SOME INVESTIGATIONS ON THE ROLE OF MICROPARTICLES ON THE LOW SALINITY PROCESS

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ABSTRACT

Several papers dealing with laboratory experiments or field operations confirm that, in some circumstances, low salinity waterflooding improves oil recovery. However, the basic mechanisms explaining the oil recovery improvement are not clearly established. The literature points out several hypotheses, among them is the role of clay particles detachment and migration.

Experiments using an intermediate-wet clayey sandstone were first performed showing an oil recovery increment when the salinity of the injected brine was reduced. Following this trail, in a second set of batch experiments we investigated the role of microparticles on the formation and stability of brine/oil emulsions when the salinity is changed. For that, we used calibrated negatively charged polystyrene latex particles and several oils (mineral, crude and a blend of the two). Emulsion samples were observed using an optical microscope to determine their typical droplet size and the water/oil interface structure. The macroscopic stability of the emulsions was also investigated. The results show that the particle wettability, which is related to its surface charge and brine salinity, plays a central role in formation and stability of water/oil emulsions. Depending on their hydrophobicity, the particles migrate toward the brine/oil interface forming a more or less stable emulsion known as "Pickering emulsion". In a third step, the same latex particles were injected in an artificial consolidated porous medium prior to two phase flow experiments and are deemed to be deposited as a mono layer all over the pore wall surface. The core low salinity waterfloods show no recovery improvement, although colloidal particles are recovered at the outlet.

This indicates that the particle mobilization is not a sufficient condition to recover additional oil so that other factors such as oil/water structure are involved.

INTRODUCTION

After several laboratory scale studies (see references in Morrow and Buckley [1]), low salinity waterflooding is now considered as a potential EOR technique that has been developed in field operations (Robertson [2], Seccombe *et al.* [3], Skrettlingland *et al.* [4]). Even if laboratory tests evidences are numerous, the recovery mechanisms are still not fully understood. The evidence is that ionic strength reduction of injected water may improve slightly oil recovery during waterflooding. The different recovery mechanisms published in the literature put forward interactions between crude oil, brine and rock

composition (especially clay presence). A mechanism based on Multicomponent Ionic Exchange between mineral surface and invading brine has been proposed by Lager *et al.* [5]. In this mechanism some polar components of the crude oil, which are complexed with clays, can be removed by uncomplexed cations present in the invading low salinity brine. This mechanism suggests that oil production is more efficient when divalent ions are present in the low salinity brine (but in a lower concentration).

McGuire *et al.* [6] put forward a mechanism similar to alkaline flooding. As pH becomes basic when low salinity brine is injected, *in situ* surfactants are generated and the interfacial tension between oil and brine decreases leading to an improvement of oil recovery.

Tang and Morrow [7] showed that the presence of potentially mobile fines and their exposure to crude oil were necessary conditions to observe low salinity effect. Moreover, it was assumed that some component of the crude oil may change the particle wettability. This germ idea has been followed by several authors (Wideroe *et al.* [8], Harsenkam *et al.* [9], Lebedeva *et al.* [10], Fogden *et al.* [11]) who studied the role of polar components of crude oil and clay particles in low salinity EOR process.

In this paper we followed this trail and present briefly in a first part core experiments performed with a clayey sandstone and crude oil showing the presence of clay particles and the positive effect of low salinity waterflooding on oil recovery. In a second part, as our objective is to study the role of particles on the low salinity recovery mechanism, we consider artificial porous media and latex particles in order to have another porous medium with controlled particle deposition. Both materials (porous medium and colloidal particles) are characterized and we were able to control the particle deposition inside the porous medium. Moreover we considered the possibility of generating water/oil emulsion stabilized by the particles known as Pickering emulsions (Binks and Lumsdson, [12],). Colloidal particles act like surfactant molecules and can adsorb onto the oil/water interface depending on their wettability (Binks, [13]). Polarity of the oil phase plays therefore an important role on the type of formed emulsion, oil in water for non-polar oils and water in oil for polar oils (Binks and Lumsdon, [14]). For that, the ability of the latex particles to stabilize water/oil emulsions has been tested in batch experiments with oils of different polarities. The first results obtained with two phase flow in porous media are presented and perspectives of further works are proposed.

EXPERIMENTS
Three kinds of experiments are presented in this section. First we consider one and two phase flow experiments in a natural clayey sandstone, then we present batch experiments performed with colloidal latex particles and different kind of oils, preliminary experiments performed on an artificial porous medium are presented briefly.

Flow in natural clayey porous medium.
Porous medium.

Consolidated sandstone outcrop core samples containing 9.2% of clays (chlorite, muscovite and illite) were used for one and two phase experiments. Permeability and porosity range between 400 mD and 800 mD and from 16.5% to 21.5% respectively.
Brines.
Three different brines have been used:
- High Salinity Brine (HSB) which contains 50g/L (90%w NaCl and 10%w $CaCl_2$)
- Low Salinity Brine (LSB) which contains 1g/L (95%w NaCl and 5%w $CaCl_2$)
- Very Low Salinity Brine (VLSB) which contains 0.1g/L (95%w NaCl and 5%w $CaCl_2$)
Crude oil.
The crude oil (μ = 8.2 10^{-3} Pa.s at T = 20°C), provided by Total, has a Total Acid Number of 0.17mg of KOH and Total Base number of 0.95 mg of KOH. It contains $2.3\%_w$ of pentane asphaltenes, the SARA analyses give a crude oil composed of 58.2% of saturated, 31.4% of aromatic and 10.4% of polar compounds.
Experimental setup and procedure.
The core, in a Hassler cell, is connected to volumetric pumps allowing injection of the different brines and crude oil. Pressure drop, pH and density were measured continuously during the one phase flow experiments. The two phase flow experiments started by a crude oil injection to reach the S_{wi} followed by an ageing of the core to modify its wettability. Then pressure drop and oil recovery were continuously monitored during the waterflooding, performed with different brines, while pH was measured separately on effluents brine samples.
More details on the experimental procedure can be found in (Cissokho *et al.* [15] and Boussour *et al.* [16]).

Artificial porous medium and latex particles.
Porous medium.
We used an artificial porous medium made from sintered crystalline and amorphous silicate grains (Aerolith-10, from Pall corporation) of which permeability and porosity are respectively 8 Darcy and 43%.
Latex particles suspensions.
The colloids particles are surfactant-free polystyrene latex microspheres (Interfacial Dynamic Corporation, Portland, OR). We considered two types of particles with diameters (dp) of 280 nm and 780 nm to generate different droplet sizes. The background solution was a 1:1 electrolyte prepared with deionized water and salt (100% NaCl) for which concentration was varied so that ionic strength ranges from 0.0 M (pure water) to 1.0 M.
The colloid particles are diluted in the background solution at concentration of 20000 ppm or 200 ppm, then pH was fixed at 7.0.
In Figure 1 we plotted the wettability of the particles, for different values of pH, as a function of ionic strength. Particle wettability was evaluated through its ability to be dispersed (hydrophilic) or aggregated (hydrophobic). The zeta potentials of latex particles and the porous medium, measured at a pH equal to 7.0 are presented in Figure 2 showing negative values under our conditions (Canseco *et al.* [17]).

Oils

We used Marcol 52$^®$ (μ = 12.10^{-3} Pa.s at T = 20°C), a mineral non-polar oil, and the crude oil described here above. Blends of the two oils have also been used for some batch experiments.

Experimental setup and procedure.

Batch experiments.

First of all we prepare a brine solution at a given value of the ionic strength (from 0M to 1M, 100%NaCl). Then we add the colloids to obtain a given value of the concentration. The suspension is transferred to glass bottles and sonicated before adding the oil (28%$_{vol}$). Emulsification is performed by stirring the mixture of suspension and oil phase for 2 min. using an Ultra-Turrax$^®$ (13500 rpm). The emulsion type and droplet size are observed using an optical microscope while the emulsion stability was directly observed in the glass bottles as a function of time.

Porous medium experiments.

The colloidal suspension with fixed concentration, pH and ionic strength is injected in the porous medium at a constant value of the flow rate (100ml/h) while effluent colloidal concentration is measured. Injection is stopped when the effluent colloidal concentration is equal to ~ 90% of the inlet colloidal concentration. This step allows us to establish the classical breakthrough curves (BTC). The porous medium is then flushed with a colloid-free solution of same ionic strength at the same flow rate in order to remove the non deposited particles. Mineral oil is then injected at constant flow rate (10ml/h) until reaching the S$_{wi}$ (25.5%) before starting waterflooding (Q = 100ml/h) with different brines. Oil recovery is measured together with colloidal concentration in the effluent water.

EXPERIMENTAL RESULTS

Flow in natural clayey porous medium.

One phase flow.

Figure 3 presents the evolution of pressure drop and pH when different salinity brines are injected in the sandstone. pH is almost constant when the HSB is injected even when temperature is increased. Pressure drop shows the same behavior. When the LSB is injected we observe an increase of pressure drop while pH, after a short decrease, increases to the value of 9.0. The injection of the VLSB provokes a dramatic pressure drop increase while pH increases to 10.0. Direct observation of the effluents (photo in Figure 3) shows that clay particles are extracted from the core when VLSB is injected while no particle production was observed during the previous brine floodings.

Two phase flow.

Results are presented in Figure 4. The core is firstly flooded with the HSB, oil recovery is equal to 43%OOIP and water effluent pH is equal to 8.0. The response to the LSB waterflooding is an increase of 4.5%OOIP and a pH increase to 9.3. The oil recovery is further increased by 6.0%OOIP when the VLSB is injected while pH value is increased

to 10.0. It is worth noting that we did not see any particle production in the brine during the VLSB injection.

Batch experiments

<u>Mineral oil and latex particles.</u>

In Figure 5a we present emulsions obtained with a suspension of latex particles (C = 20000ppm, dp = 780nm, pH = 7.0) and mineral oil (Marcol 52®) for different values of ionic strength. Figure 5b shows the same emulsions after 10 days rest. Three different behaviors can be pointed out.

- For low values of ionic strength (I = 0 and 0.04M) we obtain a direct emulsion (oil in water). After 10 days we see a slight creaming of the emulsion with a little oil at the top of the vessel. This behavior can be represented schematically (Figure 6a) and described in the following way. For low values of the ionic strength the latex particles are preferentially hydrophilic (Figure 1) and preferentially water wet at the oil/water interface. The oil droplets in the emulsion are sufficiently stabilized by formation of a monolayer of adsorbed particles at the interface with limited coalescence. This leads to a limited creaming effect, and oil migrates by gravity towards the top of the mixture.

- For high values of the ionic strength (I = 0.6, 0.8 and 1M) we clearly see in Figure 5a that the emulsion is on the top of the vessel while water, particle-free, appears on the bottom. Figure 6b describes schematically this behavior. The latex particles are now of intermediate wettability (see Figure 1) with a great tendency to flocculation but are still wetted by water arising hence in formation of oil in water emulsions. In this case however, we obtain Pickering emulsions (oil droplets coated by solid particles) which stabilized oil droplets are embedded in a 3D network of particles. Hence clusters encompassing several droplets migrate more rapidly toward the top of the vessel while water phase appears at the bottom of the vessel. It is worth noting that these emulsions are very stable with time (Figure 5b).

- For intermediate ionic strength (I = 0.4M) we obtain an unstable emulsion even if latex particles are preferentially hydrophobic; this ionic strength being close to the critical flocculation concentration. The microscopic observation of the emulsion samples presented in Figures 7a for low values of ionic strength and 7b for high values of I confirm the role of particles, especially its ability to be aggregated or not and its influence on emulsion stability.

These experiments show clearly the effect of ionic strength on water/mineral oil emulsions which can be stabilized by latex particles of different wettability as it may be monitored by salt addition.

<u>Crude oil and latex particles.</u>

For these batch experiments we used 280nm diameter particles at a concentration of 20000ppm and a blend of 20%$_{vol}$ of crude oil and 80%$_{vol}$ of Marcol 52® to get intermediate wettability conditions. The emulsion was obtained following the same experimental procedure as previously described (continuous stirring with the Ultra Turrax® device).

Results are presented in Figures 8a (initial emulsion) and 8b (emulsion after 5 days rest) for different values of I. The emulsion obtained with the particle-free system is not stable at all with rapid phase separation. This is due to the absence of particles that could

stabilize the emulsion against coalescence. When particles are present we obtain pseudo solid emulsions that are inverse (water in oil) emulsions as latex particles are preferentially oil wet in case of polar oils. The stability of formed emulsions is seen to depend strongly on ionic strength. This behavior, which is related to the oil polarity, has been extensively described in the literature dealing with Pickering emulsions (Binks and Lumsdon [14]).

Flow in artificial porous medium.

The objective of this preliminary study is to perform two phase flow in an "analogous" porous medium, i.e. a porous medium of which deposited particles are well controlled, in order to understand the role of solid particles during the low salinity process. Therefore the first step of the experiment, after brine saturation of the core, is to inject the colloidal suspension (C_0 = 200 ppm, dp=780 nm, I = 0.04M) to deposit the particles on the pore surface. This step corresponds to the part 1 of Figure 9 where the particle relative concentration in effluents is plotted as a function of injected pore volume (BTC). When particle deposition is over, the porous medium is flushed with the particle-free brine in order to remove the non deposited particles (part 2 of Figure 9). Part 3 of the same figure corresponds to the high salinity waterflooding while part 4 corresponds to the pure water waterflooding. We clearly see that no particles are coming out of the core during the high salinity waterflooding while particles are present in the effluent water during the pure water injection. In Figure 10 we plotted the oil recovery during high salinity waterflooding and pure water injection. We see that there is almost no production increment during the pure water injection. It is worth noting that we did not see any particle in the produced oil phase. This result shows that a part of already deposited particles are removed from the core when pure water is injected and that those particles, which are hydrophilic when I = 0 (Figure 1) are present in the water phase.

Conclusions and perspectives

Understanding mechanisms of low salinity waterflooding is a challenging task. According to several results from literature it appears that fines migration is a possible trail to explain the mechanism. The main conclusions of this paper are the following ones:

- Fines migration together with a drastic permeability reduction are observed during one phase low salinity injection in case of clayey consolidated sandstone porous media.
- Low salinity waterflooding increases oil recovery and the process is accompanied by pH increase of the effluent water.
- Pickering emulsions of different kinds can be formed with latex particles. Stability of the emulsions depends strongly on particles wettability that depends on ionic strength and on oil polarity.
- Latex particles can be deposited in an artificial porous medium under controlled physico-chemical suspension properties.

- Low salinity waterflooding in an artificial porous medium containing deposited latex particles did not lead to oil recovery increase while particles were detached and recovered in the effluent water.

These preliminary results show that oil recovery increment is not observed on a water wet medium even if particle detachment is effective. However we think that particle wettability, which depends strongly on salinity, is a key parameter, that oil type can play an important role and that more complex phenomena including Pickering emulsion formation has to be considered.

ACKNOWLEDGEMENTS

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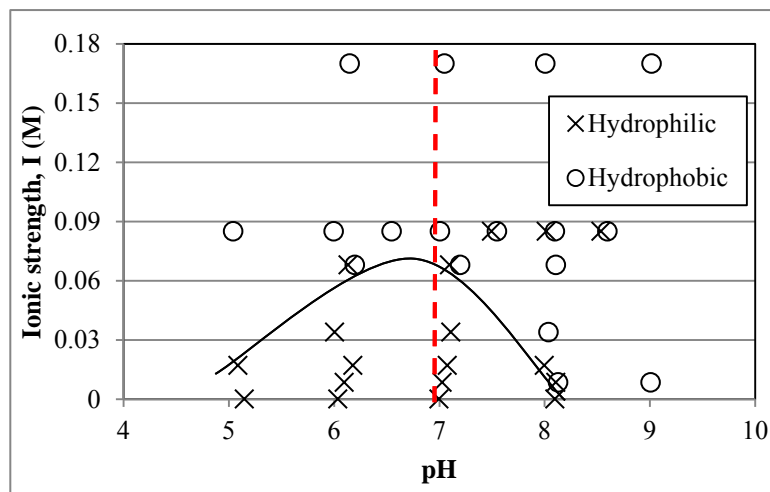
Figure 1: Phase diagram of latex particles (dp = 780nm)(the curve indicates the upper limit of the zone where the particles remain dispersed).
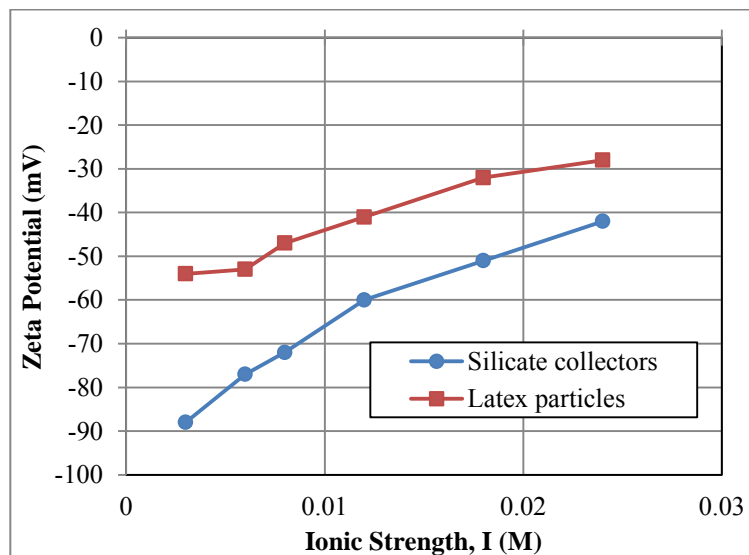
Figure 2: Zeta potential for the silicate collectors and the latex particles (dp = 780nm) at pH = 7.0.
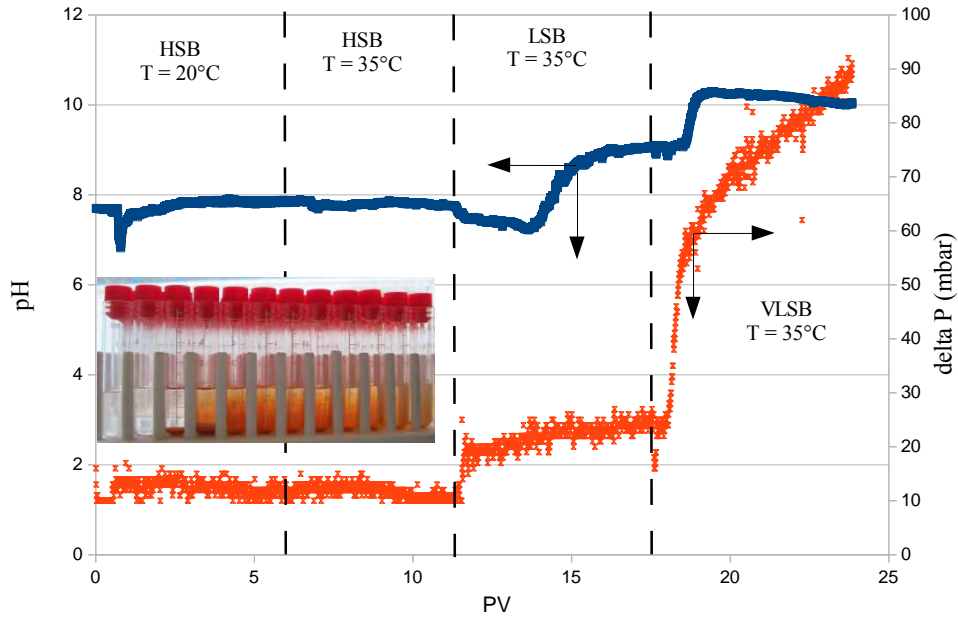
Figure 3: One phase flow in the clayey sandstone for different brines
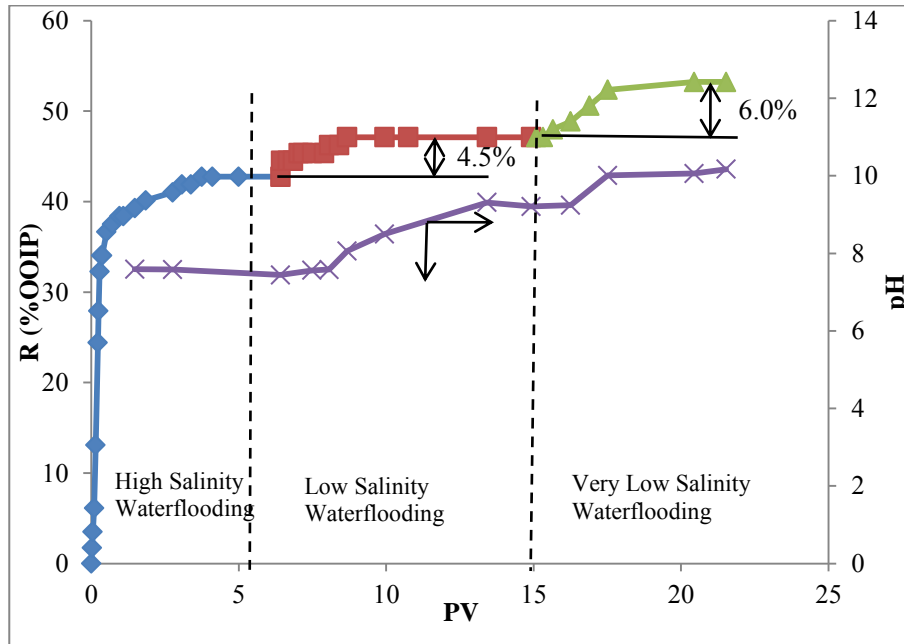

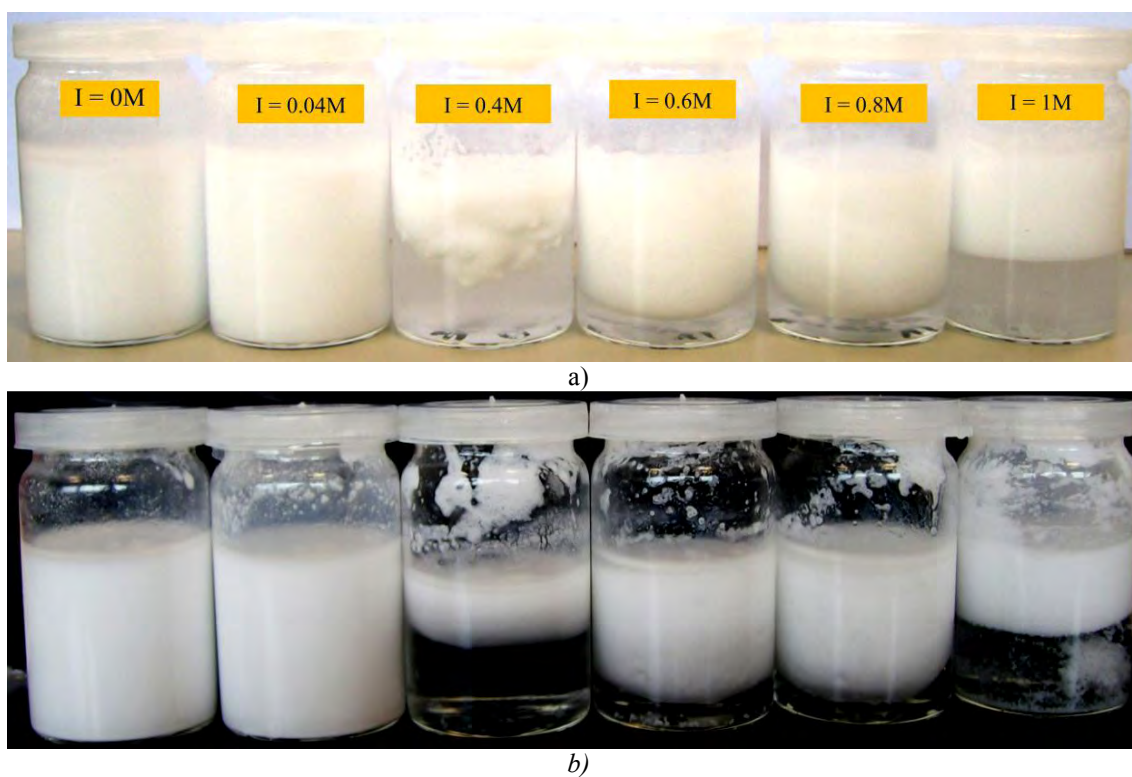*Figure 4: Oil recovery and pH evolution for different salinity brines waterflooding in a clayey sandstone*

Figure 5: Oil water emulsions obtained for different values of ionic strength. a) initial emulsion; b)emulsion after 10 days rest.
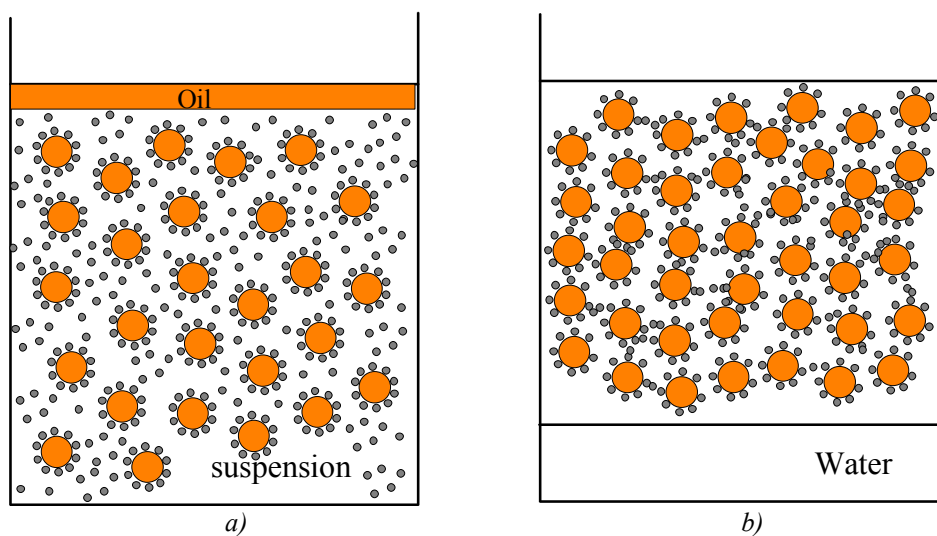

Figure 6: Schematic representation of the oil-water emulsions: a) low values of ionic strength ; b) high values of ionic strength.
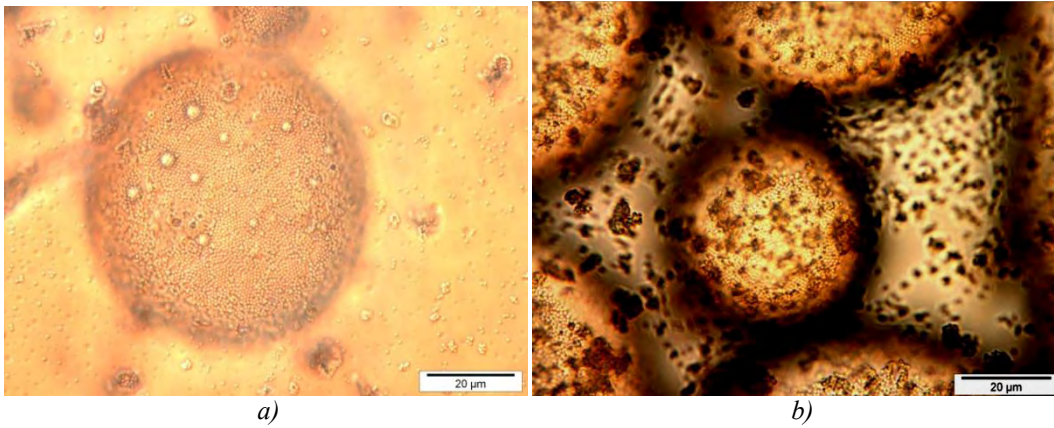
a)   *b)*

Figure 7 : Microscope view of an emulsion (C = 2000ppm, dp = 780 nm); a) I=0.04M ; b) I = 1M

a)

b)

Figure 8 : Emulsions obtained with a blend crude oil (20%vol. and Marcol 52 80%vol). (1: particle-free water; 2: dp = 280nm, I = 0.0M, 3: dp = 280nm, I = 0.004M; 4: dp = 280nm, I = 1M)
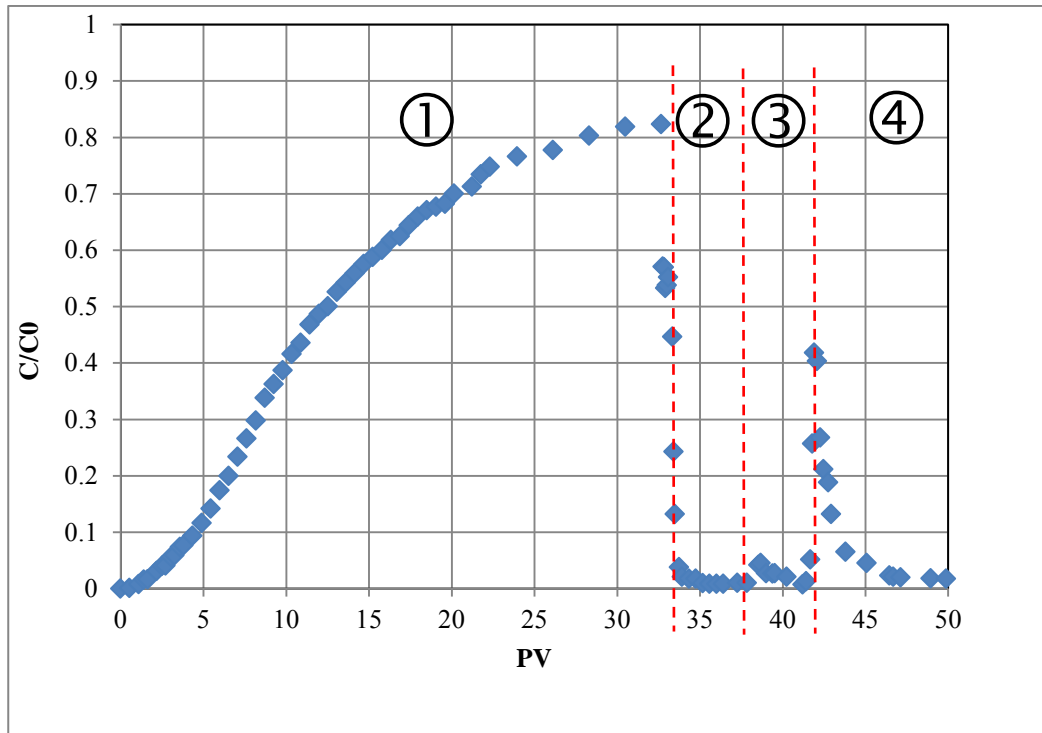
Figure 9 : Relative value of particle concentration in water effluent at the different stages of the experiment. (1 : particle deposition; 2 : particle-free flooding, 3 :secondary waterflooding, 4 : tertiary waterflooding).
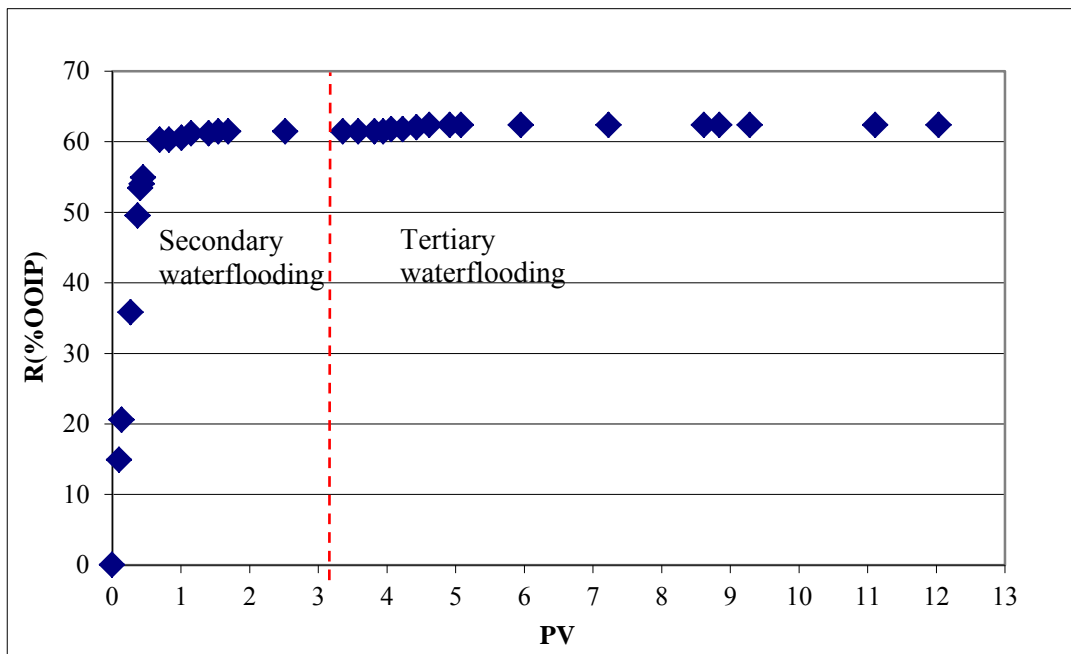

Figure 10 : Oil recovery during waterflooding experiments (secondary corresponds to high salinity brine waterflooding, tertiary corresponds to pure water injection).