

# Sulfonamide Derivatives as Novel Surfactant/Alkaline Flooding Processes for Improving Oil Recovery

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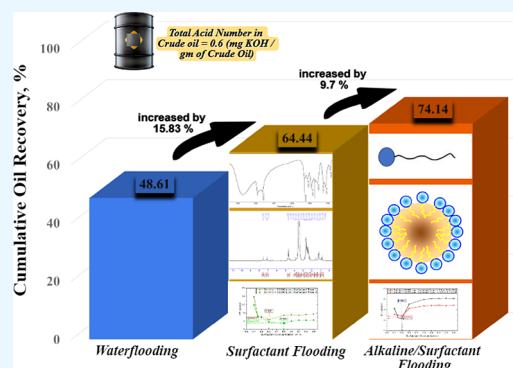
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**ABSTRACT:** Over time, oil consumption has increased along with a continuous demand for petroleum products that require finding ways to increase hydrocarbon production more economically and effectively. So, enhanced oil recovery technologies are believed to be very promising and will serve as a key to meeting the future energy demand. This paper aims to introduce an innovative method to boost the EOR by using two novel types of surfactants synthesized from sulfonamide derivatives. Types I and II surfactants were analyzed using Fourier transform infrared spectroscopy, and their characterization was further performed using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy. Additionally, the evaluation of these surfactants included interfacial tension measurements at concentrations up to 0.9 wt %. The combination of types I and II surfactants with alkaline (NaOH) was also investigated by the measurements of interfacial tension. A series of coreflood and sandpack tests under high-salinity conditions were carried out to assess the effects of a surfactant alone and alkaline–surfactant as a combination on improving oil recovery. The rock wettability was evaluated using relative permeability saturation curves, and the oil displacement efficiency was determined using fractional flow curves. The coreflood results demonstrated that alkaline–surfactant flooding with the chemical formula 0.2 wt % surfactant type II plus 0.5 wt % NaOH achieved a higher oil recovery of 74% OOIP compared to surfactant flooding with the chemical formula 0.5 wt % surfactant type II (64% OOIP) and waterflooding (saline solution with a 35,000 ppm salinity: 48% OOIP). Moreover, the experimental results showed that under both core and sandpack flood conditions, there was a noticeable reduction in oil–water interfacial tension, a change in rock wettability to more water-wet, and higher efficiency of oil displacement when alkaline was added to the surfactant. Based on current research, the alkaline–surfactant formulation is strongly recommended for chemical flooding because of its high efficacy and relatively low cost.



## 1. INTRODUCTION

Currently, the world is experiencing a major energy crisis and the depletion of conventional oil resources, which affects countries' economic stability and sustainability.<sup>1</sup> In addition, the recent political conflicts of the Russo–Ukrainian War have disturbed the market. As a result, the majority of countries stopped importing hydrocarbon products from Russia, and the price of oil increased.<sup>2</sup> To compensate for the obvious deterioration in the oil market, the world requires a boosting technology such as enhanced oil recovery (EOR). Globally, all researchers and scientists are looking into alternative low-cost technologies and materials to effectively enhance oil recovery.<sup>3</sup>

Enhanced oil recovery (EOR) techniques are utilized to increase the recovery of oil even further.<sup>4</sup> Accurately predicting water saturation and areal sweep efficiency, along with conducting thorough reservoir characterization, is crucial for the success of enhanced oil recovery techniques, as they have the potential to increase production rates and ultimately improve oil

recovery rates.<sup>5–10</sup> EOR techniques encompass chemical flooding, which involves the utilization of polymers, surfactants, alkalis, or a combination of these chemicals,<sup>11–20</sup> gas flooding, which utilizes carbon dioxide,<sup>21,22</sup> and thermal injection that involves the application of steam or in situ combustion.<sup>23–25</sup> Alkalis and surfactants are commonly utilized in chemical-based oil recovery techniques to enhance both the microscopic and macroscopic sweep efficiency of oil.<sup>26,27</sup>

Alkaline/surfactant (AS) flooding is a proven chemical flooding technique that has been shown to be successful in increasing the recovery of oil from fields that have been depleted.

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As a result of injecting these chemicals, the efficiency of oil displacement is improved, and the capillary forces in a porous medium are reduced by minimizing the oil/water interfacial tension and favorably modifying the wettability of reservoir rock.<sup>28</sup> In addition, the combination of alkalis with the surfactant allows for in situ saponification of the crude oil in the reservoirs while also aiding in decreasing the surfactant adsorption.<sup>29</sup>

In the chemical EOR process, the two most frequently utilized alkalis are sodium hydroxide (NaOH) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>).<sup>30</sup> An important aspect of alkali is its ease of synthesis and cost-effectiveness, which makes it a popular chemical agent in enhanced oil recovery.<sup>31</sup> The alkali reacts with the organic acids that are present in the crude oil, thereby forming an in situ surfactant.<sup>32</sup> Johnson<sup>33</sup> provided a summary of three potential approaches to alkaline flooding that can enhance the recovery of conventional oil. These include a reduction in interfacial tension between oil and water and also induce spontaneous emulsification, resulting in the formation of stable oil–water emulsions that facilitate the displacement and mobilization of trapped oil. Furthermore, alkali can alter the wettability of the reservoir rock, transitioning it from oil-wet to water-wet, which enhances the ability of the displacing fluid to access and recover the oil. Samanta et al.<sup>34</sup> studied the interactions between acidic crude oil and alkali solutions and their effects on enhanced oil recovery (EOR). They investigated the behavior of acidic crude oil when exposed to alkali solutions, specifically analyzing the changes in interfacial tension and wettability. The findings suggested that alkalis can significantly reduce the interfacial tension between oil and water, leading to improved oil recovery. Additionally, the alkali treatment results in wettability alteration of the rock surface, enhancing the displacement of oil by water. In a porous medium, there are a lot of factors that affect the formation of emulsions, including the acid number of crude oil, the salinity of the formation of water, pore-throat structure, and pH values.<sup>35</sup> The ability for emulsification during alkaline flooding increases with increasing the concentration of acid, resulting in transitioning from partial to complete emulsification.<sup>36</sup> Transparent microfluidic experiments have identified two kinds of emulsions, water in oil (W/O) and oil in water (O/W).<sup>37</sup> During the heavy oil waterflooding process, water/oil emulsions are more likely to form, showing non-Newtonian behavior, which means that the viscosity changes over time.<sup>38</sup> According to Arhuoma et al.,<sup>39</sup> the viscosity of a water/oil emulsion can be higher than that of the oil phase alone. This behavior results in a decrease in the mobility of water, which in turn enhances the sweeping efficiency of oil. Alternatively, the oil recovery can be enhanced by oil/water emulsions whereby crude oil is dispersed and entrained in the water phase, resulting in the improved flow toward the producing well.<sup>40,41</sup>

Surfactants, also known as surface-active agents, provide several benefits that include reducing interfacial tension (IFT),<sup>42,43</sup> modifying rock wettability,<sup>44,45</sup> forming emulsions,<sup>46</sup> and controlling mobility.<sup>47</sup> A microemulsion can form when a surfactant solution, oil, and salt are present under specific conditions that make it thermodynamically stable.<sup>48</sup> Winsor presented a classification system for microemulsions based on their phase behavior, with three distinct types identified as type I, type II, and type III.<sup>28,49</sup> Various types of microemulsions have different phase behavior transitions based on salinity, oil composition, temperature, pressure, and surfactant chemical structure and concentration.<sup>50</sup> Several studies have shown that optimizing the surfactant structure is critical for achieving

ultralow IFT under harsh conditions for any type of reservoir crude oil.<sup>51–57</sup>

Many researchers have conducted extensive studies on surfactant-based enhanced oil recovery, which include investigating surfactant flooding and its variations such as alkaline–surfactant flooding.<sup>58–61</sup> Thigpen et al.<sup>62</sup> conducted coreflood tests with oil having an API gravity of 27 to study the impact of surfactant addition to the alkaline solution on the oil–water interfacial tension. The results revealed that the addition of a surfactant increased the effectiveness of alkaline flooding, allowing for more residual oil to be extracted from the reservoir. This was attributed to the formation of low interfacial tension (IFT) between the aqueous solution and the reservoir oil. Rudin et al.<sup>63</sup> performed a study to analyze the impact of surfactant-enhanced alkaline flooding systems on oil/water emulsification and interfacial tension. Two crude oils containing organic acids with API gravities of 24.9 and 41.95 were used, respectively. The results revealed that the equilibrium interfacial tension (IFT) value was diminished to an extremely low level when the surfactant was added. Samanta et al.<sup>64</sup> investigated the interactions among an alkali, surfactant, and polymer in ASP (alkali–surfactant–polymer) slugs. Experimental tests were conducted to evaluate the influence of the alkali and surfactant on polymer viscosity, determining the optimal polymer concentration required for effective mobility control in the presence of other chemicals. Furthermore, the impact of the alkali and polymer on the surface tension of the polymer solution was examined, leading to the identification of the optimum surfactant concentration needed to reduce the interfacial tension between oil and water. The efficacy of the ASP system for enhanced oil recovery (EOR) was assessed through a series of flooding experiments conducted in sandpack systems. The results demonstrated recovery efficiencies ranging from 23 to 33% of the original oil in place, surpassing those achieved through conventional water flooding. Various mechanisms, such as interfacial tension reduction, emulsification of oil and water, solubilization of interfacial films, wettability alteration, and viscosity improvement, were identified as contributors to the EOR process. Based on the experimental findings and considering the relative cost of different chemicals, the study recommends specific concentration ranges for the alkali (0.7–1.0 wt %), polymer (1500–2500 ppm), and surfactant (0.2 wt %) to achieve successful ASP flooding. Kumar and Mandal<sup>65</sup> studied the interfacial properties and wettability changes in crude oil and aqueous surfactant–salt–alkali solution systems for enhanced oil recovery. Both ionic and nonionic surfactants are investigated, along with the influence of alkalis and salt (NaCl). The findings indicate that surfactants effectively reduce interfacial tension, with ionic surfactants showing higher efficiency due to their charged monolayer formation. The presence of salts enhances the accumulation of surface-active species, further reducing interfacial tension. Alkalis lead to a significant reduction in interfacial tension, with optimal concentrations providing suitable –OH levels for in situ surfactant production. Surfactants with alkalis induce wettability alteration, particularly CTAB and SDS.

This study aims to evaluate the potential of alkaline/surfactant flooding on oil recovery performance. Along with alkaline (NaOH), two novel types of surfactants synthesized from sulfonamide derivatives were evaluated as EOR agents through measuring the interfacial tension and applying flooding tests on both core and sandpack systems, where the sulfonamide agent has shown great success in the medical field, as it is used in

the treatment and diagnosis of cancer and it is cheap and easy to synthesize.<sup>66</sup> A set of flooding experiments were performed to evaluate the effect of the selected chemical formulations on oil recovery. The potential of the flooding solutions to alter the wettability of rock was studied through using relative permeability saturation curves,<sup>67</sup> while the oil displacement efficiency was determined through the fractional flow curves.

## 2. EXPERIMENTAL WORK

In this work, oil/water interfacial tension (IFT) measurements, wettability evaluation using relative permeability saturation curves, oil displacement efficiency determination using fractional flow curves, coreflood tests, and sandpack flood tests were carried out. All these experiments were conducted under ambient conditions.

**2.1. Fluids and Chemicals.** **2.1.1. Crude Oil.** The experimental evaluation of crude oil involved the determination of its key properties, including viscosity, density, API gravity, and acid number, as tabulated in Table 1. The crude oil exhibited a

**Table 1. Physical Properties of Crude Oil**

density (g/mL)	API gravity (° API)	viscosity @ 25 °C (mPa s)	acidity number (mg KOH per g of crude oil)
0.7946	46.58	2.464	0.6

density of 0.7946 g/mL (API = 46.58) and a viscosity of 2.464 mPa s at a temperature of 25 °C. The total acidity number

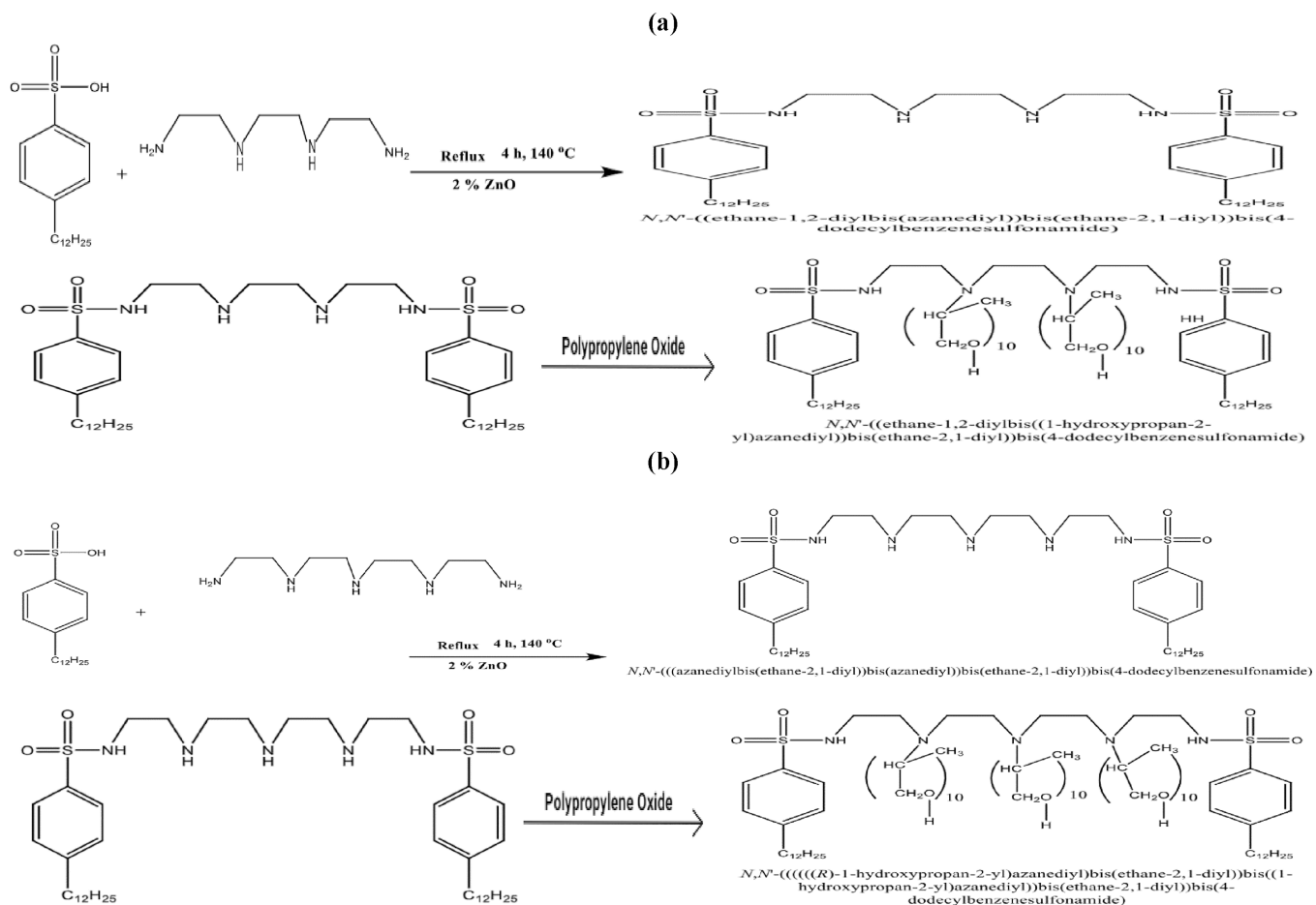
(TAN) was measured by titrating the crude oil with potassium hydroxide (KOH) until the pH was neutralized or reached a value of 7. At a pH of 7.0, the acid number obtained for the oil was 0.60 mg KOH per gram of crude oil.

**2.1.2. Brine.** For the experiments, formation water was prepared through mixing the salt (NaCl) with distilled water to achieve a salinity of 20 wt % (200,000 ppm). In addition, saline water containing 3.5 wt % (35,000 ppm) NaCl was used as the base fluid for waterflooding, as well as for all injection solutions used during the flooding process.

### 2.1.3. Surfactant Synthesis and Characterization.

#### 2.1.3.1. Synthesis of the Sulfonamide Derivative Surfactant.

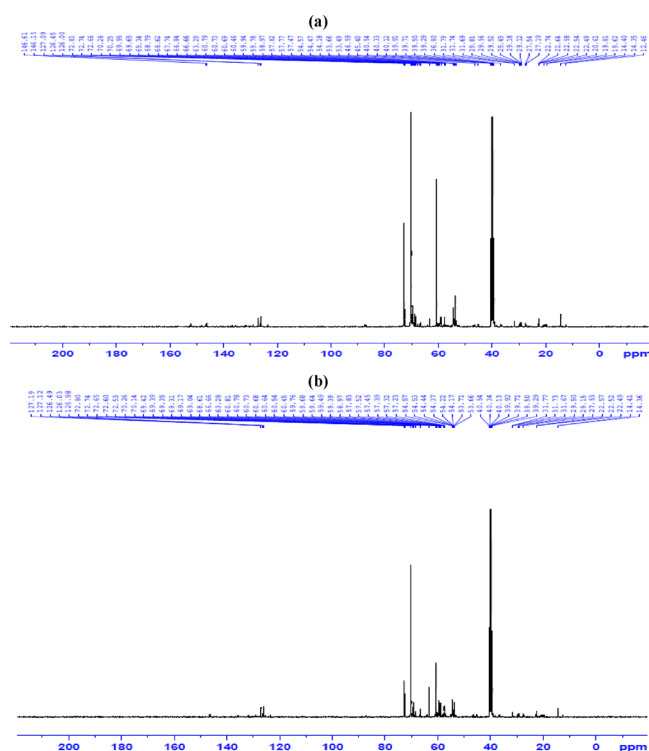
The synthesis of surfactant type one involved the combination of two moles of linear alkyl benzene sulfonic acid with one mole of triethylene tetramine in the presence of a 2 wt % ZnO catalyst. This mixture was dissolved in 100 mL of a xylene solvent and subjected to reflux at 140 °C for four hours using a three-neck round flask equipped with a mechanical stirrer, a Dean–Stark trap, a water condenser, and a dropping funnel. Following reflux, the produced water (36 mL) was efficiently removed, and the solvent was subsequently stripped out using a rotary evaporator. The obtained sulfonamide product was then dissolved in 30 mL of isopropanol. In the subsequent step, sulfonamide was reacted with molar ratios of polypropylene oxide in a stainless-steel high-pressure autoclave through a propoxylation reaction. The heating process was terminated, and the contents were cooled to ambient temperature. Upon cooling, the product was obtained, discharged, and weighted. For the synthesis of



**Figure 1.** Chemical reactions of the two types of surfactants; (a) surfactant type I and (b) surfactant type II.







**Figure 4.**  $^{13}\text{C}$  NMR spectra of (a) surfactant type I and (b) surfactant type II.

14.35, 14.40, 19.62, 19.81, 20.46, 20.61, 21.03, 22.49, 22.54, 22.58, 22.64, 31.69, 31.74, 36.80, 36.57, and 36.40.

In the  $^{13}\text{C}$  NMR spectrum of surfactant type II (Figure 4b), peaks were observed at chemical shifts of  $\delta$  C 136.92 and 135.82, corresponding to 1-benzene  $-\text{S}(=\text{O})(=\text{O})\text{N}$  and  $-\text{C}-\text{C}-\text{C}-\text{C}-$ , respectively. Additionally, peaks at  $\delta$  C 66.66 and 66.82 were observed, representing the carbon atoms in the propylene oxide units. Moreover, the CH protons in the aliphatic group dodecyl showed peaks at chemical shifts of  $\delta$  C 12.47, 14.35, 14.41, 22.52, 20.46, 20.61, 21.03, 22.49, 27.61, 29.10, and 38.18.

**2.1.4. Alkaline.** Crude oil with a high total acidity number (TAN) of 0.60 mg KOH/g oil is a good indicator of the surface activity of alkaline, which can potentially undergo chemical reactions with the organic acids present within the crude oil. As a result of this reaction, petroleum soap or an in situ anionic surfactant can be formed, which in turn lowers the oil–water interfacial tension, modifies the wettability of rock from oil-wet to water-wet, and facilitates the emulsification of oil and water. This emulsification process aids in the dispersion and mobilization of trapped oil within the reservoir, enabling its recovery.

Among the different types of alkalis, sodium hydroxide is generally preferred over others because of better interface activity, stronger emulsification ability, higher solubility in water, higher pH, easy availability, and low cost.<sup>34,68,69</sup> Based on Almalik et al.'s work,<sup>70</sup> sodium hydroxide (NaOH) with a concentration of 0.5 wt % achieved the lowest interfacial tension. Thus, sodium hydroxide (NaOH) at a concentration of 0.5 wt % was employed as the alkaline agent.

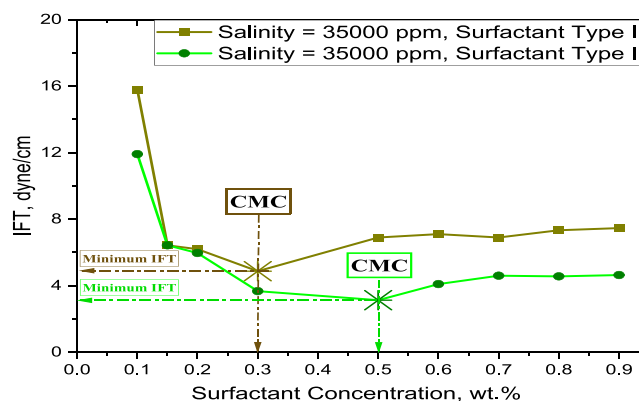
**2.2. Interfacial Tension Measurements.** In the presence of the various chemical solution systems, the interfacial tension (IFT) between oil and brine was measured using an EZ tensiometer (Model 201, USA). The EZ tensiometer employs the rod pull method, which involves slowly withdrawing a solid

rod from the interface between the two liquids. The force required to pull the rod was recorded and served as a measure of the interfacial tension between the oil and brine. A set of IFT tests were performed under a temperature of 25 °C and an ambient pressure of 1 atm. The optimal concentration of each injection solution that resulted in minimal interfacial tension is presented in Table 2.

**Table 2. Optimal Concentration of Injection Solutions That Resulted in Minimal IFT**

injection solution	optimum concentration, wt %	IFT, dyne/cm
surfactant type I	0.3	4.872
surfactant type II	0.5	3.129
surfactant type I plus NaOH	0.2 + 0.5	2.304
surfactant type II plus NaOH	0.2 + 0.5	2.786

**2.2.1. IFT Behavior of the Surfactant Type and Concentration.** The injection of surfactant solution allows for the mobilization of residual oil through a significant reduction in the interfacial tension between oil and water. This reduction in interfacial tension leads to a substantial increase in the capillary number ( $N_c$ ) by several orders of magnitude, ultimately reaching the necessary range for efficient oil recovery. The effect of different concentrations of the surfactant (up to 0.9 wt %) on IFT was investigated for both types I and II. The observed trends in Figure 5 indicate that each type of surfactant is characterized



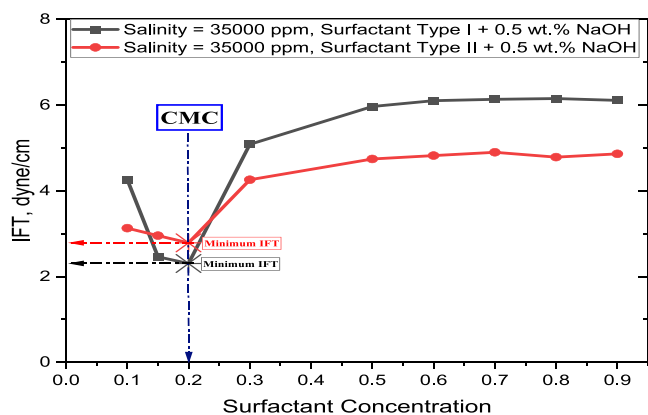
**Figure 5.** Interfacial tension of crude oil/brine as a function of surfactant concentration with a salinity of 35,000 ppm.

by an initial decline in interfacial tension (IFT) followed by the achievement of a minimum value. Subsequently, it starts to increase until a specific concentration of the surfactant is reached, after which it stabilizes. At lower concentrations, the surfactant molecules exhibit a strong affinity for adsorbing at the interface between oil and water. This preferential adsorption leads to a rapid reduction in the interfacial tension of the solution. As the interface becomes saturated with surfactant monomers, the IFT values reach a minimum, known as the critical micelle concentration (CMC). Once the critical micelle concentration (CMC) is reached, the introduction of additional surfactant molecules primarily affects the structure and size of micelles, leading to an increase in their numbers. Consequently, the effective concentration of the surfactant undergoes a slight reduction as a result of micelle solubilization in the aqueous phase. This ultimately leads to an increase in interfacial tension. For the curve of surfactant type I, a minimum IFT with a value of

4.872 dyne/cm was observed at 0.3 wt %. In addition, the surfactant type II achieved a minimum IFT with a value of 3.129 dyne/cm at 0.5 wt %. Thus, 0.3 wt % surfactant type I and 0.5 wt % surfactant type II were selected for the coreflood tests.

**2.2.2. IFT Behavior for a Combination of the Alkaline and Surfactant.** Alkali plays a significant role in alkali–surfactant (AS) flooding, and its impact is attributed to a range of mechanisms. These mechanisms encompass the reduction of surfactant adsorption, the generation of new soap, the achievement of low interfacial tension (IFT), wettability alteration, emulsification, and entrapment.

To investigate the interaction of alkaline–surfactant (A/S), the crude oil–brine interfacial tension was measured for both systems containing (up to 0.9 wt %) surfactant type I plus 0.5 wt % NaOH and (up to 0.9 wt %) surfactant type II plus 0.5 wt % NaOH. By comparing Figures 5 and 6, it can be observed that



**Figure 6.** Interfacial tension of crude oil/brine as a function of surfactant concentration plus 0.5 wt % NaOH with a salinity of 35,000 ppm.

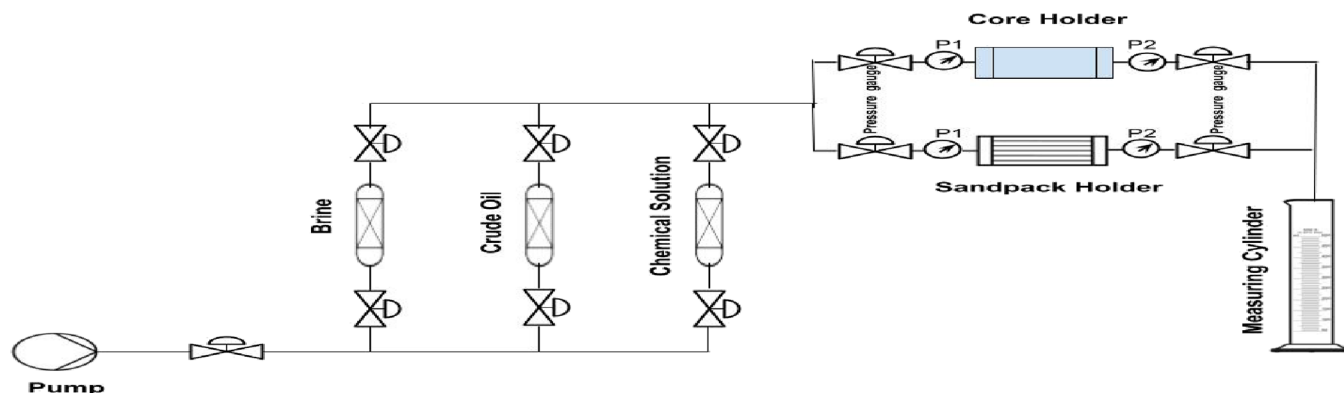
the introduction of alkaline caused a significant reduction in the interfacial tension between the crude oil and brine phases. As demonstrated in Figure 6, the minimum IFT was obtained at 0.2 wt % for both type I and type II surfactants when 0.5 wt % NaOH was added, resulting in IFT values of 2.304 and 2.786 dyne/cm, respectively. Thus, 0.2 wt % surfactant type I plus 0.5 wt % NaOH and 0.2 wt % surfactant type II plus 0.5 wt % NaOH were selected for the coreflood tests and sandpack flood tests, respectively.

**2.3. Flooding Procedure.** All the chemical flooding tests were carried out in the laboratory using an experimental flooding

system. The flooding experimental system consisted of a core holder for core plugs, a sandpack holder for unconsolidated sand, accumulators for storing the chemical solution, brine, and crude oil, a displacement pump for displacing the fluids into the sandpack or core plug, and graduated cylinders for receiving the samples. Core and sandpack flood tests were performed horizontally under ambient conditions of pressure and temperature (1 atm, 25 °C). The details of the schematics of the apparatus are shown in Figure 7.

**2.3.1. Core Preparation and Physical Properties.** In this study, sandstone core plugs, which are classified as clastic sedimentary rocks, were subjected to flooding runs through the coreflooding system. In the coreflooding system, the experimental procedure was briefly explained as follows: the porosity of core plugs was determined through using the saturation method, where the dry weight of each core was recorded. The cores were subsequently fully saturated by immersing them in a saline solution with a salinity of 200,000 ppm, and their weights were recorded after saturation. The bulk volume was determined by using a Vernier caliper, which measures cylindrical core plugs' length and diameter. In addition, the liquid permeability of the core plugs was measured by utilizing a permeameter device. The fully saturated core plugs were mounted into the core holder, where the flooding experiments were conducted. The next step involved injecting the crude oil into the core plugs through using a displacement pump until the formation water was no longer ejected. After the crude oil was injected into the core plugs, the displaced brine was considered as the initial oil saturation ( $S_{oi}$ ), whereas the formation water remaining inside the core was considered as the connate water saturation ( $S_{wc}$ ). Table 3 provides the properties and dimensions of the five core plugs utilized in this study.

**2.3.2. Sandpack Preparation and Physical Properties.** On the other hand, the sandpack employed in this study had a length of 28.81 cm and a diameter of 5.212 cm. To prepare the sandpack for injection, unconsolidated sand with a size of 0.149–0.297 mm was used. Additionally, to ensure uniform fluid flow and prevent sand migration and loss during the flooding experiments, both the inlet and outlet of the sandpack were equipped with screens and filters. The experimental process in the sandpack flooding system can be summarized as follows: first, unconsolidated sand was packed into the sandpack, and it was saturated with formation water containing a salinity level of 200,000 ppm. Permeability was subsequently measured. Following that, the sandpack was subjected to an oil injection process until water production was almost negligible, with a



**Figure 7.** Schematic diagram for the flooding experimental system.

**Table 3. Dimensions and Properties of the Sandstone Core Samples Used in This Study**

core no.	length ( <i>L</i> ) (cm)	diameter ( <i>D</i> ) (cm)	area ( <i>A</i> ) (cm <sup>2</sup> )	bulk volume ( <i>V<sub>b</sub></i> ) (cc)	pore volume ( <i>V<sub>p</sub></i> ) (cc)	porosity ( <i>φ</i> ) (%)	permeability ( <i>K</i> ) (mD)
A1	4.3	3.8	11.34	48.76	5.287	10.84	484.77
P1	3.5	3.8	11.34	39.69	5.394	13.60	504.18
P2	4.7	3.8	11.34	53.30	6.500	12.20	493.28
R1	6.6	3.8	11.34	74.84	11.600	15.50	515.46
R2	3.8	3.8	11.34	43.24	8.455	19.55	438.04

water cut of less than 1%, in order to determine the initial oil saturation and connate water saturation. Table 4 introduces the dimensions and characteristics of the sandpack.

**Table 4. Sandpack Properties**

properties, unit	values
sand size, mm	0.149–0.297
length, cm	28.81
diameter, cm	5.212
area, cm <sup>2</sup>	21.34
bulk volume, cc	614.67
pore volume, cc	135
porosity, %	21.96
permeability, mD	579.25

### 3. RESULTS AND DISCUSSION

**3.1. Oil Recovery Tests.** A series of experiments were conducted to study the effect of surfactant flooding and alkaline–surfactant flooding on the recovery of oil during the secondary stage. The experiments involved both coreflood tests and sandpack flood tests. Moreover, the wettability was determined through using the relative permeability saturation curve. In addition, the oil displacement efficiency for the displacing fluids was calculated by using the fractional flow curves. The flooding runs' experimental details and results are summarized in Table 5.

**3.1.1. Coreflood Study.** In order to examine the efficiency of using surfactant flooding alone and alkaline–surfactant flooding as a combination for improved oil recovery through the oil/water emulsification process, a set of coreflood tests (runs 1 to 5) were performed as secondary oil recovery. In all these tests, the oil volume, water volume, pressure drop, and displacing time were reported at each injected pore volume. In these tests, the effects of saline solution with 35,000 ppm salinity, 0.3 wt % surfactant type I, 0.5 wt % surfactant type II, 0.2 wt % surfactant type I plus 0.5 wt % NaOH solution, and 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution were investigated. Table 5 presents the outcomes of the coreflooding experiments.

**3.1.1.1. Effect of the Surfactant.** As depicted in Figure 8a, it was evident that the cumulative oil recovery for surfactant flooding (types I and II) was higher than that achieved through waterflooding. In addition, the maximum oil recovery was achieved by surfactant type II at 0.5 wt %. At this type of surfactant, a maximum oil recovery factor of 64.44% was achieved compared to oil recovery factors of 48.61 and 60.81% in the case of waterflooding and surfactant type I at 0.3 wt %. These findings can be attributed to the significant reduction in interfacial tension (IFT) achieved through surfactant flooding, as evidenced by the observed IFT results presented in Figure 5.

In this study, the evaluation of rock wettability through relative permeability saturation curves (Figure 8b) revealed important insights. At the intersection points of the water and oil

relative permeability curves, the water saturations were 0.502, 0.573, and 0.6025 for the saline solution with 35,000 ppm salinity, 0.3 wt % surfactant type I, and 0.5 wt % surfactant type II, respectively. It is evident that the use of two types of surfactants can result in a slight increase in the wettability of rocks toward water-wet, especially surfactant type II.

In addition, the fractional flow curves were calculated for waterflood, surfactant type I flood, and surfactant type II flood to assess the impact of surfactant flooding on oil displacement efficiency as the IFT is reduced and rock wettability is altered to be more water-wet. The results from the fractional flow curves of the three displacing fluids indicated that the use of 0.5 wt % surfactant type II caused a greater shift toward the right side. This shift signifies a higher flood front water saturation at breakthrough ( $S_{wBT}$ ), a higher average water saturation at breakthrough ( $S_{wBT}$ ), more efficient oil displacement (ED), and lower residual oil saturation ( $S_{or}$ ) as demonstrated in Figure 8c. In addition, the two types of surfactants have  $S_{wBT}$ ,  $S_{wBT}$ , and ED higher than waterflooding. Table 6 provides a summary of the displacement efficiency results for the three fluids that were injected.

**3.1.1.2. Effect of Alkaline–Surfactant.** The effect of alkaline–surfactant flooding on oil recovery was studied as a secondary recovery stage as shown in Figure 9. It was found that the tests with 0.2 wt % surfactant type I plus 0.5 wt % NaOH solution and 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution have a high increase in oil recovery. As depicted in Figure 9a, 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution achieved the maximum oil recovery factor of 74.14%, compared to 68.75 and 48.61% in the case of 0.2 wt % surfactant type I plus 0.5 wt % NaOH solution.

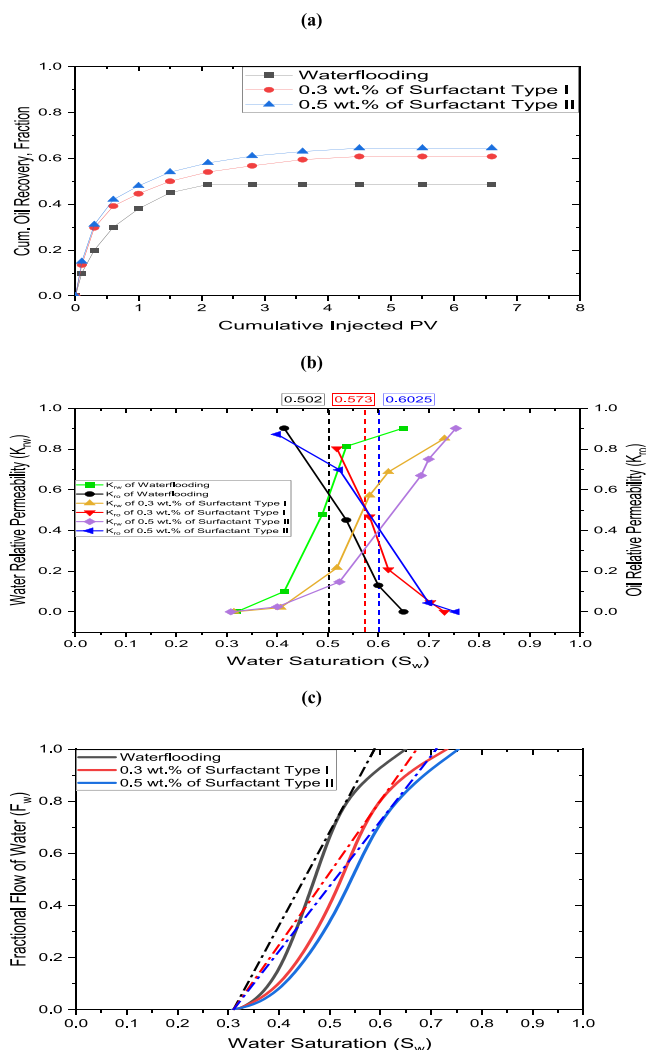
As demonstrated by Figure 9b, it was observed that the water saturations at the crossover points of relative permeability curves, where relative permeabilities are equal to each other in the case of saline solution with 35,000 ppm salinity, 0.2 wt % surfactant type I plus 0.5 wt % NaOH solution, and 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution, were 0.502, 0.612, and 0.69, respectively. This behavior proves that alkaline–surfactant solutions, especially surfactant type II plus NaOH, can alter the wettability of rock, transforming it from a state of weak water-wet to strong water-wet.

The significant reduction in IFT and alteration of wettability toward water-wet due to alkaline–surfactant solutions, as depicted in Figure 6 and Figure 9b, respectively, resulted in a significant acceleration of oil displacement. Consequently, this was reflected in the shift of the fractional flow curves from the left side (in the case of waterflooding) to the right side (in the case of alkaline–surfactant flooding). The chemical formula containing 0.2 wt % surfactant type II plus 0.5 wt % NaOH was more shifted to the right as depicted in Figure 9c, indicating a lesser amount of residual oil. The results of displacement efficiency for the three injected fluids are presented in Table 7.

**3.1.1.3. Comparison.** Upon comparing the effects of surfactant flooding and alkaline–surfactant flooding with

Table 5. Summary of Flooding Experiments

secondary oil recovery by core	injected fluid	slug conc. (g/L)	slug conc. (lb)	slug size (PV)	saturation (% PV)						recovered oil × 10 <sup>-5</sup> (bbl)	oil recovery (% OPIP)	
					V <sub>p</sub> (cc)	V <sub>oi</sub> (cc)	V <sub>wc</sub> (cc)	V <sub>or</sub> (cc)	S <sub>oi</sub>	S <sub>wc</sub>			S <sub>or</sub>
secondary oil recovery by core	A1 brine	35	0.0772	2.1	5.287	3.6	1.687	1.85	68.092	31.908	34.991	1.75	48.61
	P1 surfactant type I	3	0.0066	4.5	5.394	3.7	1.694	1.45	68.595	31.405	26.882	2.25	60.81
	P2 surfactant type II	5	0.011	4.5	6.5	4.5	2	1.6	69.231	30.769	24.615	2.9	64.44
	R1 surfactant type I plus NaOH	(2 + 5)	(0.0044 + 0.011)	3.6	11.6	8	3.6	2.5	68.966	31.034	21.552	5.5	68.75
	R2 surfactant type II plus NaOH	(2 + 5)	(0.0044 + 0.011)	2.8	8.455	5.8	2.655	1.5	68.598	31.402	17.741	4.3	74.14
secondary oil recovery by sandpack	brine	35	0.0772	4.5	135	100	35	39.8	74.074	25.962	29.481	60.2	60.20
	surfactant type I plus NaOH	(2 + 5)	(0.0044 + 0.011)	4.5	135	100	35	26.53	74.074	25.926	19.652	73.47	73.47
	surfactant type II plus NaOH	(2 + 5)	(0.0044 + 0.011)	4.5	135	100	35	16.75	74.074	25.926	12.407	83.25	83.25



**Figure 8.** Curves of three injected fluids. (a) Cumulative oil recovery of the three injected fluids relative to the injected pore volume, (b) oil and water relative permeability saturation curves, and (c) fractional flow curves.

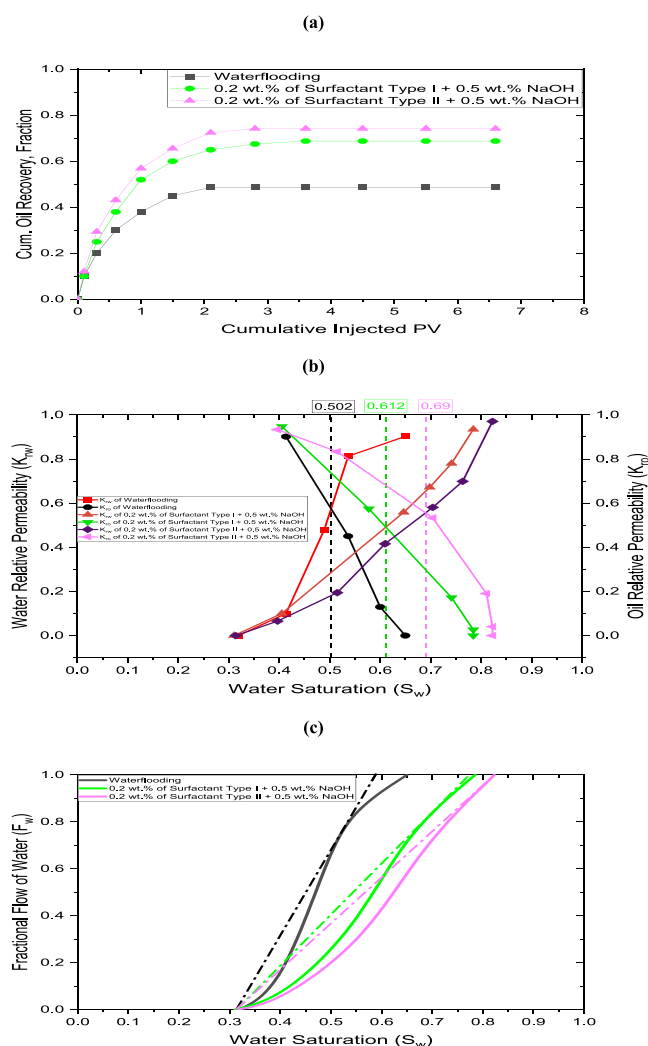
conventional waterflooding, several key observations emerged. In terms of cumulative oil recovery, both surfactant flooding and alkaline–surfactant flooding outperformed conventional waterflooding. This superiority can be attributed to the substantial reduction in IFT achieved through the emulsification mechanisms employed by the surfactants. During the emulsification process, surfactant molecules adsorb at the oil–water interface, with their hydrophilic heads interacting with the aqueous phase and their hydrophobic tails aligning with the oil phase. This arrangement allows for the formation of surfactant–oil–water microemulsions, causing a significant decrease in IFT. This reduction in IFT facilitates the detachment and mobilization of trapped oil droplets from the porous rock, enabling more efficient displacement and enhanced oil recovery.

Additionally, the reduction in IFT contributes to altering the wettability of the rock surface toward a more water-wet state. As the surfactant molecules adsorb onto the rock surface, they induce modifications in the surface properties, promoting a stronger affinity for water relative to oil. Consequently, the rock surface becomes more favorable for water infiltration, enhancing the displacement of oil and contributing to the overall efficiency of surfactant flooding.



**Table 6. Displacement Efficiency for the Two Types of Surfactants in the Case of Coreflood Tests**

injected fluid	$S_{wc}$ fraction	$S_{wf}$ @ breakthrough, fraction	$S_w^-$ @ breakthrough, fraction	$S_{or}$ fraction	ED @ breakthrough, %
waterflooding	0.3191	0.520	0.589	34.991	39.64
0.3 wt % surfactant type I	0.3141	0.590	0.673	26.882	52.33
0.5 wt % surfactant type II	0.3077	0.620	0.711	24.615	58.26

**Figure 9.** Curves of three injected fluids. (a) Cumulative oil recovery of the three injected fluids relative to the injected pore volume, (b) oil and water relative permeability saturation curves, and (c) fractional flow curves.

Under high-salinity conditions, surfactant flooding and alkaline–surfactant flooding have demonstrated superior performance in terms of achieving high oil recovery, efficient oil displacement, and altering wettability toward a strong water-wet state, surpassing the capabilities of the conventional water flooding technique. These findings are consistent with Al-Sahhaf et al., Gurkov et al., and Bera et al., who highlighted that the presence of salts could impact the distribution of surface-active

agents between the oil phase and the aqueous phase. Consequently, the presence of salts amplifies the tendency of surface-active agents to concentrate at the interface, leading to an enhanced reduction in interfacial tension (IFT).<sup>71–73</sup>

On the other hand, upon comparing the effects of surfactant flooding and alkaline–surfactant flooding, it was revealed that the alkaline–surfactant solutions are superior to surfactant solutions due to the fact that NaOH is a strong alkali. Figure 10a demonstrates that combining alkali (NaOH) with a surfactant to displace oil resulted in significant cumulative oil recovery, highlighting the cost-effective benefits of using NaOH. As a result, alkaline–surfactant (AS) flooding exhibits substantial potential for the development of conventional crude oil, as the addition of NaOH to the surfactant considerably lowers the oil–water interfacial tension (IFT) and facilitates oil dispersion in water. This accords with the outcomes observed in the interfacial tension (IFT) measurements shown in Figure 6.

As shown in Figure 10a, the formula containing 0.2 wt % surfactant type II plus 0.5 wt % NaOH could enhance the oil recovery by 13.33, 9.7, and 5.39% more than those of the formulas containing 0.3 wt % surfactant type I, 0.5 wt % surfactant type II, and 0.2 wt % surfactant type I plus 0.5 wt % NaOH. The recovery difference between the two systems (waterflooding and 0.2 wt % surfactant type II plus 0.5 wt % NaOH) is greater than 25%. This significant difference in oil recovery is consistent with the rule that alkaline–surfactant solutions have a significant impact on improving crude oil recovery.

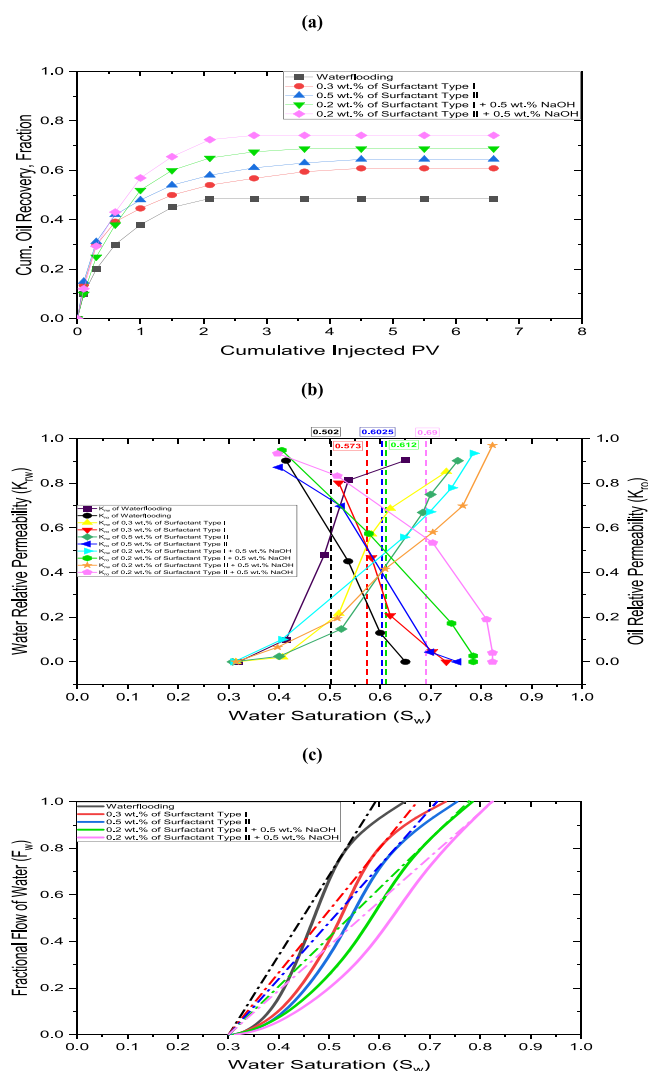
In addition, the results also indicated that the alkaline–surfactant solutions, especially the formula containing “0.2 wt % surfactant type II plus 0.5 wt % NaOH”, are more suitable and effective than the surfactant-only solutions. The reason for this is that the alkaline–surfactant solutions caused a change in the wettability of sandstone core plugs from weakly water-wet to strongly water-wet conditions, resulting in a notable reduction in the residual oil saturation ( $S_{or}$ ) value to a low level, as illustrated in Figure 10b.

Lowering the oil–water interfacial tension and inducing rock wettability to shift toward more water-wet can enhance the efficiency of oil displacement. This was consistent with the results of fractional flow curves demonstrated in Figure 10c, which showed that the alkaline–surfactant solutions shift toward the right side, especially the formula containing “0.2 wt % surfactant type II plus 0.5 wt % NaOH”. This indicates a higher flood front water saturation at breakthrough ( $S_{wBT}$ ), higher average water saturation at breakthrough ( $S_{wBT}$ ), greater efficiency of oil displacement, and lower residual oil saturation.

Consequently, the improved oil recovery with the use of alkaline–surfactant flooding can be attributed to multiple

**Table 7. Displacement Efficiency for the Alkaline–Surfactant Solutions in the Case of Coreflood Tests**

injected fluid	$S_{wc}$ fraction	$S_{wf}$ @ breakthrough, fraction	$S_w^-$ @ breakthrough, fraction	$S_{or}$ fraction	ED @ breakthrough, %
waterflooding	0.3191	0.520	0.589	34.991	39.64
0.2 wt % surfactant type I plus 0.5 wt % NaOH	0.3103	0.70	0.773	21.552	67.09
0.2 wt % surfactant type II plus 0.5 wt % NaOH	0.3140	0.79	0.810	17.741	72.30



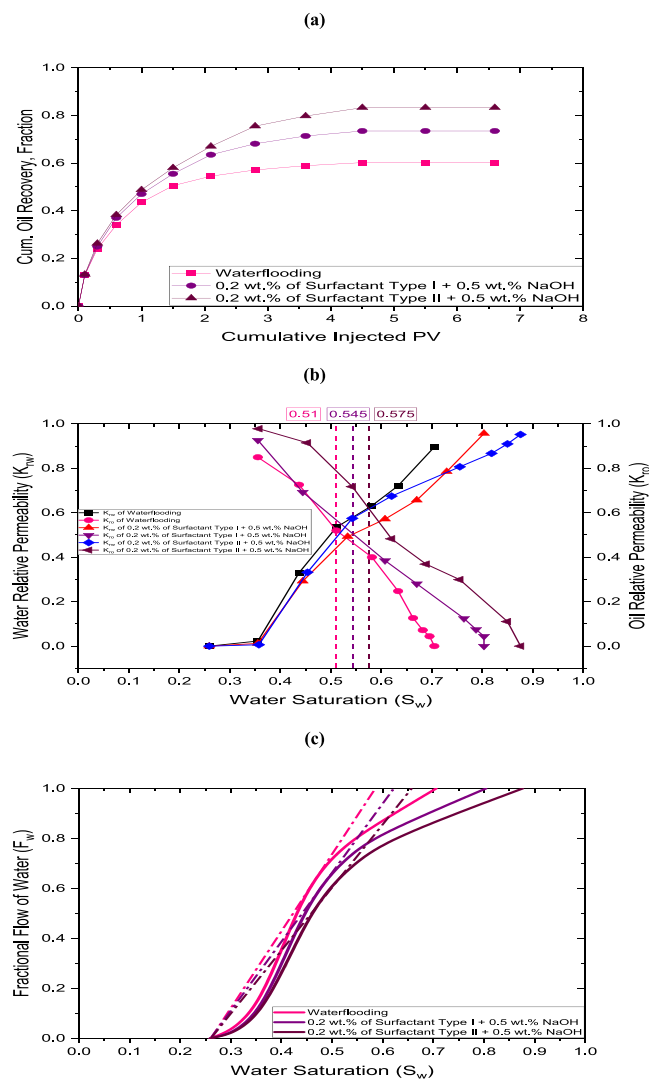
**Figure 10.** Curves of three injected fluids. (a) Cumulative oil recovery of the three injected fluids relative to the injected pore volume, (b) oil and water relative permeability saturation curves, and (c) fractional flow curves.

mechanisms. These mechanisms include a decrease in the oil–water interfacial tension (IFT), the creation of surfactants in situ via the chemical reaction between alkali and organic acids that exist in the crude oil, modification of rock wettability, and the oil–water emulsification, all of which result in better sweep efficiency.

**3.1.2. Sandpack Flood Study.** The results from the interfacial tension measurements and coreflood tests indicate that the most efficient chemical solutions that yielded minimal IFT and high oil recovery are alkaline–surfactant solutions. For more investigation into the effect of alkaline–surfactant solutions on oil recovery efficiency, flooding tests were carried out in sandpack. The tests evaluated the potential of saline solution with 35,000 ppm salinity, 0.2 wt % surfactant type I plus 0.5 wt % NaOH solution, and 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution as a secondary oil recovery. Table 5 presents a summary of the sandpack flood results. For each flood test conducted in the sandpack, the cumulative oil recovery and water cut were observed, recorded, and analyzed.

In the three flood tests conducted in the sandpack, it was observed that the tests with 0.2 wt % surfactant type I plus 0.5 wt

% NaOH solution and 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution significantly increased oil recovery compared to the waterflooding. Figure 11a shows the relationship between



**Figure 11.** Curves of three injected fluids. (a) Cumulative oil recovery of the three injected fluids relative to the injected pore volume, (b) oil and water relative permeability saturation curves, and (c) fractional flow curves.

cumulative injected PV and cumulative oil recovery. The optimum chemical solution in a secondary recovery stage was 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution, which achieved the maximum cumulative oil recovery of 83.25% compared to cumulative oil recoveries of 73.47 and 60.20% in the cases of 0.2 wt % surfactant type I plus 0.5 wt % NaOH solution and waterflooding, respectively.

As shown in Figure 11b, the water saturations at the crossover points were observed on the right of the 50% water saturation in the case of 0.2 wt % surfactant type I plus 0.5 wt % NaOH solution and 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution, with values of 0.545 and 0.575, respectively. Thus, the alkaline–surfactant solutions can change the wettability of unconsolidated sand more toward water-wetness, especially surfactant type II plus NaOH solution.

Furthermore, the fractional flow curves were calculated for the three injected fluids under sandpack conditions. The results

**Table 8. Displacement Efficiency for the Alkaline–Surfactant Solutions in the Case of Sandpack Flood Tests**

injected fluid	$S_{wo}$ fraction	$S_{wf}$ @ breakthrough, fraction	$S_w$ @ breakthrough, fraction	$S_{or}$ fraction	ED @ breakthrough, %
waterflooding	0.2593	0.460	0.585	0.2948	43.97
0.2 wt % surfactant type I plus 0.5 wt % NaOH	0.2593	0.475	0.620	0.1965	48.70
0.2 wt % surfactant type II plus 0.5 wt % NaOH	0.2593	0.490	0.657	0.1241	53.70

revealed that 0.2 wt % surfactant type II plus 0.5 wt % NaOH solution was more shifted to the right side than the other injected fluids, resulting in higher flood front water saturation at breakthrough ( $S_{wBT}$ ), higher average water saturation at breakthrough ( $S_{wBT}$ ), more efficient oil displacement (ED), and lower residual oil saturation ( $S_{or}$ ) as demonstrated in Figure 11c. The displacement efficiency results are presented in Table 8.

These findings revealed that the combination of the alkaline and surfactant was crucial to achieving optimal enhanced oil recovery. In addition, the alkaline–surfactant solutions are effective in decreasing the oil–water interfacial tension, as well as changing the wettability to a more water-wet state under both core and sandpack flood conditions. These effects ultimately led to increased oil recovery.

#### 4. CONCLUSIONS

A set of experiments including coreflood tests and sandpack flood tests were performed to assess the suitability and effectiveness of a surfactant alone and alkaline–surfactant as a combination to enhance oil recovery as a secondary oil recovery stage through the oil/water emulsification process. The results showed the following:

- (1) In coreflood tests, approximately 48, 60, and 64% of OOIP were recovered for the crude oil by injecting a saline solution with 35,000 ppm salinity, 0.3 wt % surfactant type I, and 0.5 wt % surfactant type II, respectively.
- (2) By injecting NaOH and a surfactant as a combination in coreflood tests, approximately 68% and 74% of OOIP were recovered by the chemical formulas containing 0.2 wt % surfactant type I plus 0.5 wt % NaOH and 0.2 wt % surfactant type II plus 0.5 wt % NaOH, respectively.
- (3) Higher additional oil recovery was obtained by alkaline–surfactant flooding compared to surfactant-only flooding since the addition of NaOH to the surfactant has a noticeable influence on the oil/water emulsification process, whereas alkali (NaOH) has the ability to react rapidly with the acidic components that exist in crude oil, leading to the creation of a surfactant (in situ). Moreover, alkaline–surfactant flooding has a high performance in modifying the wettability of rock from being weakly water-wet to strongly water-wet.
- (4) In sandpack flood tests, approximately 60, 73, and 83% of OOIP were recovered for the crude oil by injecting a saline solution with 35,000 ppm salinity, 0.2 wt % surfactant type I plus 0.5 wt % NaOH, and 0.2 wt % surfactant type II plus 0.5 wt % NaOH, respectively.
- (5) The chemical formula containing 0.2 wt % surfactant type II plus 0.5 wt % NaOH achieved the maximum oil recovery under both coreflood and sandpack flood experiments.
- (6) Considering the affordable cost of the surfactant and alkaline materials used in the study, the combination of alkaline and surfactant flooding appears to be a cost-

effective and viable method for improving oil recovery in both core and sandpack flood scenarios.

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##### Notes

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