ORIGINAL PAPER

Interfacial properties of asphaltene–brine systems and analysis of adsorption kinetics: effects of ion and water injection for EOR

Agatha Densy S. Francisco[1] · David C. Santos[1,2] · Maria M. C. Santos[2] · Leandro A. Cavadas[1] · Ana Mehl[2] · Paulo Couto[1,3]

Abstract

Asphaltenes are the heaviest crude oil components and active agents on the oil–water interface. Understanding the key parameters related to interfaces phenomenon, such as the adsorption kinetics, allows for the more efficient development of new E&P technologies. Therefore, this work aimed to study fluid–fluid interactions between a Brazilian Pre-salt asphaltene and customized water for enhanced oil recovery (EOR) purposes. The crude oil was characterized by SARA analysis, the total number of acids (TAN), the total number of basic (TBN), and density. The asphaltenes were characterized by FTIR and particle size. The dynamic interfacial tension (IFT) measurements through the pendant drop method were performed at 60 °C using a Drop Shape Analyser (DSA). 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 of characterization showed many active compounds in the asphaltenes structure, such as OH, NH, C=O. The interfacial activity of the system indicated that customized brine is more efficient than NaCl or $MgCl_2$ solutions in reducing the IFT of asphaltene-brine systems confirming that these ions act together on the interface. Furthermore, the customized brine containing NaCl $CaCl_2$, $MgCl_2$, KCl, $SrCl_2$, $NaHCO_3$, and Na_2CO_3 (brine #2) presented higher diffusion coefficient patterns. This system contains high content of divalent ions, pH adjusted, and specific ions are the main ones responsible for the highest IFT reduction rate and diffusion coefficient.

✉ Agatha Densy S. Francisco
agathadensy@petroleo.ufrj.br

1   LRAP (Enhanced Oil Recovery, Lab), Federal University of Rio de Janeiro, Cidade Universitária, RJ 21945-970, Brazil

2   School of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, RJ 21945-970, Brazil

3   Civil Engineering Program, COPPE, Federal University of Rio de Janeiro, Cidade Universitária, RJ 21945-970, Brazil

Springer   ABEQ Associação Brasileira de Engenharia Química

Graphical abstract
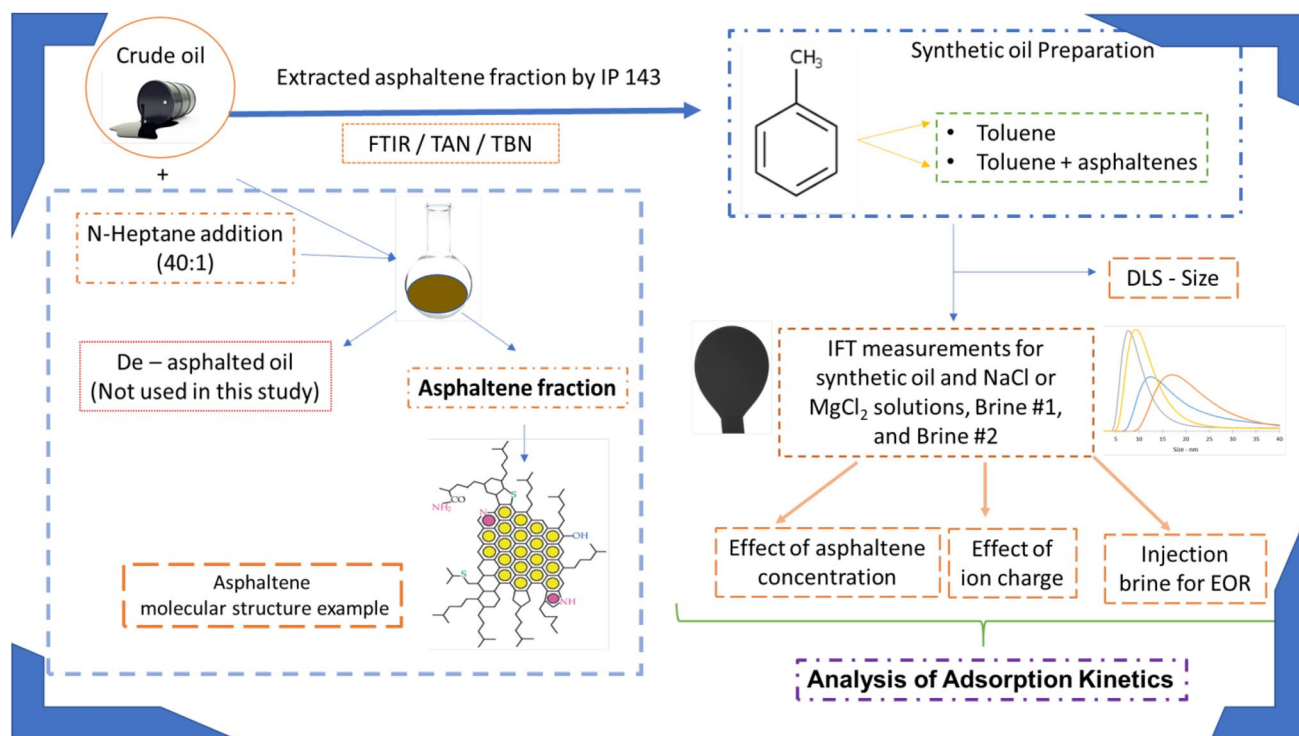
Introduction

Water flooding is a common and well-known technique for oil recovery, and seawater is usually used during this flooding due to its cost and availability. 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), such as the injection of smart water and low salinity water (LSW). This method uses customized water, which is brines composed of a complex mix of ions, to reduce the capillary forces in the reservoir and aims to increase the oil recovery factor by improving displacement efficiency (Sheng 2010). In this context, the presence of asphaltene in oils can significantly affect oil production, as they affect rock wettability, and cause emulsion stabilization and flow assurance issues during oil production. Therefore, asphaltene behavior is an important factor to be considered to choose the appropriate EOR strategy to reduce capillary forces during water flooding in the oil reservoir. Thus, understanding the asphaltene effect on the interface between oil/water is crucial to preparing efficient, customized water from seawater.

The main effects of custom water injection are wettability alteration, fine migration, pH increase, multi-ion exchange, and salting-in (Al-Shalabi and Sepehrnoori 2016). However, there is still no consensus on the real mechanism of interaction between the injection and reservoir fluids. For instance, some authors reported a significant improvement in the recovery factor after flooding, on the other hand, other studies revealed a negative influence on the recovery factor (Al-Shalabi and Sepehrnoori 2016; Webb et al. 2005; Zahid et al. 2012). For example, Webb et al. (2005) showed that 40% of original oil in place (OOIP) was recovered from chalk cores spontaneously using seawater compared to formation water, and the recovery increased from 40 to 60% with forced seawater injection. The authors proposed the evaluation of the mechanism of action from the change in the capillary pressure curves considering the rock wettability alteration as a key parameter (Webb et al. 2005). Their tests were performed using a reservoir temperature of 90 °C, and reservoir pressure (pore) of 275 bar with a confining pressure of 405 bar, and the core plug used showed the porosity was about 40% and the permeability near 2.3 mD. Furthermore, Zahid et al. (2012) performed core flooding experiments on outcrop chalk carbonate plugs to investigate the effect of low salinity water (LSW). The flooding tests were carried out with a sleeve pressure of 30 bars and a back pressure of 5 bars, also at 90 °C. They used the core

plug which the porosity was about 25% and the permeability near 0.973 mD. They showed that there was no additional recovery from the outcrop chalk plugs at different temperatures. Also, Zahid et al. (2012) pointed out that the LSW system presented acceptable performance only associated with pressure increasing due to fine migration (Zahid et al. 2012). Besides distinct mechanisms of action, the contrast in Webb's and Zahid's results could be due to petrophysics properties differences between core plugs but also, there were significative changes in the thermodynamic conditions. These scenarios become hard to obtain a consensus about the main mechanism of the LSW system. In both cases, they did not consider the fluid–fluid interactions in their systems.

Additionally, some studies pointed out that the type of interaction depends on the salts and oil composition (Sauerer et al. 2021). Therefore, understanding the key parameters of this interaction can improve the development of new technologies. For instance, the total acid number (TAN) and total basic number (TBN) are related to the rate of interfacial tension reduction (IFT) as a function of the brine pH. Another interesting point is the choice of the ionic compound, in which $MgCl_2$ or $MgSO_4$ solutions presented different interfacial behaviors (Behrang et al. 2021; Lashkarbolooki and Ayatollahi 2016). In this context, Drexler et al. (2020) reported the effect of CO_2 on the IFT between crude oil, or model oil, and formation brine, relating the presence of asphaltene and TAN number to interfacial activity.

Regarding oil composition, asphaltenes are considered the most complex components. They are 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. They are known as natural surfactants due to amphiphilic structure (Mahmoudvand et al. 2019). These characteristics favor high interfacial activity and may act as the capillary forces in the oil reservoir. The main capillary forces from the reservoir are related to rock wettability and interfacial tension. As a natural surfactant, asphaltenes interact with injection fluids decreasing the IFT and consequently alter the capillary forces of the reservoir. In addition, the asphaltenes are known to turn the rock to oil wet because of interactions between them. The adsorption/desorption of asphaltenes from the rock also could alter the capillary forces of the reservoir.

Considering the relation of asphaltenes to capillary forces, studying the interaction of asphaltenes with the injection water is crucial to optimize the EOR processes in the Brazilian pre-salt reservoirs, as well as to avoid flow assurance issues. For instance, several studies on the interfacial behavior of asphaltenes and resins in low and high salinity scenarios reported that the interfacial activity of these compounds depends on some characteristics of the oil, such as source, acidic number, and heavy fraction composition. Also, the pH of the aqueous phase presented significant importance (Alves et al. 2022; Hamidian et al. 2020; Lashkarbolooki et al. 2016b; Lashkarbolooki et al. 2014; Lashkarbolooki and Ayatollahi 2018a; Mahmoudvand et al. 2019). Lashkarbolooki et al. (2018a; b) observed that the IFT reduction depends on the partition of asphaltenes and resins. The authors reported a correlation between the content of nitrogen and oxygen, the brine pH, and the IFT trend. In this context, it was reported that, in acidic solutions, the higher the nitrogen concentration, the lower the IFT. However, for basic solutions, the higher the oxygen concentration, the lower the IFT (Lashkarbolooki and Ayatollahi 2018a). Hamidian et al. (2020) showed that resins have greater activity at the interface than asphaltenes. It means that the IFT of resins is lower than the IFT of asphaltenes due to their lower aromaticity and the greater number of heteroatoms in this specific case. In the same study, chloride salts were more active at the interface than sulfate (Hamidian et al. 2020). The activity and interfacial properties of asphaltenes and resins depend on their chemical structure, size, and electrical properties (Tajikmansori et al. 2023). It is unusual to associate the resins to flow assurance issues or rock wettability and because of these factors, the interfacial properties of asphaltenes are more studied than one.

Moreover, other physicochemical parameters have already been studied through dynamic IFT curves, such as IFT reduction rate, diffusion coefficient, and kinetic adsorption at the water/oil interface (Mohammadi et al. 2020; Zhang et al. 2018). These factors also are affected by the size of asphaltene particles, which depends on the solvent type, concentration, and temperature. The asphaltene's size tends to decrease with the reduction in the concentration of asphaltenes and the addition of a dispersant additive (Mansur et al. 2012). The asphaltene particle size is important, mainly in the migration of clusters to the interface, which may affect the diffusion of materials and their adsorption kinetics in the interface (Wang et al. 2021; Zhang et al. 2018). Furthermore, the achievement of consistent IFT equilibrium values at reservoir conditions is expensive and time-consuming (Zhang et al. 2018). Thus, a common way to determine the equilibrium IFT is by fitting the experimental IFT kinetics curves using adsorption models. Equilibrium IFT is obtained using models based on the Gibbs–Duhem diffusion equation for long-term adsorption (Zhang et al. 2018). Previous studies have shown that the asphaltene adsorption process presents three stages as a function of time (the so-called Regimes I, II, and II) (Mohammadi et al. 2020; Zhang et al. 2018). Hu et al. (2016) studied the interfacial properties of asphaltenes at the heptol−brine interface. The authors used a mixture of NaCl and $NaHCO_3$ to prepare the brine. As a result, higher temperatures and higher asphaltene concentration lowered

the IFT. In addition, the presence of silica particles contributed to the IFT decrease (Hu et al. 2016).

Mohammadi et al. (2020) investigated the adsorption kinetics of asphaltenes at the heptol – water interface to evaluate the effect of the solvent ratio between toluene and heptane. They concluded that the presence of n-heptane favors the asphaltene migration to the interface causing a reduction of the IFT values. They also observed that the higher the asphaltene concentration, the lower the IFT. Zhang et al. (2018) studied the kinetics of interfacial tension reduction. They demonstrated that in the short period (Regime I), this phenomenon is mainly driven by molecular diffusion of asphaltenes from the bulk to the oil-brine interface. This process has been modeled by the Ward–Tordai equation (Zhang et al. 2018; Mohammadi et al. 2020). In Regime II, the steric hindrance from the adsorbed asphaltenes at the oil/brine interface inhibited further adsorption. In Regime III, there is continuous adsorption of asphaltenes to the interface sublayer, and changes in their configuration due to adsorption might contribute to the dynamic IFT value (Zhang et al. 2018).

Since the interaction between asphaltene and brine is crucial for the success of customized water for EOR processes, this work aims to conduct an experimental study on the interactions of the asphaltenes-brine systems, demonstrating the impact of the charge of ions and the asphaltene concentration on the fluid–fluid interactions. This study also estimated the interfacial properties of asphaltenes and the analysis of the adsorption kinetics at the oil-brine interface by different adsorption models.

Methodology and materials

Materials

The crude oil sample used in this work was from a Brazilian ultra-deep Pre-salt reservoir. The asphaltene fraction used in this study was extracted from this crude oil. NaCl, KCl, $SrCl_2$, $CaCl_2$, $NaHCO_3$, Na_2SO_4, Na_2CO_3, and $MgCl_2$ salts were used to prepare the customized brines that were purchased from Sigma Aldrich and utilized without previous treatment. The oil was characterized by SARA analysis (percentage by mass of saturates, aromatics, resins, and asphaltenes), total acid number (TAN), and total basic number (TBN). Asphaltenes were characterized by infrared spectroscopy (FTIR), and also by TAN and TBN. The SARA analysis was performed by LRAP laboratory, whose experimental procedure was based on IP 143, which uses the precipitation of asphaltenes in n-heptane and a mixture of solvents with different polarity for the precipitation of saturates, aromatics, and resins. TAN and TBN are performed following the standard ASTM D664 e D2896, and these

properties quantify the range of polar groups in the crude oil (Xinheng and Tian 2011).

Preparation and characterization of brine solutions

The customized brine named brine #1 and brine #2 was prepared by dissolving a mix of salts in distilled water according to Table 1. NaCl at 58,440 ppm and $MgCl_2$ at 95,211 ppm solutions were used as brine models, and these concentrations correspond to 1 mol L^{-1}. All brine was prepared at ambient temperature conditions and degassed with the auxiliary vacuum pump. They were characterized by pH and density. The pH measurements were performed on a pH analyzer model pH 300 (Analyser) at ambient temperature. Density measurements were carried out in a densitometer Mettler Toledo model DM040 at 25 °C until 60 °C. The density results in the function of temperature for all systems are available at the support materials, this procedure was done to validate the density result.

Asphaltenes extraction

The asphaltene fraction was precipitated from the oil sample following the procedure described by Franco et al. (2013a, b) based on IP 143. Asphaltenes were extracted by diluting the Pre-salt oil in n-heptane with a ratio of 1:40. The mixture was sonicated (Hielscher, model UP205) for two hours 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 (Franco et al. 2013a, 2013b). The solid was dried at 60 °C and characterized by Fourier-transform infrared spectroscopy (FTIR). FTIR measurements were performed at the Instrumentation Laboratory of the Institute of Chemistry at UFRJ with the aid of the Nicolet 6700 equipment with a DTGS KBr detector. Asphaltenes were dissolved in toluene to obtain the solutions at 10,000 ppm and 1 000 ppm.

Table 1 Composition of customized water (Brine #1 and Brine #2)

Brine #1	ppm	Brine #2	ppm
NaCl	27,936	NaCl	30,348
$CaCl_2$	371	$CaCl_2$ $6H_2O$	2733
$MgCl_2$ $6H_2O$	1275	$MgCl_2$ $6H_2O$	14,220
KCl	748	KCl	953
Na_2SO_4	57	$SrCl_2$ $6H_2O$	27
		$NaHCO_3$	139
		Na_2CO_3	55

Preparation of solutions of asphaltenes in toluene

Asphaltenes were dissolved in toluene to obtain the solutions at 10,000 ppm and 1 000 ppm. Using an analytical balance, 0.100 and 1.00 g of asphaltenes were weighed in a becker. Then, toluene was added to the beaker and the system was taken to an oven at 60 °C to improve the solubilization step. The solution was transferred to a volumetric flask of 0.1 L. Additional toluene was used to adjust the solution concentration. These solutions were used in the density, interfacial tension, TAN, TBN, and particle size tests. The density tests were performed in the same conditions and equipment as the brine system.

Dynamic light scattering

The asphaltene particle size in the solutions was determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instrument, Germany). This technique is based on a measure of the particle diffusion rate due to Brownian motion and can measure particle diameters ranging from 1 to 1000 nm. Furthermore, to determine the asphaltene particle size, it is necessary to measure, a priori, the refractive index (RI) of asphaltene solutions. The experiments were carried out by analyzing light scattering at a wavelength of 410 nm using the Zetasizer Nano ZS. All asphaltene solutions were submitted to sonication for 30 min before DLS tests to break some agglomerates in these solutions. Each analysis was carried out in triplicate at 60 °C.

Interfacial tension measurements

The effect of asphaltenes concentration, ion charge, and customized water composition on the interfacial properties was evaluated by dynamic IFT tests using the pendant drop method. The IFT measurements between the aqueous phase (water, Brine #1, Brine #2, NaCl, and MgCl$_2$) and asphaltenes solutions were performed in a Drop Shape Analyzer equipment (DSA 100E–Kruss) at 60 °C and atmospheric pressure. Dynamic IFT measurements were performed in duplicate. Each experiment lasted 5400 s (1 h

30 min). Figure 1 shows the schematic experimental apparatus to measure IFT.

Analysis of adsorption kinetics

The experimental IFT of asphaltene solution at the initial stages of adsorption (Regime I) was described using the Ward–Tordai model (Eq. 1), which is only valid for the purely controlled diffusion process in the short term. This model assumes that the IFT values in the initial stages of adsorption change linearly with $t^{1/2}$. A model previously reported in the literature for long-term adsorption was employed to obtain the equilibrium IFT of asphaltene solutions. According to this model, the dynamic reduction of IFT over a long time in Regime III is proportional to the reciprocal square root of time ($1/t^{1/2}$) (Zhang et al. 2018), as described by Eq. 2.

$$\gamma_t = \gamma_0 2RT\sqrt{\frac{D}{\pi}}C_0\sqrt{t} \tag{1}$$

$$\gamma_{t\rightarrow\infty} = \gamma_{eq} + \frac{Rt\Gamma_{eq}^2}{C_0}\sqrt{\frac{7\pi}{12Dt}} \tag{2}$$

where γ_0 and γ_t are the interfacial tension at $t=0$ and an arbitrary time t, R is the gas constant with the value of 8.314 J/(mol·K), and T is the absolute temperature in Kelvin. D is the diffusion coefficient of asphaltenes moving to the interface, C_0 is the asphaltene bulk concentration, γ_{eq} is the IFT at equilibrium state, and Γ_{eq} is the equilibrium surface excess concentration.

Results and discussion

Preparation and characterization of brine solutions

Table 2 shows the pH and density of brine solutions. The density of all solutions was measured, a priori, as a function of temperature using Mettler Toledo DM-40 densimeter at

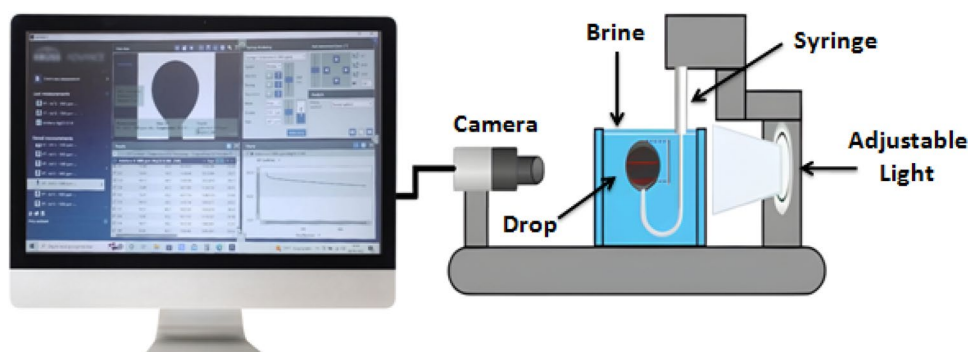**Fig. 1** Schematic of the pendant drop method used in this work

Table 2 pH and density, ρ, of brine solutions

Brine	pH	ρ/g·cm^{-3} (60 °C)
NaCl	6.89 ± 0.39	1.0186 ± 0.0005
MgCl$_2$	5.58 ± 0.21	1.0679 ± 0.0005
Brine #1	6.42 ± 0.02	1.0199 ± 0.0005
Brine #2	7.75 ± 0.05	1.1061 ± 0.0005

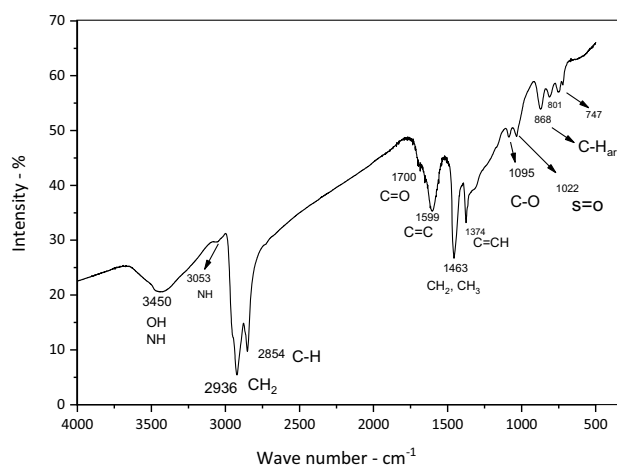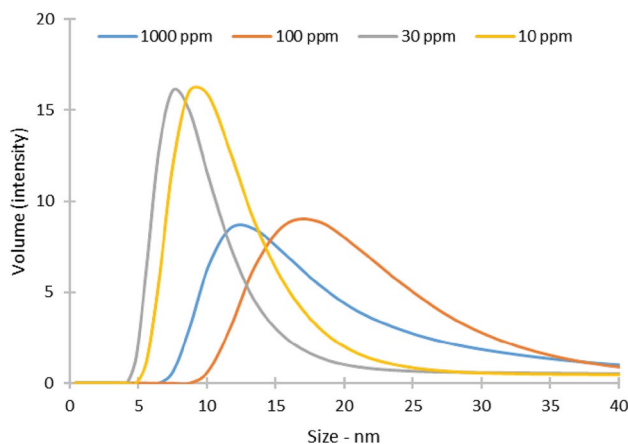**Table 3** SARA analysis composition, TAN, and TBN for the Brazilian pre-salt oil

Crude oil properties	Concentration
Saturated	32% wt
Aromatics	31% wt
Resin	24% wt
Asphaltenes	13% wt
TAN	0.33 mg KOH/g
TBN	5.88 mg KOH/g

Fig. 2 Asphaltene spectrum by FTIR

Fig. 3 Particle size distribution of asphaltenes in the function of concentration at 60 °C

atmospheric pressure. The densities were used as input data to calculate interfacial tension using ADVANCE software provided by Kruss. According to the Young–Laplace equation, the IFT depends on the $\Delta\rho$ (density difference).

Crude oil and asphaltene characterization

Table 3 presents the results of crude oil properties such as the oil's SARA analysis composition, TAN, and TBN. If the oil's TAN is higher than 0.50 mg KOH/g, it is classified as acidic oil (Behrang et al. 2021; Xinheng and Tian 2011; Thomas 2004). Thus, the oil used in this work is classified as non-acid. Besides, TBN showed the presence of significative basic compounds in its. These polar compounds can be active depending on the pH media during IFT tests. TAN and TBN are related to all acidic and basic compounds present in crude oil, including asphaltenes, resins, naphthenic acids, and/or other compounds. However, as the asphaltenes are considered natural surfactants, TAN and TBN values are closely related to their composition. The TAN and TBN of the asphaltene solution are shown in the supplementary materials.

Figure 2 shows the FTIR spectrum of asphaltene, where it is possible to identify the main functional groups presented in the asphaltene fraction. Their diversity confirms the complexity of the asphaltene class. It corroborates with the TAN and TBN results since these tests suggested the presence of acidic and basic compounds. Furthermore, the FTIR confirmed the presence of these functional groups of C=O, OH, NH$_2$, and others in the asphaltene molecular structure. The density of asphaltenes solutions at 60 °C is 0.829 g/cm^3 and 0.831 g/cm^3 to 1000 ppm and 10,000 ppm, respectively.

Dynamic light scattering (DLS) measurements

Figure 3 shows the results of the asphaltene particle size analyses in the function of the concentration. According to Mullins et al. (2011, 2012), the asphaltene molecule has an average size of 1.5 nm (Mullins 2011; Mullins et al. 2012). However, in the present work, the asphaltene's size was larger than one, suggesting a formation of clusters.

Figure 3 shows that the higher the asphaltene concentration, the higher the particle size, as seen and discussed by Mansur and other authors (Mansur et al. 2012; Wang et al. 2021; Zhang et al. 2018). It is possible to note a large size distribution in these curves. This behavior might be related to molecular interactions, where the lateral hydrophobic chains of asphaltenes interact through van der Waals forces, therefore forming cluster aggregates of different sizes.
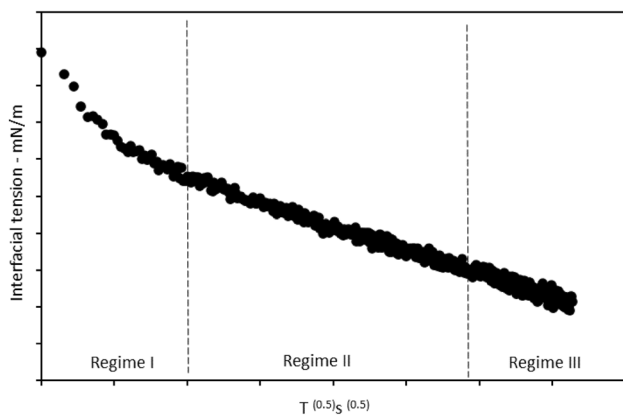
Fig. 4 The schematic diagram for the typical experimental IFT curve vs. square root of time obtained from our data—1000 ppm Asphaltene–NaCl system, at 60 °C—P atm. This curve was smoothed

Fig. 5 Interfacial tension as a function of time between NaCl solution and asphaltenes solutions at 1000 ppm and 10,000 ppm. T = 60 °C and P = 14 psi

Dynamic interfacial tension

Figure 4 shows a schematic diagram of a typical experimental IFT curve from our data as a function of the time obtained in this study. As one can see, the IFT curves can be divided into three different regimes, denoted as Regime I, Regime II, and Regime III, as suggested by Zhang et al. (2018). Regime I is related to the asphaltene adsorption process only due to diffusion. In this Regime, the experimental IFT data at the initial stages of adsorption changes linearly with $T^{0.5}$, which can be described using the Ward–Tordai model (Eq. 1). Therefore, at the start of IFT measurements, the adsorption process is controlled by asphaltene diffusion from bulk into the oil/brine interface. Regime II is a non-diffusion-controlled regime, an intermediate transition between Regime I and Regime III. During this transition regime, the adsorbed asphaltenes could provide steric hindrance for the interfacial diffusion of additional asphaltenes, i.e., the diffusion of additional bulk asphaltene to the interface would be affected by their interactions with the interfacial asphaltenes already adsorbed in the Regime I. Therefore, decreasing the rate of reduction of IFT values (as shown in Fig. 4). Regime III is a long-term stage that gradually approaches the equilibrium stage. In this Regime, the adsorption of asphaltenes occurs at the interface sublayer. Thus, molecular arrangement and reconfiguration of adsorbed asphaltenes at the interface might also contribute to the long-term decrease of dynamic IFT. The magnitude of these phenomena depends on the type of brine since each kind of ion presents specific interaction with asphaltenes and their concentration.

Effect of asphaltene concentration on IFT data

Figure 5 shows the dynamic interfacial tension as a function of asphaltene concentration. It is possible to observe that the
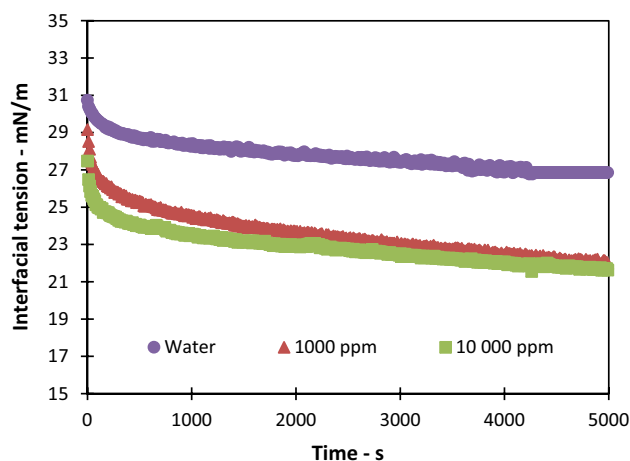
system without asphaltenes, that is, the water-toluene system showed the highest IFT. On the other hand, the presence of asphaltene increases the polarity of the oil phase, allowing interactions between phases and reducing the interfacial tension. In this case, as the asphaltene concentration increases, the IFT value decreases. It is due to the migration of asphaltenes from the bulk to the interface. However, regardless of asphaltene concentration, both systems presented similar IFT equilibrium suggesting that both systems can saturate the interface. Asphaltene adsorbs onto the oil–water interface due to its amphiphilic structure. However, as seen in the FTIR results, the presence of oxygen, nitrogenous, and sulfur atoms in its structure allows intermolecular interactions such as the electrostatics, polar, and hydrogen bonds with aqueous media (Mohammadi et al. 2020; Zhang et al. 2018).

The experimental IFT curves were modeled using diffusion Eqs. 1 and 2 to obtain the equilibrium IFT and the interfacial diffusion coefficients (Table 4), respectively. It is possible to note that IFT decreases sharply during the first minutes of measurement (Regime I), and then the reduction decreases with time (Regime III). Regime II does not show a linear correlation between IFT and time. The adsorption model of Ward and Tordai also provides a theoretical scheme regarding the energy barrier of asphaltene adsorption at the interface in Regime I. This model proposes that an area ΔA must be created for a new interface material to diffuse and move onto the interface. Based on Ward and Tordai model, Zhang et al. (2018) presented the following expression to calculate the adsorption rate at the interface:

$$ln(d\Pi/dt) = ln(b) - \frac{\Pi \Delta A}{k_B T} \qquad (3)$$

Table 4 Results of adsorption kinetics parameters obtained from IFT measurements of NaCl solutions at 1000 and 10,000 ppm of asphaltene
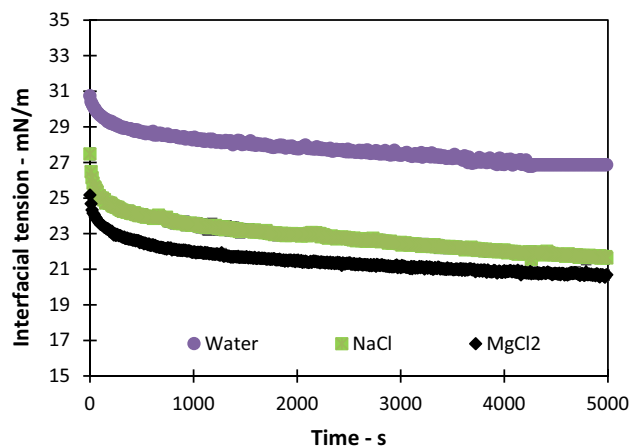
Concentration–ppm	D (m²/s)	ΔA (nm)	IFT_{final} (mN/m)	IFT_{eq} (mN/m)	Δ_{IFT} (mN/m)
1000	$3.56 \cdot 10^{-15}$	6.77	21.92	17.96	3.96
10,000	$3.88 \cdot 10^{-17}$	6.63	21.50	18.74	2.76
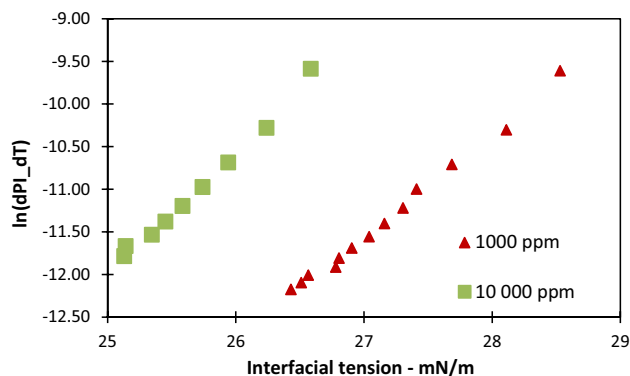
Fig. 6 Short-term IFT in Regime I replotted by ln(dPI_dT) vs. Interfacial tension using Eq. 1. Asphaltene solutions at 1000 ppm and 10,000 ppm–T = 60 °C and P = 14 psi

Fig. 7 Interfacial tension as a function of time between Water, NaCl and MgCl₂ solutions and asphaltenes at 10,000 ppm. T = 60 °C and P = 14 psi

where b is a constant related to the bulk concentration, Π is the surface pressure ($\Pi = \gamma_0 - \gamma_t$), ΔA is the area for asphaltenes to move the interface, k_B is the Boltzmann constant, and T is the temperature.

According to the Ward–Tordai adsorption model, data related to the Regime I can be well-fitted with Eq. 3. Figure 6 shows the IFT data in Regime I by showing ln(dΠ/dt) vs. IFT, which was then fitted using Eq. 3 for two different asphaltene concentrations. In Fig. 6, the fitting lines presented almost the same slope, which indicates that the area created at the interface during Regime I is almost constant regardless of asphaltene concentration. Table 4 shows the diffusion coefficient of asphaltenes moving to the interface, the area occupied for asphaltenes molecules, ΔA, the IFT at the end of measurements, and the equilibrium IFT calculated by Eq. 2. The average value of the standard deviation of the measurements was around 0.5 mN/m and is not shown in the graph due to the scale and the number of points in the curve.

As shown in Table 4, the asphaltene solution 1000 ppm showed a diffusion coefficient two orders of magnitude higher than the solution 10,000 ppm. As shown by the DLS analysis presented in this study, asphaltenes could be in the form of clusters and aggregates in solutions. Thus, the higher the asphaltene concentration, the greater the aggregate. Therefore, its ability to move from bulk to interface decreases with increasing aggregate size. This premise is in full agreement with the calculated diffusion coefficients by Ward–the Tordai adsorption model (Eq. 1). On the other

hand, the equilibrium IFT and the area for asphaltenes to move in does not change significantly.

The 10,000 ppm asphaltene solution presented the lowest diffusion coefficient. From the next section onwards, the discussion of the evaluation of the ion charge and the composition of the customized water will be made only in this scenario because these effects are better observed in solutions with a high concentration of asphaltene.

Ions and ionic strength effects

Figure 7 shows the dynamic IFT between water, NaCl, MgCl₂, and asphaltene solutions. It is possible to note that the dynamic IFT values decreased significantly in the presence of brine when compared with distilled water. As discussed in Section "Effect of asphaltene concentration on IFT data", the increase of ionic strength and the polarity of the aqueous phase (caused by salts) favored the migration of asphaltenes to the interface due to the amphiphilic nature of asphaltenes. Also, as seen in the FTIR results (Fig. 2), the asphaltene molecule presented basic and acid functional groups, which also favor its migration to the interface. As a result, there were significant interactions between ions with surface-active components at the interface. In the dynamic IFT curves, the MgCl₂ solution showed the lowest IFT during all tests containing asphaltenes. It indicates that the interactions between asphaltene-Mg²⁺ are stronger

than with asphaltene-Na$^+$ ions, possibly due to the increasing ionic strength and higher electrostatic potential of the divalent ion. However, this is not always observed. In the n-alkanes system, monovalent salt (NaCl) has the highest effect on IFT when compared with divalent salts (MgCl$_2$ and CaCl$_2$), for example (Kakati and Sangwai 2017). In this case, it is related to Gibb's adsorption isotherm due to the surface excess concentration (or superficial density) of a species. Since the interaction of cations with the hydrocarbon phase is a non-covalent type of interaction, an excess of positive charge can drive these ions away from the interface, and as Mg^{2+} ions have more charge than Na$^+$, its presence in the interface becomes less attractive (Kakati and Sangwai 2017). On the other hand, systems containing crude oil, or asphaltenes and resins showed otherwise behavior, and the preference for monovalent or divalent ions is mainly due to TAN or TBN, the functional groups, and heteroatoms distributed in their structures. (Lashkarbolooki et al. 2016b; Lashkarbolooki and Ayatollahi 2016, 2018b).

Some features of the asphaltene molecule can also be considered, such as the heteroatoms and the acid or basic compounds, as discussed in Section "Crude oil and asphaltene characterization". According to Pejmannia et al. (2022), the main factor in reducing IFT is the competition between the repulsive forces between active agent molecules at the interface and the adsorption of ions into the active agents' structure. Repulsive forces can be generated due to the alignment of the polar asphaltene compounds on the interface. However, they might be smoothed by the adsorption of ions at the interface, stabilizing the surface charge (Pejmannia et al. 2022). In this context, dominant interactions are ion–dipole which are the strongest for MgCl$_2$. Therefore, the stronger interaction between asphaltenes and divalent ions at the interface can be considered one of the driving factors for the more accentuated reduction of IFT values. Another phenomenon that contributes to understanding these results is the salting-in effect, in which salts accelerate the diffusion of surface-active components from the bulk solution to the interface at low concentration. Divalent ions have higher hydration energy and stabilization power than monovalent ones. It favors the salting-in effect considering the direct Hofmeiters series, usually used for proteins (Santos et al. 2021).

Table 5 shows the IFT at equilibrium and diffusion coefficient between asphaltene, NaCl, and MgCl$_2$ solutions. Divalent ions have higher surface activity than the monovalent system (Hamidian et al. 2020; Lashkarbolooki et al. 2016b; Lashkarbolooki and Ayatollahi 2018a, b; Lashkarbolooki et al. 2014). The results showed that the diffusion coefficient of the NaCl solution was higher than the MgCl$_2$ solution; in other words, the asphaltenes migrated to the interface faster in the presence of sodium ions, despite the Mg^{2+} ions presenting higher electrical potential. This behavior can

Table 5 Interfacial tension at equilibrium condition of oil/brine systems and asphaltene (10,000 ppm) interfacial diffusion coefficient obtained by modeling

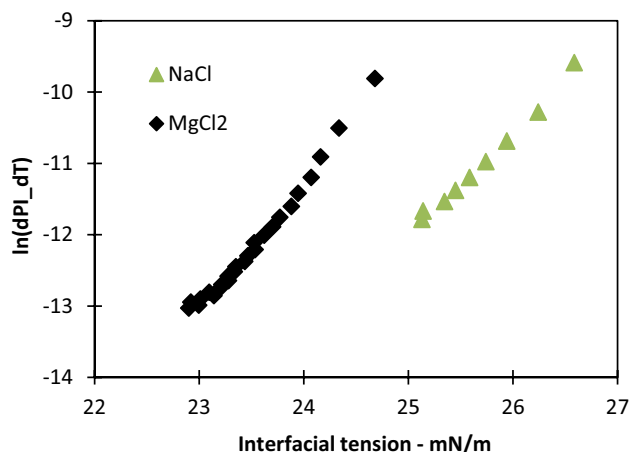| Salt solutions	IFT (mN/m)	D (m^2/s)
NaCl	19.89	$3.88 \cdot 10^{-17}$
MgCl$_2$	19.11	$1.28 \cdot 10^{-17}$

Fig. 8 Short-term IFT in Regime I replotted by ln(dPI_dT) vs. Interfacial tension using Eq. 1—NaCl or MgCl$_2$ solutions for 10,000 ppm asphaltene at 60 °C and P = 14 psi

be explained by the analysis of the pH of the brines (see Table 2). In an acidic medium, there is no ionization of the acid components presented in the asphaltene molecule (see Fig. 3). On the other hand, in these scenarios, there may be protonation of the basic components (R–NH$_3^+$) quantified by TBN, which can make the interface more positive and less attractive to Mg^{2+} ions. The consequence was an extension of Regime I for the MgCl$_2$ solution compared to NaCl as can be seen in Fig. 8.

Water injection for EOR effect

Brine #1 shows a typical composition of seawater supplied by the oil company. On the other hand, brine #2 (desulphated water) was customized to improve some interfacial properties. The desulfation process is commonly employed for water flooding in oil production operations to avoid operational scale and flow assurance problems. Thus, using a desulphated fluid is a form of customizing the injection fluid for EOR purposes. Furthermore, the customized water (brine #2) was doped with divalent ions due to their better performance on the reduction of IFT, as presented in Section "Ions and ionic strength effects". The concentrations of CaCl$_2$ and MgCl$_2$ were increased and added the SrCl$_2$ to widen the potential electrical. The strontium ions can reduce

the oil/brine interfacial tension and have performed well in some works in the literature (Santos et al. 2021). As the crude oil used in this work was obtained from the carbonated reservoir, which presents rock dissolution issues, Na_2CO_3 and $NaHCO_3$ salts were added to the composition of brine #2 to approach the field scenario.

Figure 9 shows the dynamic IFT between water, brine #1 and #2 solutions, and asphaltene solutions at 60 °C. Customized water showed lower IFT than distilled water. As previously discussed, the polarity of brine favors the migration of asphaltenes to the interface. Another interesting behavior observed was that desulphated brine (brine #2) showed higher interfacial activity than sulfated one (brine #1).

The main differences between this brine are the presence of sulfate, the content of divalent ions, carbonated salts, and the pH (see Table 2). It is important to note that the pH of the brine may influence the migration of asphaltene to the interface due to the ionization of acidic or basic compounds. The increase in pH promotes the interfacial activity of natural surfactants due to the ionization of active agents. Its behavior promotes the migration of asphaltenes to the interface, where they interact with divalent ions, thus reducing the IFT of the system. On the other hand, the interaction between sulfate ions was not favorable. It suggests a repulsion between sulfate ions and negative groups of asphaltene molecules at the interface. Some studies in the literature showed that sulfate ions do not contribute to the reduction of IFT, mainly due to electrostatic repulsion and due to the absence of positive compounds both in the oil and in the asphaltenes (Karimi et al. 2016; Lashkarbolooki and Ayatollahi 2016). Even though the capability of using sulfate anion as a wettability modifier is established in the EOR process, there are few explanations for fluid–fluid interactions (Deng et al. 2020; Standnes and Austad 2000). According to Lashkarbolooki et al. (2016b), ionic solutions formed from Na_2SO_4 and Mg_2SO_4 show similar behavior on IFT values
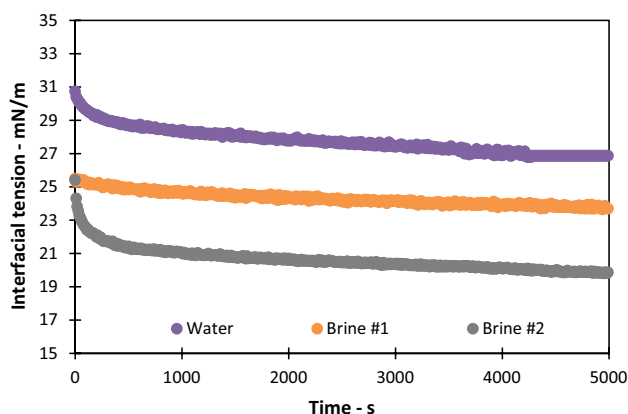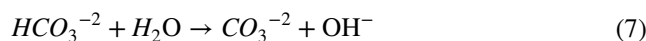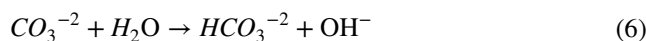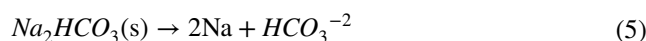
in systems similar to those evaluated in this study, regardless of salt concentrations. The authors related their results to the compressing of asphaltene's electrical double layer due to cations, which promotes the reduction of the intermolecular distance at the interface due to the weak electrostatic repulsion (Lashkarbolooki and Ayatollahi 2016). Mahmoudvand et al (2019) reported that IFT in crude oil and asphaltenes systems is not affected by Na_2SO_4 solutions. This means that there are not enough positive polar head groups in the oil to interact with anions adsorbed at the aqueous phase interface. On the other hand, Na_2SO_4 showed activity on the interface in a system containing maltene components (Mahmoudvand et al. 2019). They proposed the presence of an amine group that may interact with sulfate ions. In our work, among the heteroatoms present in the oil phase, there are nitrogen groups, which are basic polar groups. These groups can induce a positive charge because they can accept protons. However, TBN results, present in the support material, showed a negligible amount of nitrogen in asphaltene compositions. In other words, basic polar groups cannot be the dominant surface-active components in the oil.

Furthermore, brine #2 does not have a sulfate ion in its composition. In addition, other anions, such as sodium carbonate, might not have a negative effect on the migration of asphaltenes to the interface. In fact, the literature has already pointed out the positive effects of carbonate ions dissolved in the brine in reducing the IFT. The presence of $NaHCO_3$ and Na_2CO_3 turns the brine alkaline, which favors the formation of surfactants in situ (asphaltenes and resins) promoting their migration to the interface. Honarvar et al. (2020) studied the effect of alkalinity in LSW systems to reduce interfacial tension. Their system was capable of significantly reducing the IFT from 13.2 mN/m to 1.1 mN/m in the LSW approach by adding basic groups (HONARVAR et al. 2020).

Based on Honarvar et al. (2020), we proposed to our case that there was a hydration reaction of $NaCO_3$ and $NaHCO_3$ salts. Therefore, a buffer solution was formed to maintain a slightly alkaline aqueous medium (Eqs. 4, 5, 6 and 7). Such behavior allows the ionization of acid compounds in asphaltenes and favors their migration to the interface.

$$Na_2CO_3(s) \rightarrow 2Na + CO_3^{-2} \qquad (4)$$

$$Na_2HCO_3(s) \rightarrow 2Na + HCO_3^{-2} \qquad (5)$$

$$CO_3^{-2} + H_2O \rightarrow HCO_3^{-2} + OH^- \qquad (6)$$

$$HCO_3^{-2} + H_2O \rightarrow CO_3^{-2} + OH^- \qquad (7)$$

In addition, brine #2 has a higher content of Mg^{2+} and Ca^{2+}, as well as higher pH than brine #1. Because of all these factors, the IFT is lower in brine #2 than in brine #1.
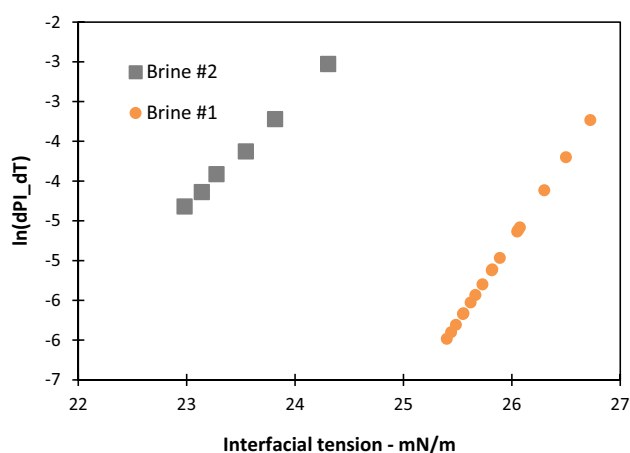

Fig. 9 Interfacial tension as a function of time between injection brine for EOR and asphaltenes solution 10,000 ppm. T = 60 °C and Pressure = 14.7 psi (left)

Fig. 10 IFT in Regime I vs. $ln(d\Pi/dT)$ for 10,000 ppm. Asphaltene solutions at 60 °C (right)

Table 6 Interfacial tension at equilibrium condition of oil/brine systems and asphaltene (10,000 ppm) interfacial diffusion coefficient

EOR system	IFT (mN/M)	D (m^2/s)
Brine #1	23.07	$1.5 \cdot 10^{-17}$
Brine #2	19.05	$1.0 \cdot 10^{-16}$

Figure 10 also 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. On the other hand, 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 interfaces than brine #1. Although asphaltenes occupy the same area on the interface, it is believed that the type of interaction and the arrangement are different. Brine #2 promoted a stronger interaction between the oil–water phase than brine #1 considering the IFT values. The IFT average value of the standard deviation of the measurements was around 0.5 mN/m and is not shown in the graph due to the scale and the number of points in the curve. Table 6 shows the interfacial tension at equilibrium conditions and the diffusion coefficient of oil/brine systems.

Conclusions

The interfacial properties of asphaltene–brine systems were evaluated through dynamic interfacial tension measurements. In this context, the analysis of adsorption kinetics considering the effects of asphaltene concentration, the ion charge, and the customized water with a high potential for application for EOR was studied using models based on Ward–Tordai and Gibbs–Duhem diffusion equations. Also, the equilibrium IFT values were determined by fitting the experimental data using the long-term adsorption equation. The results showed that customized water systems are more efficient than NaCl or MgCl$_2$ solutions in reducing the IFT of asphaltene-brine systems. This study also showed that the asphaltene adsorption kinetics at the oil-brine interface depended on the customized brine composition. Each Regime is related to different patterns of asphaltene migration into the interface. Also, the brine composition controlled the IFT reduction rate and diffusion coefficient. The presence of divalent ions and, the absence of sulfate ions were favorable to reducing the IFT of the evaluated systems. This result pointed out that the optimal condition for water injection can be achieved by the brine composition assessment.

Author contributions All authors contributed to the study's conception and design. Material preparation, data collection, and analysis were performed by ADSF, DCS, MMCS, LAC, AM, and PC. The first draft of the manuscript was written by ADS. Francisco and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data availability Not applicable.

Code availability Not applicable.

Declarations

References

Al-Shalabi EW, Sepehrnoori K (2016) A comprehensive review of low salinity/engineered water injections and their applications in sandstone and carbonate rocks. J Petrol Sci Eng 139:137–161

Alves CA et al (2022) Influence of asphaltenes and resins on water/model oil interfacial tension and emulsion behavior: comparison of extracted fractions from crude oils with different asphaltene stability. J Pet Sci Eng 208:2021

Behrang M, Hosseini S, Akhlaghi N (2021) Effect of pH on interfacial tension reduction of oil (heavy acidic crude oil, resinous and asphaltenic synthetic oil)/low salinity solution prepared by chloride-based salts. J Pet Sci Eng 205:108840

Deng X et al (2020) A review on wettability alteration in carbonate rocks: wettability modifiers. Energy Fuels 34:31–54

Drexler S, Correia EL, Jerdy AC, Cavadas LA, Couto P (2020) Effect of CO_2 on the dynamic and equilibrium interfacial tension between crude oil and formation brine for a deepwater Pre-salt field. J Petrol Sci Eng 190:107095. https://doi.org/10.1016/j.petrol.2020.107095

Franco C et al (2013a) Kinetic and thermodynamic equilibrium of asphaltenes sorption onto nanoparticles of nickel oxide supported on nanoparticulated alumina. Fuel 105:408–414

Franco CA et al (2013b) Nanoparticles for inhibition of asphaltenes damage: adsorption study and displacement test on porous media. Energy Fuels 27(6):2899–2907

Hamidian R, Lashkarbolooki M, Amani H (2020) Evaluation of surface activity of asphaltene and resin fractions of crude oil in the presence of different electrolytes through dynamic interfacial tension measurement. J Mol Liq 300:112297

Honarvar B et al (2020) Favorable attributes of low salinity water aided alkaline on crude oil-brine-carbonate rock system. Colloids Surf a: Physicochem Eng Aspects. https://doi.org/10.1016/j.colsurfa.2019.124144

Hu C et al (2016) Interfacial properties of asphaltenes at the heptol-brine interface. Energy Fuels 30(1):80–87

Kakati A, Sangwai JS (2017) Effect of monovalent and divalent salts on the interfacial tension of pure hydrocarbon-brine systems relevant for low salinity water flooding. J Petrol Sci Eng 157:1106–1114

Karimi M et al (2016) Impact of sulfate ions on wettability alteration of oil-wet calcite in the absence and presence of cationic surfactant. Energy Fuels 30(2):819–829

Lashkarbolooki M, Ayatollahi S (2016) Effect of asphaltene and resin on interfacial tension of acidic crude oil/sulfate aqueous solution: experimental study. Fluid Phase Equilib 414:149–155

Lashkarbolooki M, Ayatollahi S (2018a) The effects of pH, acidity, asphaltene and resin fraction on crude oil/water interfacial tension. J Petrol Sci Eng 162:341–347

Lashkarbolooki M, Ayatollahi S (2018b) Effects of asphaltene, resin and crude oil type on the interfacial tension of crude oil/brine solution. Fuel 223:261–267

Lashkarbolooki M, Ayatollahi S, Riazi M (2014) Effect of salinity, resin, and asphaltene on the surface properties of acidic crude oil/smart water/rock system. Energy Fuels 28(11):6820–6829

Lashkarbolooki M et al (2016a) Low salinity injection into asphaltenic-carbonate oil reservoir, mechanistic study. J Mol Liq 216:377–386

Lashkarbolooki M et al (2016b) Synergy effects of ions, resin, and asphaltene on interfacial tension of acidic crude oil and low-high salinity brines. Fuel 165:75–85

Mahmoudvand M, Javadi A, Pourafshary P (2019) Brine ions impacts on water-oil dynamic interfacial properties considering asphaltene and maltene constituents. Colloids Surf a: Physicochem Eng Aspects 579:123665

Mansur CR, de Melo AR, Lucas EF (2012) Determination of asphaltene particle size: influence of flocculant, additive, and temperature. Energy Fuels 26(8):4988–4994

Mohammadi M, Zirrahi M, Hassanzadeh H (2020) Adsorption kinetics of asphaltenes at the heptol-water interface. Energy Fuels 34(3):3144–3152

Mullins OC (2011) The asphaltenes. Annu Rev Anal Chem 4(1):393–418

Mullins OC et al (2012) Advances in asphaltene science and the Yen-Mullins model. Energy Fuels 26(7):3986–4003

Pejmannia S, Hosseini S, Akhlaghi N (2022) Effect of resin as a surface active agent (natural surfactant) on the interfacial tension of high and low salinity solutions prepared by chloride-based salts. J Pet Sci Eng 211(September 2021):110082

Santos D et al (2021) Strontium-based low salinity water as an IOR/EOR method: oil-brine interaction. J Pet Sci Eng 202:108549

Sauerer B et al (2021) Effect of formation water salinity on interfacial tension of reservoir fluids. J Pet Sci Eng 204:108700

Sheng J (2010) Modern chemical enhanced oil recovery: theory and practice. Gulf Professional Publishing

Standnes DC, Austad T (2000) Wettability alteration in chalk: 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. J Pet Sci Eng 28(3):123–143

Tajikmansori A et al (2023) New insights into effect of the electrostatic properties on the interfacial behavior of asphaltene and resin: an experimental study of molecular structure. J Mol Liq 377:121526

Thomas JE (2004) Fundamentos de Engenharia de Petróleo. 2ª edição. Editora Interciência

Wang Y, Cheng T, Zhou G (2021) Study on the mechanism of asphaltenes reducing oil-water interfacial tension. Chem Res Chinese Univ 38(2):616

Webb KJ, Black CJJ, Tjetland G (2005) A Laboratory study investigating methods for improving oil recovery in carbonates. In: Paper presented at the International Petroleum Technology Conference, Doha, Qatar, November 2005. https://doi.org/10.2523/IPTC-10506-MS

Xin-heng C, Tian SB (2011) Review and comprehensive analysis of composition and origin of high acidity crude oils. Chin Pet Process Petrochem Technol 13:6–15

Zahid A, Shapiro A, Skauge A (2012) Experimental studies of low salinity water flooding in carbonate reservoirs: a new promising approach. All Days. Anais. SPE, 16 Apr

Zhang S et al (2018) Adsorption kinetics of asphaltenes at oil/water interface: effects of concentration and temperature. Fuel 212:387–394