Oil displacement by aqueous solutions of surfactants at various temperatures

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Abstract. To generalize the experimental data on the displacement of oil by aqueous solutions of surface-active substances (surfactants) at temperatures of 40, 60, 80 °C, we studied the influence of an additional parameter of the ratio of the work of adhesion during the displacement of oil by water to oil adhesion during the displacement of an aqueous solution of surfactant \( W = \frac{W_w}{W} \). This parameter characterizes the intensity of mass transfer of oil particles from the surface of the rock using surfactants at different temperatures. The parameter \( W \) in combination with the capillary number \( Ca \) characterizes the value of residual oil saturation in oil reservoirs. A criterion equation is obtained that allows one to calculate the displacement coefficient from two dimensionless parameters: the capillary number and the relative work of oil adhesion.

1. Introduction

Recently, in connection with the widespread use of surface-active substances (surfactants) to increase oil recovery, studies are increasingly being conducted to reduce residual oil saturation during displacement. [1] Moreover, if the initial oil saturation is determined by the initial geological conditions of the reservoir, the residual oil saturation depends on the surface tension forces arising from the interaction of oil with a displacing agent and other parameters. [2]

Capillary forces, and, consequently, residual oil saturation, depend on the size and type of surfactant micelles, surfactant concentration, and temperature. The decrease in residual oil saturation with increasing temperature can be explained by the weakening of intermolecular interactions of asphaltenes in the volume of structured oils.

Thus, as shown by numerous experimental studies and their analysis, the residual oil saturation depends on the dimensionless capillary number. An extensive review of the results of experimental studies of the effect of capillary number on residual oil saturation during oil displacement by water for core samples from various fields of the world is given in the book by Yu.E. Baturin. [5] However, this parameter alone is not enough to estimate the amount of residual oil saturation. [6]

2. Objects and research methods

The use of an aqueous surfactant solution instead of water as a displacing agent leads to a decrease in residual oil saturation. [1,3] According to the results of laboratory studies on core material, the injection of an aqueous surfactant solution into a porous medium with all relevant reactions leads to a relative
decrease in residual oil saturation, which can be up to 30%. [4, 5] This occurs due to a decrease in capillary forces, which are characterized by the capillary number $Ca$. The form of this number is:

$$Ca = \frac{v \cdot \mu_d}{\sigma}$$

(1)

where $v$ - displacement fluid filtration rate, m$^3$/m$^2$·s; $\mu_d$ – displacement fluid viscosity, Pa·s; $\sigma$ – surface tension at the oil-displacing fluid interface, N/m.

The capillary number characterizes the ratio between capillary forces, the value of which determines the surface tension at the water-oil interface, the structure of the pore space and the hydrodynamic pressure, which determines the rate of fluid filtration. An analysis of the parameters included in the capillary number formula shows that it is virtually impossible to significantly increase the hydrodynamic forces in a real reservoir. The introduction of surfactants can have a significant effect on capillary forces.

The addition of a surfactant reduces the marginal angles of selective wetting, i.e., increases the wettability of the rock with water. The criterion for the wetting ability of a surfactant is the energy of the interaction of oil with the rock surface, defined as the work of oil adhesion. A decrease in contact angles together with a decrease in interfacial tension entails a significant decrease in the binding energy of oil and the rock surface. The binding energy can be judged by the decrease in the work of adhesion of oil to the surface from the Dupre-Young equation [7]:

$$W = \sigma \cdot (1 - \cos \theta)$$

(2)

where $W$ - oil adhesion work, J/m$^2$; $\sigma$ - interfacial tension at the oil - water phase, N/m; $\theta$ - marginal angle of selective wetting, deg.

In the framework of the studies, the surface tension was measured at the interface “oil - aqueous surfactant solution” on an ST-1 stalagmometer by the drop volume method. The results of these studies are given in [8].

![Figure 1. Characteristic dependence of the dynamic viscosity and density of oil on temperature](image)

Filtration studies were carried out on a composite column consisting of three sand cores with similar lithological and porosity and permeability properties. The average open porosity of the samples in water is $(22.65 \pm 0.2)\%$; helium gas permeability - $(372 \pm 20)$ mD.
An oil with the following characteristics was used: dynamic viscosity at 20 °C $\mu = 15.2$ mPa∙s; density at 20 °C $\rho = 840$ kg/m$^3$.

A typical form of changes in the dynamic viscosity and density of oil in the temperature range of 20 - 80 °C is shown in Figure 1.

As the aqueous phase, we took aqueous solutions of three surfactants in a reservoir water model. Distilled water with a NaCl salt content of 20 g/L was used as a model of produced water. Surfactants used: synthanol ALM-1, ne Lonol AF 9-12 - belong to the class of nonionic surfactants, sodium lauryl sulfate - anionic surfactant. The concentration of aqueous surfactant solutions was 0.5% of the mass.

The adhesion work $W$ was found by the formula (2), where the contact angle was determined by the method of a lying drop. The technique for measuring the contact angles of wetting is based on placing a drop of oil on the bottom surface of the plate suspended horizontally and placed in a cuvette with an aqueous phase. Instead of a core sample, a quartz surface acted as a plate, which models the wetting conditions of the rock pore walls. Using a microscope, the maximum diameter and height of the drop were measured. The diameter of the drop should be from 2 to 5 mm; this ensures that the contact angle will not depend on the diameter. In the case of very small drops, the influence of the surface tension of the liquid itself will be large (spherical drops will form), and in the case of large drops, gravity forces begin to dominate [9, 10]. The contact angle was calculated by the formula:

$$ \tan \left( \frac{\theta}{2} \right) = \frac{2h}{d_{\max}} $$

where $\theta$ – contact angle, $h$ – drop height, $d_{\max}$ – maximum drop diameter.

Filtration was carried out on the PIK-OFP/EP-3 installation, designed to simulate a two-phase flow through a composite column of core samples in reservoir conditions. Filtration experiments were carried out at a mountain pressure of 250 atm, an operating pressure of 30 atm, and a linear filtration rate of 1.7 m/day at three temperatures: 40, 60 and 80 °C.

The oil displacement coefficient was determined by the formula [11]:

$$ K_{\text{oil}} = \frac{1-S_w-S_p}{1-S_w} \times 100 \% $$

where $S_w$ – initial residual water saturation; $S_p$ – residual oil saturation.

The value of residual water saturation was determined by centrifugation. [12]

3. Research results

The results of oil displacement experiments for various aqueous surfactant solutions at temperatures of 40, 60, 80 °C, as compared with produced water are shown in Figure 2. The obtained value of the residual oil saturation can be used in determining the dependences of the relative phase permeabilities of oil and water using the methods [13, 14].
Figure 2. Comparison of oil displacement coefficients with aqueous solutions of various surfactants at different temperatures

Table 1 shows the calculated parameters of the studied system at different temperatures: oil displacement coefficient $K_{dis}$, surface tension at the oil-aqueous surfactant interface $\sigma$, capillary number calculated by the formula (1) $Ca$, selective contact wetting angles $\theta$, parameter of relative oil adhesion work $\bar{W}$.

| $T$, °C | Displacing agent | $K_{dis}$, % | $\sigma$, mN/m | $Ca \cdot 10^6$ | $\theta$, deg | $W$, mJ/m$^2$ | $\bar{W}$ |
|--------|-----------------|-------------|--------------|----------------|-------------|---------------|--------|
| 40     | Water           | 44          | 36.9         | 0.41           | 76          | 27.9          |        |
| 60     | Synthanol ALM-1 | 54          | 35.8         | 0.35           | 70          | 23.5          | 1      |
| 80     |                 | 59          | 35           | 0.26           | 47          | 11.1          |        |
| 40     | Neorol AF 9-12  | 61          | 26           | 0.49           | 55          | 11.0          | 2.1    |
| 60     | Sodium lauryl   | 66          | 20           | 0.75           | 67          | 12.2          | 2.2    |
| 80     | sulfate         | 61          | 4.8          | 3.1            | 57          | 2.2           | 12.8   |

Table 1 shows that there is a monotonic dependence of the displacement intensity on the work of adhesion. With increasing temperature, the adhesion work $W$ decreases, due to which the oil recovery increases. Thus, the dimensionless parameter of the relative adhesion work $\bar{W}$ can be used to evaluate oil displacement by aqueous surfactant solutions.

Based on the conducted experimental studies, the dependence of the oil displacement coefficient on two dimensionless parameters was revealed: the capillary number $Ca$ and the relative adhesion work $\bar{W}$ in the form:

$$K_{dis} = C \cdot f_1(Ca) \cdot f_2(\bar{W})$$

(5)
where the dimensionless constant $C, f_1(Ca)$ and $f_2(W)$ are functional dependencies on $Ca$ and $W$.

Obviously, when displacement occurs without adding a surfactant, the parameter of the relative adhesion work $W$ is 1. The function of the dependence on the capillary number for $W = 1$ can be found for specific deposits according to the set of points summarized in the book by Yu.E. Baturin. [5]

We present the experimental data in the logarithmic form adopted in the theory of heat and mass transfer [15,16]:

$$\lg K_{dis} = \lg a_0 + m_1 \cdot \lg Ca$$

(6)

In this case, the criterial equation of mass transfer during oil displacement by water has the form:

$$K_{dis} = a_0 \cdot Ca^{m_1}$$

(7)

As an example, Figure 3 shows the experimental dependence $K_{dis} = K_{dis}(Ca)$ at a temperature of 60 °C in logarithmic coordinates.

Figure 3. Value of the displacement coefficient depending on the capillary number in the logarithmic coordinates for the Abrams field [5]

Thus, as a function $K_{dis} = K_{dis}(Ca)$ in the logarithmic coordinates, a straight line was taken with approximation reliability of 0.84, which is typical for the criterion equations of mass transfer. [15,16]

From the approximation equation, empirical coefficients $a_0$ and $m_1$ were found for the studied temperatures.

The general form of the criterion equation for the dependence of the displacement coefficient on dimensionless parameters and temperature is taken in the form:

$$K_{dis} = a_0(T) \cdot Ca^{m_1(T)} \cdot W^{m_2}.$$ 

(8)

The value of the coefficient $m_2$ was found analytically from a system of equations with known data on the displacement coefficient, capillary number, and relative work of adhesion. The found value of the coefficient $m_2 = 0.07$. According to the calculations, it was found that the value of this coefficient does not depend on temperature. While the coefficients $a_0$ and $m_1$ are functions of temperature.
According to calculations, the empirical coefficients were:

\[ a_0(T) = 2600 \cdot T^{-0.748}, \]
\[ m_1(T) = 17,115 \cdot T^{-1.392}, \]
\[ m_2 = 0.07. \]

Figure 4 shows the types of surfaces of the displacement coefficients on the parameters of the capillary number Ca and the relative work of oil adhesion \( \bar{W} \) for various temperatures.

**Figure 4.** Surfaces of displacement coefficients depending on two dimensionless criteria for temperatures: a – 40 °C; b – 60 °C; c – 80 °C
Table 2 shows the experimental values and values calculated by the formula (8) of the displacement coefficient for various temperatures.

| Displacing agent | $T = 40 \, ^\circ\text{C}$ | $T = 60 \, ^\circ\text{C}$ | $T = 80 \, ^\circ\text{C}$ |
|-------------------|----------------------------|----------------------------|----------------------------|
|                   | $K_{\text{dis, exp}}$ | $K_{\text{dis, calc.}}$ | $K_{\text{dis, exp}}$ | $K_{\text{dis, calc.}}$ | $K_{\text{dis, exp}}$ | $K_{\text{dis, calc.}}$ |
| Water             | 44.2                      | 43.7                      | 54.0                      | 53.7                      | 59.2                      | 57.8                      |
| Synthanol ALM-1   | 51.1                      | 49.3                      | 57.4                      | 57.7                      | 61.1                      | 59.1                      |
| Neonol AF 9-12    | 66.3                      | 64.2                      | 73.3                      | 74.0                      | 75.1                      | 74.0                      |
| Sodium lauryl sulfate | 74.0                    | 73.1                      | 79.7                      | 80.6                      | 80.4                      | 79.1                      |

As can be seen from Table 3, the calculated values within the measurement error coincide with the experimental data, which confirms the adequacy of the obtained criteria equation. Thus, choosing the right surfactant, using the above methodology, it is possible to predict the possibility of additional oil displacement with aqueous solutions of surfactants.

4. Conclusion
1. A procedure has been developed for calculating additional oil displacement with aqueous surfactant solutions, based on the obtained criterion equation for mass transfer based on the experiments performed, which allows predicting the influence of the type of aqueous solution of surface-active substances, the temperature of the solution and the ratio of pressure forces and surface tension forces in the "oil - aqueous surfactant solution - core" system.
2. Experimental studies of oil filtration with aqueous solutions of three different surfactants and without them in the temperature range of 40 - 80 °C were conducted. The increase in oil displacement with the use of additives, as well as with increasing temperature, is shown.
3. It is shown that with increasing temperature, oil displacement by aqueous surfactant solutions increases. However, the use of surfactants is more rational at low temperatures. With increasing temperature, the washing ability of water increases significantly, so the percentage of displacement compared with produced water decreases. So, for example, at a temperature of 40 °C the additional displacement for sodium lauryl sulfate was 68%, and at 80 °C - 35%.

References
[1] Semikhina L P, Shtykov S V, Pashchina A M and Karelin E A 2015 Effect of temperature on the ability of aqueous reagent solutions to wash oil from a solid surface Bulletin of the Tyumen State University. Physical and mathematical modeling. Oil, gas, energy 1 3(3) 39-51
[2] Akhmetova Z R 2016 Residual oil saturation structuring to substantiate oil recovery technology National University of Oil and Gas "Gubkin University" Moscow
[3] Moreau P, Morvan M, Rivoal P (Rhodia), Bazin B, Douarche F, Argillier J-F and Tabary R 2010 (IFP) An integrated workflow for chemical EOR pilot design SPE 129865 presented at the SPE Improved Oil Recovery Symposium held in Tulsa Oklahoma USA 24-28
[4] Flaaten A A, Quoc Nguyen and Pope G 2008 A systematic laboratory approach to low-cost, high performance chemical flooding SPE 113469 presented at the SPE/IOR Symposium Tulsa 19-23
[5] Baturin Yu E 2016 Design and development of oil and gas and oil fields in Western Siberia (Surgut: OJSC “Surgutneftegaz”, Advertising and publishing information center “Oil of the Ob region”) 2 204
[6] Kuzina O A, Semikhina LP and Shabarov A B 2019 Effect of capillary number and adhesion work on oil displacement by aqueous solutions of surfactants Bulletin of the Tyumen State University. Physical and mathematical modeling. Oil, gas, energy 5 3
[7] Babalyan G A 1983 Development of oil fields using surfactants (Moscow: Nedra) 216
[8] Grigoriev B V, Vazhenin D A and Kuzina O A 2016 Effect of surfactant concentration of aqueous solutions and temperature on the surface tension coefficient Bulletin of the Tyumen State University. Physical and mathematical modeling. Oil, gas, energy 2 3 35-48.
[9] Aslan S, Najafabadi N F. Firoozabadi A 2016 Non-monotonicity of the contact angle from NaCl and MgCl2 concentrations in two petroleum fluids on atomistically smooth surfaces Energy Fuels 30 2858-2864
[10] Lu Y, Najafabadi N F and Firoozabadi A 2019 Effect of Low-concentration of 1-Pentanol on Wettability of Petroleum Fluid-Brine-Rock Systems Langmuir American Chemical Society
[11] OST 39-195-86 Oil. Method for determining the coefficient of oil displacement by water in laboratory conditions
[12] Kuznetsov A M, Baishev A B and Kuznetsov V V 2010 Determination of initial water saturation and capillary curve by centrifugation Oil industry 1 49-51
[13] Shabarov A B and Shatalov A V 2016 Pressure loss during oil-water mixture flow Bulletin of the Tyumen State University. Physical and mathematical modeling. Oil, gas, energy 2 2 50-72
[14] Shabarov A B, Shatalov A V, Markov P V and Shatalova N V 2018 Methods for determining the functions of relative phase permeability in multiphase filtering problems Bulletin of the Tyumen State University. Physical and mathematical modeling. Oil, gas, energy 4 1 79-109
[15] Isachenko V P, Osipova V A and Sukomel A S 1975 Heat transfer (Moscow: Energiya) 488
[16] Lukanin V N, Shatrov M G et al. 2009 Heat engineering (Moscow: Vyshaya shkola) 671