



EVALUATION OF INTERFACIAL PROPERTIES FOR BRINE/OIL SYSTEMS

Josefa M. S. Gonçalves¹, Denisson Santos¹, Fabiane Serpa¹, Elton Franceschi¹, Claudio Dariva¹, Gustavo R. Borges¹

¹ Center for Study on Colloidal Systems (NUESC), Institute of Technology and Research (ITP), Tiradentes University, 300, Murilo Dantas Av., Aracaju-SE, Brazil, denisson_santos@itp.org.br*

Abstract

Technological investment is fundamental for economic development, mainly in the oil and gas industry. Thus, enhanced oil recovery methods are used in the search for greater efficiency in oil production. In this way, different fluids are used to increase the oil recovery factor. The oil recovery through low salinity water injection has been studied as one of those improved methods. In this context, the present work aims to evaluate the influence of sulfate, carbonate, and nitrate ions on the interfacial properties of crude oil. The pendant drop tensiometry was used to measure the rheological properties of the interfacial film formed by crude oil and brines with distinct ionic strengths at the temperature of 25 °C for up to 24 h. The results indicated that the sulfate ion promoted a greater reduction of the interfacial tension compared to the other ions. This is because it improves the solubilization of surfactant components, which migrate more easily to the interface. The presence of this anion also favored the formation of a more viscoelastic interface. It was concluded that the sulfate ion induced the formation of a more rigid interfacial film.

Keywords

Low salinity water; oil recovery; interfacial properties; sulfate.

Introduction

The oil industry suffered a major impact due to the coronavirus (COVID-19) pandemic in early 2020, even though it is a sector used to economic uncertainty and price volatility. The drastic reduction in global economic activity and mobility has resulted in the reduction of global energy demand and the oil price [1].

The IEA (2021) report [2] stated that not all drops in world energy demand were a result of Covid-19. The continuation of the current climatic conditions such as global warming is greatly influenced by the carbon dioxide released by fossil fuels. To reverse this situation, many countries are paving the way for renewable energy.

Oil industries make production decisions on an economic basis and analyze how much can be produced with economic viability [3]. This intensifies the need for more advanced techniques to improve the ultimate recovery of oil while economic viability remains. Among the methods used to improve oil production, the technique of low salinity water injection has gained prominence [4]. This method improves the interaction of the injection fluid with the oil/rock system, altering the mobility of the hydrocarbons contained in the reservoir by both fluid/fluid interactions and by fluid/rock interactions, thus creating favorable conditions for the reduction of residual oil saturation and increased oil recovery [5].

There are few works available in the literature related to this topic. Thus, to better understand the mechanism of low salinity injection water on the oil recovery efficiency, it is necessary to conduct studies that allow the understanding of the oil/brine interfacial behavior. The pendant drop tensiometry technique is well used in the rheological evaluation of these systems [6-9]. This work aims to analyze the influence of electrolytes (carbonate [CO₃²⁻], nitrate [NO₃⁻], and sulfate [SO₄²⁻] in the aqueous phase on the interfacial properties of an oil/water emulsion. In this way, it seeks to understand the mechanisms that favor the stability of interfacial films and clarify the actions of surfactants in petroleum/brine systems.

Methodology

Materials

A Brazilian crude oil henceforth called oil 1 was sampled in an oil field and used in this study. The characteristics of this oil are summarized in Tab. 1.

Table 1: Characteristics of the oil used in the study.

Property	Oil 1	Methodology
Density (°API)	29,95 ± 0,012	ASTM D-5002
Viscosity at 25 °C (cSt)	19,3 ± 0,12	ASTM D-7042
Water content (v/v)	1,27% ± 0,06	ASTM D6304-16.

Strontium carbonate [SrCO₃], strontium nitrate [Sr(NO₃)₂], strontium sulfate [SrSO₄] and deionized water were used to prepare the brine solutions. They were prepared at different concentrations, as shown in Tab. 2.

Experimental Procedure

The brine solutions were prepared as a function of the ionic strength of the [SrSO₄] salt saturated in an aqueous solution, which was the salt with lower solubility at the investigated pH and temperature conditions.

The ionic strength values of the solutions and their respective masses are described in Tab. 2 under temperature conditions (25 °C).

Table 2: Data for preparing [SrSO₄], [SrCO₃], and [Sr(NO₃)₂] solutions.

strontium sulfate [SrSO ₄]	
molar concentration (g mol ⁻¹)	ionic strength
5,60E-04	2,20E-03
4,30E-04	1,70E-03
3,10E-04	1,20E-03
1,90E-04	7,00E-04
strontium carbonate [SrCO ₃]	
molar concentration (g/mol)	ionic strength
5,60E-04	2,20E-03
4,30E-04	1,70E-03
3,10E-04	1,20E-03
1,90E-04	7,00E-04
strontium nitrate [Sr(NO ₃) ₂]	
molar concentration (g/mol)	ionic strength
7,30E-04	2,20E-03
5,60E-04	1,70E-03
4,10E-04	1,20E-03
2,40E-04	7,00E-04

* ionic strength = $I = 1/2 \sum C_i z_i^2$
 where C is the molar concentration of compound *i* and z is the charge of compound *i*

Study of interfacial properties

To evaluate the influence of different ions on the interfacial properties of the oil/water emulsion, the pendant drop tensiometry technique was used. In summary, a sample of oil was inserted into a syringe containing a U-shaped needle, which was immersed into the brine phase. The interfacial tension measurements were performed by the drop profile variation, which was digitalized using a CCD camera and transferred to a personal computer. Interfacial tension was analyzed for 4 hours.

In the dynamic oscillatory tests, the total dilatational (E), elastic (E'), and viscous (E'') moduli were determined. It can be correlated with the rigidity of the interfacial film. These tests are obtained through sinusoidal oscillations around the interfacial area of the drop and the analysis of the droplet volume, pre-defined oscillation frequency and amplitude. The ideal drop volume tests as well

as the study of the oscillation amplitude and frequency were based on the publication of ALVES et al., 2014 [6]. Table 3 presents the initial parameters chosen to perform the dynamic tests.

Table 3: Initial parameters adopted for tensiometry tests under ambient temperature and pressure conditions.

Volume (mm ³)	Area (mm ²)	Amplitude (mm ²)	Period (s)	Frequency (Hz)
28,57	43,8	3,5	10	0,1

Stability tests

To identify the stability of the analyzed systems, breakage tests were carried out through conventional heating in a thermostatic bath and the use of a demulsifier.

Emulsions were prepared using oil 1, deionized water, and brine phases with ionic strengths of 0.0007 and 0.0012 M, respectively. Initially, the mass of oil and solutions were obtained gravimetrically using an analytical balance. The proportion of emulsions was 30% of aqueous solution and 70% of the petroleum (v/v). Oil samples and brine solutions were homogenized by handshaking for about 5 minutes.

Then, the emulsions were subjected to a shearing process for 2 minutes under rotation of 6500 rpm through an ultra-turrax homogenizer. Soon after, 10 µL of DISSOLVAN-6521® demulsifier was added and homogenized for 1 min under the same rotation. These samples were transferred to graduated glass tubes and deposited on supports immersed in water in a thermostatic bath at a temperature of 60°C. The free water level was measured at times of 15 min, 30 min, 1 hr, 2 hrs, 3 hrs, 4 hrs, and 24 hours after the demulsifier addition to observe the phase separation.

Results and Discussion

Study of interfacial properties

Figure 1 shows the behavior of the interfacial tension for systems containing oil/brine over 4 hours of contact and a temperature of 25 °C.

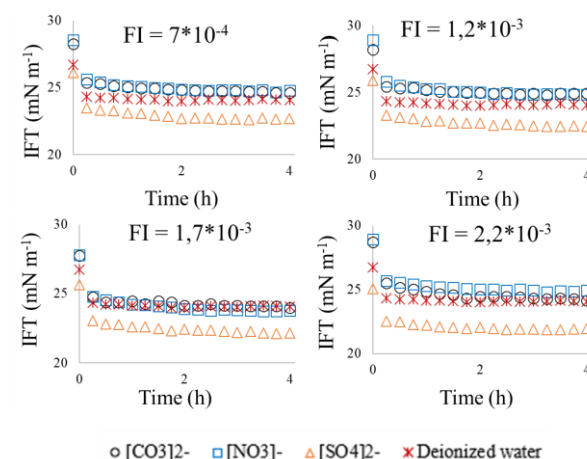


Figure 1: Dynamic interfacial tension of systems containing different aqueous phases at 25 °C.

As one may see in Figure 1, a reduction in interfacial tension was observed in the first minutes of the tests (10 min). According to PERLES et al. (2012) [10], the process of the interfacial film formation happens initially with the accumulation of surfactant fractions of the oil, and depends on the kinetics of these molecules migration to the oil/water interface. Then, the spatial reorganization of the molecules in this film occurs and the intermolecular forces are maximized.

It is also observed in Fig. 1 that there were no significant changes in the interfacial tension when comparing the different ionic strengths. It is verified that the ion $[SO_4^{2-}]$ had a greater influence on the interfacial tension. In general, the type of ion present in water favors the migration and dissociation of surface-active compounds at the interface. It results in the formation of a more active interfacial film which may favor the reduction of the interfacial tension of the system [11].

Viscoelastic properties

Figure 2 shows the behavior of interfacial elasticity (total modulus) for the petroleum/brine solution.

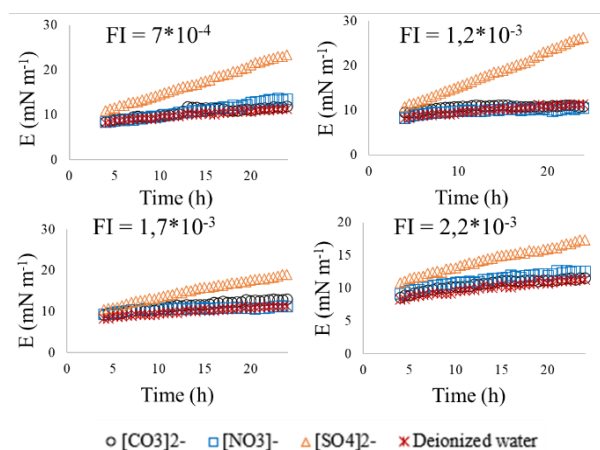


Figure 2: Viscoelastic properties of the oil 1/brine system as a function of ionic strength at 25 °C and atmospheric pressure. FI stands for ionic strength.

Figure 2 shows an increase in the total modulus over time. At the beginning of the oscillatory tests (after 4 hours of aging), the elasticity is more pronounced for $[SO_4^{2-}]$ and even greater with the reduction of the ionic strength. As for the ions $[CO_3^{2-}]$ and $[NO_3^-]$, which obtained similar results, a slight increase in elasticity was observed over time. The total dilatational modulus, Fig. 2, which corresponds to the combination of elastic and viscous moduli, is used as a parameter of film resistance to modifications applied in the interfacial area. In summary, the higher modules indicate stronger films [12].

Some works available in the literature report the presence of electrolytes in the aqueous phase as a major influence on the modification of interfacial behavior. PERLES et al. (2012) [10] stated that the presence of metal ions in the aqueous phase could form complexes with the polar groups in the active interface species, which increased the film rigidity

and thickness. Thus, it contributed to the increase in the surface's total area, allowing the adsorption of particles at the oil-water interface.

ALVES et al. (2014) [6] investigated an oil/brine system and observed an initial increase in elasticity over time. The results were evidenced in the presence of $[NaCl]$ in the aqueous phase. According to the authors, salt increased the electrostatic interactions between the ions in the brine phase and the surface-active compounds in the oil phase of the water/oil (W/O) emulsions. This mechanism drives a greater interaction of the surfactants at the interface due to a polarity increase in the aqueous phase, thus stiffening the interfacial film. Figures 3 and 4 show the evolution of the dilatational modulus components.

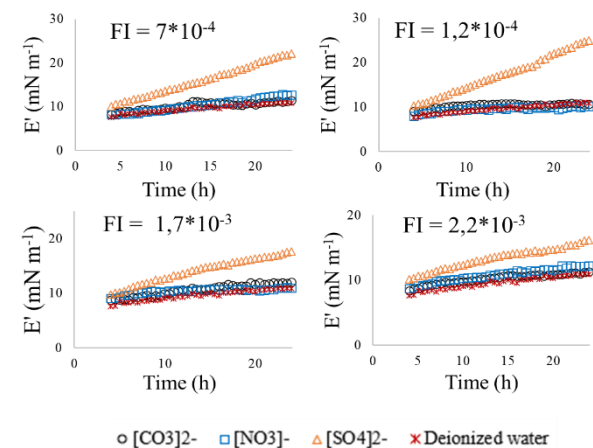


Figure 3: Modulus of elasticity of the oil 1/brine system as a function of ionic strength at 25 °C and atmospheric pressure.

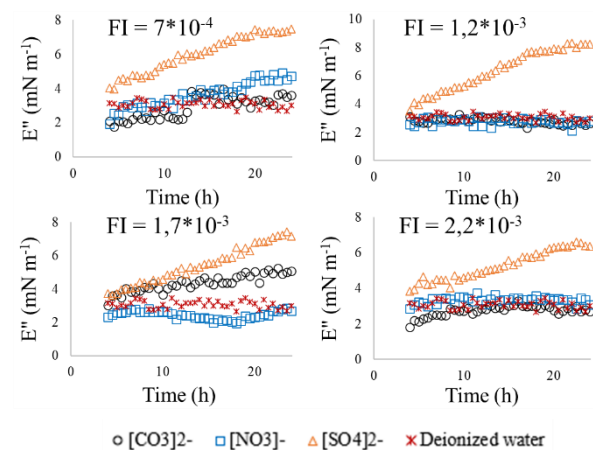


Figure 4: viscous module of the oil1/brine system as a function of ionic strength at 25 °C and atmospheric pressure.

Comparing Figs. 2, 3, and 4, a similarity is observed in the values of the total and elastic moduli, while the viscous modulus presents itself with a lower magnitude. This circumstance indicates that the interface is more elastic and resistant to changes during oscillatory tests [13]. Figs. 2, 3, and 4 also show a significant increase in the elastic modulus as the concentration of the anion $[SO_4^{2-}]$ is reduced. The literature [12] stated

that there is a tendency for greater stability at lower salinity concentrations. The sulfate ion provides a higher viscous modulus when compared to other individual ionic brines. It can be noted the higher stability of the brine system at lower $[\text{SO}_4]^{2-}$ concentration in comparison to the other studied ions. This is due to the evolution of viscoelastic modules that prove a greater rigidity of the interfacial film [6]. The comparison of the interfacial behavior verified in the presence of electrolytes suggests that the sulfate ion interacts at the oil/water interface to improve the stability of the interfacial film, as suggested by MANSHAD *et al.*, (2016) [14].

Stability tests

Figure 5 shows the demulsification results with different aqueous phases – without the presence of ions and with the presence of ions $[\text{CO}_3^{2-}]$, $[\text{NO}_3^-]$, and $[\text{SO}_4^{2-}]$ – with ionic strength = 0.0007 and 0.0012 (molar) in a 24-hour stability test time.

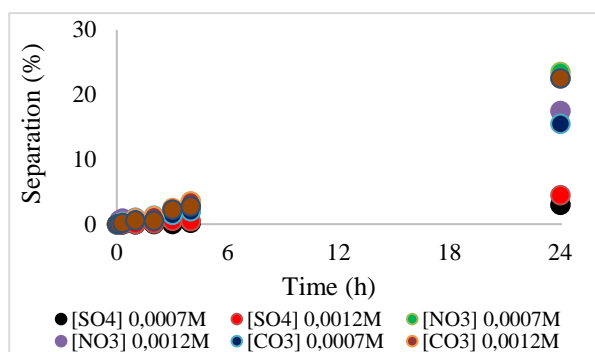


Figure 5: Stability tests of systems with and without salt heated at 60°C.

Figure 5 shows the highest stability of the emulsion containing the aqueous phase with the ion $[\text{SO}_4]^{2-}$. There was almost no formation of free water during the 4 hours of the test. This result is consistent with the values of the interfacial properties obtained in this work. Figure 5 shows the experimental results obtained for systems with deionized water and in the presence of the ions $[\text{NO}_3^-]$ and $[\text{CO}_3]^{2-}$. It is possible to observe a small content of free water (below 5%) during the 4 hours of testing. After this time, the phase separation occurs faster, reaching a level of almost complete separation over the 24 hours of testing.

Conclusions

It can be concluded from the obtained results that the presence of the ion $[\text{SO}_4]^{2-}$ as well as the reduction of its concentration increased the values of the total elastic modulus, which induced the formation of a more rigid interfacial film. In addition, the presence of this ion corresponded to a stronger interfacial activity of the surfactants that improve the interfacial elasticity of the film and may result in greater oil production. The stability tests showed that the presence of the sulfate anion made it difficult to separate the oil/water phases and

corroborated satisfactorily with the obtained results of the interfacial properties.

Acknowledgments

The authors thank to CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil) - Finance Code 001 and ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis) for financial support and scholarships.

Responsibility Notice

The authors are the only ones responsible for the paper content.

References

- [1] Chofreh, G. *et al.*, Renewable and Sustainable Energy Reviews, v. 139, p. 110643, 2021.
- [2] IEA. International Energy Agency. Global Energy Review 2021. Disponível em: < <https://www.iea.org/reports/global-energy-review-2021>>. Acesso em: 20 abr. 2022.
- [3] Halttunen, K.; *et al.*, Energy Research & Social Science, v. 85, p. 102407, 2022.
- [4] Farajzadeh, R *et al.*, Journal of cleaner production, v. 235, p. 812-821, 2019.
- [5] Mcguire, P. L. *et al.*, Proceeding of the SPE western regional meeting, p. 1–15, 2005.
- [6] Alves, D. R. A *et al.*, Fuel, v. 118, p. 21-26, 2014.
- [7] Ling, N. N. A *et al.*, Energy & Fuels, vol 32, p. 10042-10049, 2018.
- [8] Kazemzadeh, Y *et al.*, Fuel, v. 243, n. July 2018, p. 15–27, 2019.
- [9] Santos, D *et al.*, Journal of Petroleum Science and Engineering, 202, p. 2 – 8, 2021.
- [10] Perles, C.E *et al.*, Energy and Fuels, v. 26, p. 6914-6924, 2012.
- [11] Chavez-Miyauchi, T. E.; *et al.*, Energy & Fuels, v. 32, p. 2192-2198, 2016.
- [12] Ayirala, S. C *et al.*, Journal of Petroleum Science and Engineering, 163, p. 640 – 649, 2018.
- [13] Wang, D *et al.*, Fuel, 286, p. 119390, 2021.
- [14] Manshad, A. K. *et al.*, Journal of Molecular Liquids, 322, p. 987-993, 2016.