Formation of a microheterophase state from planar nanoparticles of graphene at the oil-water interface

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Abstract. It has been found that N aqueous suspension of planar graphite nanoparticles exhibits properties of displacement fluid at the oil–water interface. Experiments with the Hele–Shaw cell showed that the process of oil displacement from the interface is not accompanied by the formation of viscous “fingers” as a result of development of instability at the oil–water interface.

1. Introduction

Most of oil deposits are known to be entering the final stage of development [1]. To completely displace oil from a seam, physicochemical oil recovery methods are combined with flooding [2]. Microemulsion flooding is considered to be the most efficient technique, but the flooding agent must have a required mobility and a low surface tension in oil. In this case, the oil-water interface is stable and viscous fingers do not form. Microemulsions are, however, sensitive to aggressive media of the seam. As a result, a stable laboratory microemulsion state becomes unstable in field operations [2].

Thus, the research objective was to form, at the oil-water interface, a transition zone with a low surface tension, which would not be a microemulsion and would have a low sensitivity to deposit water temperature and hardness. To meet these requirements, a water suspension based on planar nanoparticles of graphene was chosen [3, 4].

It is known that a low surface tension at the oil–water interface is related to the formation of a structure consisting of liquid-crystalline layers of macromolecules [2]. These layers can be formed, in particular, by planar graphite nanoparticles with dimensions below 400 nm. Stability of this suspension is determined by the condition [4]

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S \leq 0 \]  

(1)

where \( \Delta G_{\text{mix}} \) is the change in Gibbs’ energy of the mixture, \( \Delta H_{\text{mix}} \) is the change in enthalpy of the system, and \( \Delta S \) is the change in entropy. Therefore, a solvent for suspension should possess a specific surface energy (\( \sigma \)) close to the energy of a monolayer of graphite nanoparticles. This requirement is satisfied by aqueous ethanol solutions [5]. By varying the concentration of ethanol, it is possible to make \( \sigma \) close to that of planar graphite particles.

Under real conditions, liquids frequently exhibit the phenomenon of bedding (e.g., motion of oil in water). In this case, solution of the problem of possible motion of the oil–water interface depends on the coefficient of proportionality of the bulk of the reservoir and the angle of the bed slope. The shape of the oil–water interface also depends on the ratio of viscosities of oil and water. The formation of transition regions leads to a decrease in the velocity of motion on the bed bottom and increase in that at the bed roof. The difference of the velocities of motion at the inner and outer contours depends on the permeability of bed solid. Even simple schemes of oil displacement exhibit distortion of the shape of
the oil–water interface with the formation of water fingers. The degree of stability is determined by the coefficient of mobility defined as,

\[ \lambda = \frac{K_{w0} \mu_{oil}}{K_{w0} \mu_B} \]  

(2)

where \( K_{w0} \) is the permeability for water in the presence of residual oil, \( K_{ow} \) is the permeability for oil in the presence of residual bound water, \( \mu_{oil} \) is the viscosity of oil, and \( \mu_B \) is the viscosity of brine. The contact front is stable provided that \( \lambda < 1 \), which implies that \( \mu_B \) must not significantly increase. Therefore, a suspension of graphite (planar) particles must have a small surface tension \( \sigma \) at the oil–water interface, while viscosity \( \mu_B \) and density \( \rho \) should obey the empirical relation \[ 0.1 \geq \frac{\mu_B}{\sqrt{\sigma \rho d}} \] 

(3)

where \( d \) is the average pore size (or capillary diameter) in the porous structure, or

\[ K_{w0} \mu_B < K_{w0} \mu_{oil} \]  

(4)

2. Results and discussion

It was discovered that, at the oil-water interface, the water graphene suspension forms a transition multilevel microheterophase state from planar nanoparticles of graphene, oil hydrocarbon molecules.

Analysis of the X-ray diffraction patterns of the carbon material obtained on a DRON-7 X-ray diffractometer (CuK\( \alpha \) radiation) showed a significant decrease in the 002 peak in the carbon material of the graphene suspension. The decrease in the 002 peak in the graphene suspension indicates the presence of a single-layered graphene in the suspension [5]. However, in the formation of the microheterophase state, the magnitude of the peak 002 increases compared to the peak that gives the carbon material isolated from the graphene suspension. In addition to the increase in peak 002, the distance between the
planes $d_{002}$ increases from 0.337nm to 0.347nm (Figure 1.). This can be explained by the fact that in the formation of a microheterophase state, graphene particles form a multilayer structure of sheets of graphene and hydrocarbons contained in oil.

To study the behavior of the water-oil interface, the radial Hele-Shaw cell was used, the geometric parameters of which were $D_0 = 2$ mm, $D_\infty = 120$ mm, $b = 0.6$mm (Figure 2) [6,7]. Displacement was carried out at a constant pressure of $p = 10$ kPa.

As a result of synthesis of planar carbon nanostructures, a suspension with a particle size of 200÷400 nm with a low surface tension $\sigma = 43$ mN/m was formed. The electron-microscopic examination of this carbon material on a UEMV-100K transmission electron microscope using standard techniques showed the presence of perfect graphite crystals with various thicknesses (Figure 3).

The addition of this suspension to an oil phase reduced the initial viscosity by 0.7%, which led to an increase in the stability of the contact front ($\lambda < 1$). When water was injected without graphene nanoparticles into the Hele-Shaw cell (with a constant pressure $p = 10$ kPa), viscous fingers formed due to the instability of the interface, indicating the breakthrough of water through the oil (Fig. 4, a). When graphene suspension is added to water with a concentration of 0.04 g/l, the displacement is a stable front.
without forming viscous fingers under the same regime with a constant pressure $p = 10$ kPa. In Figure 2, b, the oil-microhetero-phase-water interface is clearly visible.

![Image](a) ![Image](b)

**Figure 4 (a, b).** Displacing oil with water in a Hele-Shaw cell (a) with viscous fingering; (b) without viscous fingering with a stable oil-graphene nanoparticles-water interface

### 3. Conclusion

The results of the research works prove promising the development of the technology involving the use of the graphene-based suspension to displace residual oil from the seam.

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