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Evaluation of interfacial activity of asphaltenes extracted from light and heavy oil of Brazilian Pre salt reservoir

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Abstract

The oil reservoirs in Brazil's Pre-Salt region exhibit a diverse range of oil compositions and properties, including varying densities and viscosities, which set significant challenges for production. In this context, studying fluid-fluid interactions using reservoir fluids can enhance the predictability of asphaltene precipitation in various Enhanced Oil Recovery (EOR) scenarios, thus improving process efficiency. Consequently, evaluating the interfacial behavior of these systems is crucial for optimizing flow assurance. This study aimed to assess the interfacial activity of asphaltenes extracted from both light and heavy oils in Brazilian Pre-Salt reservoirs, considering factors such as solvent type, pressure, and brine composition. Initially, asphaltenes were extracted using n-heptane and characterized by Fourier Transform Infrared Spectroscopy (FTIR). Carboxylic, aromaticity, and hydrophobicity indices were calculated from the FTIR spectra. Subsequently, the interfacial tension of asphaltene solutions in the presence of heptol, with varying proportions of heptane and toluene, was evaluated based on the composition of the aqueous phase. This aqueous phase included a model brine (NaCl-1M) and an EOR fluid, desulphated water (DSW). The effects of pressure (ranging from 1000 to 5000 psi) were analyzed using Drop Shape Analyser (DSA) equipment designed for high pressure and high temperature (HPHT). The results indicated that asphaltenes extracted from light oil exhibited greater interfacial activity compared to those from heavy oil, with a correlation to the FTIR indices. Additionally, increasing the temperature led to a reduction in interfacial tension values, while the opposite effect was observed with increasing pressure. The findings suggest that asphaltenes from light oil are more susceptible to precipitation than those from heavy oil.

Keywords

Asphaltenes; EOR; Interfacial tension;

Introduction

The Brazilian Pre-Salt oil reservoirs exhibit a wide variety of oil compositions and properties, including differences in density and viscosity, which present significant challenges to production processes [1].

Enhanced Oil Recovery (EOR) methods are designed to increase the oil recovery factor and improve system efficiency. These methods often involve reducing capillary forces within the reservoir, such as interfacial tension, and altering rock wettability. In this context, asphaltene molecules are known to affect these interfacial properties because they adsorb at the oil-water-rock interfaces. Asphaltenes also pose challenges for flow assurance as they can precipitate within production lines, reducing the efficiency of oil extraction [2].

Asphaltenes are the heaviest and most polar components in crude oil, characterized by conjugated aromatic ring systems with aliphatic chains that contain heteroatoms. Their size, charge, and interfacial activity are influenced by the origin of the oil. Due to their amphiphilic structure, asphaltenes act as natural surfactants, which contributes to their high interfacial activity and impacts capillary forces within the oil reservoir [3].

The injection of smart water is a well-established and efficient EOR technique that utilizes customized water with a complex mix of salts to reduce capillary forces in the reservoir. Desulphated water (DSW) has demonstrated effective performance as an EOR fluid in some studies [4].

Understanding the interfacial behavior of asphaltenes is crucial for predicting their precipitation in various EOR scenarios and improving flow assurance during oil transport. It is known that changes in CO_2 concentration and pressure can promote asphaltene precipitation; however, this effect is dependent on asphaltene composition and gas ratios among other factors [5].

Therefore, the objective of this study was to evaluate the interfacial activity of asphaltenes extracted from light and heavy oils in Brazilian Pre-Salt reservoirs, focusing on the effects of solvent type, pressure, and brine composition. This preliminary study aims to enhance the predictability of asphaltene precipitation in EOR scenarios.

Methodology

Experimental Procedure

Petroleum: Crude oils from a Brazilian Pre-Salt reservoir, including both light and heavy grades, were characterized using a variety of analytical methods. These methods included SARA analysis (which measures saturates, aromatics, resins, and asphaltenes), total acid number (TAN), density, and viscosity. Subsequently, the asphaltene fractions were extracted from these crude oils for further investigation.

Preparation and characterization of brine solutions: A 1M NaCl solution was used as the model brine. Additionally, desulphated water (DSW), utilized as the EOR fluid, was prepared by dissolving a specific mixture of salts (as detailed in Table 1) in distilled water. The DSW was characterized by its pH and density. pH measurements were conducted using a pH analyzer model pH 300, while density measurements were performed with a Mettler Toledo DM040 densitometer and an Anton Paar HPHT densitometer. The density data obtained were subsequently used as input parameters for the ADVANCE software in the Drop Shape Analyser (DSA).

Table 1: Desulphated water - DSW composition

Salts	ppm
NaCl	30 348
$CaCl_2.6H_2O$	2 733
$MgCl_2.6H_2O$	14 220
KCl	953
$SrCl_2.6H_2O$	27
$NaHCO_3$	139
Na_2CO_3	55

Note: All materials were used without previous treatment.

Asphaltenes extraction and solution preparation: The asphaltene fraction was precipitated from light and heavy crude oils from a Brazilian Pre-Salt reservoir. Heptane was added to the crude oil at a ratio of 40:1. The mixture was then sonicated for 2 hours at 60°C and subsequently placed in a thermostatic stirring bath, where it was stirred at 220 rpm for 24 hours. Following this period, the mixture was centrifuged at 3300 rpm for 15 minutes. The solid asphaltene extract was washed multiple times with n-heptane until it displayed a shiny black color. The asphaltenes were then dried at room temperature.

Characterization of the asphaltenes was performed using Fourier Transform Infrared Spectroscopy (FTIR), from which carboxylic, aromaticity, and hydrophobicity indices were calculated. The asphaltenes were dissolved in either toluene or heptol (a mixture of heptane and toluene in varying proportions), and the resulting solutions were characterized by density measurements under both atmospheric and high pressure and high temperature (HPHT) conditions.

Interfacial tension measurements: Interfacial tension measurements between 1M NaCl or DSW solutions and asphaltene solutions were conducted using the pendant drop method. The measurements were taken with a Drop Shape Analyzer (HPHT DSA) from Krüss at temperatures of 60°C or 80°C and pressures ranging from atmospheric pressure to 5000 psi. The dynamic interfacial tensions were monitored over a period of 5400 seconds (1 hour and 30 minutes). Additionally, all experiments were performed in duplicate to ensure the reliability of the results.

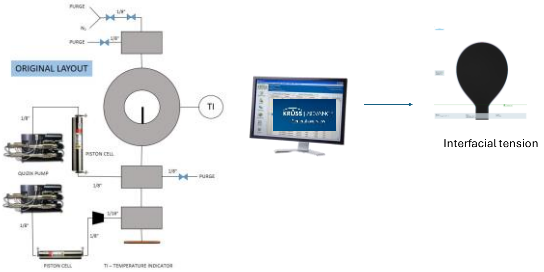

Figure 1: HPHT DSA layout for interfacial tension measurements

Results and Discussion

The properties of both crude oils used in this work are shown in tab. 1.

Table 2: Oil properties

Properties	Light Oil	Heavy Oil
°API	27.8	20.6
Density at 15 °C – g/cm³	0.888	0.930
Viscosity at 15 °C – mPa.s	62.5	2506.9
TAN - mg KOH/g	0.37	0.72
Saturates - % wt.	56.3	44.5
Aromatics - % wt.	20.5	19.7
Resins - % wt.	22.2	30.6
Asphaltenes wt. - %	0.5	5.8

Asphaltenes extracted from light and heavy reservoirs were designated as G and H, respectively. FTIR spectra (Fig. 2) indicated that both types of asphaltenes exhibit similar functional groups related to the aliphatic and aromatic fractions; however, they differ in the content of polar components. The G asphaltenes displayed intense bands corresponding to O-H (3400–3500 cm⁻¹), C=O (1600–1700 cm⁻¹), and C-O (1050 cm⁻¹). In contrast, the H asphaltenes exhibited low-intensity bands of amide (3060–3200 cm⁻¹) and the associated carbonyl group. These FTIR results suggest that the G asphaltenes contain a higher concentration of polar compounds, which may confer greater interfacial activity compared to the H asphaltenes. Indices of aromaticity, hydrophobicity, and the distribution of heteroatoms were found to be distinct according to the FTIR data [6].

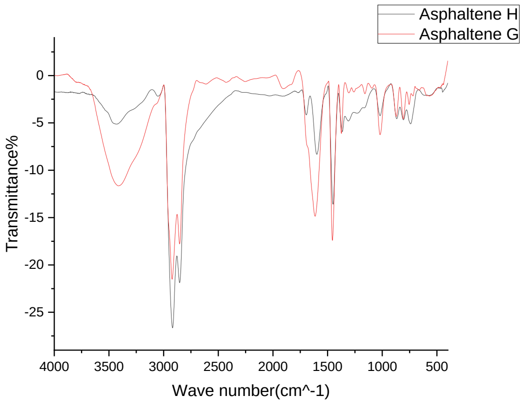

Figure 2. FTIR spectrum of asphaltenes extracted from the G and H fields

Figure 3 presents images of asphaltene solution droplets as a function of the solvent composition, specifically the heptane-toluene ratio in heptol. Variations in the droplet profile can be observed depending on the solvent, which correspondingly affects the interfacial tension values (Table 2). Asphaltenes are soluble in toluene but insoluble in heptane. An increase in the heptane content within the heptol fractions promoted the gradual precipitation of asphaltenes over time. The results indicate that as the proportion of n-heptane in the solvent increases, the migration of asphaltenes from the solution to the oil/water interface becomes more pronounced, leading to the bleaching of the solution. This bleaching is indicative of asphaltene precipitation.

Figure 3. Images of drops of G and H asphaltenes solution in heptol containing different proportions of heptane and toluene – Surrounding phase: NaCl 1M, T = 60°C and P atm

Table 3 presents the interfacial tension results for 1000 ppm solutions of G and H asphaltenes as a function of the heptane-toluene ratio in the heptol solution. No significant changes in equilibrium interfacial tension were observed in these scenarios, except for the system containing toluene with G asphaltenes. This observation suggests that 1000 ppm may exceed the critical aggregation concentration (CAC) of asphaltenes, a region where the oil-water interface is saturated with asphaltene molecules, leading to a stabilization of interfacial tension without sudden variations.

Table 3. Interfacial tension results in the equilibrium between asphaltene solution G or H dissolved in different proportions of heptol and 1M NaCl solution at 60 °C and P atm

Solvent	**IFT – G Asphaltene – mN/m**	**IFT – H Asphaltene – mN/m**
Toluene	10.79 ± 1.79	17.52 ± 0.94
Heptol – 25/75	16.27 ±0.16	17.39 ± 0.43
Heptol – 50/50	17.68 ± 5.16	16.96 ± 3.56
Heptol – 75/25	16.70 ± 0.55	15.11 ± 1.45

The interfacial behavior of asphaltenes under high pressure and high temperature conditions is crucial for predicting their precipitation in enhanced oil recovery (EOR) scenarios. For this reason, an EOR fluid, specifically DSW, was employed under these conditions. Figure 5 presents the effect of pressure on the interfacial tension of systems containing G asphaltenes and DSW. The results indicate that increasing pressure reduces the interfacial activity of G asphaltenes. In contrast, the interfacial properties of H asphaltenes remained unaffected by pressure (Table 3). The increase in pressure likely enhances the interaction between asphaltene molecules, which may lead to their rearrangement at the interface or to precipitation.

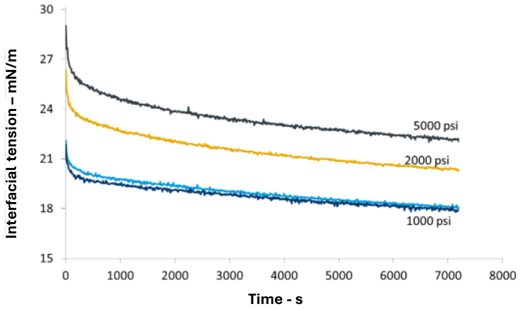

Figure 4. Effect of Pressure - Interfacial tension as a function of time between a solution of asphaltene G at 1000 ppm dissolved in toluene and the DSW brine at different pressures (1000 psi to 5000 psi) and T = 60 °C

A comparison between Table 3 and Table 4 reveals that DSW exhibited greater interfacial activity than the NaCl solution, as evidenced by the lower interfacial tension values for the EOR fluid. This increased activity can be attributed to the specific composition of DSW, which includes ions such as Mg^{2+} and Ca^{2+} that interact more effectively with asphaltenes. Additionally, the pH of DSW (pH 7.9) favors the migration of ionic molecules to the interface, whereas the NaCl solution has a pH of 7.0. The slightly basic environment of DSW enhances the interaction between carboxylic groups and divalent ions.

Table 4. Interfacial tension of asphaltene H solution in 1000 ppm toluene and DSW brine at T = 60 °C – Effect of pressure

Pressure – psi	IFT – mN/m
1000	22.24 ± 1.11
1500	21.91 ± 0.92
2000	22.03 ± 0.94
3000	22.31 ± 0.94
4000	22.52 ± 0.88

Figure 5 presents the interfacial tension results as a function of the type of asphaltene. It is evident that G asphaltenes exhibit greater interfacial activity than H asphaltenes, as they more effectively reduce interfacial tension. The interfacial activity of G and H asphaltenes is primarily determined by their chemical composition. As indicated by the FTIR results, G asphaltenes contain a higher concentration of polar groups, which gives them a greater affinity for the ions present in DSW compared to H asphaltenes. This affinity facilitates the migration of asphaltenes and ions to the interface, thereby promoting the reduction of interfacial tension. FTIR analysis suggests that the interactions between asphaltenes and ions are predominantly electrostatic, occurring through interactions between carboxylate and/or amine groups. Additionally, interactions can also occur between aromatic compounds and ions due to the resonance effect within the chemical structure of asphaltenes.

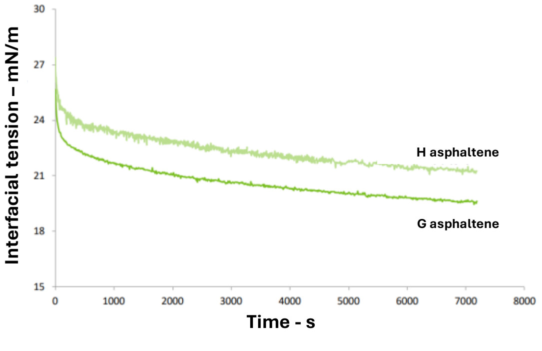

Figure 5. Effect of the type of asphaltene - Interfacial tension as a function of time between a 1000 ppm asphaltene solution from the G or H field in toluene and the DSW at 4000 psi and T = 60 °C

Despite its high interfacial activity, G asphaltene is more prone to precipitation during oil production than H asphaltene, largely due to its pressure-dependent interfacial behavior and the asphaltene content in the oil. According to SARA analysis, light oil contains a lower asphaltene content (0.5 wt%) compared to heavy oil (5.8 wt%). In light oil, the reduced presence of similar molecules, such as asphaltenes and resins, creates an unfavorable condition for stabilizing G asphaltene, thereby increasing the likelihood of precipitation.

Conclusions

The interfacial activity of asphaltenes extracted from light and heavy oils from Brazilian Pre-Salt reservoirs was evaluated through interfacial tension measurements under varying conditions of solvent composition, pressure, and brine composition. Asphaltenes from light oil exhibited a higher number and greater diversity of heteroatoms in their structure, resulting in greater interfacial activity compared to asphaltenes from heavy oil. An increase in pressure led to a reduction in interfacial activity for the asphaltenes from light oil, whereas the interfacial properties of asphaltenes from heavy oil remained unaffected by pressure. Additionally, the interfacial tension between the asphaltenes and DSW was lower than that with the NaCl solution. Under reservoir conditions during oil production, these findings suggest that asphaltenes from light oil are more prone to precipitation than those from heavy oil.

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Responsibility Notice

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