

The Effect of Calcium and Magnesium Ions on a Crude Oil-Brine-Carbonate Rock System for Enhanced Oil Recovery by Sophorolipid Solution

Rudarsko-geološko-naftni zbornik
(The Mining-Geology-Petroleum Engineering Bulletin)
DOI: 10.17794/rgn.2026.2.6

Original scientific paper



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Abstract

The interaction between crude oil, brine and carbonate rock systems is critical for implementing enhanced oil recovery (EOR). Surfactants, such as sophorolipid biosurfactants, incorporated in the displacing fluid are able to reduce the interfacial tension (IFT) and alter the wettability in these systems. However, the presence of divalent ions, especially calcium (Ca^{2+}) and magnesium (Mg^{2+}), complicates this interaction, affecting the effectiveness of EOR techniques. This study examines the influence of divalent ions on crude oil-brine-carbonate rock systems with the introduction of sophorolipids through experimental work. Interfacial tension and emulsion viscosity experiments evaluate the fluid-to-fluid interactions, while contact angle and static adsorption measurements characterize the interaction between the fluids and the rock, which are highly pertinent to the EOR mechanism. The Ca^{2+} and Mg^{2+} ions (2000 ppm) to sodium chloride (NaCl) solutions (10,000–15,000 ppm) with a 0.5 wt.% sophorolipid concentration at Critical Micelle Concentration (CMC) increased the water-wetness of the carbonate rock surface. In addition, while the ions reduced the interfacial tension (IFT), they did not significantly affect the viscosity of the oil-water emulsion of the NaCl solution with 0.5 wt.% sophorolipid. At low salinity (5000 ppm NaCl solution), these ions decreased the adsorption rate of the sophorolipid solutions on Indiana Limestone samples. The addition of these divalent ions to the injection solution significantly reduced the oil recovery efficiency, by about 28% for light oil and 32% for medium oil, during the biosurfactant flooding process.

Keywords:

Sophorolipids, divalent ions, carbonate, salinity conditions, enhanced oil recovery

1. Introduction

Carbonate reservoirs, which contain about 60% of the world's oil reserves, present unique challenges for oil extraction due to their complex pore structure and wettability characteristics (Ayirala et al., 2021; Sheng, 2013). Carbonate reservoirs are often heterogeneous, having varying degrees of porosity and permeability, which further complicates the oil production process (Mogensen & Masalmeh, 2020; Nazari et al., 2019). These reservoirs are usually oil-wet or mixed-wet, which reduces the effects of traditional water-flooding methods (Hao et al., 2019; Mohammed & Babadagli, 2015). This means large residual oil reserves are often left in carbonate rocks (Mogensen & Masalmeh, 2020; Xu et al., 2020), awaiting innovative solutions to increase oil recovery.

The injection of surfactants into carbonate rocks for enhanced oil recovery (EOR) is critical, but it has environmental impacts. Concerns about this have prompted research into sustainable alternatives, such as biosurfactants. Consequently, the use of sophorolipids as green surfactants has attracted increased research interest. Sophorolipids – a class of biosurfactants – have attracted interest for their potential in EOR applications owing to their biodegradability, low toxicity and relatively low cost (Díaz De Rienzo et al., 2015; Ganji et al., 2020). Sophorolipids can lower the interfacial tension (IFT) between crude oil and brine, mobilising trapped oil (Esfandyari et al., 2021; Hou et al., 2021; Shekhar et al., 2015). These biosurfactants can modify the wettability of carbonate rocks from oil-wet to water-wet, and reduce the surfactant adsorption by carbonate rock, hence improving oil recovery (Akanji et al., 2021; Bhardwaj, 2013; Elshafie et al., 2015; Magri et al., 2018).

Crude oil-brine-carbonate rock systems are common in petroleum engineering studies, and oil recovery can be significantly enhanced from these. The crude

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Received: 18 June 2025. Accepted: 13 October 2025.

Available online: 13 March 2026

oil–brine–carbonate rock system represents a complex interaction of multiple components that substantially affect the efficiency of EOR methods. Fluid-to-fluid interactions in biosurfactant injection processes impact the microemulsion viscosity and lower the IFT (Marhaendrajana et al., 2025; Megayanti et al., 2023; Udoh & Vinogradov, 2019). Changes in the wettability and the degree of rock adsorption are usually measured to evaluate fluid-to-carbonate rock interactions (Bassir & Shadzadeh, 2020; Shaik et al., 2020).

Salinity affects the interactions between fluids and the mechanisms of biosurfactant application in fluid-to-fluid and fluid-to-rock interactions. In specific instances, biosurfactants have demonstrated optimal performance at particular salinity levels, at which point the IFT reaches its minimum value (Mohammadi et al., 2019; Yutkin et al., 2022). The viscosity and stability of the microemulsion generated during the EOR biosurfactant process are influenced by salinity levels (Irvani et al., 2025; Khodaparast & Johns, 2020). The salinity level of the solution can potentially decrease biosurfactant adsorption, thereby increasing the availability of biosurfactant molecules to alter the rock-wetting properties (Hou et al., 2022). In elevated salinity conditions, the solubility of biosurfactants in the brine solution may decrease due to aggregate (e.g. micelle) formation or precipitation, and the biosurfactant's effectiveness may be reduced. Thus, the optimal salinity must be established for each reservoir, considering the intricate interactions between the biosurfactant and the carbonate rock (Ghaedi et al., 2023).

Elevated IFT between crude oil and brine can impede the mobilisation of entrapped oil. Incorporating surfactants, including sophorolipids, markedly decreases the IFT, promoting oil displacement (Baccile & Kleinen, 2025; Esfandyari et al., 2021; Fu et al., 2024; Gazem et al., 2025). Divalent ions reduce the IFT between oil and aqueous surfactant solutions, achieving very low values at optimal concentrations. This phenomenon is crucial for applications such as EOR (Jha et al., 2018). The presence of divalent ions can also improve the effectiveness of sophorolipids in reducing the IFT, these ions interacting with the surfactant molecules and the crude oil, leading to a more effective reduction in IFT (Koh et al., 2016).

Carbonate rocks are primarily composed of calcite (CaCO₃) minerals. In the formation of dolomite, magnesium ions (Mg²⁺) replace some of the calcium ions (Ca²⁺) in the limestone's mineral structure. The chemical formula for dolomite is CaMg(CO₃)₂. Derikvand (2020) discovered that including Mg²⁺ and Ca²⁺ in brine solutions can improve oil recovery by modifying the surface characteristics of the crude oil–brine–carbonate rock system (Derikvand et al., 2020; Zheng et al., 2024).

This modification has been ascribed to the capacity of these ions to engage both with the rock surface and the crude oil, thereby changing the wettability and IFT (Derikvand et al., 2020; Eslahati et al., 2020). Divalent

ions, including Ca²⁺ and Mg²⁺, are also essential in modifying rock wettability and thereby enhancing oil mobilisation (Bai et al., 2021; Gandomkar & Reza, 2017; Marhaendrajana et al., 2018; Zaeri et al., 2019). The presence of Ca²⁺ and Mg²⁺ significantly affects the adsorption rate (Anachkov et al., 2015; Herawati et al., 2022; Hou et al., 2022). The reactive properties of Ca²⁺ and Mg²⁺ are also strongly influenced by salinity (Derikvand et al., 2020; Prabhakar & Melnik, 2018; Zaeri et al., 2019).

The interaction of these three components can significantly impact the fluid movement mechanism in a reservoir and the oil recovery efficiency using sophorolipids. The objective of the study is to evaluate the effects of brine with various salinities (5000–15,000 ppm) and sophorolipid concentration (0–2 wt.%) on medium and light oil samples using Indiana Limestone (IL). In addition, the study investigates the role of divalent ions (Ca²⁺ and Mg²⁺) in enhancing and optimising biosurfactant-based EOR system through IFT, oil–water emulsion viscosity, contact angle, static adsorption and core flooding tests. Incorporating sophorolipids into EOR represents an innovative approach to addressing the challenges associated with carbonate reservoirs. This strategy not only improves recovery efficiency but also provides environmental and operational benefits that align with the industry's increasing commitment on sustainable practices.

2. Experimental Methodology

2.1. Material and Sample Preparation

2.1.1. Crude Oil Sample

The crude oil samples used in this study were collected from two oil fields in Indonesia. The light oil properties presented in Table 1 were cited by Swadesi et al. (2015). The medium oil properties were obtained from laboratory analyses conducted by Lemigas. Based on API gravity, each sample represents the characteristics of light and medium oils.

Table 1. Crude Oil Characteristics

Property	Light Crude Oil	Medium Crude Oil
API Gravity (°API)	43.45	33.1
Saturates (%)	71.60	74.67
Aromatics (%)	25.49	24.07
Resins (%)	2.14	1.15
Asphaltenes (%)	0.78	0.106
Total Acid Number, TAN (mg KOH/g)	1.23	0.178
Viscosity (cP) at Corresponding reservoir temperature	0.9 (66°C)	4.38 (60°C)

Note. KOH, potassium hydroxide.

2.1.2. Sophorolipids

We used a sophorolipid biosurfactant purchased from Shanghai Yuchuang Chemical Technology Co., Ltd., which has a light yellow to brown liquid appearance, as shown in **Figure 1**. This product is water soluble and has the sophorolipid specifications shown in **Table 2**. Sophorolipids consist of hydrophilic sophorose groups covalently bonded to hydrophobic fatty acid groups. Two glucose units are linked by a glycosidic bond (β -1,2') to form sophorose, a disaccharide (2-O- β -D-glucopyranosyl- β -D-glucopyranose) (**Pal et al., 2023**).

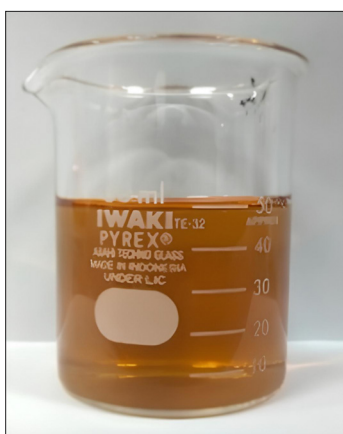


Figure 1. Example of a Sophorolipid Sample

Table 2. Sophorolipids Specification

Items	Specifications
Solid Content	51.50%
pH	3.95
Solubility (Water)	Soluble

2.1.3. Core Sample

Indiana Limestone was used for the rock-fluid test in this study. Based on laboratory testing, this limestone is characterized by 20% porosity and 135 mD permeability, as measured by a PORG-200 porosimeter and PERG using gas N₂. The mineral composition based on X-ray diffraction data from IL, is shown in **Table 3**.

Table 3. Mineral Composition of Indiana Limestone

Items	Specifications
Quartz	0.84%
Calcite	94.08%
Clay	1.94%
Pyrite	1.61%
Dolomite	1.53%

2.2. Experiment Design

The overall fluid-to-fluid and fluid-to-carbonate rock testing involved synthetic brines with various composi-

Table 4. Synthetic Brine Composition

Number	Synthetic Brine		
	NaCl	CaCl ₂	MgCl ₂
1	5,000 ppm	-	-
2	5,000 ppm	2,000 ppm	-
3	5,000 ppm	-	2,000 ppm
4	10,000 ppm	-	-
5	10,000 ppm	2,000 ppm	-
6	10,000 ppm	-	2,000 ppm
7	15,000 ppm	-	-
8	15,000 ppm	2,000 ppm	-
9	15,000 ppm	-	2,000 ppm

Note. NaCl, sodium chloride; CaCl₂, calcium chloride; MgCl₂, magnesium chloride.

tions, as shown in **Table 4**. The scenarios totalled 90 tests, incorporating two samples of crude oil and five sophorolipid concentrations, from 0 to 2 wt.%.

The technique of attributing reaction rates to the distance from equilibrium (X) becomes troublesome when dealing with magnesian calcites, and there has been debate regarding the precise definition of this equilibrium. Uncertainties in free energy values, the more general issue of whether magnesian calcites ever achieve a truly metastable equilibrium state, and the best way to depict this connection in thermodynamic calculations are some of the causes of this issue.

Thus, far more attention has been paid to the problem of how magnesium substitution impacts solubility than to the impact on dissolution rate alone. To address this issue, **Thorstenson & Plummer (1977)** proposed the concept of stoichiometric saturation. They suggested that the product of activities provides the equilibrium constant for a magnesian calcite with the composition Ca_(1-x)Mg_xCO₃.

$$IAP_{mag\ cal} = (Ca^{2+})^{1-x} (Mg^{2+})^x (CO_3^{2-}) \quad (1)$$

Where x = mole fraction of lattice magnesium. Magnesian calcite is thus assumed to react as a one-component phase having a fixed composition (**Morse & Arvidson, 2002; Thorstenson & Plummer, 1977**).

2.3. Procedure

2.3.1. Interfacial Tension Test

The IFT measurement was conducted using a spinning-drop tensiometer (see **Figure 2**) to determine the biosurfactant's ability to reduce the IFT between the oil and brine solutions. The measurement time was 30 min at 6000 rpm and a temperature of $60 \pm 0.5^\circ\text{C}$.

2.3.2. Viscosity Emulsion

A Brookfield viscometer measures the torsional force exerted on a cylindrical rotor (spindle) immersed in a flu-

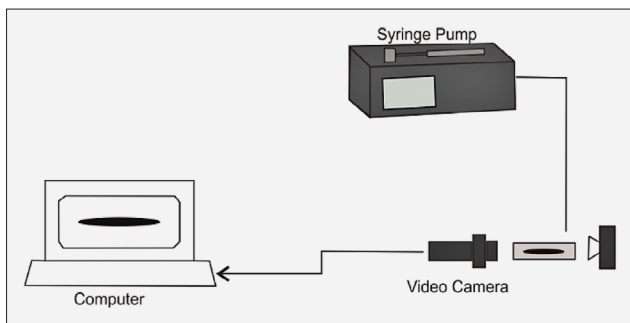


Figure 2. Schematic of the Spinning Drop Tensiometer

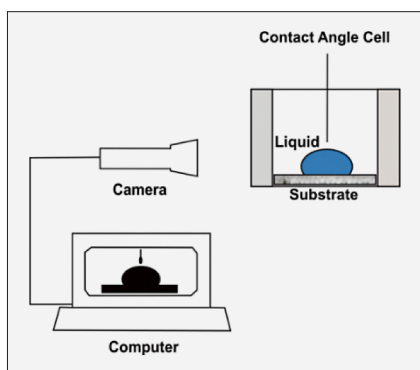


Figure 3. Schematic of the Optical Tensiometer Tool

id, which gives the measurement of viscosity. In this experiment, the viscometer was used to measure the viscosity of an oil–water emulsion. The sample mixture was 1:1, with 5 mL each of oil and sophorolipid solution, stirred for 10 min at $60 \pm 0.5^\circ\text{C}$ to promote emulsification.

2.3.3. Contact Angle Measurement

A Theta Lite Optical Tensiometer TL100 (OneAttention) tool was used to measure the contact angle on a thin-section of the IL. The IL thin-section was immersed in crude oil for 24 h at $60 \pm 0.5^\circ\text{C}$ to adjust the rock conditions to the initial wettability of the reservoir by inducing the adsorption of oil molecules and polar compounds, such as asphaltene and resins, onto the rock surface. During the procedure, water droplets were placed on the oil-soaked rock surface, and the contact angle was measured, as shown in Figure 3. A similar procedure had previously been used by Abdallah et al. (2007) and Al-Maamari & Buckley (2003).

2.3.4. Static Adsorption

The adsorption test was performed to evaluate the adsorption efficacy of the sophorolipids on the IL and to ascertain whether other factors, such as the interaction of

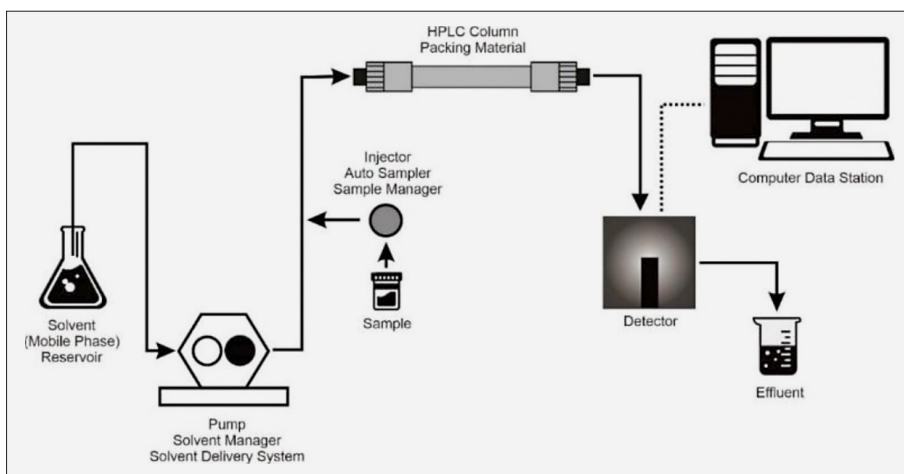


Figure 4. Schematic of The High-Performance Liquid Chromatography (HPLC) Apparatus

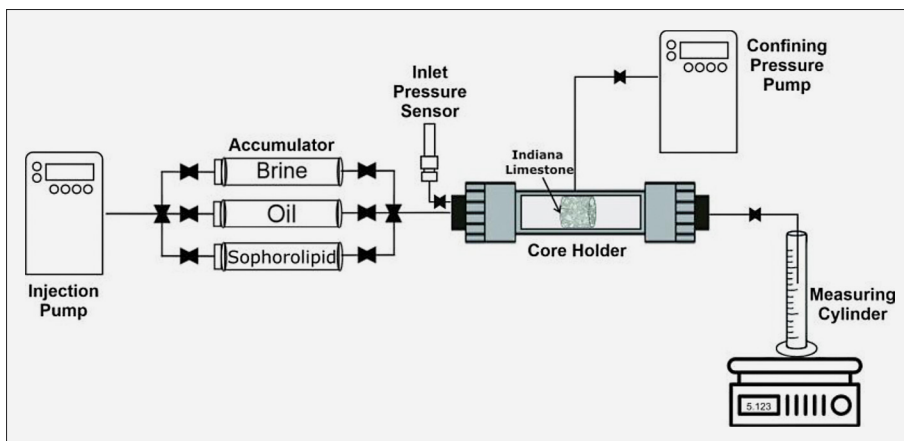


Figure 5. Schematic of the Core Flooding Apparatus

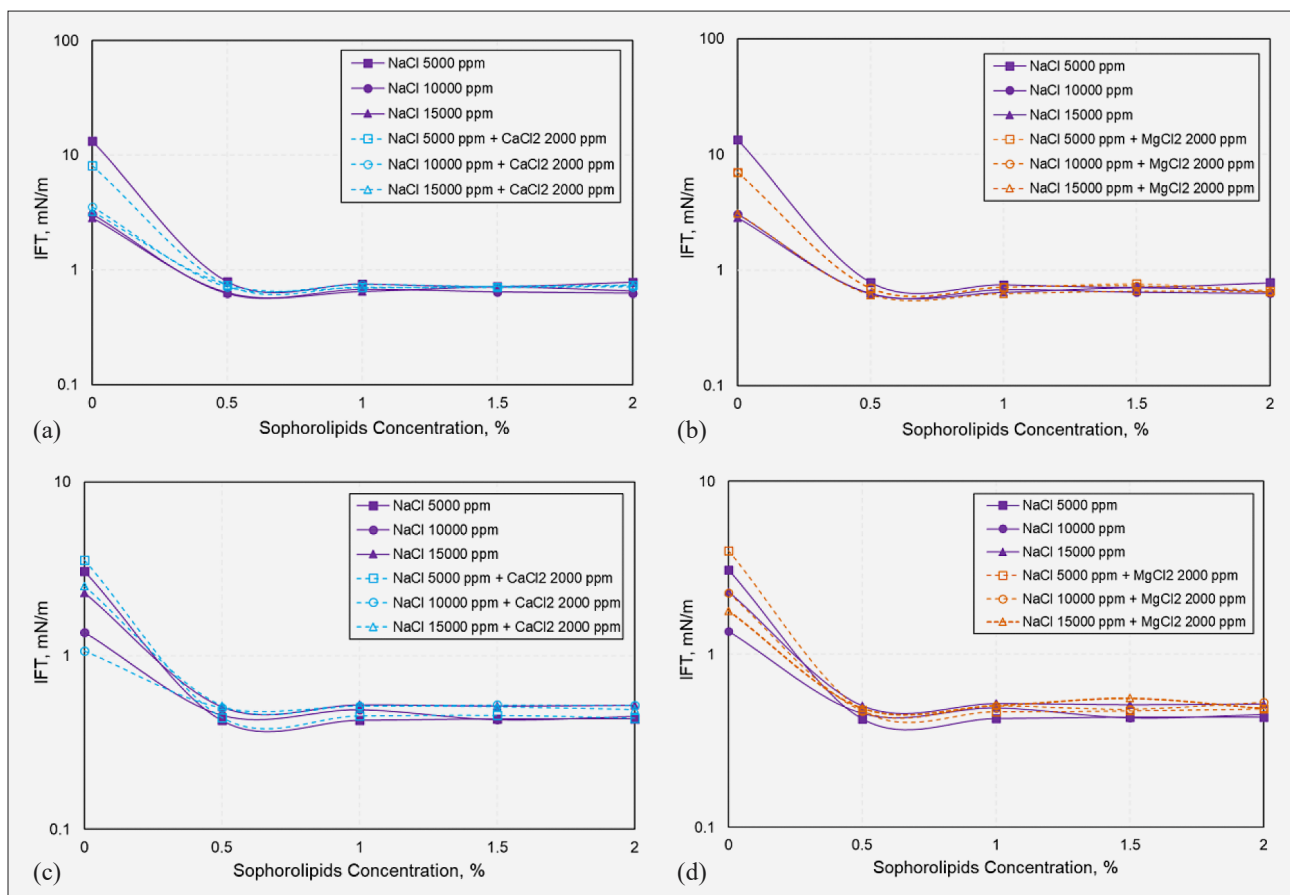


Figure 6. Oil-water Interface Tension vs. Various Sophorolipids Concentrations: (a and b) Medium Oil; and (c and d) Light Oil, both with Added CaCl₂ and MgCl₂.

water with the rock surface, changed the adsorption features. In a volumetric flask, a sample of IL grain (80 mesh) was soaked in a solution of sophorolipids at 0.5% and 2 wt.%. The mass ratio between the grain and the solution was 1:4. The flask was shaken for 48 h, and then the liquid was filtered through 4 micro-sized filter papers. The adsorption analysis was conducted using a high-performance liquid chromatography apparatus (see **Figure 4**). The test was performed by introducing the fluid (all particles analysed had to be in liquid form) into the injection port.

2.3.5. Core Flooding

The core flooding test involves fluid, or a combination of fluids, being injected into a rock sample. This test is commonly used to determine the optimal development options for oil reservoirs and often helps in evaluating the effects of injecting fluids specifically designed to enhance or increase oil recovery. A core plug sample of IL was immersed in crude oil for 24 h at $60 \pm 0.5^\circ\text{C}$ after water injection. The concentration of the sophorolipid solution was 0.5 wt.% under CMC conditions and the brine concentration was 10,000 ppm, representing the field conditions in Indonesia. Divalent ions were added to this fluid. The test was conducted using the core flood-

ing apparatus, with a confining pressure of 100 psia and an injection rate of 0.3 cc/min, as shown in **Figure 5**.

3. Results

3.1. Interfacial Tension

Measurement of the IFT in sophorolipid solutions was carried out on 90 samples, with the effects of the addition of Ca²⁺ and Mg²⁺ ions, respectively in the forms of CaCl₂ or MgCl₂ at concentrations of 2000 ppm, to the solutions that had varying NaCl and sophorolipid concentrations. In general, the presence of CaCl₂ or MgCl₂ affected the IFT values in very subtle ways (see **Figure 6**). This suggests that the sophorolipids were not significantly affected by the divalent ions in either the medium crude oil (see **Figures 7a** and **b**) or light crude oil (see **Figures 6c** and **d**) cases. The sophorolipids were found to be optimum for reducing the oil-water IFT at a concentration of approximately 0.5 wt.%.

3.2. Oil-Water Emulsion Viscosity

In the oil-water emulsion viscosity test, observations were made at a sophorolipid concentration of 0.5 wt.%. In the medium oil (see **Figure 7a**), the Ca²⁺ caused an

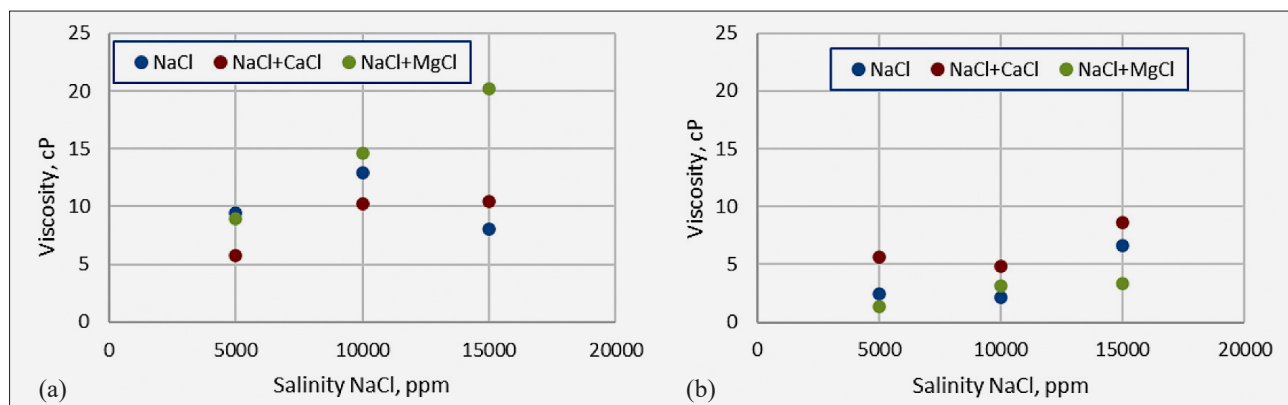


Figure 7. Mix Viscosity at Various Salinity of 0.5%wt Sophorolipids: (a) Medium Oil; and (b) Light Oil with added CaCl_2 and MgCl_2

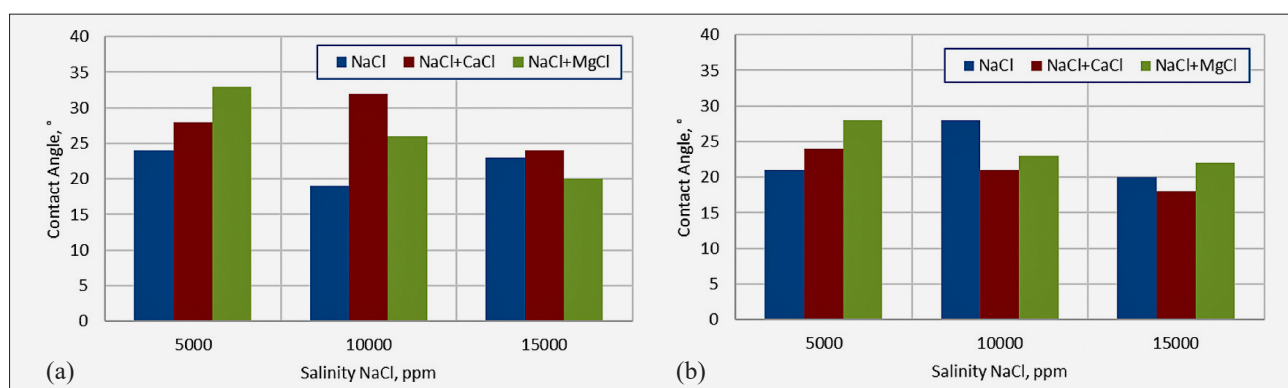


Figure 8. Effect of CaCl_2 and MgCl_2 on the Contact Angle of 0.5 %wt Sophorolipids in Various NaCl Concentrations: (a) Medium Oil; and (b) Light Oil

increase in the viscosity of the oil–water emulsion at high salinity (15,000 ppm) and the Mg^{2+} increased the viscosity even more, especially at medium to high salinities. In the light oil (see **Figure 7b**), the Ca^{2+} and Mg^{2+} effects were less critical, but both still increased the viscosity at a specific salinity. The impacts of the Ca^{2+} and Mg^{2+} were more significant in the medium oil than the light oil. In the light oil, the initial viscosity was lower, and the impact of the sophorolipids and additional ions was less pronounced. The structure of light oils tends to be simpler, which might explain this. Sophorolipids can affect the viscosity of oil–water emulsions depending on the oil type, optimum salt concentration, and the presence of divalent ions. Adding Ca^{2+} and Mg^{2+} increases the viscosity of medium oils in particular because the interaction between the ions and the sophorolipid micelles strengthens the structure, thus increasing flow resistance. The combination of NaCl and divalent ions showed synergistic effects in modifying the viscosity, especially at the Critical Micelle Concentration of sophorolipids.

3.3. Wettability Alteration

The influence of divalent ions on the alteration of wettability by sophorolipids is a complex subject that

encompasses the interactions between biosurfactants and ionic compositions in aqueous solutions. Divalent ions, especially Ca^{2+} and Mg^{2+} , significantly influence the wettability of surfaces, particularly those altered by sophorolipids. In the case of 0.5 %wt sophorolipids concentration, Ca^{2+} and Mg^{2+} ions cause a significant increase in contact angle at NaCl salinity of 5,000 ppm and 10,000 ppm. At the same time, the effect is not noticeable at 15,000 ppm (see **Figure 8**).

The observation is almost similar for the light oil case. The contact angle increases at low salinity (5,000 ppm); it decreases at 10,000, and finally it tends to stabilize at 15,000 ppm. The effect of the addition of divalent ions on wettability alteration does not always have a clear pattern, but it is highly dependent on the specific conditions of the system and the combination of ions used (**Gandomkar & Reza, 2017**).

3.4. Static Adsorption

Static adsorption tests were conducted at 5,000, 10,000 and 15,000 ppm NaCl salinity and 0.5 wt.% sophorolipid concentrations. At low NaCl salinity (5,000 ppm), the presence of a divalent ion was able to reduce the adsorption (see **Figure 9**). At NaCl salinities of 10,000 and 15,000 ppm, the addition of Ca^{2+} or Mg^{2+} did not affect

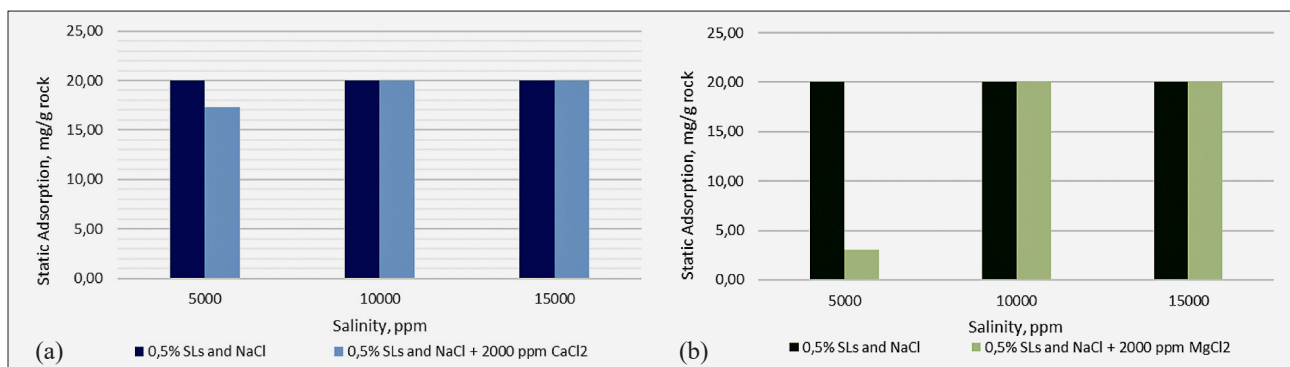


Figure 9. Static Adsorption of Sophorolipids on Carbonate Rocks-Effects of: (a) CaCl₂; and (b) MgCl₂

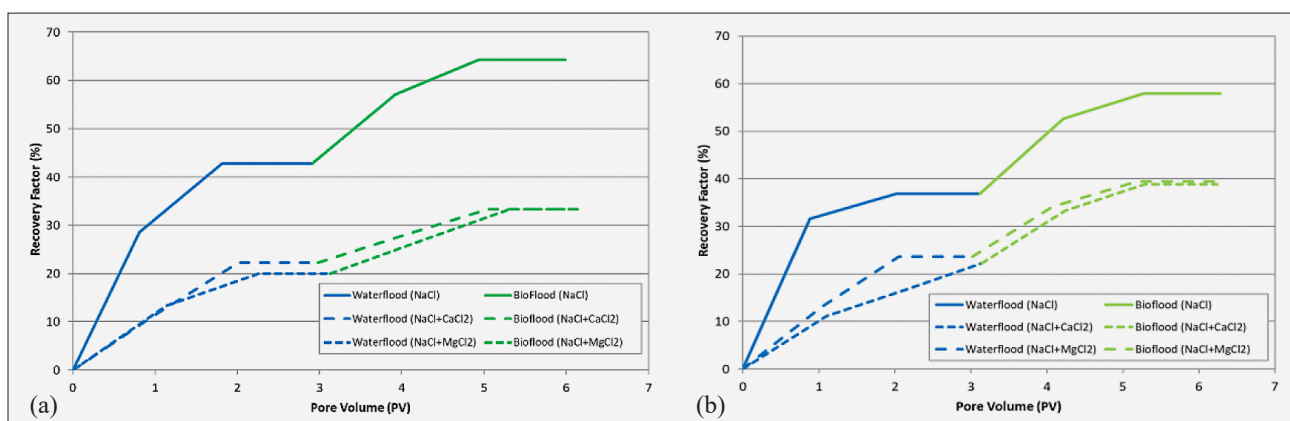


Figure 10. Effects of CaCl₂ and MgCl₂ on Waterflooding and Biosurfactant Flooding of 0.5 wt% sophorolipids in Various NaCl Concentrations: (a) Medium Oil; and (b) Light Oil.

the adsorption of sophorolipids. It is assumed that the sophorolipid molecules act directly on the surface, their distribution being more even under diverse ion circumstances (i.e. in the presence of Na⁺, Na⁺ + Ca²⁺ or and Na⁺ + Mg²⁺), resulting in a consistent adsorption rate.

3.5. Core Flooding

The addition of Ca²⁺ and Mg²⁺ to the injection solution significantly decreased the oil recovery efficiency in both the water flooding and sophorolipid flooding processes, regardless of the crude oil grade, whether medium or light. During water flooding, the recovery factor decreased from approximately 44% to 20–23% for medium oil and from 37% to about 25% for light oil when divalent ions were added. In the biosurfactant flooding, the recovery factor decreased significantly, from approximately 65% to 33% for medium oil and from 58% to 40% for the light crude (see Figure 10). In carbonate rock reservoirs, the presence of divalent ions, such as Ca²⁺ and Mg²⁺, has a more complex effect than in sandstone reservoirs. This is because carbonate rocks are composed mainly of calcite (CaCO₃), which can chemically interact directly with these ions. Divalent ions interact with the sophorolipid solution and the rock, causing a decrease in biosurfactant activity, an increase in

adsorption, and the formation of mineral scales that inhibit permeability. Elevated divalent-ion concentrations (Ca²⁺/Mg²⁺) in carbonate systems alter surface charge and promote Ca²⁺-mediated surface complexation, which diminishes wettability alteration and reduces incremental recovery (Mahani et al., 2015).

4. Discussion

The interaction between divalent ions (Ca²⁺ and Mg²⁺), sophorolipid molecules, and carbonate mineral surfaces plays a crucial role in determining the overall recovery performance. These ions are known to engage in surface complexation reactions with carbonate minerals, leading to changes in surface charge and electrostatic potential. At moderate salinity levels (5,000–10,000 ppm NaCl), Ca²⁺ and Mg²⁺ ions tend to compete with the carboxyl and hydroxyl functional groups of sophorolipid molecules for adsorption sites on the carbonate surface. This competition reduces biosurfactant adsorption, enhancing the availability of active sophorolipid molecules in solution and promoting water-wet conditions. Conversely, at higher salinities (≥15,000 ppm), the accumulation of these divalent ions at the mineral interface promotes the formation of Ca–CO₃ or Mg–CO₃ surface

complexes, which can hinder the ability of sophorolipids to interact effectively with the rock, thus diminishing wettability alteration efficiency. Mg^{2+} ions, due to their stronger hydration shell, induce greater charge shielding and restrict surfactant adsorption, resulting in more stable but less reactive interfaces. In contrast, Ca^{2+} can bridge between negatively charged sophorolipid headgroups and carbonate surfaces, promoting partial aggregation of micelles at the interface. This bridging effect explains the observed increase in emulsion viscosity for medium oils and the reduced recovery during coreflooding tests. These mechanistic insights align with previous findings by Bai et al. (2021) and Derikvand et al. (2020), suggesting that the balance between ion concentration, salinity, and biosurfactant molecular structure must be optimized to achieve effective EOR performance in carbonate reservoirs.

5. Conclusions

The findings show that divalent ions – especially Ca^{2+} and Mg^{2+} – affect the interactions between crude oil, brine solutions, and carbonate rocks, to a certain degree, when biosurfactant sophorolipids are added to the brine as the EOR agent. These ions decrease the IFT between the brine and sophorolipid at least a tenth of the time, in both light and medium oil. Meanwhile, these ions tend to increase the water contact angle at low salinities (5000–10,000 ppm) and decrease the water contact angle at higher salinities (10,000–15,000 ppm). The adsorption of the sophorolipids onto the IL decreased in the presence of Ca^{2+} and Mg^{2+} at low salinities. These results suggest Ca^{2+} and Mg^{2+} can improve the performance of sophorolipids if used as an EOR agent in a carbonate reservoir. Incorporating Ca^{2+} and Mg^{2+} enhances the viscosity of the mixture, particularly in medium oils, due to the interaction of these ions with sophorolipid micelles, thereby fortifying the structure and augmenting flow resistance. This may potentially create a more stable displacement front for improved oil recovery.

The recovery factor in biosurfactant flooding decreased significantly, dropping from approximately 65% to 33% for the medium oil and from 58% to 40% for the light crude oil. In carbonate rocks, the adverse effects of divalent ions are more complex because they stabilize the carbonate minerals, reducing the potential for changes in wettability required to increase recovery. Increased divalent-ion concentrations (Ca^{2+}/Mg^{2+}) in carbonate systems modify surface charge and facilitate surface complexation, hence decreasing wettability alteration and limiting incremental recovery.

Acknowledgement

This study was funded by the Center of Higher Education Funding and Assessment, Ministry of Higher Education, Science, and Technology of the Republic of

Indonesia through Grant No: 0742/J5.2.3/BPI.06/10/2021. The experiments were conducted in the Laboratory of Enhanced Oil Recovery (EOR), Institut Teknologi Bandung, and UPN Veteran Yogyakarta.

Funding

This research was funded by the Center of Higher Education Funding and Assessment, Ministry of Higher Education, Science, and Technology of the Republic of Indonesia, grant number 0742/J5.2.3/BPI.06/10/2021.

6. References

- Abdallah, W., Buckley, J. S., Carnegie, A., Edwards, J., Herold, B., Fordham, E., Graue, A., Habashy, T., Seleznev, N., Signer, C., Hussain, H., Montaron, B., & Ziauddin, M. (2007). Fundamentals of wettability. *Oilfield Review*, 19(2), 44–61.
- Akanji, L. T., Rehman, R., Onyemara, C. C., Ebel, R., & Jamal, A. (2021). A novel technique for interface analysis: Behaviour of sophorolipids biosurfactant obtained from *Meyerozyma* spp. MF138126 during low-salinity heavy-crude experiments. *Fuel*, 297(April 2020), 120607. <https://doi.org/10.1016/j.fuel.2021.120607>
- Al-Maamari, R. S. H., & Buckley, J. S. (2003). Asphaltene precipitation and alteration of wetting: The potential for wettability changes during oil production. *SPE Reservoir Evaluation and Engineering*, 6(4), 210–214. <https://doi.org/10.2118/84938-PA>
- Anachkov, S. E., Tcholakova, S., Dimitrova, D. T., Denkov, N. D., Subrahmaniam, N., & Bhunia, P. (2015). Adsorption of linear alkyl benzene sulfonates on oil-water interface: Effects of Na^+ , Mg^{2+} and Ca^{2+} ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 466, 18–27. <https://doi.org/10.1016/j.colsurfa.2014.10.059>
- Ayrala, S., Sofi, A., Li, Z., & Xu, Z. (2021). Surfactant and surfactant-polymer effects on wettability and crude oil liberation in carbonates. *Journal of Petroleum Science and Engineering*, 207(June), 109117. <https://doi.org/10.1016/j.petrol.2021.109117>
- Baccile, N., & Kleinen, J. (2025). Biosurfactants and bioamphiphiles, survey, perspectives and applicative potential from a colloid science point of view. *Current Opinion in Colloid and Interface Science*, 75, 101891. <https://doi.org/10.1016/j.cocis.2024.101891>
- Bai, S., Kubelka, J., & Piri, M. (2021). Wettability Reversal on Dolomite Surfaces by Divalent Ions and Surfactants: An Experimental and Molecular Dynamics Simulation Study. *Langmuir*, 37(22), 6641–6649. <https://doi.org/10.1021/acs.langmuir.1c00415>
- Bassir, S. M., & Shadizadeh, S. R. (2020). Static adsorption of a new cationic biosurfactant on carbonate minerals: Application to EOR. *Petroleum Science and Technology*, 38(5), 462–471. <https://doi.org/10.1080/10916466.2020.1727922>
- Bhardwaj, G. (2013). Biosurfactants from Fungi: A Review. *Journal of Petroleum & Environmental Biotechnology*, 04(06). <https://doi.org/10.4172/2157-7463.1000160>

- Derikvand, Z., Rezaei, A., Parsaei, R., Riazi, M., & Torabi, F. (2020). A mechanistic experimental study on the combined effect of Mg^{2+} , Ca^{2+} , and SO_4^{2-} ions and a cationic surfactant in improving the surface properties of oil/water/rock system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 587(September 2019), 124327. <https://doi.org/10.1016/j.colsurfa.2019.124327>
- Díaz De Rienzo, M. A., Banat, I. M., Dolman, B., Winterburn, J., & Martin, P. J. (2015). Sophorolipid biosurfactants: Possible uses as antibacterial and antibiofilm agent. *New Biotechnology*, 32(6), 720–726. <https://doi.org/10.1016/j.nbt.2015.02.009>
- Elshafie, A. E., Joshi, S. J., Al-Wahaibi, Y. M., Al-Bemani, A. S., Al-Bahry, S. N., Al-Maqbali, D., & Banat, I. M. (2015). Sophorolipids production by *Candida bombicola* ATCC 22214 and its potential application in microbial enhanced oil recovery. *Frontiers in Microbiology*, 6(NOV), 1–11. <https://doi.org/10.3389/fmicb.2015.01324>
- Esfandyari, H., Moghani Rahimi, A., Esmaeilzadeh, F., Davarpanah, A., & Mohammadi, A. H. (2021). Amphoteric and cationic surfactants for enhancing oil recovery from carbonate oil reservoirs. *Journal of Molecular Liquids*, 322, 114518. <https://doi.org/10.1016/j.molliq.2020.114518>
- Eslahati, M., Mehrabianfar, P., Isari, A. A., Bahraminejad, H., Manshad, A. K., & Keshavarz, A. (2020). Experimental investigation of Alfalfa natural surfactant and synergistic effects of Ca^{2+} , Mg^{2+} , and SO_4^{2-} ions for EOR applications: Interfacial tension optimization, wettability alteration and imbibition studies. *Journal of Molecular Liquids*, 310, 113123. <https://doi.org/10.1016/j.molliq.2020.113123>
- Fu, L., Ren, Z., Chen, W., Liu, Q., Ye, M., Qiu, X., Zhang, Y., Zheng, Y., Liao, K., & Shao, M. (2024). Polyetheramine enhanced biosurfactant/biopolymer flooding for enhanced oil recovery. *Journal of Molecular Liquids*, 411(May), 125757. <https://doi.org/10.1016/j.molliq.2024.125757>
- Gandomkar, A., & Reza, M. (2017). The impact of monovalent and divalent ions on wettability alteration in oil / low salinity brine / limestone systems. *Journal of Molecular Liquids*, 248, 1003–1013. <https://doi.org/10.1016/j.molliq.2017.10.095>
- Ganji, Z., Beheshti-Maal, K., Massah, A., & Emami-Karvani, Z. (2020). A novel sophorolipid-producing *Candida keroseneae* GBME-IAUF-2 as a potential agent in microbial enhanced oil recovery (MEOR). *FEMS Microbiology Letters*, 367(17), 1–8. <https://doi.org/10.1093/femsle/fnaa144>
- Gazem, A., Krishna, S., & Al-Yaseri, A. (2025). Low-salinity enhanced oil recovery using biosurfactant-ZnO nanoparticle-xanthan gum formulations: A comparative study of rhamnolipid and sophorolipid systems. *Journal of Molecular Liquids*, 432(May), 127894. <https://doi.org/10.1016/j.molliq.2025.127894>
- Ghaedi, A., Nabipour, M., Azdarpour, A., & Gandomkar, A. (2023). Mechanistic investigation of using low salinity alkaline surfactant solutions in carbonate reservoirs based on polarity of crude oil. *Journal of Molecular Liquids*, 390(PB), 123098. <https://doi.org/10.1016/j.molliq.2023.123098>
- Hao, J., Mohammadkhani, S., Shahverdi, H., Esfahany, M. N., & Shapiro, A. (2019). Mechanisms of smart waterflooding in carbonate oil reservoirs - A review. *Journal of Petroleum Science and Engineering*, 179(January), 276–291. <https://doi.org/10.1016/j.petrol.2019.04.049>
- Herawati, I., Permadi, P., Rochliadi, A., & Marhaendrajana, T. (2022). Adsorption of anionic surfactant on sandstone reservoir containing clay minerals and its effect on wettability alteration. *Energy Reports*, 8, 11554–11568. <https://doi.org/10.1016/j.egy.2022.08.268>
- Hou, J., Du, J., Sui, H., & Sun, L. (2021). Surfactants enhanced heavy oil–solid separation from carbonate asphalt rocks-experiment and molecular dynamic simulation. *Nanomaterials*, 11(7). <https://doi.org/10.3390/nano11071835>
- Hou, J., Lin, S., Du, J., & Sui, H. (2022). Study of the Adsorption Behavior of Surfactants on Carbonate Surface by Experiment and Molecular Dynamics Simulation. *Frontiers in Chemistry*, 10(April), 1–19. <https://doi.org/10.3389/fchem.2022.847986>
- Iravani, M., Simjoo, M., & Chahardowli, M. (2025). Screening key parameters affecting stability of graphene oxide and hydrolyzed polyacrylamide hybrid: Relevant for EOR application. *Heliyon*, 11(4), e42875. <https://doi.org/10.1016/j.heliyon.2025.e42875>
- Jha, N. K., Iglauer, S., & Sangwai, J. S. (2018). Effect of Monovalent and Divalent Salts on the Interfacial Tension of n-Heptane against Aqueous Anionic Surfactant Solutions. *Journal of Chemical and Engineering Data*, 63(7), 2341–2350. <https://doi.org/10.1021/acs.jced.7b00640>
- Khodaparast, P., & Johns, R. T. (2020). A continuous and predictive viscosity model coupled to a microemulsion equation of state. *SPE Journal*, 25(3), 1070–1081. <https://doi.org/10.2118/190278-PA>
- Koh, A., Linhardt, R. J., & Gross, R. (2016). Effect of Sophorolipid n-Alkyl Ester Chain Length on Its Interfacial Properties at the Almond Oil-Water Interface. *Langmuir*, 32(22), 5562–5572. <https://doi.org/10.1021/acs.langmuir.6b01008>
- Magri, A., Baldo, C., Pedrine, M. A., & Celligoi, C. (2018). Review: Sophorolipids A Promising Biosurfactant and its Applications Study of probiotics in different matrices View project Optimization and scale-up of liquid-liquid extraction process with ionic liquids (ILs) as a sustainable tool for the separation of. *International Journal of Advanced Biotechnology and Research(IJBR)*. <http://www.bipublication.com>
- Mahani, H., Keya, A. L., Berg, S., Bartels, W.-B., Nasralla, R., & Rossen, W. R. (2015). Insights into the Mechanism of Wettability Alteration by Low-Salinity Flooding (LSF) in Carbonates. *Energy & Fuels*, 29(3), 1352–1367. <https://doi.org/10.1021/ef5023847>
- Marhaendrajana, T., Ridwan, M. G., Kamil, M. I., & Permadi, P. (2018). Wettability alteration induced by surface roughening during low salinity waterflooding. *Journal of Engineering and Technological Sciences*, 50(5), 635–649. <https://doi.org/10.5614/j.eng.technol.sci.2018.50.5.4>
- Marhaendrajana, T., Widiyaningsih, I., Kurnia, I., & Sulistyarso, H. B. (2025). Fluid-to-Fluid and Fluid-to-Rock Interaction on Sophorolipids Biosurfactant for Enhanced Oil Recovery: A Literature Review. *Scientific Contributions Oil and Gas*, 48(1), 63–76. <https://doi.org/10.29017/SCOG.48.1April.1688>

- Megayanti, R., Hidayat, M., Cahyaningtyas, N., Sanmurjana, M., Nur Muhammad Yahya, Z., Sagita, F., Kadja, G. T. M., & Marhaendrajana, T. (2023). Effect of Titanium Dioxide Nanoparticles on Surfactants and Their Impact on the Interfacial Properties of the Oil-Water-Rock System. *ACS Omega*, 8(41), 38539–38545. <https://doi.org/10.1021/acsomega.3c05365>
- Mogensen, K., & Masalmeh, S. (2020). A review of EOR techniques for carbonate reservoirs in challenging geological settings. *Journal of Petroleum Science and Engineering*, 195(May). <https://doi.org/10.1016/j.petrol.2020.107889>
- Mohammadi, S., Kord, S., & Moghadasi, J. (2019). The hybrid impact of modified low salinity water and anionic surfactant on oil expulsion from carbonate rocks : A dynamic approach. *Journal of Molecular Liquids*, 281, 352–364. <https://doi.org/10.1016/j.molliq.2019.02.092>
- Mohammed, M., & Babadagli, T. (2015). Wettability alteration: A comprehensive review of materials/methods and testing the selected ones on heavy-oil containing oil-wet systems. *Advances in Colloid and Interface Science*, 220, 54–77. <https://doi.org/10.1016/j.cis.2015.02.006>
- Morse, J. W., & Arvidson, R. S. (2002). The dissolution kinetics of major sedimentary carbonate minerals. *Earth-Science Reviews*, 58(1–2), 51–84. [https://doi.org/10.1016/S0012-8252\(01\)00083-6](https://doi.org/10.1016/S0012-8252(01)00083-6)
- Nazari, M. H., Tavakoli, V., Rahimpour-Bonab, H., & Sharifi-Yazdi, M. (2019). Investigation of factors influencing geological heterogeneity in tight gas carbonates, Permian reservoir of the Persian Gulf. *Journal of Petroleum Science and Engineering*, 183(March), 106341. <https://doi.org/10.1016/j.petrol.2019.106341>
- Pal, S., Chatterjee, N., Das, A. K., McClements, D. J., & Dhar, P. (2023). Sophorolipids: A comprehensive review on properties and applications. *Advances in Colloid and Interface Science*, 313(February), 102856. <https://doi.org/10.1016/j.cis.2023.102856>
- Prabhakar, S., & Melnik, R. (2018). Influence of Mg²⁺, SO₄²⁻ and Na⁺ ions of sea water in crude oil recovery: DFT and ab initio molecular dynamics simulations. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 539(July 2017), 53–58. <https://doi.org/10.1016/j.colsurfa.2017.12.009>
- Shaik, I. K., Song, J., Biswal, S. L., Hirasaki, G. J., Bikkina, P. K., & Aichele, C. P. (2020). Effect of brine type and ionic strength on the wettability alteration of naphthenic-acid-adsorbed calcite surfaces. *Journal of Petroleum Science and Engineering*, 185(October 2019), 106567. <https://doi.org/10.1016/j.petrol.2019.106567>
- Shekhar, S., Sundaramanickam, A., & Balasubramanian, T. (2015). Biosurfactant producing microbes and their potential applications: A review. *Critical Reviews in Environmental Science and Technology*, 45(14), 1522–1554. <https://doi.org/10.1080/10643389.2014.955631>
- Sheng, J. J. (2013). Review of Surfactant Enhanced Oil Recovery in Carbonate Reservoirs. *Advances in Petroleum Exploration and Development*, 6(June), 1–10. <https://doi.org/10.3968/j.aped.1925543820130601.1582>
- Swadesi, B., Marhaendrajana, T., Septorato Siregar, H. P., & Mucharam, L. (2015). The effect of surfactant characteristics on IFT to improve oil recovery in tempino light oil field Indonesia. *Journal of Engineering and Technological Sciences*, 47(3), 250–265. <https://doi.org/10.5614/j.eng.technol.sci.2015.47.3.2>
- Thorstenson, D. C., & Plummer, L. N. (1977). Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase; example, the magnesian calcites. *American Journal of Science*. <https://doi.org/10.2475/ajs.277.9.1203>
- Udoh, T., & Vinogradov, J. (2019). A synergy between controlled salinity brine and biosurfactant flooding for improved oil recovery: An experimental investigation based on zeta potential and interfacial tension measurements. *International Journal of Geophysics*, 2019. <https://doi.org/10.1155/2019/2495614>
- Xu, Z. X., Li, S. Y., Li, B. F., Chen, D. Q., Liu, Z. Y., & Li, Z. M. (2020). A review of development methods and EOR technologies for carbonate reservoirs. *Petroleum Science*, 17(4), 990–1013. <https://doi.org/10.1007/s12182-020-00467-5>
- Yutkin, M. P., Radke, C. J., & Patzek, T. W. (2022). Chemical Compositions in Modified Salinity Waterflooding of Calcium Carbonate Reservoirs: Experiment. *Transport in Porous Media*, 141(2), 255–278. <https://doi.org/10.1007/s11242-021-01715-x>
- Zaeri, M. R., Shahverdi, H., Hashemi, R., & Mohammadi, M. (2019). Impact of water saturation and cation concentrations on wettability alteration and oil recovery of carbonate rocks using low-salinity water. *Journal of Petroleum Exploration and Production Technology*, 9(2), 1185–1196. <https://doi.org/10.1007/s13202-018-0552-2>
- Zheng, C., Wang, Z., Zhang, X., Wang, Y., & Zhang, L. (2024). Effect of salt ions (Na⁺, Ca²⁺ and Mg²⁺) and EOR anionic and nonionic surfactants on the dispersion stability of cellulose nanocrystals. *International Journal of Biological Macromolecules*, 282(October). <https://doi.org/10.1016/j.ijbiomac.2024.136761>

SAŽETAK

Utjecaj iona kalcija i magnezija na sustav sirove nafte, slojne vode i karbonatnih stijena tijekom povećanja iscrpka nafte soforolipidnom otopinom

Interakcija između sirove nafte, slojne vode i karbonatnih stijena ključna je za primjenu metoda povećanja iscrpka nafte (engl. *Enhanced Oil Recovery*, EOR). Površinski aktivne tvari (surfaktanti), kao što su biosurfaktanti soforolipidi, koji su sastavni dio istiskivajućega fluida, mogu smanjiti međufaznu napetost (engl. *interfacial tension*, ITF) i promijeniti moćivost takvih sustava. Međutim, prisutnost dvovalentnih iona, posebice kalcija (Ca^{2+}) i magnezija (Mg^{2+}), čini ovu interakciju složenijom, utječući na učinkovitost EOR metoda. U ovome je radu eksperimentalno ispitan utjecaj dvovalentnih iona na sustav sirova nafta – slojna voda – karbonatne stijene uz dodatak soforolipida. Izražen je utjecaj dvovalentnih iona na uzorke srednje teške i lake nafte dodavanjem različitih koncentracija Ca^{2+} i Mg^{2+} iona u otopinu soforolipida u trima različitim uvjetima saliniteta. Eksperimenti s međufaznom napetošću i viskoznošću emulzije procjenjuju interakcije fluida, dok mjerenja kontaktnoga kuta i statičke adsorpcije karakteriziraju interakciju između fluida i stijene, što je vrlo važno za EOR mehanizam. Dodavanje Ca^{2+} i Mg^{2+} iona (2000 ppm) otopinama natrijeva klorida (NaCl) (10 000 – 15 000 ppm) s koncentracijom soforolipida od 0,5 % težinski pri kritičnoj micelnoj koncentraciji (engl. *Critical Micelle Concentration*, CMC) povećalo je moćivost karbonatne stijene na vodu. Uz to, iako su ioni smanjili međufaznu napetost (ITF), nisu znatno utjecali na viskoznosti emulzije nafte u vodenoj otopini NaCl s 0,5 % (težinski) soforolipida. U uvjetima niskoga saliniteta (otopina s 5000 ppm NaCl) ovi su ioni smanjili brzinu adsorpcije u soforolipidnim otopinama na uzorcima vapnenaca iz Indiane. Dodavanje ovih dvovalentnih iona u otopinu za utiskivanje znatno je smanjilo učinkovitost istiskivanja nafte, za oko 28 % u slučaju lake nafte i 32 % u slučaju srednje teške nafte, tijekom navodnjavanja biosurfaktantima.

Ključne riječi:

sforolipidi, dvovalentni ioni, uvjeti saliniteta, povećanje iscrpka nafte

Author's contribution

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All authors have read and agreed to the published version of the manuscript.