The Use of Nanoparticles to Displace Oil from a Porous Medium

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Abstract. The formation of supramolecular structures forming a transition region at the oil-nanofluid interface with a low surface tension is studied as a result of a synergistic effect in the interaction of planar graphene nanoparticles and silicon carbide nanoparticles coated with graphene layers (Core-shell). In model experiments on a Hele-Shaw cell, it was shown that in a porous medium such hybrid nanofluids have a high displacing ability of residual oil. At the same time, the oil – nanofluid interface remains stable, without the formation of sticky fingers. In the process of research using power electron microscopy, a transition region was observed, in the structuring of which nanoparticles were directly involved. The efficiency of displacement by hybrid nanofluid depends on the concentration of nanoparticles and their interaction.

Introduction

Nanofluids have unique characteristics that over the past two decades have found application in various fields of science and technology, reflected in the reviews [1-7]. Of particular interest are fluids based on graphene-like nanostructures (GLN): single-layer graphene; graphene oxide; reduced graphene; multilayer graphene; graphene with quantum dots. Thus, the optical properties of GPNF are widely used in solar energy. Due to its high thermal conductivity, GLN are actively used in heat removal systems. High electrical conductivity of GLN has found application in electronics [7]. However, the use of GLN runs into a number of difficulties. For example, a change in the rheological properties of the base fluid leads to a rapid increase in the viscosity of the GLN, which negatively affects the performance of nanofluids. The use of a combination of various nanostructures allows one to partially solve the difficulties encountered. So, in a review [7], nanofluids with a combination of nanostructures are considered. Among the many types of nanoparticles used in combination with graphene, the following are common: metals Ag, Cu, [8,9]; metal oxides Al2O3, Fe3O4, CuO [10.11]; carbides TiC, SiC, [12]; carbon in various forms (nanodiamonds, graphite), single-, double- and multi-wall carbon nanotubes, composites from fullerenes [13-15].

In recent years, GLN have become widely used in the oil and gas industry [16-17]. The use of single-layer graphene as a displacing agent [18] has shown high efficiency with increased oil recovery. In [19], graphene oxide was used as such an agent, and in [20], sulfonated graphene (Sulfonated graphene) was...
used. In [21], fluids based on multilayer graphene were used to increase oil recovery. Creating at the oil-water interface a transition region with a low surface tension, which is not a microemulsion, is an urgent task in oil production. The solution to this problem allows us to develop technologies that increase oil recovery from the oil reservoir of the bottomhole zone [22]. It is known that low surface tension at the oil−water interface is associated with the formation of a structure from liquid crystalline monolayers of macromolecules [23]. Such layers can be formed from planar graphene nanoparticles [24]. In this study, the displacing properties of hybrid nanofluids based on multilayer graphene and Core-shell structures - SiC crystallites coated on top with several layers of graphene are studied.

**Materials and methods**

Planar graphene nanoparticles were obtained in aqueous graphene suspension by ultrasonic dispersion of polycrystalline graphite [25]. Carbon nanoparticles and Core-shell structures were synthesized using a high-performance process − rapid cyclic compression in a chemical reactor [26]. Aqueous suspensions of Core-shell nanoparticles, as well as carbon, were obtained by the same method [27]. We used 12 different samples of nanofluids, the mass concentration of graphene and core-shell nanoparticles in the base fluid (distilled water) in which is shown in the table 1.

**Table 1.** Graphene nanofluids (GNF), Core-shell nanofluids (C-sNF), hybrid nanofluids (GNF+C-sNF).

| GNF        | C-sNF       | GNF+C-sNF                  |
|------------|-------------|----------------------------|
| wt 0,0050% | wt 0,0050%  | wt 0,0025%+ wt 0,0025%     |
| wt 0,0100% | wt 0,0100%  | wt 0,0050%+ wt 0,0050%     |
| wt 0,0150% | wt 0,0150%  | wt 0,0075%+ wt 0,0075%     |
| wt 0,0200% | wt 0,0200%  | wt 0,0100%+ wt 0,0100%     |

As a model of a porous medium, to study the behavior of the interface, in this work, we used the Hele−Shaw radial cell, whose geometric parameters were $R_0 = 2$ mm, $R_\infty = 120$ mm, $b = 0.6$ mm [3]. All experiments on the Hele-Shaw cell were carried out at room temperature. Prepared, dehydrated oil from a Western Siberian field with viscosity $\mu_{20} = 4.08$ mPa*s and density $\rho_{20} = 838$ kg/m$^3$ was placed in the cell. At constant overpressure, nanofluid was injected into the cell. Further, the $P_{crit}$ value increased until the oil−water interface degenerated into instability. The unstable displacement parameter was used to consider the ratio $\delta / R = 0.4$, where $R$ is the radius of the unperturbed surface and $\delta$ is the perturbation amplitude [28].

**Results and discussion**

The size and shape of the particles in the aqueous suspension was determined using an Ntegra Aura atomic force microscope (AFM) (NT-MDT) and a MIRA 3 scanning electron microscope (SEM) (TESCAN). (Figure 1-a, b). SiC crystallites with a size of 3−7 nm, coated with several layers of graphene (Core-shell structure) are shown in Figure 2. Images were obtained by TEMR method using a JEM-2010 electron microscope (JEOL, Japan). At a lower magnification, it can be seen that particles with a size of 40-50 nm form dendrite couplings - aggregates of many round-shaped particles (Figure 3). Particles of fluids were deposited on a silicon single crystal. From the analysis of particles, it can be concluded that graphene particles are predominantly cylindrical in diameter with $D = 30 \pm 5$ nm.
Figure 1. Images of graphene nanoparticles on a silicon substrate, obtained by (a) - SEM, (b) - AFM semi-contact method.

Figure 2. Image of nanoscale crystallites of SiC coated with 2-5 layers of graphene - (Core-shell structure).

Figure 3. Image of Core-shell nanoparticles forming extended dendrite aggregates (resolution 100 nm).

The results of modeling the motion in a porous medium on a Hele-Show cell are given below. In Figs. 4a, c, the undisturbed motion of the GNF and C-sNF nanofluids with equal mass concentrations wt 0.005% was observed. When critical pressure was reached, the oil – nanofluid interface turned into a perturbed state and the front degenerated with the formation of “sticky fingers” (Figures 4-b, d).
It was established that the boundary region between oil and nanofluids is more stable in contrast to the movement of distilled water (table 2). The perturbation of the oil-water interface occurs at lower critical pressures, in contrast to the oil-nanofluid interface (table 2). The critical pressure for displacement with distilled water is $p_{\text{crit}} = 8$ kPa. With increasing concentrations of nanoparticles in the base fluid, the critical pressure $p_{\text{crit}}$ also increases. However, when the concentration reaches wt $0.015\%$ for GNF and C-sNF, the critical pressure value ceases to increase. Combined nanofluids No. 1 and No. 2 (see table 2) showed greater stability of the interface. For combination No. 2, the critical pressure value was $92 \pm 1$ kPa, which exceeds the values of monofluids GNF and C-sNF at concentrations wt $0.015\%$ by $\Delta p = 12 \pm 1$ kPa. For combination No. 3, $p_{\text{crit}}$ differs little from the values for monofluids GNF and C-sNF at
Concentration, wt%  | GNF $p_{\text{crit}}$, kPa | C-sNF $p_{\text{crit}}$, kPa | GNF+ C-sNF $p_{\text{crit}}$, kPa |
--- | --- | --- | --- |
0 (dis. water) | 8±1 | 8±1 | |
0.005 | 55±1 | 60±1 | Combined Fluid № 1 | 85 |
0.010 | 70±1 | 75±1 | Combined Fluid № 2 | 92 |
0.015 | 80±1 | 81±1 | Combined Fluid № 3 | 79 |
0.020 | 79±1 | 80±1 | Combined Fluid № 4 | 60 |

Table 2. Critical pressure $p_{\text{crit}}$ for GNF, C-sNF and GNF+ C-sNF nanofluids

The stability of the oil – nanofluids interface, in comparison with distilled water, can be explained by the appearance of an ordered film at the interphase boundary [21,25]. This film is the result of self-organization of graphene nanoparticles and hydrocarbon oil molecules. To test this mechanism of strengthening the boundary region of the ball, a film was grown at the GNF boundary and molten paraffin (mixture of saturated hydrocarbons) (Figure 5-a). Using the SEM, the transition region of graphene nanoparticles can be observed in the selected area (Figure 5-b). The formation of a structured region at the hydrocarbon-nanofluid interface can indicate a low surface tension. Therefore, it can be assumed that nanoparticles are directly involved in the structuring of the transition region.

Figure 5. Graphene film: (a) a graphene film grown at the hydrocarbon (paraffin) - GNF interface; (b) SEM image of a graphene film.

The reason that the displacing ability of nanofluids is reduced is the increase in viscosity of the base fluid. It is known that an increase in the concentration of nanoparticles in the base fluid leads to a quadratic increase in the viscosity of nanofluid [29].

Conclusions
Nanofluids, when displaced from a model of a porous medium (Hele-Shaw cells), exhibit greater interphase stability. With an increase in the concentration of nanoparticles in the base fluid, the critical pressure value increases, i.e. a transition to a disturbed state is carried out. Combinations of graphene nanoparticles and Core-shell enhance the displacing ability of nanofluids, however, when certain nanoparticle concentrations are reached, the effect weakens. Research data can be used to create technology that improves oil recovery.

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