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Effect of Salinity on Microemulsion Used for Residual Oil Recovery and Restoration of Initial Wetting State of a Capillary Medium

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Abstract

An important volume of oil remains trapped in the porous medium due to wettability alteration. Microemulsions are widely used in laboratory core flooding experiments to enhance residual oil recovery and restore the initial wetting state. This study presents the formulation of a microemulsion using two surfactants: sodium dodecyl benzene sulfonate (SDBS) and Tergitol 15-S-12, with the optimal salinity determined by Huh's method for draining a capillary system with altered wettability (oil-wet). The results show that the optimal salinity lies between 70 and 90 g/l, with a decrease in interfacial tension of approximately 0.01 mN/m. The percentage of oil recovered after brine drainage is 33.13%, compared with 89.96% after microemulsion injection at 25ºC. These results support the use of experimentally prepared surfactant formulations from the laboratory scale to the reservoir rock scale.

Keywords: *Microemulsion; Surfactant; Capillary medium; Salinity, Oil recovery; Interfacial tension.*

1. Introduction

Numerous applications of nanoparticles in the oil and gas sector have been studied and proven. Utilising nanoparticles for improved oil recovery (EOR) applications highlights how small they are relative to the size of the pore throats in rocks; as a result, they can be readily transported into porous rocks without altering permeability or retention. By improving the fluid's characteristics and the fluid-rock interaction, nanoparticles can greatly boost oil recovery [1]. Surfactants are organic molecules with a polar (hydrophilic) head and a non-polar (hydrophobic) tail that function as surface-active agents. For the surfactant slug to mobilise residual oil and form an oil bank where water and oil flow as a single continuous phase, it must first reach an ultralow IFT [2]. An anionic surfactant has a negative charge. Due to its extremely low adsorption on sandstone rock with a negative surface charge, this surfactant is the most commonly employed in the EOR process. The molecular structures of ammonium lauryl sulfate (ALS) and sodium dodecyl sulfate (SDS) are shown. Nonionic: A nonionic surfactant is primarily used to enhance system phase behaviour because it does not naturally carry any ionic charge [3].

The nature of the mixed fluids (oil and water) determines the emulsion's physical characteristics. Because oils contain a variety of constituents, hydrocarbons may differ in their composition, affecting physical properties such as density and viscosity. These attributes could be determined by the final emulsion's physical characteristics [4]. As a thermodynamically unstable system, an emulsion tends to separate into two incompatible phases, moving the system to a lower energy state. This phase separation can be caused by various destabilisation mechanisms [5-6]. In the following sections, we first present materials and methods. Then, we summarise the experimental procedures relevant to oil recovery by water flooding in an altered

wettability capillary system. Finally, we present the findings regarding surfactant solution injection and oil recovery, and highlight the conclusions. The results show that the microemulsion increases oil recovery and restores the initial wetting state.

2. Materials and methods

2.1. Altered-wettability capillary micromodel

The device mainly consists of six (06) glass capillaries into which PVC channels are introduced, simulating the first phase of asphaltene precipitation (Formation of hydrophobic films). All the capillaries have the same diameter of 0.2 cm and the same length of 24 cm, as shown in Figure 1.

Figure 1. Glass capillary.

2.2. Brine

The brine used in all experiments was prepared in the laboratory and had a salinity of 300 g/L. In order to prepare this brine, 300g of NaCl was dissolved in one litre of distilled water. This brine is used for liquid/liquid displacements.

2.3. Oil

The oil was used in all single- and two-phase flow experiments and also served as the base fluid in the microemulsion formulation. The oil used is marketed by the company Naftal®, whose characteristics are represented in Table 1.

Table 1. Properties of the used oil.

Density at 15°C	0.828 g/cm^3	Pour point	- 14°C
Dynamic viscosity at 20°C	5.6 mPa s	Initial boiling point	152°C
Surface tension at 20°C	30 mN/m	Final boiling point	320°C
Flash point	88°C		

2.4. Microemulsion

The preparation of the microemulsion relies on the use of three compounds: anionic surfactant: sodium dodecyl benzene sulfonate (SDBS), whose chemical structure is shown in Figure 2. A reference concentration of 0.8 g/L in SDBS was chosen. Thus, it is readily soluble in solution. Non-ionic surfactant: Tergitol 15-S-12, whose chemical structure is shown in Figure 3. This surfactant was chosen for its good efficiency in recovering additional oil from sand. A reference concentration of 1 g/L in Tergitol 15-S-12 was chosen. Thus, it is completely soluble in water at room temperature. Co-surfactant: butanol, whose role is to ensure the mutual miscibility of oil and water (IFT 23 mN/m at 25°C, solubility: completely soluble in polar organic solvents and 125 g/L in water at 25°C). The typical performance properties of the surfactants used are shown in Table 2.

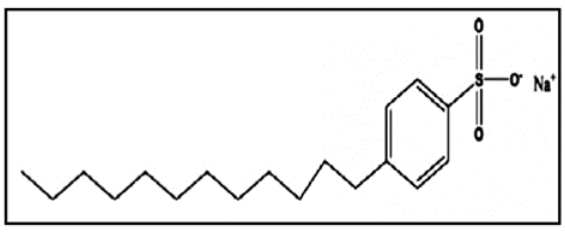

Figure 2. Chemical structure SDBS surfactant.

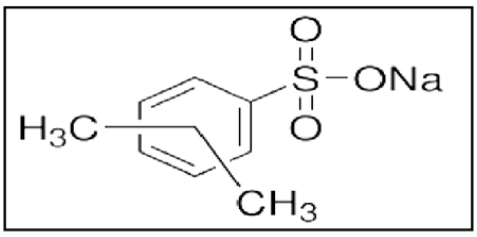

Figure 3. Chemical structure Terginol 15 S-12.

Table 2. Typical performance properties of the used surfactants.

Typical properties	SDBS	Tergitol 15-S-12
HLB	10.638	14.50
Surface tension (dyne/cm)	36	33
IFT (mN/m)	4.1	3.5
CMC (ppm)	612	104
Stability and solubility	Soluble in water. Chemically stable under standard ambient conditions (room temperature).	Soluble in water. Soluble in polar organic solvents. Chemically stable in the presence of acids, bases, and diluted salts. Compatible with anionic, cationic, and other non-ionic surfactants.

3. Experimental procedures

3.1. Determination of the optimal salinity of the WINSOR III system

In a Winsor I system, the surfactant is mainly dissolved in the aqueous phase, whereas in a Winsor II system it is dissolved in the oily phase. In a Winsor III system, an intermediate zone contains a microemulsion. The salinity at which this zone appears is called the "optimal salinity," meaning the interfacial tension between the aqueous phase, the surfactant, and the oil phase is at a minimum. This Winsor system classification is widely used in EOR, where the optimal formulation is determined by preparing test tubes at different salinities and optically detecting the appearance of the Winsor III phase. At this salinity, the interfacial tension between water and oil is the lowest.

The salinity determination is carried out by preparing test tubes, each containing the same composition of oil and aqueous phases, surfactants, and 3% butanol as a co-surfactant to promote the dissolution of SDBS and, on the other hand, to favour the appearance of the Winsor III phase [7]. It is necessary to change the salinity of the brines used in each tube.

Once the fluids are introduced, the test tubes are mixed (ambient pressure and temperature conditions) and left to rest for 3 days to ensure that the microemulsion is stabilized. Subsequently, a salinity diagram can be established. To ensure the effectiveness of the prepared formulation, the interfacial tension was estimated using Huh's method [8]. The estimation of the interfacial tension is done using the respective volumes of the oil phase and the aqueous phase solubilized in the intermediate phase (Equation 1 and 2) for a given concentration of surfactants, such as:

$$\gamma_O = \frac{V_O}{V_S} \quad (1)$$

$$\gamma_W = \frac{V_W}{V_S} \quad (2)$$

where, V_O, V_W, V_S representing respectively the volumes of oil, water, and surfactants solubilized in the microemulsion.

Knowing the heights of each phase in the test tubes, we can determine the solubilization ratios for each formulation. Next, we introduce Huh's relation (Equation 3), such that:

$$\gamma = \frac{C}{\delta_i^2} \quad (3)$$

where, C being the Huh constant; γ the interfacial tension; and δ_i^2 the solubilization ratio of phase i.

The solubilization ratio of phase i is measured by calculating the difference between the volume of phase i introduced and the volume of phase i measured after the microemulsion has stabilised. In this case, we can observe the evolution of interfacial tension as a function of salinity using Huh's correlation.

3.2. Drainage tests

Drainage tests on the capillary micromodel with altered wettability are performed under two conditions, as shown in Figure 4. All steps are carried out at room temperature. The pressure is determined using a capillary system (in cm of H_2O), as shown in Figure 5.

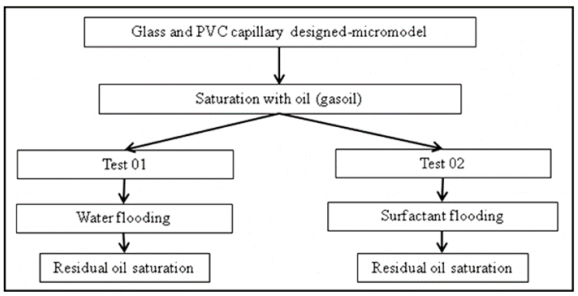

Figure 4. Flowchart of drainage tests in an altered-wettability capillary micromodel.

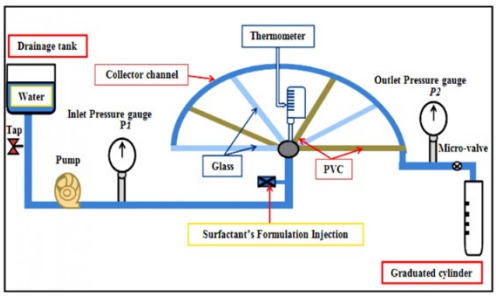

Figure 5. Different components of altered-wettability capillary micromodel.

4. Results and discussion

4.1. Optimal salinity of the Winsor III system

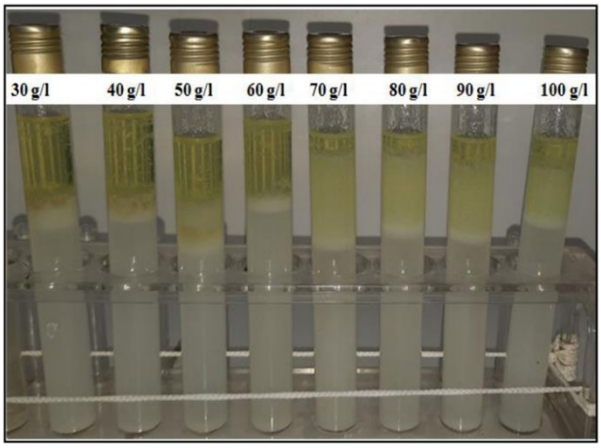

Figure 6. Tests to determine the salinity of the surfactant formulation: each tube has the same composition; only the NaCl concentration varies.

Figure 6 represents the systems obtained after varying the salinity in the test tubes. According to the results obtained, it is observed that the salinity range for which a Winsor I type microemulsion (surfactant soluble in the aqueous phase) is found is between 0 and 60 g/L. The Winsor III-type microemulsion (a central intermediate phase composed of the oily and aqueous phases and surfactants), indicative of very low interfacial tension (mutual miscibility), is observed at salinities between 70 and 90 g/L. For NaCl concentrations above 100 g/L, the surfactants are mostly soluble in oil (Winsor II system). We can determine the heights of each phase based on salinity to calculate the solubilization ratios. The results are shown in Figure 7.

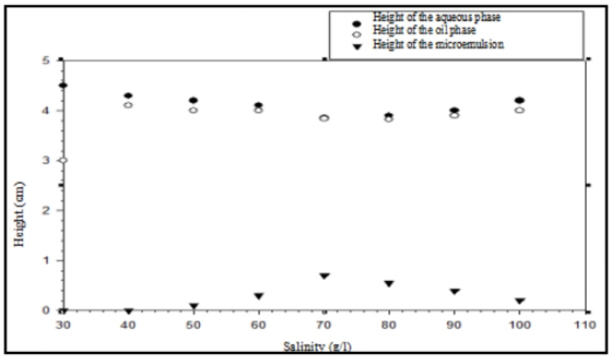

Figure 7. Evolution of the height of each phase of the Winsor III system as a function of salinity.

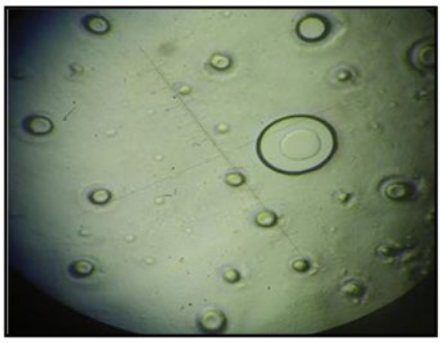

Figure 8. Image of the shape of the micelles in the prepared microemulsion.

We observe that the height of the micro-emulsion increases significantly at a salinity of 70 g/L. This means an optimal salinity for the surfactant formulation. On the other hand, it involves reciprocal miscibility between the oily and aqueous phases, resulting in minimal interfacial tension. Characterisation of the surfactant formulation using a polarising microscope yields micellar images (water/oil and oil/water), as shown in Figure 8.

4.2. Drainage test results

The volume of the designed capillary system with altered wettability is 19.4 cm^3. So the initial water saturation is 100%. After injecting the oil, we obtain a brine volume of 17.2 cm^3, which in turn represents the initial oil volume in the capillary system. We use this volume as a reference to evaluate the effect of wettability on the fluid's preferential path. The difference between the two volumes represents the irreducible water saturation (Swi) of 11.34%, equivalent to 2.2 cm^3 of brine wetting the system. The results of oil drainage by brine are shown in Table 3.

Table 3. Drainage of the oil by brine at 25ºC.

Tests	ΔH (cm)	Pressure (ΔP en atm)	Volume of oil recovered (mL)	Recovery yield (%)
01	H_{in} = 7 H_{out} = 5 ΔH = 2	$1.9363*10^{-3}$ + 1.01325 ΔP = 1.01518	5	29.06
02	H_{in} = 7 H_{out} = 3 ΔH = 4	$3.8726*10^{-3}$ + 1.01325 ΔP = 1.01712	6.4	37.20
Medium	ΔH = 3	ΔP = $2.9045*10^{-3}$	5.7	33.13

We find that 66.86% (11.50 cm^3) of the oil remains in the capillary system (within the hydrophobic PVC capillaries), attributable to the affinity of PVC films for the organic phase. The capillary environment in this case is highly oil-wettable. On the other hand, the contact angle (always measured in the denser fluid) is greater than 90° at the water/oil and water/petroleum interfaces in PVC capillaries; hence, the wetting state is oil-wet.

In the case of surfactant-enhanced drainage, the reference volume is that remaining after brine drainage, as shown in Table 4. Based on the results, we find that oil recovery rates increase significantly after surfactant injection. This means the effectiveness of our formulation. The chosen surfactants play a key role in forming the specific microemulsion that reduces the interfacial tension of the trapped oil [9].

Table 4. Drainage of oil by the prepared surfactant formulation at 25°C.

Tests	ΔH (cm)	Pressure (ΔP en atm)	Volume of oil recovered (mL)	Recovery yield (%)
01	H_{in} = 7 H_{out} = 2.5 ΔH = 4.5	$4.5367*10^{-3}$ + 1.01325 ΔP = 1.01760	10	86.51
02	H_{in} = 7 H_{out} = 2 ΔH = 4	$4.8408*10^{-3}$ + 1.01325 ΔP = 1.01809	10.63	92.43
Medium	ΔH = 4.75	ΔP = $4.5988*10^{-3}$	10.315	89.96

5. Conclusions

In this work, we attempted to use a mixture of SDBS and Tergitol 15-S-12 with low interfacial tension, so both components tend to minimise residual saturation in the oily phase. On the other hand, the chosen surfactants readily adsorb onto the surface of hydrophobic films and improve the durability of the process for restoring the initial wetting state (water-wet). The addition of butanol enriches the coating mechanism and ensures mutual miscibility between the polar and non-polar phases by breaking the oil/water emulsion, due to an unstable lubrication film around the oil droplets. The formulation also prevents the aggregation of oil droplets detached from the surface of oleophilic films by forming layers around them, keeping them in suspension and allowing their production while minimising the residual oily phase.

Nomenclature

γ_O	*interfacial tension of oil phase (mN/m)*
V_O	*solubilized oil volume (ml)*
V_S	*solubilized surfactant volume (ml)*
γ_W	*interfacial tension of water phase (mN/m)*
V_W	*solubilized water volume (ml)*
γ	*interfacial tension (mN/m)*
C	*Huh constant*
δ_i^2	*solubilization ratio of phase i*

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