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# Application of Multifunctional Agents During Enhanced Oil Recovery

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Additional information is available at the end of the chapter

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## Abstract

During the application of enhanced oil recovery (EOR) processes, complex operational issues, such as the deposition of organic compounds (i.e., wax, resins, and asphaltenes, among others), reservoir formation damage, rock wettability alteration, and high fluids viscosity negatively affect oil recovery. This chapter presents the experimental evaluation of the multifunctional properties of two novel chemical agents recently developed: a zwitterionic surfactant (ZS) and a supramolecular complex (named here as AMESUS) for chemical EOR applications. The performance of the new multifunctional agents and the mechanisms in play on the removal/control of organic compounds deposition oil recovery, asphaltenes inhibition-dispersion activity, reduction in heavy crude oil viscosity, rock wettability modification, and relative permeability are discussed in this chapter.

**Keywords:** chemical enhanced oil recovery, multifunctional surfactants, asphaltenes, formation damage, viscosity reduction

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## 1. Introduction

On average, only one-third of the original oil in place (OOIP) is economically recoverable after the application of primary and secondary oil recovery (SOR) methods. The implementation of enhanced oil recovery (EOR) processes is increasing due to the decline in the discovery of new oil fields during the last decades [1–3]. EOR is defined as a process to reduce oil saturation below the residual oil saturation [4], and it refers to the injection of any fluid (i.e., steam, polymer solution, solvents, etc.) into the reservoir to change and/or to modify the existing rock/oil/brine

interactions. It has been reported that for light and medium oil reservoirs, the residual oil saturation ranges from 50 to 60% of the OOIP, whereas for heavy crude oil reservoirs, it could range from 80 to 95% [1, 5]. Several EOR methods have been reported such as the use of chemical products (polymers and surfactants), thermal methods (steam stimulation, in-situ combustion, electrical heating, vibrational methods etc.), miscible gas injection, and microbial EOR, among others [4]. However, the application of EOR technologies can modify in an adverse way the flow and phase behavior of the reservoir fluids as well as the formation rock (FR) properties that can promote oil productivity decline. Some of these issues include organic compounds deposition leading to formation damage, plugging of the formation rock (within the reservoir and at the wellbore), as well as flow restrictions in tubing, flow lines, and production facilities [2, 3].

Deposition of heavy organics such as asphaltenes can take place at the oil producing slots and at the rock formation face, while the deposition of solid phases (i.e., asphaltenes) over pore surface and/or across pore throats within the oil formation can reduce significantly the effective permeability of the reservoir and severely impair the flow of crude oil through the porous medium (formation damage). The deposition of organic components also renders rock wettability changes from water-wet to oil-wet. Another issue could be the increase in the viscosity of the oil phase due to the formation of water in oil emulsions [6, 7].

This complicated association of problems can occur simultaneously during oil recovery processes. Several methods to remediate these operational problems are available such as the use of chemical additives, which have been used in the field without testing their actual effectiveness in remediating the situation [7, 8]. The removal and control of formation damage caused by asphaltenes deposition are usually achieved by the application of chemical treatments based on aromatic solvents that are applied in both at the wellbore and deeper within the formation. However, there is an economical limitation due to the transient effect of such cleanup methods. Moreover, aromatic solvents do not efficiently dissolve the heavy organic deposits or extract the asphaltenes fractions that remain fixed onto carbonated and clay minerals surfaces [7, 9, 10]. In the case of heavy crude oils, some of the methods that have been reported for viscosity reduction include dilution with lighter crudes or alcohols, the use of chemical additives such as polymers, or nanoparticles, and the use of surfactants to stabilize emulsions [11].

Chemical flooding using surfactants is a method that has been widely studied over several decades; it is considered an efficient process to achieve incremental recovery of residual oil with great potential as an EOR process for the petroleum industry. Although the mechanisms involved in the interactions of the surfactants with oil and brine within the porous media are complex, interfacial-tension reduction and formation rock wettability alteration are the most accepted mechanisms responsible for recovering residual oil saturation [4, 7, 12, 13].

This chapter presents the experimental evaluation of the multifunctional properties of two novel chemical agents recently developed: a zwitterionic surfactant (ZS) and a supramolecular complex (named here as AMESUS) for chemical EOR applications. The performance of the new multifunctional agents and the mechanisms in play on the removal/control of organic compounds deposition oil recovery, asphaltenes inhibition-dispersion activity, reduction in

the viscosity of the heavy crude oil, rock wettability modification, and relative permeability are presented and discussed in this chapter.

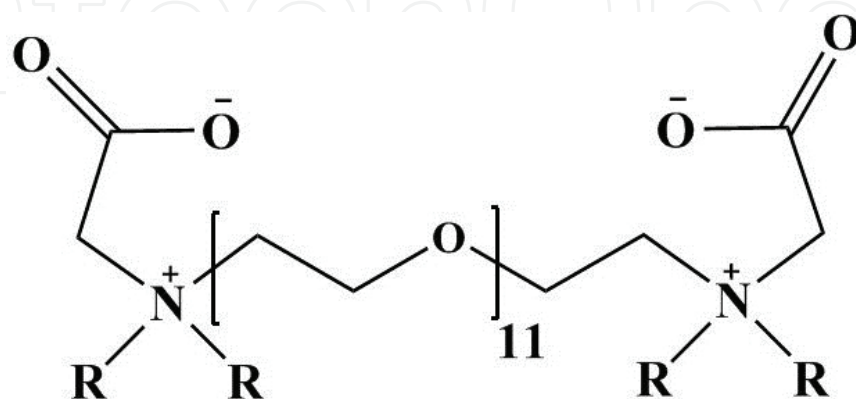
## 2. Multifunctional agents

### 2.1. Zwitterionic surfactant (ZS)

Surfactants that are composed of two hydrophilic and two hydrophobic groups have been the subject of significant research interest since the early 1990s. These surfactants are called “Gemini” because their chemical structures can be perceived as two classic surfactant molecules chemically connected at or near the head groups. Their chemical arrangement provides a rich array of aggregate morphologies and solution properties that are dependent upon the nature and size of the linking group and/or head groups. These types of surfactants with unsymmetrical geometry have interesting characteristics in terms of self-assembly into aggregates and packing at interfaces [14].

Zwitterionic surfactants (ZSs) are considered among the surfactant molecules that can be applied in EOR with molecular structures made up by two hydrocarbon chains, a bridge, and two polar groups of zwitterionic type that can be a cation and an anion in different atoms of the same molecule. ZSs are electrically neutral, and they can behave as bases or acids (acceptor or donor) according to the properties of the medium where they are found. Therefore, zwitterionic surfactants can play a role as smart wettability modifiers that react efficiently according to the characteristics and properties of the specific medium [8, 15–17].

**Figure 1** displays the general chemical structure of zwitterionic surfactants (ZSs), which corresponds to a recently developed alkyl betaine zwitterionic gemini surfactant with polyethylene spacers [17]. This molecule was designed as a wettability modifier of rock surfaces such as limestone, dolomite, sand, quartz or heterogeneous lithology in the presence of brines with high content of divalent ions (i.e., calcium, magnesium, barium, and strontium), high temperature, and high pressure for EOR applications.



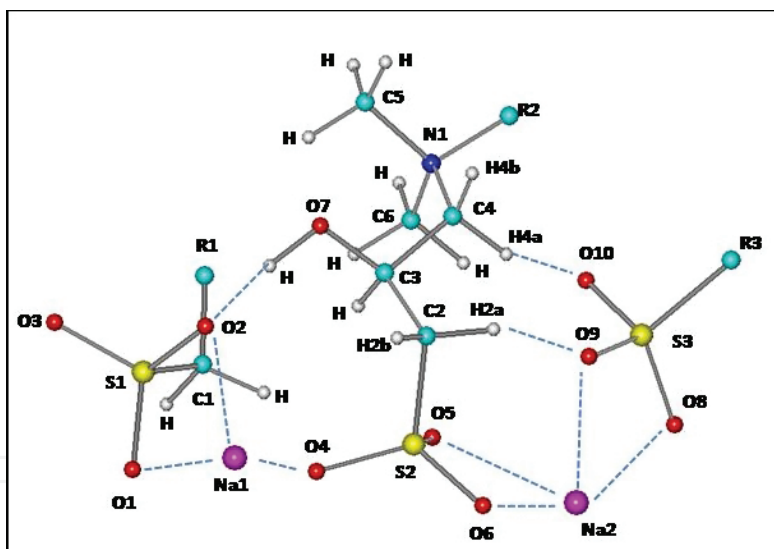
**Figure 1.** General chemical structure of the geminal zwitterionic surfactant. R is dodecyl radical [17].

## 2.2. Supramolecular complex

Supramolecular chemistry is based on the phenomenon of molecular recognition through weak forces between molecules, which promotes self-assembly [18]. This is a promising technology that has impacted the design of new materials with interesting applications in the chemical industry including the petroleum industry [7, 19, 20].

Supramolecular technology has been used for EOR applications. For instance, supramolecular assemblies, such as micellar structures, have been developed for applications in wettability alteration where it is beneficial to modify the rock formation wettability from oil-wet to preferentially water-wet to enhance oil recovery [19, 20]. It has also been reported that supramolecular agents can interact with crude oil fractions within the reservoir to reduce their viscosity promoting additional recovery of residual oil [7, 19, 20].

The supramolecular complex, AMESUS, is a surfactant developed from the interactions among cocamidopropyl hydroxysultaine (CAHS), sodium dodecyl alpha-olefin sulfonate, and sodium dodecyl hydroxyl sulfonate. AMESUS offers multifunctional features including foaming, corrosion-inhibition, and wettability-alteration properties. AMESUS can be used in high salinity brines at reservoir conditions without alteration of its molecular structure [19]. **Figure 2** shows the characteristic chemical structure of a supramolecular structure.



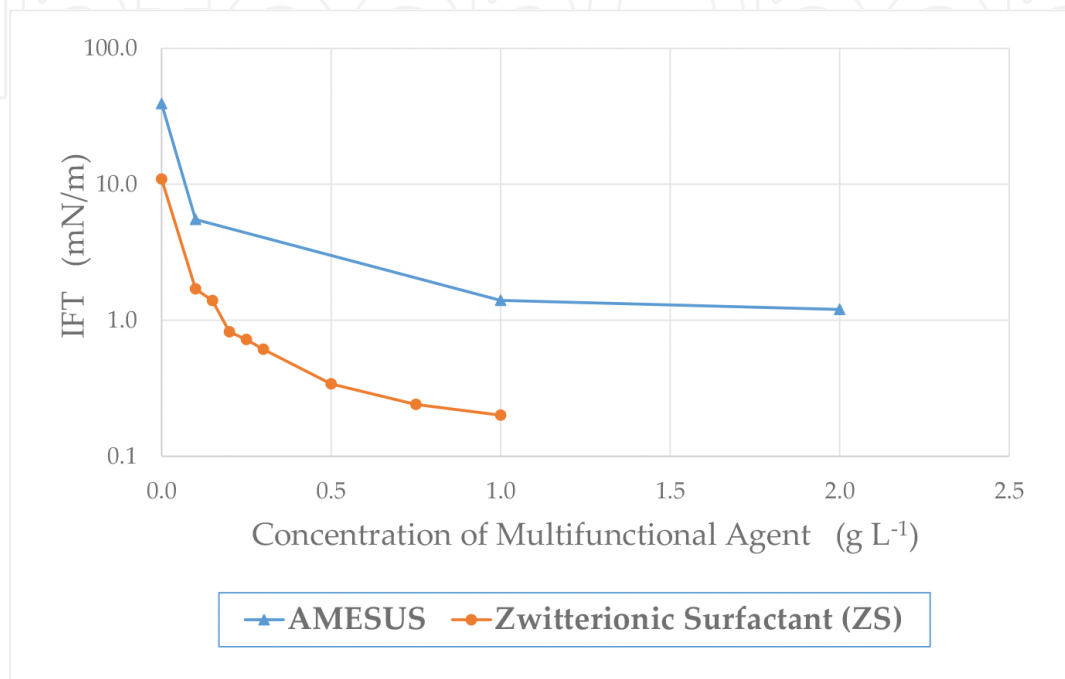
**Figure 2.** Characteristic chemical structure of the supramolecular complex, wherein R1, R2, and R3 are alkyl, alkenyl linear, or branched chains, whose length ranges from 1 to 30 carbon atoms [19].

## 3. Evaluation of the multifunctional properties

### 3.1. Interfacial tension (IFT) and contact angle

The dominant oil recovery mechanisms during surfactant flooding are interfacial tension (IFT) reduction and wettability alteration [12, 13]. The mobilization of residual oil requires the

reduction in the interfacial tension at the oil-brine interfaces to ultralow values to overcome the capillary forces responsible for trapping residual oil at the pore scale [8]. Therefore, IFT reduction mechanism depends on the surfactant effectiveness in reducing the oil-water IFT by four to six orders of magnitude. **Figure 3** shows the interfacial tension as a function of surfactant concentration and surfactant type (AMESUS and a ZS) obtained from a light crude oil (31° API)—high-salinity brine (2.6 wt.% NaCl) system.



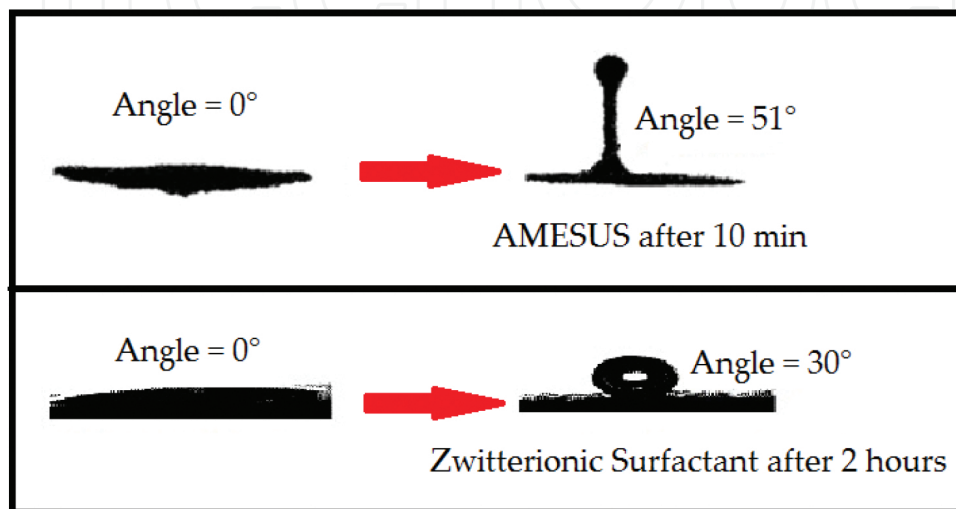
**Figure 3.** Interfacial tension (mN/m) as a function of surfactant concentration and surfactant type.

As expected, multifunctional agents (surfactants) decrease the interfacial tension as the concentration of surfactant increases until the critical micelle concentration is reached. According to the data presented in **Figure 3**, “ultra-low” IFT values were not obtained for this system with these surfactants. However, it is important to realize that oil recovery is not only influenced by IFT reduction, there are other several factors affecting the mobilization of oil at pore scale such as rock wettability (contact angle), capillary and viscous forces, and fluid properties, among others [4, 8, 12, 13]. Wettability determines the adhering tendency of a fluid toward a solid surface in the presence of other immiscible fluids, and it is a function of the interfacial chemistry of the phases present in the system. Contact angle is the point at which the oil or water interface meet at the solid (i.e., rock) surface; therefore, it indicates the affinity of the solid surface for any of the fluids present in the system. Contact angle determination is commonly used to establish wettability changes of solid surfaces [21]. In this regard, reliable wettability alteration measurement tools are necessary for the accurate evaluation and monitoring of wettability alteration treatments.

**Figure 4** shows the effect of multifunctional agents (i.e., surfactant) addition on the contact angle for each system as a function of time. The solid surfaces used were carbonate minerals



(dolomite), and the concentration of multifunctional agents was 0.1 g/L in high salinity brine concentrations (3.2 wt.% NaCl). As observed in **Figure 4**, both multifunctional agents changed the contact angle between oil and the solid surface. In the AMESUS system, the contact angle was changed from 0 to 51°, while for the ZS system the contact angle changed from 0 to 30°. These results demonstrate the effectiveness of these additives as wettability modifiers. Therefore, these results show that despite the slow decrease in interfacial tension, these multifunctional agents are efficient in altering the rock wettability.



**Figure 4.** Effect of multifunctional agents on contact angle between oil and the solid surface.

### 3.2. Asphaltenes aggregation inhibition and dispersion activity

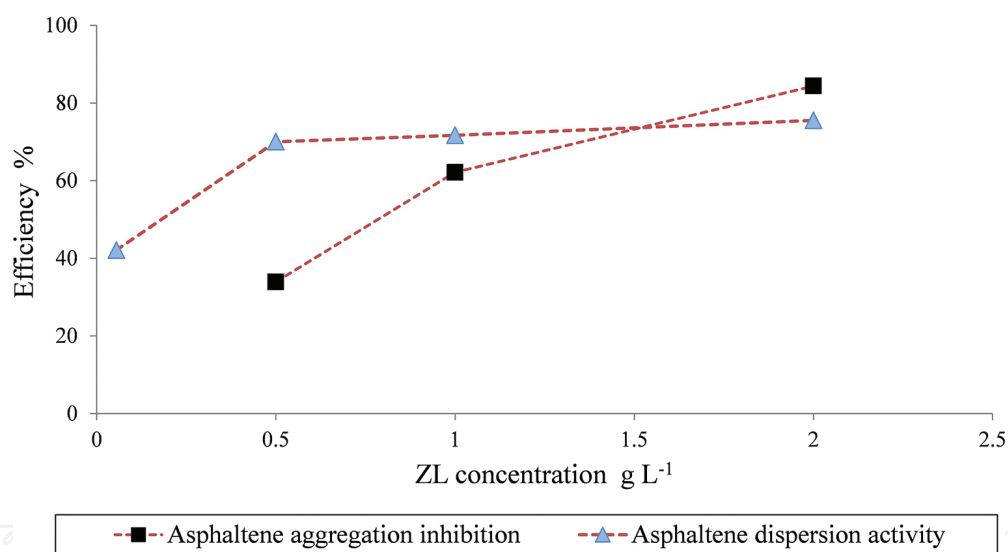
Asphaltenes can be defined according to their solubility as the fraction of oil that is insoluble in low-molecular-weight alkanes, specifically n-pentane and n-heptane, but completely soluble in aromatic hydrocarbons, such as benzene and toluene. Asphaltenes fraction is formed of associated systems of polynuclear aromatics bearing alkyl side chains and organic molecules containing oxygen, nitrogen, sulfur, vanadium, and nickel porphyrins [22]. Asphaltenes are known to aggregate due to the propensity of their fused aromatic ring systems to stack via  $\pi$ -bonding [23].

Oil production operations can induce asphaltenes precipitation because of pressure and temperature decrease and oil-phase compositional changes. The disruption of the initial reservoir conditions could induce undesirable phase separation that negatively impacts every stage of the oil production process. As mentioned earlier, deposition of asphaltenes aggregates onto the rock surface can modify the wettability of the reservoir from water-wet to oil-wet, affecting significantly the oil displacement efficiency during the oil recovery processes. Thus, surfactants agents designed for chemical enhanced oil recovery must effectively interact with the heavy fractions of the crude oil such as asphaltenes and resins. Surfactants must inhibit their aggregation and/or disperse their aggregates to prevent their deposition or accumulation

onto the rock surface, which would alter the wettability and the effective permeability of the formation rock affecting oil sweep efficiency.

Multifunctional agents used as asphaltenes aggregation inhibitors have been evaluated through ultraviolet-visible (UV-vis) spectroscopy by determining the concentration of asphaltenes remaining in solution after induced precipitation with *n*-heptane [8]. This study was carried out taking advantage of the insolubility of the asphaltenes fraction in low-molecular-weight alkanes such as *n*-heptane. However, under these conditions, the addition of the chemical agents promotes a colloidal stability to the asphaltenes particles in the liquid phase by preventing their aggregation through steric hindering or by modifying the electrostatic forces involved in the system [8].

The asphaltenes used in this experimental study were extracted from a Mexican heavy crude oil sample (18°API) using *n*-heptane. The solvent (volume) to heavy oil (mass) ratio was 40:1 (cm<sup>3</sup>/g of oil). The solution was mixed for 8 h, filtered (1 µm porous size membrane), and dried under vacuum at 60°C. The obtained fraction of asphaltenes was redissolved at a concentration of 10 wt.% in methylene chloride, reprecipitated using *n*-heptane, and refiltered.



**Figure 5.** Performance of zwitterionic surfactant on asphaltenes aggregation inhibition and dispersion activity.

**Figure 5** shows the effect of the zwitterionic surfactant (ZS) on asphaltenes aggregation inhibition and dispersion activity. The evaluations of the inhibition properties were carried out using solutions (1000 µL) of 5.0 g/L of asphaltenes in toluene mixed with *n*-heptane solutions (9000 µL) at different concentrations (0.5, 1, and 2 g/L) of ZS according to experimental techniques described elsewhere [8]. The dispersion activity experiment was performed using a sample of sediment extracted from a light crude oil (35° API) by centrifugation and with a composition of 59.99 wt.% saturates, 20.82 wt.% aromatics, 17.47 wt.% resins, and 1.45 wt.% asphaltenes [8]. **Figure 5** shows that the efficiency of asphaltenes aggregation inhibition increases as the concentration of ZS increases, while the dispersion activity efficiency increases



initially as the concentration of ZS increases but it levels off at a concentration of ZS of 0.5 g/L.

The mechanism by which ZS inhibits asphaltenes aggregation can be elucidated through interactions between asphaltenes and ZS resulting in the formation of ion-dipole pairs that generate disorder in the system by steric effects [8]. This multifunctional agent (ZS) not only inhibits asphaltenes aggregation but also exhibits suitable asphaltenes dispersion performance (**Figure 5**).

### 3.3. Formation damage

The assessment, control, and remediation of formation damage are among the most important issues to be resolved to ensure the efficient exploitation of hydrocarbon reservoirs. Formation damage is a detrimental operational and costly problem that could arouse during several stages of oil and gas production. Formation damage can occur during drilling, production, hydraulic fracturing, workover operations, and EOR [24].

Organic deposition is one of the main factors that can induce formation damage due to permeability impairment. For instance, asphaltenes deposition is a common cause of formation damage [24, 25]. It has been reported that asphaltenes induced formation damage can be explained by three mechanisms: (1) increase in the reservoir fluid viscosity due to the formation of water-in-oil emulsions and/or due to the increased concentration of asphaltenes particles in the bulk of the oil phase, especially in the near wellbore region as the oil converges radially toward the wellbore; (2) change in the wettability of the reservoir formation from water-wet to oil-wet by the adsorption of asphaltenes onto the rock surface; and (3) reduction in the reservoir formation permeability by plugging of pore throats and/or constrictions by asphaltenes particles [24].

This section summarizes the experimental evaluation of the effectiveness of multifunctional agent AMESUS in removing and inhibiting the deposition of heavy organics components onto the porous media. As heavy crude oil flows through porous media, the interactions between the asphaltenes aggregates contain in the heavy oil and some of the mineral compounds present in the rock surface induce the adsorption of asphaltenes onto the rock surfaces, which results in the gradual decrease in the effective permeability of the rock [7, 25].

This experimental work was performed by conducting coreflooding tests at reservoir conditions: temperature of 150°C, average pore pressure of 2400 psi, and overburden pressure of 3500 psi.

The experimental procedure was carried out as follows: (1) core damage was generated by flowing a sample of crude oil (1 ml/min) with high propensity for asphaltenes precipitation, through the porous medium (at least 50 pore volumes, PV). It was assumed that core impairment was caused by asphaltenes deposition. The degree of core damage was evaluated through the determination of permeability reduction; (2) application of the corresponding chemical treatment either xylene or AMESUS solutions dissolved in brine at a concentration of 2.0 g/L to the damaged core. The volume of treatment applied was five PV injected at a flow rate of 1 ml/min that was followed by a soaking period of 6 h; (3) injection of crude oil through the

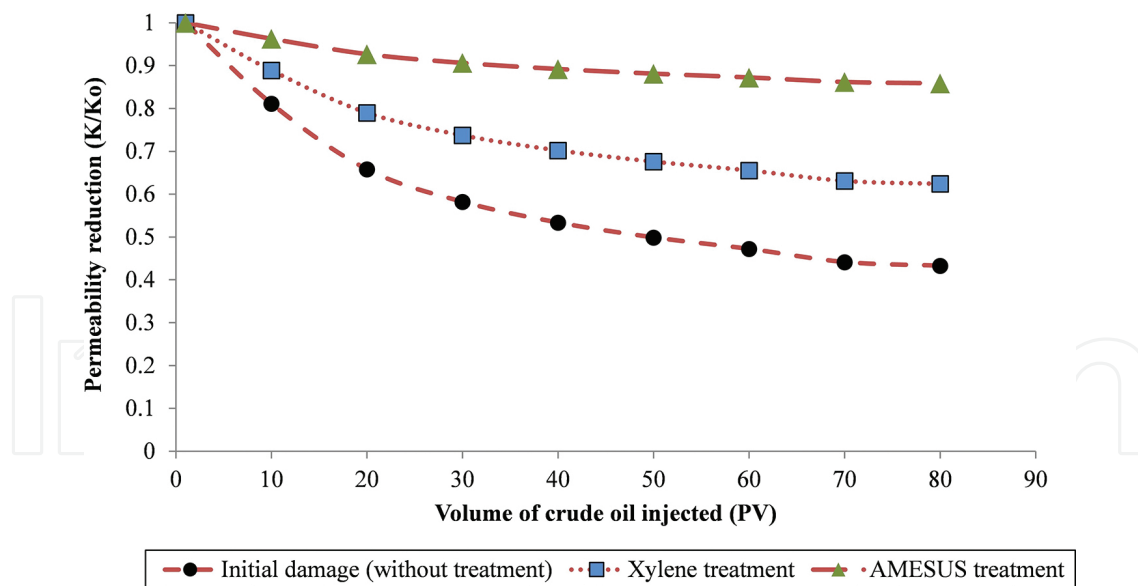
treated core plug in order to evaluate the effectiveness of the applied chemical treatment in removing the damage previously caused to the core [7]. **Table 1** summarizes the composition and other properties of the crude oil sample, and **Table 2** lists some petrophysical properties of the core plug used (Bedford limestone).

API° gravity	36.7°
SARA analysis (wt.%)	
Saturates	63.65
Aromatics	24.11
Resins	11.68
Asphaltenes	0.56
Colloidal instability index	1.79
Acidity (mg KOH/g)	0.1

**Table 1.** Composition and other physical properties of the crude oil.

Mineralogy	Length (cm)	Diameter (cm)	Porosity (%)	Pore volume (cm <sup>3</sup> )	$K_{\text{absgas}}$ (mD)
Calcite (~100%)	6.9	3.8	20	14.4	104

**Table 2.** Some petrophysical properties of the core plug sample.



**Figure 6.** Performance of chemical treatments in removing and inhibiting the deposition of asphaltenes.

**Figure 6** plots the experimental results obtained during the application of different remediation treatments. The reference case (black solid circles in **Figure 6**), in which the core plug was flooded with 80 pore volumes (PV) of crude oil without a previous chemical treatment, shows a severe permeability reduction due to the retention and adsorption of asphaltenes and resins

within the porous medium sample [7]. The application of the xylene treatment to the damaged core (blue solid square symbols in **Figure 6**) shows that permeability is recovered to some extent, while the application of AMESUS (green solid triangles in **Figure 6**) revealed a significant recovery of the core plug permeability. These results demonstrate the effectiveness of the supramolecular complex (AMESUS) in simultaneously removing the organic deposits and inhibiting the further adsorption of asphaltenes onto the core plug during the second stage of crude oil injection. It seems that the application of AMESUS changes the surface properties of the core by adhesion to the mineral surface forming a film that alters its wettability and thus inhibits the adsorption of asphaltenes and prevents further formation damage [7].

3.4. Effect of the multifunctional agents on crude oil viscosity

Residual oil saturation in heavy crude oil reservoirs has been reported to range from 80 to 95% of the OOIP, after primary and secondary oil recovery [1, 5]. The most practical approach to enhance the recovery of heavy oil is viscosity reduction through thermal EOR.

This section of the chapter describes the effectiveness of the multifunctional agents in reducing the viscosity of heavy oil. An Anton-Paar Physica MCR-301 rheometer equipped with a 50 mm PP50 plate-plate configuration and a gap of 1 mm was used to determine the viscosity of the oil samples. **Figure 7** summarizes the composition, API°, and viscosity behavior of the heavy oil as a function of temperature and shear rate.

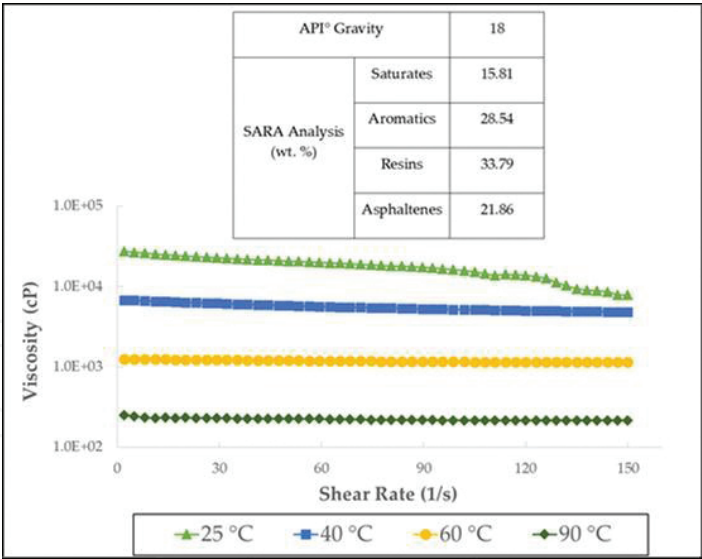
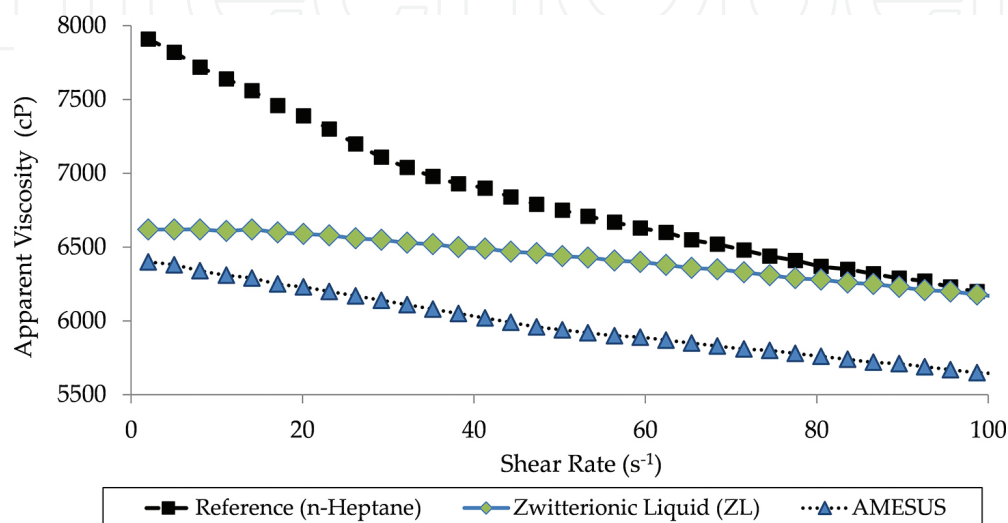


Figure 7. Heavy crude oil: composition and viscosity as a function of temperature and shear rate.

The high viscosity of this heavy oil can be attributed to its high content of resins and asphaltenes (33.79 and 21.86%, respectively). In addition, this heavy oil exhibits a non-Newtonian rheological behavior at 25°C (**Figure 7**), most likely due to the formation of wax-resin aggregates within the bulk of the oil phase at this temperature.

The multifunctional agents — AMESUS and the zwitterionic surfactant — were diluted in a fixed volume of n-heptane (1 ml) at preestablished concentrations to achieve a final concentration of the chemicals in the crude oil sample of 0.5 g/L. For comparative purposes, a reference system was prepared by dosing the heavy oil sample with the equivalent fixed volume of n-heptane that was used for dilution of the chemical agents. **Figure 8** plots the apparent viscosity of the crude oil as a function of shear rate and chemical treatment. The experiments were conducted at 25°C, and the range of shear rate evaluated was 0.1/s to 100.0/s.



**Figure 8.** Apparent viscosity as a function of shear rate and chemical treatment.

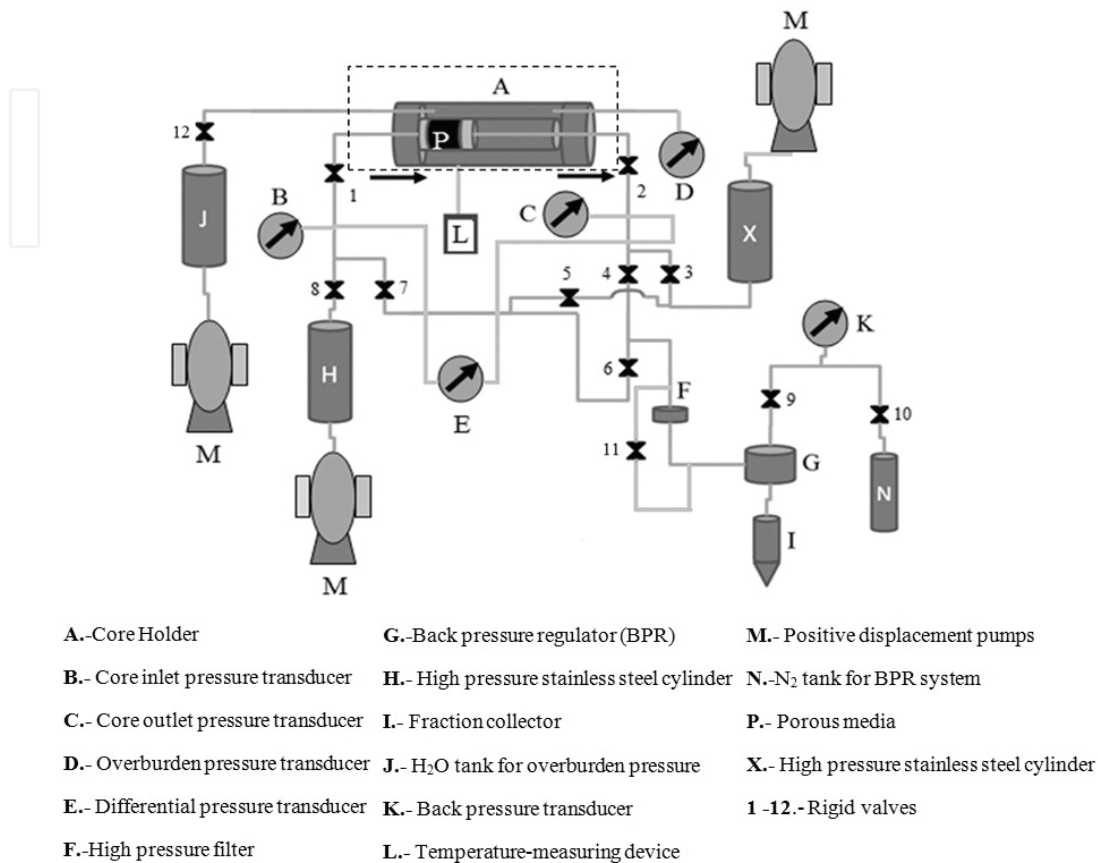
**Figure 8** indicates that the viscosity of the samples (baseline and chemical treated oil) decreases as the shear rate increases following a shear thinning behavior. The chemical-treated oil samples show lower viscosities when compared with the viscosity of the reference sample. Therefore, both multifunctional agents are effective in decreasing the viscosity. Nevertheless, AMESUS offers a better performance in reducing the viscosity of the heavy oil than the ZS agent. Moreover, the performance of the ZS agent is hindered as the shear rate increases.

These experimental observations demonstrate that the multifunctional agents interact with the asphaltenes and resins contained in the heavy oil sample providing a significant viscosity reduction. The AMESUS supramolecular complex exhibits a suitable performance in preventing the aggregation of asphaltenes and resins which allows reducing the viscosity of the heavy crude oil evaluated [7].

### 3.5. Oil recovery

This section describes the experimental evaluation of the multifunctional agents as chemical additives for enhanced oil recovery (EOR) through coreflooding displacement tests at reservoir conditions. **Figure 9** displays the experimental setup of the coreflooding apparatus [7, 8]. The dead volumes of the flow lines were measured and accounted for in all material balance

calculations. The performance of the corresponding chemical EOR applications was estimated in terms of incremental oil recovery [7, 8].



**Figure 9.** Experimental setup for coreflooding displacement tests.

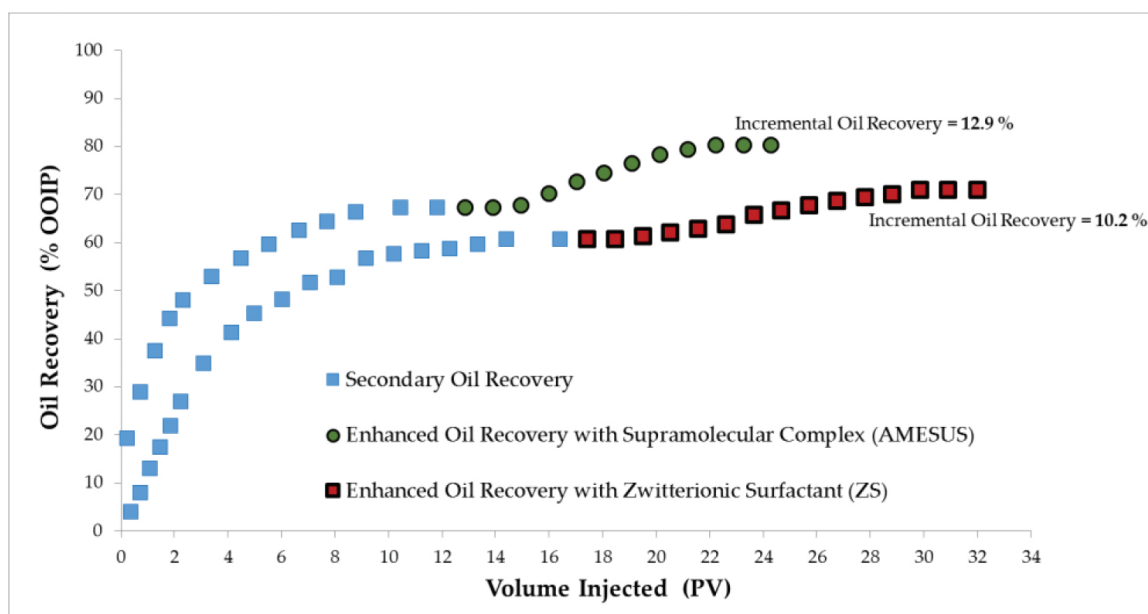
The protocol used during coreflooding testing was as follows:

1. *Core plug preparation.* First, the core was cleaned using solvents such as toluene/methanol; afterward, the core was dried at 120°C for 24 h. The clean core plug was positioned into a standard core holder (manufactured by Core Laboratories). Flooding conditions were set at: temperature, 90°C; average core pressure, 2400 psi, and overburden pressure, 3500 psi. A Bedford limestone (BL), core plug was used, which consists of 100 wt.% CaCO<sub>3</sub>. The dimensions of the core plug were 6.7 cm in length and 3.8 cm in diameter. The absolute permeability of the core plug was 139 mD and the porosity 20%.
2. *Brine injection.* Brine with a concentration of 2.6 wt.% in NaCl was used. In this step, the core plug was saturated with brine at a flow rate of 1 ml/min.
3. *Crude oil injection.* **Table 1** displays the composition and some physical characteristics of the crude oil used in this experimental section. The core plug was flooded with crude oil at a constant flow rate of 1 ml/min. In this stage, the irreducible water saturation ( $S_{wi}$ ) and initial oil saturation ( $S_{oi}$ ) were determined.

4. *Waterflooding (WF) stage.* Waterflooding as a secondary oil recovery (SOR) process was carried out by injecting brine at a constant flow rate of 1 ml/min. The produced fluids were collected using graduated centrifuge flasks. Pressure profile data along the core plug were recorded. The residual oil saturation ( $S_{or}$ ) was established when the production of crude oil became negligible. Oil recovery (% OOIP) was calculated by material balance as a function of time.
5. *Surfactant flooding (SF) stage.* This stage was carried out injecting the corresponding multifunctional agent dissolved in brine at a fixed concentration of 1.0 g/L at a flow rate of 1 ml/min [7, 8].

**Figure 10** shows the experimental results of oil recovery (OOIP %) as a function of the volume of fluid injected, recovery stage, and type of surfactant treatment (AMESUS or ZS).

An incremental oil recovery of 12.9% was obtained for the AMESUS chemical flooding, whereas an incremental oil recovery of 10.2% was achieved for the ZS chemical flooding. Therefore, the multifunctional agents evaluated are effective in mobilizing and displacing residual oil. This indicates that the proper physicochemical interactions among the chemical solutions, rock, and crude oil were established during surfactant flooding.



**Figure 10.** Oil recovery (OOIP %) versus volume of fluid injected (PV), recovery stage, and surfactant type.

Rock permeability, porosity, and the spatial distribution of these parameters within the porous media influence oil recovery [26]. Thus, in order to evaluate the effect of permeability on oil recovery during surfactant flooding, coreflooding displacement tests were conducted using two different core plugs. A formation rock (FR), which consists of 92% calcite and 8% clays (kaolinite and sodium montmorillonite), having an absolute permeability of 9 mD, a porosity of 19%, a length of 8.3 cm, and a diameter of 3.8 cm. The second core plug was a Bedford limestone (BL), containing 100 wt.%  $\text{CaCO}_3$ , an absolute permeability of 139 mD, 20% porosity,



a length of 6.7 cm, and a diameter of 3.8 cm. In terms of rock wettability and as shown below in section 3.6 by using oil-water relative permeability curves, the FR rock is more oil-wet than the BL core [8].

API° gravity		31°
SARA analysis (wt.%)	Saturates	41.05
	Aromatics	36.66
	Resins	20.32
	Asphaltenes	1.97
Colloidal instability index		0.75
Acidity (mg KOH/g)		0.13

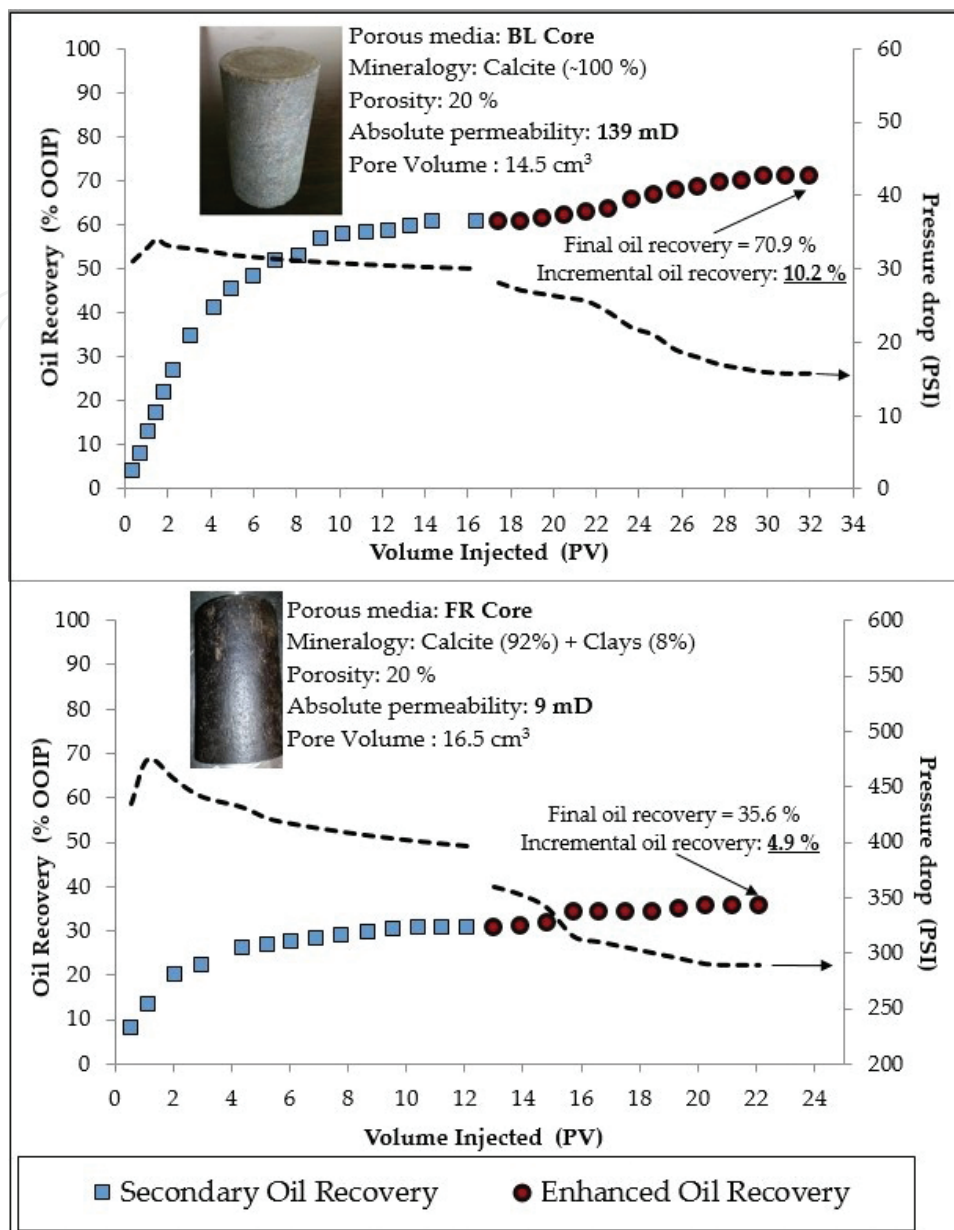
**Table 3.** Composition and some physical characteristics of the crude oil.

A sample of crude oil with the properties presented in **Table 3** and brine (2.6 wt.% NaCl) were used in these experimental runs. The displacement tests were conducted following the injection protocol previously described. During the surfactant flooding stage, the ZS chemical was used at a concentration of 1.0 g/L. **Figure 11** summarizes these experimental observations, which indicate that the secondary oil recovery stage is significantly affected by the core permeability and mineralogy: the heterogeneous FR core with lower permeability ( $K_{\text{absgas}} = 9$  mD) had the higher residual oil saturation ( $S_{\text{or}} = 56.4\%$ ) after waterflooding, whereas a lower residual oil saturation of 39.3% was obtained for the homogeneous BL core sample ( $K_{\text{absgas}} = 139$  mD). As expected, the higher the permeability of the rock, the higher the oil recovery. Furthermore, a higher oil recovery by waterflooding was obtained from the more water-wet or BL core, as previously reported [7].

As **Figure 11** shows, after the waterflooding stage, surfactant EOR flooding was carried out. An incremental oil recovery of 10.2% of the OOIP was obtained from the BL core plug, while only an incremental oil recovery of 4.9% was obtained from the FR core plug.

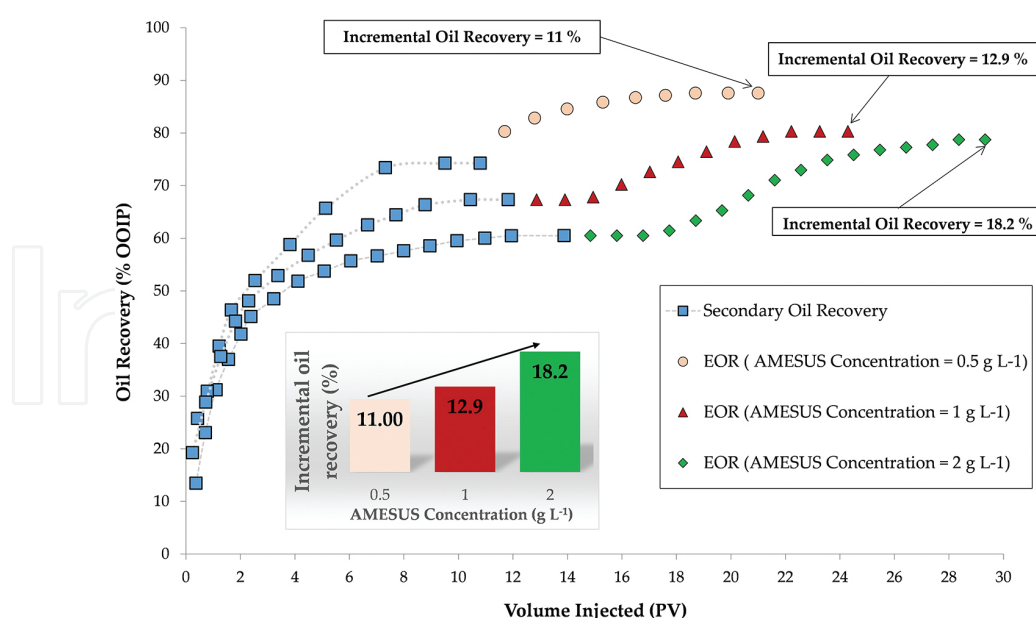
The higher incremental EOR obtained from the BL core sample might be explained by the higher permeability and wettability conditions (more water-wet) of this core as has been previously reported [8]. Nonetheless, the ZS multifunctional agent is effective in rendering incremental EOR from both porous media that otherwise would not be recovered.

**Figure 11** also shows the pressure drop profiles as a function of volume injected. Both porous media show similar behavior. At the beginning of waterflooding, the pressure drop rises slightly as oil production increases; however, as soon as brine breakthrough at the production end, pressure drop declines progressively, as well as oil production. During surfactant flooding, the pressure drop rapidly decreases, whereas oil production increases slowly. The pressure drop profiles exhibited in **Figure 11** also show that despite the high salinity characteristics of the brine used (2.6 wt.% NaCl), surfactant precipitation and/or blockage of the core plug was not observed during the flooding processes [8].



**Figure 11.** Influence of porous media on oil recovery performance of zwitterionic surfactant (ZS).

The effectiveness of AMESUS during surfactant flooding was also evaluated. In these experiments, the rock sample used was a Bedford limestone (BL) (100 wt.% CaCO<sub>3</sub>), with absolute permeability of 139 mD, a porosity of 20% porosity, a length of 6.7 cm, and a diameter of 3.8 cm. Samples of crude oil (31° API) and brine (2.6 wt.% NaCl) were used following the injection sequence previously described. Furthermore, in these coreflooding tests, different concentrations of AMESUS (0.5 g/L, 1 g/L, and 2 g/L) were evaluated to establish the effect of surfactant concentration on oil recovery. **Figure 12** presents oil recovery as a function of pore volume of fluid injected and surfactant concentration. These experimental results indicate that as the concentration of AMESUS increases, oil recovery increases.



**Figure 12.** Effect of AMESUS concentration on oil recovery performance.

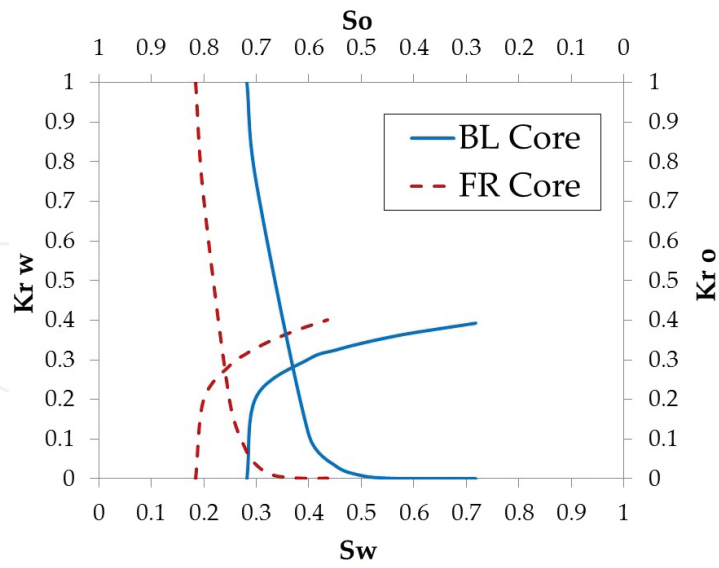
### 3.6. Relative permeability

Oil-water relative permeability data offer relevant insights into the simultaneous flow of crude oil and brine that allows predicting the performance of waterflooding processes. Oil-water relative permeability is influenced by several variables such as fluids saturation, fluids saturation history, interfacial tension, fluids viscosity, overburden pressure, temperature, flow rate, wettability, and capillary end effects [27]. In addition, relative permeability curves provide information on the wettability of the porous media, which significantly affect oil recovery processes [7, 8].

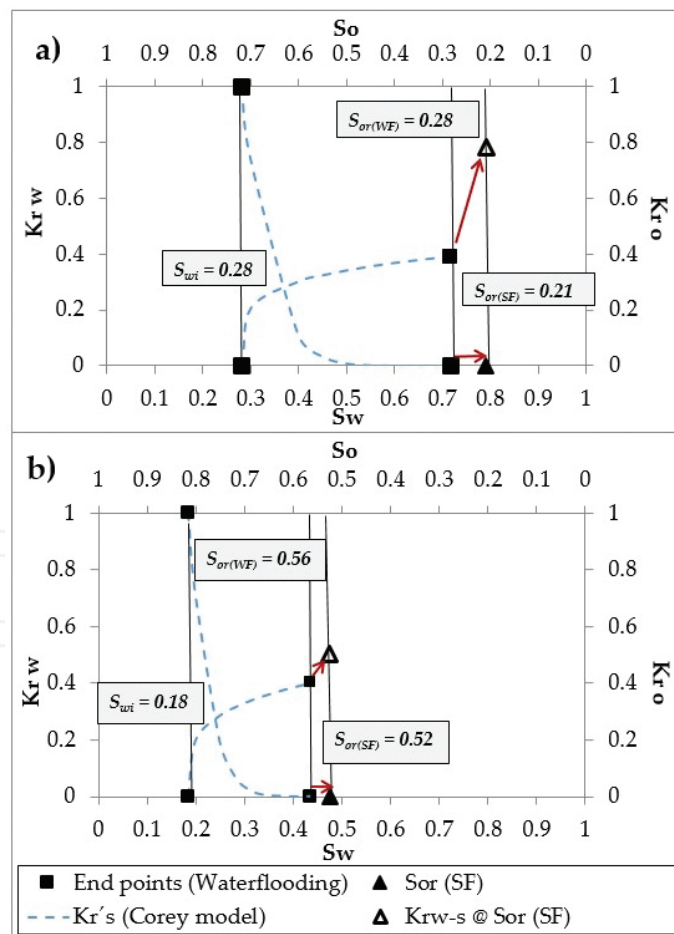
In this study, the oil-water relative permeability curves were obtained following the Johnson-Bossler-Neumann (JBN) method and the data were fitted using a Corey-type correlation [7, 8, 28–30].

The effect of the multifunctional agent ZS on the oil-water relative permeability curves was evaluated to establish their efficiency in altering rock wettability.

In this experimental work, the wettability of the core plugs was determined after waterflooding. **Figure 13** presents the oil-water relative permeability curves after waterflooding. The crossover point (equal relative permeabilities) of the oil and water relative permeability curves shown in **Figure 13** indicates that both porous media (BL and FR rocks) are predominantly oil-wet, which is expected for calcite rock formations [31]. However, the FR core plug is more oil-wet (crossover point more shifted toward the left side of the relative permeability curves) than the crossover point of the BL core, which also explains the waterflooding oil recovery behavior presented in **Figure 11**, where a higher secondary oil recovery was obtained from the rock sample showing less oil-wetting tendency (i.e., BL core plug).



**Figure 13.** Relative permeability curves after waterflooding.



**Figure 14.** Effect of ZS chemical agent on the relative permeability curves. (a) BL core and (b) FR core.

The effect of rock wettability on oil recovery has been reported in the literature [32, 33]. **Figure 14** displays the effect of surfactant flooding (SF) using the ZS agent on the oil-water relative permeability curves corresponding to the oil-recovery coreflooding results previously discussed (**Figure 11**). **Figure 14** shows the end points of the relative permeability curves of both waterflooding (WF) and surfactant flooding (SF) processes. For the WF process, the initial water saturation ( $S_{wi}$ ) and the residual oil saturation ( $S_{or}$ ) are presented, whereas for the SF process, the final residual oil saturation ( $S_{or(SF)}$ ) and the final relative permeability ( $K_{rw-S}$  at  $S_{or(SF)}$ ) obtained for both the BL and the FR core plugs are presented.

These results demonstrate that the injection of ZS alters the wettability of both core plugs toward more water-wet conditions, which is in agreement with the incremental oil recovery previously presented [8].

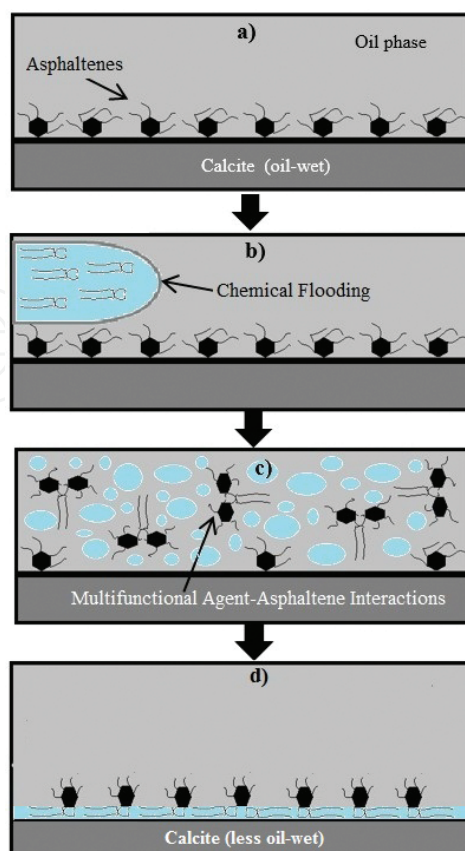
## 4. Mechanisms

Key mechanisms involved in the multifunctional activity of the chemical agents evaluated in this work are proposed and discussed in this section.

In the context of this study, formation damage is caused by the deposition of polar heavy organic fractions present in the crude oil, such as asphaltenes and resins, which could form a hydrophobic layer on the rock surface altering its wettability toward more oil-wet [**Figure 15(a)**]. Remediation of this type of formation damage by chemical treatment using the multifunctional agents AMESUS and ZS takes place due to the strong interactions established between the chemicals and the deposited layer of asphaltenes and resins, as sketched in **Figure 15(a)** and **(b)**. The interactions between the chemical agents and asphaltenes are different for each of the multifunctional agents. For instance, the ZS-asphaltenes interactions are of the ion-dipole pair types [16], whereas the asphaltenes-AMESUS interactions are of the dipole-dipole pair types [7]. As a result, the deposited asphaltenes are desorbed, disaggregated, and dispersed within the crude oil phase by the multifunctional agents, while simultaneously part of the chemical agents is adsorbed onto the rock surface replacing the previously deposited asphaltenes molecules [**Figure 15(d)**]. Moreover, the adsorption of the multifunctional agents onto the mineral surface modifies the wettability of the rock toward more water-wet condition and inhibits the further adsorption of asphaltenes, which prevents formation damage. Furthermore, the interactions of the multifunctional agents with the crude (bulk) oil indicate their effectiveness in inhibiting the formation of asphaltenes aggregates. Therefore, these surfactants are efficient in dispersing these heavy oil fractions within the crude oil reducing its viscosity [7, 8, 16].

It is important to emphasize that the mechanisms proposed here might be dependent on the characteristics of the brine/rock/crude oil system including resins and asphaltenes content, rheological properties of crude oil, brine composition, and the mineralogy of the porous media [7, 8]. Therefore, wettability alteration and reduction in crude oil viscosities are considered the key mechanisms that allow the multifunctional agents to increase oil recovery.





**Figure 15.** Sketch of the suggested mechanisms: (a) initial conditions, asphaltenes adsorbed onto the rock surface (oil-wet core condition), (b) chemical flooding, (c) multifunctional agent-asphaltene interactions promoting asphaltenes desorption, and (d) wettability alteration to less oil-wet conditions due to the adsorption of the chemical agents onto the rock surface.

## 5. Conclusions

This chapter summarizes the evaluation of the multifunctional properties of two novel chemical agents applied for enhanced oil recovery (EOR). These chemical agents demonstrate suitable performance during surfactant flooding at reservoir conditions (i.e., temperature and pressure) and high salinity brine concentration. These chemical agents are effective as asphaltenes aggregation inhibitors. Similarly, they are suitable asphaltenes dispersants. Therefore, these agents are applicable for the removal and prevention of asphaltenes deposition and/or adsorption onto the rock surface. Furthermore, these multifunctional agents can significantly decrease the viscosity of heavy oil through the breaking and dispersion of asphaltenes and resin aggregates within the bulk oil phase.

The dominant mechanisms responsible for the multifunctional activity of these chemical agents are the reduction in the viscosity of the heavy oil and the modification of the rock wettability. Finally, the novel multifunctional chemical agents have the potential of providing



a feasible technological solution to the complex problems related to the heavy crude oil viscosity reduction and formation damage commonly found in the petroleum industry.

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