show extraordinary water solubilization capacity which again makes them capable for excellent injecting fluids in chemical enhanced oil recovery techniques. From the reducing interfacial tension at the oil boundary point of view, surfactant solutions and nanosized emulsions have approximately the same characteristics. In this case, an important advantage of nanoemulsions compared to surfactant solutions is a significant reduction in the adsorption surfactants on the surface of the rock material, so it possible to use much lower surfactant concentrations in displacement fluids and to improve the environmental indicators of production processes, as it was shown in [10]. It also was found in [11], that the nano-emulsion flooding can be an effective enhancement for an oil recovery method for a heavy oil reservoir which is technically sensitive to the thermal recovery method. It was shown there, that the nano-particle stabilized emulsions can long-distance drive oil in the reservoir, since the nano-particle size is 2-4 times smaller than the pore throat. In the investigation [12] were obtained, that substantial additional recoveries were more than 25% of original oil in place over conventional water flooding. In [13] were concluded, that microemulsion systems are efficient in the oil extraction process, in that they possessed higher viscosities than the oil itself. A recovery factor achieved the value of 87.5% in that experimental investigation.

In addition, the viscosity of surfactant solutions is much lower than the viscosity of natural oils. Due to this the inhomogeneous breakthroughs of long "jets" displacing the fluids around unaffected volumes of the stratum may take place, and, lead to a decrease in the achieved values of oil recovery coefficient as a result. Nanosized emulsions based fluids have significantly higher viscosity values, which exclude the formation of breakthroughs.
The use of nanosuspensions is another promising method of increasing oil recovery. A significant increase in the oil recovery factor by means of the addition of nanoparticles was shown in [14,15]. Thus, SiO₂ nanoparticles with dimensions of 20-70 nm were used for this purpose in [14]. A 5% NaCl solution with a density of 1.05 g/cm³ and a viscosity of 1.09 cP was used as a model of the stratum water. The displacing nanofluid was prepared by adding nanoparticles in this solution, the concentration of which was equal to 4 g/l. The displacement of natural oil with a viscosity of 11.014 cP and a density of 859.3 kg/m³ from the carbonate manifold cores was investigated. Increase the oil recovery factor from 47% to 76% in comparison with stratum water by means of nanofluids was shown as a result. The authors explained this effect by the fact that the rock material acquires the properties of water-wetting by the adsorption of nanoparticles, which facilitates the extraction of both film and capillary-retained oil. TiO₂ nanoparticles with an average size of about 50 nm used for oil displacement in [15]. Heavy natural oil with a density of 920 kg/m³ and a dynamic viscosity of 41.21 cP was used in the experiments. Increase in oil displacement coefficient at least 1.3 times by means of nanofluid was shown as the results of the measurements.

Change in rock wettability, which facilitates the extraction of both film and capillary-retained oil is the main reason to use surfactants in methods of increasing oil recovery. A lot of laboratory experiments, which confirmed the high efficiency of various nanoparticles in the case of interfacial angle reduction on the surface of various materials was carried out in recent years [14,16-18]. For example, the studies of changes in the interfacial angle by SiO₂ nanoparticles with dimensions of 20-70 nm describes in [14]. It was shown that, in the absence of modification by nanoparticles, the value of the contact angle was 146 degrees (oil-wetted), and after modification, the contact angle decreased to 50 degrees, that means the rock became water-wetted, with a weak adherence of oil droplets to the surface. It was concluded in [17], that the wettability conditions is changed when on of the liquids contain nanoparticles. At that, SiO₂ nanoparticles alter the wettability of the rock matrix and the amount of nanoparticles absorbed on the pore walls. It leads to reduce of interfacial tension due to positioning of nanoparticles on the interface between oil and water.

Emerging environmental problems of using the highly toxic surfactants can be solved by replacing ones to nanoparticle suspensions. Therefore, conducting systematic studies of the application of nanofluids in the operation of oil wells is extremely important for the oil and gas industry. The aim of this research is to investigate experimentally the effect of volume concentration and average diameters of nanoparticles on the contact angle of wetting between nanofluids and different substrates to enhance the original oil in place recovery and to increase the oil recovery factor.

2. Experimental apparatus and procedures
An experimental study of the dependence of the equilibrium contact wetting angle between the surface and the nanofluid in the air atmosphere was carried out in this work. All the experiments were conducted at room temperature. Nanofluid was prepared using the distilled water and nanoparticles of aluminium oxide (Al₂O₃) with average sizes from 43 nm to 150 nm. Nanoparticles were purchased from Plasmotherm, Moscow. The volume concentration of nanoparticles ranged from 0.0625 to 1%. A standard two-step method was used to prepare nanofluids. After adding the required amount of nanopowder to water, the tank with the nanofluid was placed in the “Sapphire” ultrasonic bath to destroy the nanoparticle conglomerates. The time of ultrasonic dispersion of powders in the water was 30 minutes. Further sonication did not lead to any changes in the properties of the considered suspensions. The sedimentation stability of metal oxides suspensions after exposure to ultrasound persisted for several days. As the substrate material in this study were used the following materials: andesite, diabase, gabbro-diabase and metabasalt.

The measurement of the contact angle of wetting was carried out using an automatic tensiometer IFT-820-F. Its principle of action based on the method of a lying drop. Structurally, the tensiometer consists of a measuring unit with an optical cell, a thermostat, a fluid dosing system, a pressure control system, an interface for an external computer, and "DropImage Advanced" software. Control of the measurement mode, the drop forming process and the processing of measurement results is carried out.
using a computer. The image of the drop and its size, as well as the calculation results, are displayed on the monitor. The IFT-820-P cell operates at pressures up to 68.95 MPa and temperatures up to 176 °C. The ramé-hart camera is used to monitor the formation and measure the parameters of the drop.

3. Results and discussion

It was found as a result of the study that the contact angle of wetting substantially depends on the volume concentration of nanoparticles, as can be seen in Fig. 1, which represent the photos of nanofluid droplets of 0 vol.%, 0.0625 vol.%, 0.25 vol.% and 1 vol.% concentrations at the particles average size of about 43 nm. Moreover, it was established, that that dependence is nonlinear. In addition, it was found that the contact angle of wetting also depends on the substrate material, on which the drop lies, as can be seen in Fig.2.

![Figure 1](image1.jpg)

**Figure 1.** The lying on metabasalt surface drop of nanofluid at the particles average size of about 43 nm and their different volume concentrations: a) 0%; b) 0.0625%; c) 0.25%; d) 1%.

Based on these experimental data, it was plotted a graph of the dependence of the contact angle of wetting between various substrates and nanofluid on the volume concentration of nanoparticles, that shown in Fig. 3a. It can be seen in this figure that the value of the contact angle for all substrates, except the gabbro-diabase, first increases sharply and then begins to decrease. Thus, for example, the contact angle of wetting between the nanofluid and the metabasalt substrate reaches a maximum value at the volume concentration of nanoparticles of 0.0625%. The relative increase of the contact angle of wetting for that case equal to 1.19 times compares to the pure water.

![Figure 2](image2.jpg)

**Figure 2.** The nanofluid drop of 1 vol.% concentrations at the particles average size of about 43 nm lying on different substrates: a) andesite; b) diabase; c) gabbro-diabase; d) metabasalt.

In the next series of experiments, the effect of the average sizes of nanoparticles on the contact angle of wetting between the surfaces and nanofluid was studied. Metabasalt was chosen as the substrate material for that experimental study. A very interesting behaviour of the contact angle of wetting with changing the average sizes of nanoparticles was found as a result. Thus, the contact angle between different substrates and nanofluids with average and huge nanoparticles (> 75 nm) increased in 1.25-1.5 times at even smallest concentration (0.0625 vol.%) and then achieved the plateau. For nanofluids with small nanoparticles sizes (< 50 nm), the dependence of the wetting angle differs radically. As was shown above, as the volume concentration of nanoparticles increases, that value reaches the maximum at the lowest concentration (0.0625 vol.%) and then gradually decreases till the values lower than for the pure water. For example, the contact angle of wetting between the metabasalt substrate and nanofluid of 1 vol.% concentration was 40% less than the value of this value for pure water.
Figure 3. The dependence of the contact angle of wetting between various substrates and nanofluid of 43 nm average diameters (a) and between metabasalt substrate and nanofluids of different average diameters (b) on the volume concentration of nanoparticles.

Thus, it can be concluded that the use of nanofluids makes it possible to modify the contact angle of wetting, and thus makes it possible to control the processes of oil recovery and increase the efficiency of its production.

Conclusions
The experimental investigations of the influence of different volume concentrations and average diameters of Al₂O₃ nanoparticles on the contact angle of wetting between nanofluids and different substrates were carried out. The concentrations of aluminium oxide nanoparticles were varied from 0.0625 vol.% to 1 vol.%. The average diameters of aluminium oxide nanoparticles were varied from 43 nm to 150 nm. The average diameters of aluminium oxide nanoparticles were varied from 43 nm to 150 nm. Andesite, diabase, gabbro-diabase and metabasalt were chosen as the substrates. The dependences of the value of the contact angle of wetting between nanofluids and different substrates were obtained as a result of the experiments. It was shown, that the contact angle of wetting nonlinearly depended on the nanoparticles volume concentration. In addition, it was found that the wetting angle also depends on the substrate material, on which the drop lies. The maximum relative increase of the contact angle of wetting between nanofluid of 43 nm average diameter and andesite substrate reached 1.37 times compared to the pure water at 0.125 vol.% concentration of nanoparticles. The same value for diabase substrate was equal to 1.17 times at 0.25 vol.% concentration of nanoparticles. For gabbro-diabase, the maximum contact angle of wetting was observed at 0 vol.% (pure water). The maximum relative increase of the contact angle of wetting between different substrates and nanofluids in sizes (> 75 nm) increased in 1.25-1.5 times at even smallest concentration (0.0625 vol.%) and then achieved the plateau. In contrast, the contact angle of wetting between different substrates and nanofluids with small nanoparticles (< 50 nm) reached maximum at a concentration of 0.0625 vol.% and after that slowly decreased till the values lower than for the pure water.

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