



## Interfacial Properties of Asphaltene–Brine systems and Analysis of Adsorption Kinetics: Effects of ion and Water injection for EOR

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### Abstract

Low salinity water (LSW) injection is an enhanced oil recovery (EOR) method with a high potential to reduce capillary forces during the water flooding in the oil reservoir. Asphaltenes are the heaviest crude oil components and are active agents on the oil-water interface. Understanding the key parameters related to interfaces phenomenon, such as the adsorption kinetics of these systems, allows for more efficient development of new E&P technologies. Therefore, this work aims to study fluid-fluid interactions between a Brazilian pre-salt asphaltene and injection water for EOR purposes. The dynamic interfacial tensions (IFT) of the systems were measured using a Drop Shape Analyser (DSA) by the pendant drop method at 60 °C. The experimental IFT curves were modeled using the Ward–Tordai and Gibbs–Duhem diffusion equations to obtain the equilibrium IFT of asphaltene solutions and the interfacial diffusion coefficient. The results showed that LSW contained customized composition water is more efficient than NaCl or MgCl<sub>2</sub> solutions in reducing the IFT of asphaltene-brine systems. Furthermore, brine containing divalent ions such as Mg<sup>2+</sup> showed a higher IFT reduction rate than monovalent ions. These results are explained in terms of diffusion coefficient patterns.

### Keywords

EOR; Asphaltene; IFT; adsorption model

### Introduction

Water flooding is a common and well-known technique for oil recovery. However, the increasing demand for oil and the significant decline in crude oil production from mature fields have encouraged the development of new technologies for enhanced oil recovery (EOR).

The main EOR methods are based on thermal, microbiological, miscible, chemical, and other processes, such as low salinity water. EOR methods aim to increase the oil recovery factor by improving displacement and sweeping efficiency. The capillary number (CN) is a parameter defined by the ratio between viscous and capillary forces that are strongly related to some oil production factors. Thus, the higher the CN, the higher the oil recovery factor.

The advantages of LSW injection as an EOR method are mainly due to its cost and benefit in reducing capillary forces. Among the main action mechanisms of LSW, it is worth highlighting the wettability alteration, fine migration, pH increase, multi-ion exchange, and salting-in. However, there is still no consensus on the actual mode of interaction between the fluids in the reservoir. On the other hand, it is believed that this interaction can be explained in terms of the type of salts and the oil composition. Therefore, understanding the

key parameters of this interaction can improve the development of new technologies [1].

Regarding oil composition, asphaltenes are considered the most complex components. Asphaltene-related problems may include precipitation during oil production, emulsions stabilization, and rock wettability alteration, among others. Also, asphaltenes play a key role in interface phenomena and problems related to flow assurance. They are defined as a solubility class soluble in aromatic solvents but insoluble in light n-alkanes. Asphaltenes are also the heaviest and most polar components, presenting conjugated systems of aromatic rings with aliphatic chains containing heteroatoms such as N, O, and S. [2]. These characteristics favor high interfacial activity and may decrease the capillary forces. From this perspective, studying how the asphaltenes interact with injection water, such as low salinity water, is crucial to optimizing EOR processes in Brazilian Pre-salt reservoirs.

Dynamic interfacial tension measurements are used to study fluid-fluid interactions. However, obtaining reliable IFT equilibrium values at reservoir conditions is expensive and time-consuming. Thus, a common way to determine the equilibrium IFT is by fitting the experimental IFT kinetics curves using adsorption models. The asphaltene adsorption process shows three stages as a function of time. The reduction kinetics of

interfacial tension at the initial state (Regime I) is diffusion-controlled, during which asphaltenes are adsorbed to the oil-brine interface. This process is described by the Ward–Tordai equation. With increasing adsorption time, in Regime II, the steric hindrance arising from the adsorbed asphaltenes at the oil/brine interface inhibited further adsorption. In Regime III, continuous adsorption of asphaltenes to the sublayer of the interface and reconfiguration of adsorbed asphaltenes might contribute to the construction of dynamic IFT. To obtain the equilibrium IFT, a model based on the Gibbs–Duhem diffusion equation for long-term adsorption has been employed [3].

Since the interaction between asphaltenes and injection water is crucial for the success of low salinity water EOR-based process, this work aims to carry out an experimental study on the fluid-fluid interactions of the asphaltenes-brine systems. The brines used in this study are composed of a complex mix of ions. The Estimation of some interfacial properties of asphaltenes and the analysis of the adsorption kinetics at the oil-brine interface by different adsorption models are also evaluated in this study.

## Methodology

### Experimental Procedure

**Materials:** The chemicals used to prepare the synthetic brines were purchased from Sigma Aldrich and used without previous treatment. Shell Brazil provided a crude oil sample from a Brazilian Pre-Salt reservoir. It was characterized through SARA analysis (saturates, aromatics, resins, and asphaltenes) and a total acid number (TAN). The asphaltene fraction was extracted from this crude oil.

**Preparation and characterization of brine solutions:** The injection water (brine 1 e brine 2) was prepared by the dissolution of a specific amount of salts (see table 1) in distilled water. In addition, NaCl 1M and MgCl<sub>2</sub> 1 M solutions were also used as brine models in this work. The brine solutions were characterized by pH and density. The pH measurements were performed on a pH analyzer model pH 300. The density measurements were carried out in a densitometer Mettler Toledo model DM040. The results were used as input data in DSA software.

Table 1. Brine composition

Brine 1	ppm	Brine 2	ppm
NaCl	27 936	NaCl	30 348
CaCl <sub>2</sub>	371	CaCl <sub>2</sub> .6H <sub>2</sub> O	2 733
MgCl <sub>2</sub> .6H <sub>2</sub> O	1 275	MgCl <sub>2</sub> .6H <sub>2</sub> O	14 220
KCl	748	KCl	953
Na <sub>2</sub> SO <sub>4</sub>	57	SrCl <sub>2</sub> .6H <sub>2</sub> O	27
		NaHCO <sub>3</sub>	139
		Na <sub>2</sub> CO <sub>3</sub>	55

### Asphaltenes extraction and solution preparation:

The asphaltene fraction was precipitated from a Brazilian Pre-salt oil following the procedure described by Franco et al. (2013), which is briefly described here. An excess of n-heptane was added to the crude oil at a ratio of 40/1. The mixture was sonicated (Hielscher, model UP205) for 2h at 25 °C. Then, it was placed on a thermostatic stirring bath (Nova technique NT230) at 220 rpm for 24 h. After this period, the asphaltenes were centrifuged at 3300 rpm for 15 min. The solid extract was washed with n-heptane several times until it showed a shiny black color. The asphaltenes were dried at room temperature. Then, it was ground and characterized by FTIR. Asphaltenes were dissolved in toluene to obtain the stock solution at a concentration of 10,000 mg/L.

**Interfacial tension measurements:** The interfacial tension measurements between brine solutions (water, Brine 1, Brine 2, NaCl 1M, or MgCl<sub>2</sub> 1M) and asphaltenes solutions were performed by the pendant drop method using a Drop Shape Analyzer equipment (DSA 100E – Kruss) at 60 °C and atmospheric pressure. The Dynamic interfacial tensions were measured over 5400 seconds (1h 30 min). Also, all the tests were performed in duplicate.

**Analysis of Adsorption Kinetics:** Adsorption models based on the equations of Ward–Tordai/Gibbs–Duhem (eq. 1) and modified Gibbs–Duhem (eq. 2) were used to fitting experimental IFT curves. Equation 1 describes the diffusion process found in regime I, whereas Equation 2 describes the long-term adsorption found in regime III.

$$\gamma t = \gamma^{\circ} 2RT C^{\circ} \sqrt{t} \quad \text{Equation 1}$$

$$\gamma(t) t \rightarrow \infty = \gamma e q + \frac{RT \Gamma^2 e}{C^{\circ}} \sqrt{\frac{7\pi}{12 D s t}} \quad \text{Equation 2}$$

## Results and Discussion

### Preparation and characterization of brine solutions:

Table 2 shows the pH and density of brine solutions. It is important to note that the pH influences the migration of ions to the interface depending on the asphaltene compositions.

Table 2. pH and density of brine solutions

Brine	pH	Density – g/cm <sup>3</sup>
NaCl 1M	6.89	1.0186
MgCl <sub>2</sub> 1 M	5.58	1.0679
Brine 1	6.42	1.0179
Brine 2	7.59	1.1061

**Asphaltenes characterization:** In table 3 the main bands are shown in the FTIR spectrum. The diversity of functional groups shown in the FTIR spectrum confirms the complexity of the asphaltenes class. The heteroatoms can be the

main ones responsible for the interface activity of these materials.

Table 3. Functional groups present in asphaltene sample by FTIR spectroscopy

Wavenumber (cm <sup>-1</sup> )	Functional group
3403	OH
2920	CH <sub>2</sub> + CH <sub>3</sub>
2850	CH <sub>2</sub> + CH <sub>3</sub>
1697	C=O
1604	C=C aromatic
1461	CH <sub>2</sub> + CH <sub>3</sub>
1376	CH <sub>3</sub>
1306	C-O
1031	C-O
872 - 719	C-H aromatic

Dynamic interfacial tension versus time: Figure 1 shows a schematic diagram of a typical experimental IFT curve in a function of time (square root) obtained in this study. It is possible to note that the IFT curves can be divided in three different regimes. Regime I is related to the asphaltene adsorption process only due to diffusion. Regime II is a meta-stable region, and Regime III is related to the adsorption of asphaltenes to the sublayer of the interface and molecular reconfiguration of adsorbed asphaltenes. The magnitude of these phenomena depends on the type of brine since each type of ion presents specific interaction with asphaltenes.

The asphaltene interfacial diffusion coefficient ( $D$ ) is obtained by modeling Regime I with the Gibbs-Duhem diffusion equation (Eq. 1). The Equilibrium IFT values were obtained by fitting the Regime III of the curves using the modified Gibbs–Duhem diffusion equation (Eq. 2). The equilibrium IFT and  $D$  parameters are shown in Table 4. From values found in Table 4, it is possible to note that the influence of the type of brine on  $D$  is more pronounced in brine 2, which is 70% higher than in the other systems. Thus, asphaltenes diffuse faster to the oil/brine 2 interface than in the other systems.

Table 4. Interfacial tension at equilibrium condition of oil/brine systems and asphaltene interfacial diffusion coefficient.

EOR system	IFT (mN/M)	$D$ (m <sup>2</sup> /s)
NaCl 1M	19.89	$5.6 \cdot 10^{-17}$
MgCl <sub>2</sub> 1 M	19.11	$1.8 \cdot 10^{-17}$
Brine 1	23.07	$1.5 \cdot 10^{-17}$
Brine 2	19.05	$1.0 \cdot 10^{-16}$

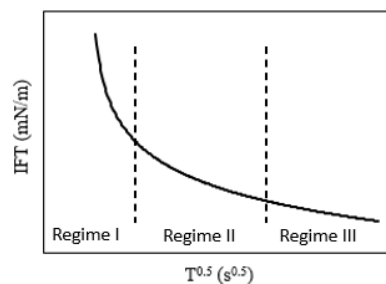


Figure 1. Schematic diagram for the typical experimental IFT curve vs. square root of time.

From the analysis of the adsorption kinetics in Regime I by the adsorption model of Ward and Tordai [3] it is possible to obtain the area for the new interface active materials (asphaltenes) to diffuse and move at the interface. For this premise to be applied to the results obtained in this study, the  $\ln$  of the partial derivative of surface pressure ( $\Pi$ ) with time ( $\ln(d\Pi/dT)$ ) must show linear dependence with the IFT values of Regime I. Fig. 2 shows the IFT values in Regime I vs.  $\ln(d\Pi/dT)$ . It is possible to note that the fitting lines show almost the same slope, which indicates that the area created in the interface during the diffusion-controlled regime (Regime I) is almost constant regardless of brine composition.

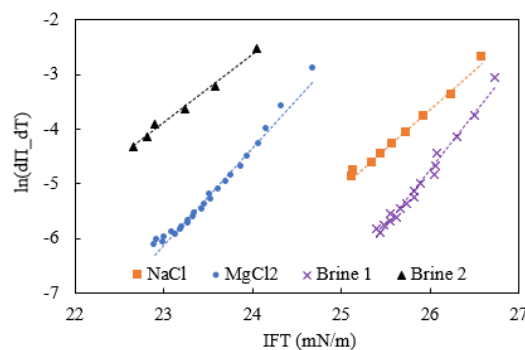


Figure 2. IFT in Regime I vs.  $\ln(d\Pi/dT)$  for 1% wt. asphaltene solutions at 60 °C.

- Ion effect: Figure 3 shows the dynamic IFT between water, NaCl, and MgCl<sub>2</sub> solutions and asphaltene/toluene solutions at 60 °C.

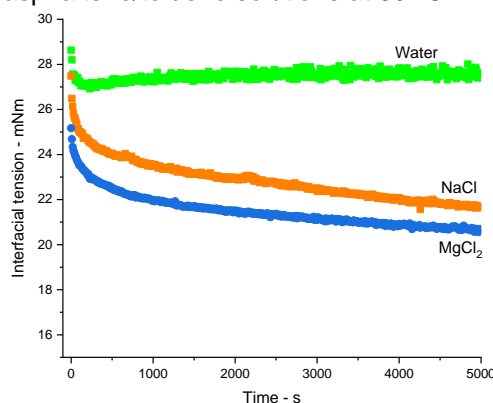


Figure 3. Interfacial tension as a function of time between Water, NaCl, or MgCl<sub>2</sub> (1 mol.L<sup>-1</sup>) solutions and asphaltenes solution 1% wt. T = 60 °C and P = 14 psi.

The dynamic IFT decreases significantly in the presence of brine when compared with distilled water. The increase of polarity of the aqueous bulk phase (caused by salts) favored the migration of asphaltenes to the interface due to the polar nature of asphaltenes. The ions have significant interactions with surface-active components at the interface. The  $MgCl_2$  solution presented a smaller IFT than the  $NaCl$  solution. FTIR results show that the asphaltene structure has a carboxylate (COOH) and alcoholic groups (OH). These groups may interact with ions reducing the IFT values. This result indicates that the interaction with  $Mg^{2+}$  is stronger than with  $Na^+$  ions, possibly due to a stronger electrostatic potential of the divalent ion. In this context, dominant interactions are ion-dipole which are stronger for  $Mg^{2+}$ . Thus, the higher the interaction between asphaltenes-ion, the lower the IFT due to the stability of the interface. Some authors have studied the impact of different ions on water-oil interfacial properties. They observed that pH changes, multi-ion exchange, salting-in, and diffusion phenomena can explain this phenomenon. Another important observation was the adsorption kinetics, the IFT decreases notably with time during the first minutes, and then the reduction slows down with time. The slope changes observed in the dynamic IFT curves indicate the magnitude of interfacial activity.

- Water injection for EOR effect: Figure 4 shows the dynamic IFT between water, brine 1, brine 2 solutions, and asphaltenes/toluene solutions at 60 °C.

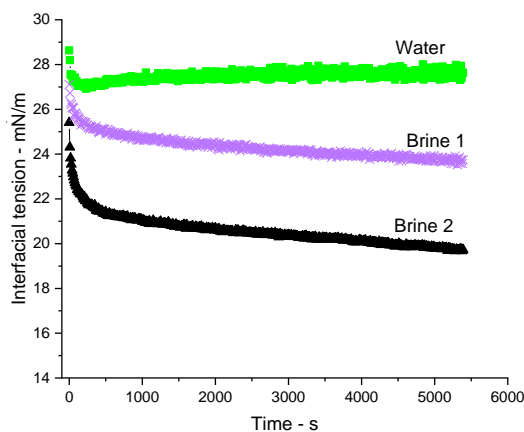


Figure 4. Interfacial tension as a function of time between injection brine for EOR and asphaltenes solution 1% wt.  $T = 60\text{ }^{\circ}\text{C}$  and Pressure = 14.7 psi.

Customized composition water (brine 1 and brine 2) showed lower IFT than distilled water. As previously discussed, the bulk brine polarity allows the migration of asphaltenes to the interface. Another interesting behavior observed was that desulphated brine (brine 2) showed more interfacial activity than sulfated ones (brine 1). The sulfate ion may be repelled from the interface due to carboxylate groups presented in the asphaltene molecule. Furthermore, brine 2 has

a higher content of  $Mg^{2+}$  and  $Ca^{2+}$  than brine 1. When interacting with asphaltenes, these divalent ions may be the main responsible for reducing the IFT of the system. Based on the acid number of the oil, the pH increase stimulates the interfacial activity of natural surfactants. Because of all these factors (medium polarity, sulfate ion, content of  $Mg^{2+}$ , and pH), the IFT is smaller in brine 2 than in brine 1.

## Conclusions

This study showed that the adsorption kinetics of asphaltenes to the oil/brine interface can be divided in three regimes. Each regime is related to different patterns of asphaltene migration into the interface. From the analysis of these patterns, it was found that asphaltenes migrate faster to the interface in the oil/brine 2 system. Also, the equilibrium IFT values have been determined by fitting the experimental data using the long-term adsorption equation (eq. 2). Considering the IFT reduction, the best result was achieved with the oil/brine 2 system. However, it is worth noting that the  $NaCl$  and  $MgCl_2$  solutions were more efficient in reducing IFT than brine 1. This result shows that the optimal condition for injection must be achieved not only by the compositional complexity of the brine (customized composition water) but also by the proper choice of the ion mixture used in the brine formulation.

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