



## Novel glycerin-based microemulsion formulation for enhanced oil recovery

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### ABSTRACT

Among enhanced oil recovery chemical methods, the use of surfactants is cited in many field studies. Microemulsions are systems composed of surfactants that aim to decrease the interfacial tensions between water and oil facilitating their flow in the porous medium. This paper proposes the use of a new microemulsion formulation, based on glycerin as the polar phase for improved oil recovery. The aim is to evaluate if the microemulsion composed of glycerin in the polar phase is as efficient as the microemulsion containing water. The proposed microemulsion was composed of commercial surfactants (DBB-7107 and DBB-7191), isopropyl alcohol, pine oil, and glycerin in substitution of distilled water. The microemulsion was characterized and the recovery tests were conducted with samples of sandstone rock in a core holder. The results showed that the formulation generated a well-defined microemulsion region and presented characteristics typical of microemulsion systems of the water-in-oil type. Recovery tests have shown that microemulsions containing glycerin in the polar phase achieved a recovery factor up to 49% of the residual oil while microemulsions containing water recovered about 36% of the residual oil.

### 1. Introduction

With respect to conventional oil recovery, it is estimated that less than 50% of the original oil can be recovered. Special oil recovery techniques are studied as an alternative to supplying energy to the reservoir when they tend to become unproductive. These techniques can be classified into thermal, miscible and chemical methods. Techniques that give more favorable interfacial conditions to the flow of petroleum are classified as chemical methods, through the addition of chemicals such as polymers or surfactants. Tenoactive chemicals or surfactants are intended to reduce interfacial tensions between water and oil, thereby increasing the miscibility of these two compounds (Kwok et al., 1995), allowing the flow in the porous medium. This technique has a high efficiency, but is very expensive due to the loss of the surfactant that is adsorbed on the reservoir rock (Curbelo et al., 2007; Liu et al., 2004). Therefore, studies are focused on the use of surfactant in diluted form, such as microemulsions.

Microemulsions were discovered by Hoar and Schulman in 1943, who described a thermodynamically stable translucent system composed of two immiscible liquids in the presence of a surfactant (Bera and Belhaj, 2016). Microemulsified systems are formed by a polar phase

and an apolar, a surfactant, and may or may not contain a cosurfactant, which is generally an alcohol. The potential success of a microemulsion flooding depends of studies about phase behavior, interfacial phenomena and particle size. In order to understand the mechanism for the penetration of the microemulsion in the porous media it is necessary to evaluate the particle size distribution (Bera et al., 2012). The particle size is usually determined by the Dynamic Light Scattering (DLS) technique that uses a relation between the particle size and its Brownian motion. According to Austad and Strand (1996) the factors that affect the phase transition of microemulsion is the molecular structure and nature of the surfactant and cosurfactant and the type of oil. Many studies evaluate interfacial tension between immiscible liquids. These analysis can be carried out by various methods such as Du Noüy ring, drop volume, Wihelmy plate, pedant drop, Neumann triangle and breaking thread method (Drelich, 2002; Sakthivel et al., 2015).

According to Austad et al. (1998) and Standnes and Austad (2000), microemulsions are able to reduce the value of the interfacial tension between petroleum and brine contained in reservoirs, stabilizing the interface against coalescence. The microemulsion flow easily through the porous medium improving oil extraction performance (Austad and Strand, 1996; Mandal et al., 2010). In the porous media the

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**Abbreviations**

A	Cross-sectional area of core	LAPEG	Petroleum and Natural Gas Laboratory
IP	Inversion Point	ME	Microemulsion
BSW	Basic sediments and water	OOIP	Original oil in place
C/S	Cosurfactant/surfactant ratio	PV	Porous volume
CAPES	Coordination of Improvement of Higher Level Personnel	OR	Residual oil
DLS	Dynamic Light Scattering	Q	Volumetric flow rate
FAPESB	Foundation for Research Support of the State of Bahia	VI	Volume injected up to a certain instant
FR	Fraction recovered	VOOIP	Volume of original oil in place
IBTR	Brazilian Institute of Technology and Regulation	VOR	Volume of displaceable oil
L	Core legenth	VPI	Injected porous volume
		VT	Total core volume
		$\Delta P$	Pressure differentials

microemulsion produce self-assembled structures, similar to micelles, capable of solubilizing the oil by incorporating it into the droplet core thereby promoting miscibility in the system (Wellington and Richardson, 1997; Santanna et al., 2013). Due to these characteristics many studies have turned to the use of microemulsion in enhanced oil recovery.

Levitt et al. (2006) evaluated the influence of salinity on the microemulsion, noting that there is an optimum value of approximately 4% by weight of salt where the solubility of the microemulsion is higher, the interfacial tension is reduced and there is little adsorption of the surfactant in the rock. Santanna et al. (2009) concluded that the higher the viscosity of the microemulsion, the higher the recovered oil fraction increasing from 78.7% for microemulsion with viscosity equal to 27 cP to 87.5% for microemulsion with a viscosity of 32 cP. Kharghoria et al. (2015) made a simulation using microemulsion for oil recovery. The obtained results showed that the microemulsion system achieved a recovery factor of 27% of the residual oil. Santanna et al. (2013) studied enhanced oil recovery using microemulsion composed of commercial anionic surfactants derived from fatty acids, achieving a recovery of 87.5% of the original oil in place, corresponding to 75% of the residual oil. Bera et al. (2014) studied a microemulsion composed of the anionic surfactant sodium dodecyl sulfate, reverse osmosis water as the polar phase, propanol as cosurfactant and the apolar phase was n-heptane. The system recovered 80% of the original oil in place. Karambeigi et al. (2016) evaluated the efficiency of the microemulsion composed of the surfactant polysorbate 80, brine, ethanol and biodiesel. The surface tension of the system was 24.2 mN/m at 75.8 °C and the interfacial tension between the microemulsion and the oil was 0.002 mN/m while the interfacial tension of the water with the oil was 0.006 mN/m. The achieved recovery factor was 39.5% of the original oil in place.

Many studies on microemulsion aim to increase their efficiency in special recovery by optimizing some properties such as interfacial tension and viscosity (Liyanae et al., 2015). The disclosed microemulsion works utilize a variety of commercial or synthetic surfactants in order to achieve a lower interfacial tension. This work proposes a new formulation for microemulsions, modifying the polar phase using glycerin instead of water in order to increase the viscosity of the system and verify its effect on enhanced oil recovery.

## 2. Materials and methods

The reagents used for the preparation of the microemulsions were DBB-7107 and DBB-7191 as surfactants, isopropyl alcohol (Synth, purity 99.5%) as cosurfactant, pine oil as apolar phase, and distilled water and glycerin (Synth, purity 99.5%) as polar phase. The use of distilled water in the polar phase was based on the work developed by Santanna et al. (2009); Santanna et al., 2013 that also used distilled water as the polar phase of the microemulsion. The commercial surfactants were supplied by Bolland (Brazil). Both are nonionic surfactants in aromatic hydrocarbon solution. Pine oil is a material produced

from turpentine, removed from the gum-resin of Pinus. The oil is in translucent form, with coloring ranging from colorless to yellow, in addition to having a characteristic pinaceous odor. Pine oil was used in the composition of the apolar phase of the microemulsion, because it contains hydrocarbons in its structure (terpenes); therefore, it is expected that it has a greater affinity with the oil and with the surfactant used in this work. The saline solution used to simulate conventional recovery method was prepared using NaCl (Sigma-Aldrich, analytical grade). The oil used in the experiments came from the Reconcavo Basin (Brazil) and had a viscosity of 13 cP and density of 0.83 g/cm<sup>3</sup>, both measured at 60 °C. The oil API grade was equal to 33.12 and BSW equal to 24%. For simulation of the porous medium, a sandstone from the Botucatu region (Paraná - Brazil) was used. The sandstone was cut into a cylindrical shape with a mean diameter of 3.81 cm and 9 cm length. The sandstone samples were previously placed in the oven at a temperature of 100 °C for 4 h to remove moisture.

### 2.1. Preparation of microemulsions

For the construction of the pseudoternary phase diagram, eleven points were determined by varying the compositions of cosurfactant/surfactant and the organic phase, from 0 to 100%. Each point was then titrated with distilled water until the mixture change the behavior from microemulsion, characterized by the Winsor IV phase, to two immiscible phases. For the accomplishment of the experimental procedure a system was built, with an analytical balance of the brand Shimadzu model AUY220, and a support for a testing tube in which the cosurfactant, surfactant and the organic phase were dripped through a micropipette. The mass of each constituent was recorded as they were added to the tube. Then the testing tube was transferred to a magnetic stirrer (Tecnal brand), where titration with water was carried out until the system change from the microemulsion characteristics (single-phase and translucent system) to a two immiscible phases. The mass of water added was then taken. With the masses of each component, at each of the 11 points, the microemulsion diagram was constructed.

The microemulsions were prepared based on the study carried out by Santanna et al. (2013) which also used distilled water as polar phase. Therefore it is possible to draw a comparison between the microemulsion used by Santanna et al. (2013) with the one used in this paper. For future studies, the effect of salinity on the phase diagram will be evaluated.

### 2.2. Characterization of microemulsions

The viscosity and the density of the microemulsions were measured using an Anton Paar DMA-4500 digital viscometer and Anton Paar DMA-5000 digital densimeter, respectively. The surface tension was measured on a Kruss model K20 tensiometer using the Du Noüy Ring method. Particle size analysis was performed on the Malvern Zetasizer Nano ZS90 particle analyzer. All analyses were done at the temperature of 60 °C, which is the temperature of the recovery tests.

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