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Synergistic anionic/zwitterionic mixed surfactant system with high emulsification efficiency for enhanced oil recovery in low permeability reservoirs

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ABSTRACT

Emulsification is one of the important mechanisms of surfactant flooding. To improve oil recovery for low permeability reservoirs, a highly efficient emulsification oil flooding system consisting of anionic surfactant sodium alkyl glucosyl hydroxypropyl sulfonate (APGSHS) and zwitterionic surfactant octadecyl betaine (BS-18) is proposed. The performance of APGSHS/BS-18 mixed surfactant system was evaluated in terms of interfacial tension, emulsification capability, emulsion size and distribution, wettability alteration, temperature-resistance and salt-resistance. The emulsification speed was used to evaluate the emulsification ability of surfactant systems, and the results show that mixed surfactant systems can completely emulsify the crude oil into emulsions droplets even under low energy conditions. Meanwhile, the system exhibits good temperature and salt resistance. Finally, the best oil recovery of 25.45% is achieved for low permeability core by the mixed surfactant system with a total concentration of 0.3 wt% while the molar ratio of APGSHS:BS-18 is 4:6. The current study indicates that the anionic/zwitterionic mixed surfactant system can improve the oil flooding efficiency and is potential candidate for application in low permeability reservoirs.

1. Introduction

With the increasing demand for energy in the world, enhancing the oil recovery of various developed reservoirs has become a hot concern. However, many reservoirs with high residual oil reserves have high temperature and salinity, low permeability and small pore throats, making crude oil difficult to be driven out. Among them, low-permeability reservoirs show low permeability, high clay content in rock composition, and significant heterogeneity in some cases. This leads to high flow resistance during water flooding, high injection pressure and low washing efficiency. The existence of natural fractures as well as artificial fractures transformed by fracturing makes the water cut rise quickly, which will potentially cause the phenomenon of water channeling. Therefore, the low-permeability reservoirs have great potential for development. Among various recovery enhancement methods, surfactant drives with low injection pressure, strong interfacial activity and good emulsification performance, have been proven to be very effective in enhancing oil recovery of low-permeability reservoirs (Lv et al., 2018; Mohsenatabar Firozjaii et al., 2018; Puerto et al., 2018; Xu et al., 2013; Yuan et al., 2015).

Surfactant has both hydrophilic and hydrophobic groups and prefers to adsorb at the oil—water interface, lowering the interfacial

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tension (IFT) and forming emulsions with crude oil (Omari et al., 2021). Some research shows that the basic principle of surfactant flooding is to reduce the interfacial tension, which in turn increases the capillary number (Feng et al., 2018a; Li et al., 2020a; Lv et al., 2018; Sarmah et al., 2020). When the interfacial tension is reduced to ultra-low ($< 1 \times 10^{-2}$ mN/m), the capillary number will increase significantly, thus enhancing the oil recovery efficiency. Other studies, on the other hand, have demonstrated that the ability of surfactants to emulsify crude oil is vital in flooding crude oil (Guo Y.B. et al., 2018, 2021; Shang et al., 2019). When a surfactant solution is injected into the pore space of the rock, the surfactant emulsifies the crude oil with the presence of the flow shear between the water and oil phases. Emulsification is an important mechanism for surfactant flooding. Firstly, the oil/water (O/W) emulsion stabilized by surfactants can reduce the viscosity of crude oil as well as the transportation of crude oil, which is crucial for improving the micro displacement efficiency. In addition, the emulsion droplets can also produce a Jamin effect via blocking the dominant seep channel, which helps to guide the fluid flow into the unswept area, and mobilize the residual oil (Kumar and Mandal, 2019; Pal N. et al., 2019a). Many studies have shown that emulsification capacity is an essential mechanism in enhancing oil recovery (Feng et al., 2018b; Yu et al., 2021; Zhang M. et al., 2021). Different from the case in high permeability reservoirs, emulsification is the dominant displacement mechanism in low permeability reservoirs (Chen et al., 2022). By proposing an artificial oil film model to simulate the micro residual oil absorbed on the rock surface, it is found that emulsifying reduces the thickness and size of the oil film and facilitates the detachment of tiny residual oil with a broad action range (Li et al., 2021). It should be noted that the surfactant system with both low interfacial tension and strong emulsification ability has the best displacement performance (Yuan et al., 2015). However, there is usually no direct relationship between the IFT and emulsification ability of surfactants (Guo et al., 2018). Since different types of surfactants have their own shortcomings, the use of a single traditional surfactant for oil flooding basically cannot meet the reservoir conditions (Han et al., 2021). The combination of various types of surfactants can bring the synergistic effects, resulting in a better performance than that of single surfactant (He and Xu, 2017), for instance, excellent temperature and salt resistance, higher interfacial activity and higher oil driving efficiency (Kumar and Mandal, 2018). Therefore, the combination of two surfactants with different properties has become a hot research topic recently (Belhaj et al., 2019; Guo J.X. et al., 2021; Kumari et al., 2019; Kurnia et al., 2020; Xiao et al., 2021; Xu et al., 2021; Zhang Z. et al., 2021; Zhong et al., 2018, 2020; Zhou et al., 2017).

The anionic/zwitterionic surfactant system, which is one of the most widely applied oil recovery surfactant compound systems, not only can bring their respective advantages, but also has a good synergistic effect to further improve sweep efficiency. Simulation studies show that the anionic surfactant sodium octadecyl sulfonate (SOS) and the zwitterionic surfactants alkyl sulfobetaine (ASB) can form a double-layer adsorption and mixed adsorption at the oil—water interface, forming a dense adsorption film and significantly lowering the IFT (Cai et al., 2018; Su et al., 2021). Meanwhile, experimental results show that the synergistic effect of anionic and zwitterionic surfactants can be used to create a variety of high-performance anionic/zwitterionic surfactant systems, such as high temperature resistance and salt resistance, ultra-low interfacial tension, massive formation of mesophase microemulsions and water-in-oil microemulsions, formation of wormlike micelles with high shear viscosity, pH-responsive emulsion (Chen et al., 2021; Kurnia et al., 2020; Wu et al., 2022; Zhang M. et al., 2021; Zhu et al., 2021). Therefore, anionic/zwitterionic surfactant systems that

achieve efficient emulsification of crude oil at low shear rates are more suitable for practical applications. However, few studies have been conducted on the emulsification effect of anionic/zwitterionic surfactant systems.

Alkyl polyglycoside (APG) surfactants have the following advantages: (1) Lower critical micelle concentration, better interface activity; (2) Strong environmental compatibility, temperature and salt resistance, acid and alkali resistance, and no cloud point (Iglauer et al., 2010); (3) The raw materials are widely available and biodegradable. APG1214 which contains extra 12—14 hydrophobic carbon chain has a better capability in reducing the interfacial tension and emulsification effect. However, the APG1214 surfactant has a limited solubility in water. Meanwhile, as non-ionic surfactant, it will encounter certain adsorption loss problem under the formation flow conditions. Therefore, the anionic surfactant APGSHS was prepared by chemical modification of the non-ionic surfactant APG1214, which could enhance its water solubility and reduce the adsorption in formation while retaining its interfacial tension reduction and emulsification behavior (Li et al., 2020b).

Alkyl polyglucoside sodium hydroxypropyl sulfonate (APGSHS) is a surface active, water-soluble, and environmentally friendly anionic surfactant with good compatibility with other surfactants (Li et al., 2019). The spontaneous emulsification system composed of APGSHS and cationic surfactant CTAB has good performance and can improve the recovery of crude oil by 14.14%. The zwitterionic surfactant octadecyl dimethyl betaine (BS-18) has good interfacial activity and temperature and salt resistance. Xu and Xu (2017) proposed the of BS-18 with anionic surfactant $C_{16/18}AEC_3$ system which can produce ultra-low interfacial tension with crude oil. However, oil displacement performance of this system was not evaluated.

To solve the above challenges, anionic surfactant APGSHS and zwitterionic surfactant BS-18 are compounded to develop a mixed surfactant system with low IFT and high emulsification ability. The impact of molar ratios of the system on emulsification capability is discussed. In addition, the synergistic recovery enhancement mechanism is investigated from an emulsification standpoint. These findings help to explore the mixed surfactant systems for enhanced oil recovery.

2. Materials and methods

2.1. Materials

The alkyl polyglucoside sodium hydroxypropyl sulfonate surfactant (APGSHS) was synthesized and purified according to previous work (Li et al., 2020a). The molecular structure of APGSHS is shown in Fig. 1(a). The commercial octadecyl dimethyl betaine BS-18 (see Fig. 1(b)), a zwitterionic surfactant aqueous solution with a concentration of 35 wt%, was purchased from Huaian Huajun New Material Technology Co. The crude oil and simulated formation water were obtained from a low-permeability reservoir in the Changqing Oilfield, China. The formation water composition is shown in Table 1. Unless otherwise indicated, all tests were conducted at 25 °C while all aqueous solutions were prepared by a Direct-Q-8UV-R Merck Millipore ultra-pure water integrated system. For all the emulsions prepared, the volumetric ratio between oil and water was 3:7.

2.2. Methods

2.2.1. Interfacial tension measurement

The IFT value between crude oil and mixed surfactant system was tested using a TX-500C Interfacial Tension Meter (Bowing Industry Corp., USA). The experiment was carried out at a speed of
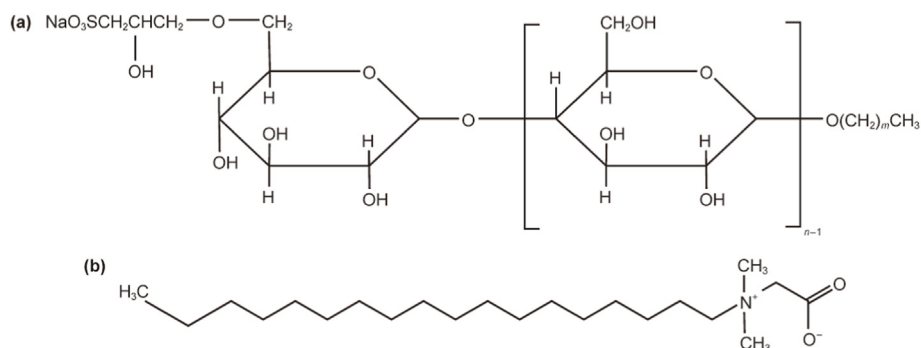
Fig. 1. Structure of APGSHS ($n = 1.3–1.5$, $m = 11/13$) (**a**) and BS-18 (**b**).

Table 1
Components of the formation water.

Ion	Concentration, mg/L
$K^+ + Na^+$	1580.9
Mg^{2+}	24.58
Ca^{2+}	53.02
Cl^-	3350.3
Total salinity	5008.8

6000 rpm at 50 °C. Each experiment was terminated when the IFT value remained unchanged.

2.2.2. Emulsify ability measurement

Emulsions were prepared with an IKA EUROSTAR 60 control overhead mixer (IKA, Germany), and experiments were performed at speeds of 50, 100, 200, 300, 400, 500, and 600 rpm for 2 min. The appearance of the solutions was captured in order to determine the degree of emulsification.

2.2.3. Droplet size and distribution of emulsion

A Leica microscope (Leica DM1000, Germany) was used to measure the average particle size and the distribution of emulsion droplets. A Delsa nanoparticle analyzer (Beckman Coulter Corp., USA) was used to determine the particle size distribution of emulsion droplets.

2.2.4. Contract angle measurement

Quartz is the most common mineral in sandstone reservoirs, usually accounting for more than 50% of the total sandstone volume. Hence, quartz thin slices were used instead of core slices for wettability improvement experiments in this study. This also avoided the problems of uneven and non-uniform surface of core slices. Using a TRACKER-H high-temperature interfacial rheometer (TECLIS, France) to measure the contact angles between quartz flakes and water before and after treated with surfactant solutions, determine the ability of different systems to change wettability, the specific steps included:

(1) Soak the quartz flakes in dimethyl silicone oil at 50 °C to make the quartz flakes oil-wet.
(2) Measure the initial contact angle between water and the quartz flakes, then immerse the quartz flakes in various systems to change the wettability.
(3) Air-dry the quartz flakes, measure the contact angle between the quartz flakes and water after treatment with various systems, and photograph the results.

2.2.5. Core flooding experiments

To evaluate the enhancing oil recovery ability of the mixed surfactant system, the following procedures were used to conduct core flooding tests, the sketch of the core-flooding setup is shown in Fig. 2.

(1) The diameter and length of the core samples were measured, and the gas-measured permeability of them was calculate.
(2) The core samples were vacuumed and saturated with formation water using a manual metering pump, the injected water volume was recorded as the pore volume (PV), and then the porosity (ϕ) was calculated.
(3) The crude oil was injected at a rate of 0.1 mL/min into the core until the produced fluid contained no water.
(4) Water flooding was conducted at a rate of 0.1 mL/min until the water cut of produced fluid was > 99%.
(5) The residual oil was flooded with 0.1 mL/min chemical slugs with 0.5 PV, then subsequent water flooding was followed at 0.1 mL/min until no oil was produced.

The core flooding experiments were performed at 50 °C. The cores used in the experiment are outcrop sandstone cores, and the initial wettability is water-wet, Table 2 lists the properties of used core samples.

3. Results and discussion

3.1. Interfacial tension

The IFT between surfactant system and crude oil is an important parameter to characterize the oil displacing ability of the system. Therefore, this section optimizes the concentration and compounding ratios of three kinds of mixed surfactant systems by evaluating the IFT.

Fig. 3 shows the interfacial tensions of APGSHS, BS-18 and the APGSHS/BS-18 mixed surfactant system with a molar ratio of 1:1 at various concentrations. As shown in Fig. 3, the IFTs of anionic surfactant APGSHS are in the range of 1–10 mN/m. IFTs of APGSHS decrease with the increase in concentration when the concentration is below 0.3 wt%. However, IFT slightly increase once the concentration is above 0.3 wt%. This is probably because some surfactant molecules enter the aqueous phase from the oil–water interface after the concentration exceeding the critical micelle concentration, forming a large quantity of micelles (Lu et al., 2015; Zhai et al., 2020). Concentration of the APGSHS exhibited small influence on the IFT between APGSHS solution and crude oil. Compared to APGSHS, the zwitterionic surfactant BS-18 has better interfacial activity and its IFT with crude oil reaches the lowest value of 9×10^{-3} mN/m at a concentration of 0.5 wt%. For BS-18, the
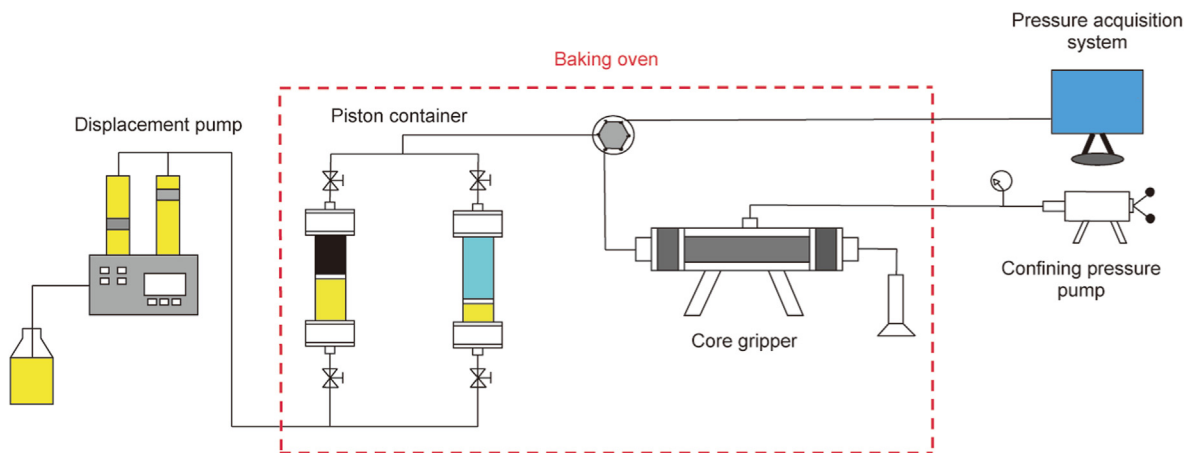
Fig. 2. Sketch of the device of core flooding experiments.

Table 2
Parameters of the core samples.

Core sample	Diameter, cm	Length, cm	Porosity, %	Permeability, 10^{-3} μm²
Core-1	2.53	10.03	21.83	38.09
Core-2	2.53	9.98	21.93	37.30
Core-3	2.53	10.06	19.78	46.12
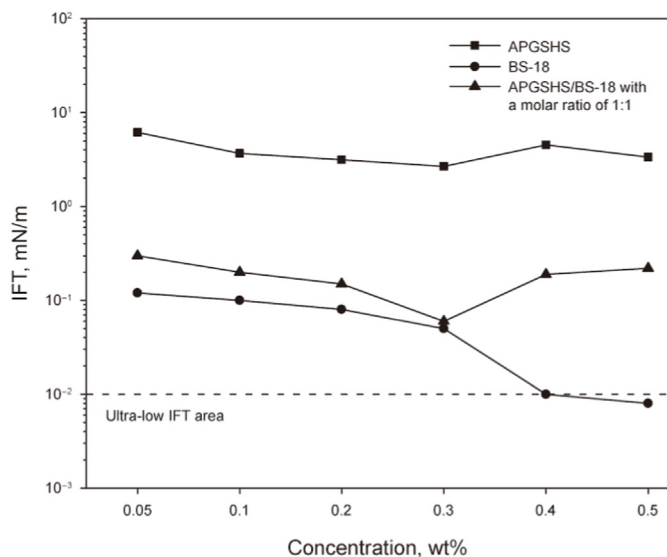
Fig. 3. IFTs between various systems and crude oil at different concentrations at 50 °C.
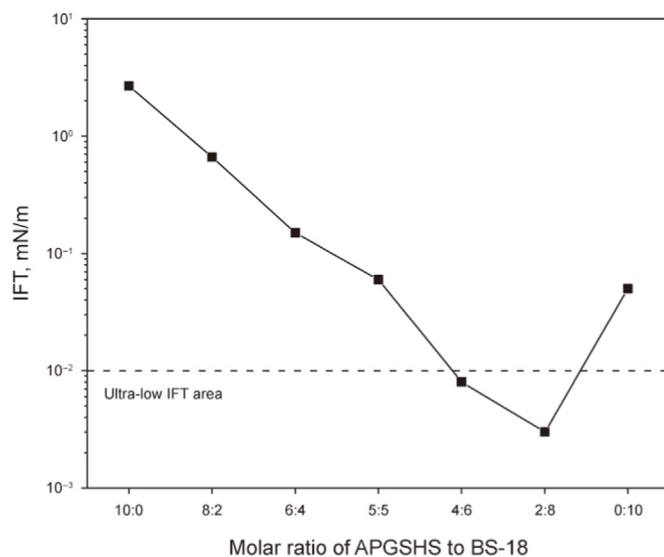

Fig. 4. IFTs between crude oil and APGSHS/BS-18 mixed surfactant systems with various molar ratios, with a total surfactant concentration of 0.3 wt%.

better ability in IFT reduction could be attributed to the interaction between the hydrophilic head group of BS-18 molecule and the water phase reaches equilibrium with the interaction between the lipophilic carbon chain and the oil phase. BS-18 molecules are evenly arranged on the oil–water interface, forming a surfactant layer with a certain thickness, which greatly reduces the interfacial tension between aqueous solution of BS-18 and crude oil (Sun et al., 2020; Zhong et al., 2018).

When the molar ratio of APGSHS/BS-18 mixed surfactant system is 1:1, the IFT values range between those of APGSHS and BS-18, and are closer to that of BS-18. The lowest IFT, with a value of 8×10^{-2} mN/m, of the mixed surfactant system is achieved with a total concentration of 0.3 wt%. It can be found that its variation

trend is similar to that of APGSHS, albeit the IFT values of the mixed surfactant system is one order of magnitude smaller than that of the APGSHS. The IFT of the mixed surfactant system increases after the concentration exceeds 0.3 wt%, which is due to the larger molecular fraction of APGSHS. The mixed surfactant system with a concentration of 0.3 wt% was selected for the subsequent study.

Fig. 4 shows the IFT of APGSHS/BS-18 mixed surfactant systems with crude oil at different molar ratios. Ultra-low oil–water interfacial tensions were achieved for the mixed surfactant systems with the APGSHS/BS-18 molar ratios of 4:6 and 2:8, indicating that the co-adsorption of the two surfactant molecules at the interface forms a more dense adsorption film (Ma et al., 2019). The cation in BS-18 has electrostatic attraction with the head group of APGSHS, weakening the electrostatic repulsion among APGSHS molecules. As proposed by Cai et al. (2018), surfactant molecules are likely distributed in two layers at the interface in anionic/zwitterionic mixed surfactant system.

To explain the synergistic effect of anionic/zwitterionic surfactants on the adsorption of oil–water interface and the reduction of interfacial tension, the Gibbs free energy change of the mixed surfactant system was analyzed. Under the condition of constant

temperature and pressure, the adsorption process of surfactant at the oil−water interface and micelle will produce Gibbs free energy change, which satisfies Eq. (1) (Manko et al., 2017):

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where ΔH and ΔS are the changes in enthalpy and entropy at a given temperature T.

The Gibbs free energy change of the surfactant aqueous solution represented by Eq. (1) is related to the standard adsorption Gibbs free energy (ΔG_{ads}^{o}) and micellization Gibbs free energy. Since the concentration of the mixed surfactant system during EOR is below the critical micelle concentration, the Gibbs free energy of micellization is not considered in this part. The transfer of the surfactant hydrophobic part from the aqueous phase to the oil phase and the change in the degree of the hydrophilic part hydration result in the standard Gibbs free energy of the adsorption of the surfactant molecules at the oil−water interface. Therefore, this energy can be expressed by Eq. (2) (Jańczuk et al., 1997):

$$\Delta G_{ads}^{o} = (\gamma_T - \gamma_{TW})A_T N_A + (\gamma_{WH_1} - \gamma_{WH})A_H N_A \tag{2}$$

where γ_T is the interfacial free energy of the hydrophobic tail; γ_{TW} is the interfacial free energy of the hydrophilic head group; A_T is the accessible area of the surfactant hydrophobic tail or its part; γ_{WH} and γ_{WH_1} are the interfacial free energies of the hydrophilic head group at different hydration degrees; A_H is the accessible area of the hydrophilic head group and the part hydrophobic tail of the surfactant; N_A is Avogadro's constant.

From Eqs. (1) and (2) above, the change of Gibbs free energy of surfactant molecules during adsorption at the oil−water interface is related to the change of enthalpy and entropy. The change in enthalpy during adsorption is usually small, and the change comes mainly from the formation of hydrogen bonds. The change of Gibbs free energy mainly originates from the change of entropy, which is primarily attributed to the releasing of water molecules bound to hydrophobic chain segments by hydration after the surfactant adsorbed at the oil−water interface. The change of Gibbs free energy of surfactant molecules transferred from water to the interface is related to the change of the free energy of the tail at interface. When the surfactant is adsorbed at the oil−water interface, the hydrophilic headgroup is still in the aqueous phase, and its Gibbs free energy remains unchanged before and after the adsorption at the oil−water interface. Hence, $\gamma_{WH_1} - \gamma_{WH}$ is equal to 0 in Eq. (2). The Gibbs free energies of the hydrophobic tail chain in the aqueous phase and the oil phase environment numerically equal to the interfacial tension values in the aqueous and oil phases, respectively. The interfacial tension value of the hydrophobic tail chain in the aqueous phase is significantly greater than its value in the oil phase. Therefore, $\gamma_T - \gamma_{TW}$ and ΔG_{ads}^{o} in the formula are negative values. According to the change of Gibbs free energy during the adsorption of surfactant at the oil−water interface, it can be concluded that the adsorption of mixed surfactant system at the oil−water interface is spontaneous. Later, the arrangement of surfactant molecules at the oil−water interface will be elucidated based on their interactions.

The APGSHS/BS-18 system produces two types of arrangement at the oil−water interface, competitive adsorption and mixed adsorption. As shown in Fig. 5(a), attributing to the large hydrophilic head groups, there are large gaps among the hydrophobic chains of the APGSHS molecules. For the APGSHS/BS-18 mixed surfactant system, BS-18 molecules are distributed in two layers at the interface. The first layer of surfactant molecules is located at the oil−water interface, the APGSHS molecules and BS-18 molecules are arranged in parallel with each other, generate competitive

adsorption. Due to the electrostatic attraction, the BS-18 molecules locate in the gaps of hydrophobic chain and form a mixed adsorption layer with APGSHS molecules (see Fig. 5(b)). The formation of the mixed adsorption layer makes the adsorption amount of the two surfactant molecules on the oil−water interface increase, forming a dense adsorption layer. When the molar ratio of the system is 4:6 and 2:8, the two surfactants form the most densely arrangement, which enables the ultra-low interfacial tension synergistically.

The performance of the mixed surfactant system in reducing interfacial tension of oil and water is related to oil composition, surfactant concentration and temperature. To explore the effective concentration range of the mixed surfactant system under different temperature conditions, plottings of IFT as a function concentration for APGSHS/BS-18 mixed surfactant system with a molar ratio of 4:6 were measured (see Fig. 6). With the increase in the concentration of the mixed surfactant system, the ability of surfactant to reduce interfacial tension gradually increases. When the critical micelle concentration is reached, the adsorption at the oil−water interface of surfactant is saturated, the rates of adsorption and desorption equilibrate, micelle begins to form, and the interfacial tension reaches its lowest value. When concentration exceeds the critical micelle concentration, the oil−water interface tension remains nearly constant. Increase in temperature favors the dissolution of surfactants in the aqueous phase and thus delays micelle formation (Pal et al., 2019b).

Interfacial tension reduction abilities of the APGSHS/BS-18 mixed surfactant system on different crude oil components, including saturated hydrocarbons, aromatic hydrocarbons, resin and asphaltenes, were measured. As shown in Fig. 7, it can be noted that the APGSHS/BS-18 mixed surfactant system has the best interfacial tension reduction performance with the saturated hydrocarbon components, which may be due to the good affinity of the hydrophobic chain segment in the surfactant due to its similar structure with the saturated hydrocarbon chain. The effect of mixed surfactant system and asphaltenes in reducing the interfacial tension is also significantly as compare to those of aromatic hydrocarbon and resin, which may be related to the interfacial activity of asphaltenes (Koreh et al., 2022).

3.2. Emulsification performance

3.2.1. Emulsifying ability

The emulsification ability of surfactant plays an important role in oil flooding (Zhou et al., 2019). On the one hand, O/W type emulsion helps to lower viscosity of crude oil, increase water phase permeability and favors the seepage of crude oil. On the other hand, the emulsion with certain viscosity can block the dominant seepage channel, leading to the improve of the sweeping area. Hence, it is essential to provide sufficient energy during the emulsion formation. From this point of view, the higher the emulsification degree of surfactant at low speed is, the stronger its emulsification ability is (Hu et al., 2022).

Fig. 8 shows the appearance of emulsions stabilized by mixed surfactant systems with various APGSHS/BS-18 molar ratios prepared at different rotation speeds. When the rotation speed is low, the oil droplets with large particle size can be clearly observed. For instance, for APGSHS/BS-18 mixed surfactant system with molar ratio of 8:2, oil droplets with large particle size could be observed immediately after be prepared by stirring at 100 and 200 rpm. After stopping stirring, the oil droplets will quickly gather and delaminate, producing an obvious oil−water interface. When the rotation speed increases up to a certain value, the crude oil can be completely dispersed in the solution, and the delamination rate is very slow, indicating that the crude oil is completely emulsified.
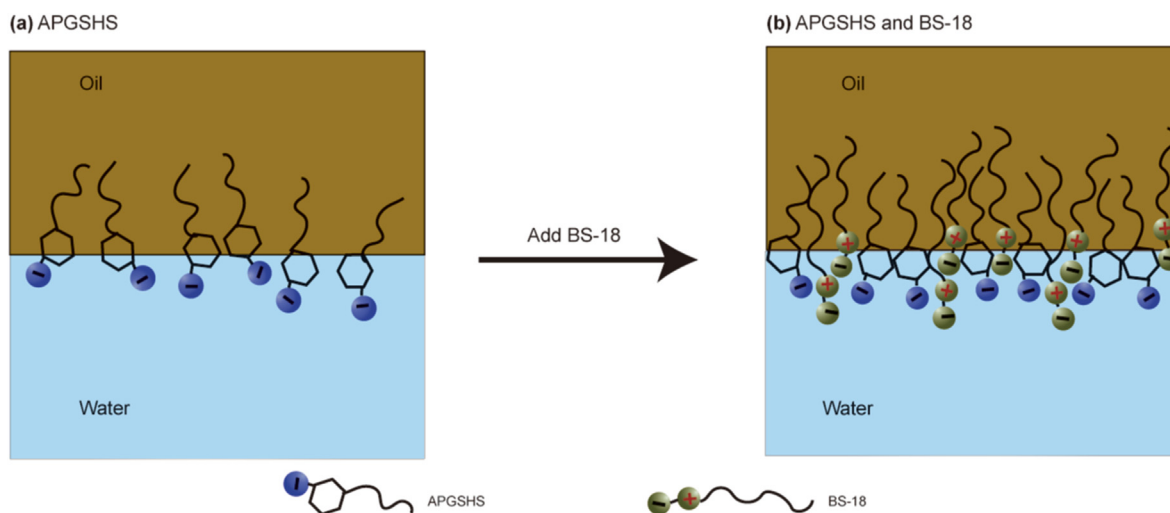
Fig. 5. Schematic arrangement of surfactant molecules at the oil–water interface: (**a**) APGSHS; (**b**) APGSHS and BS-18 mixed surfactant system.
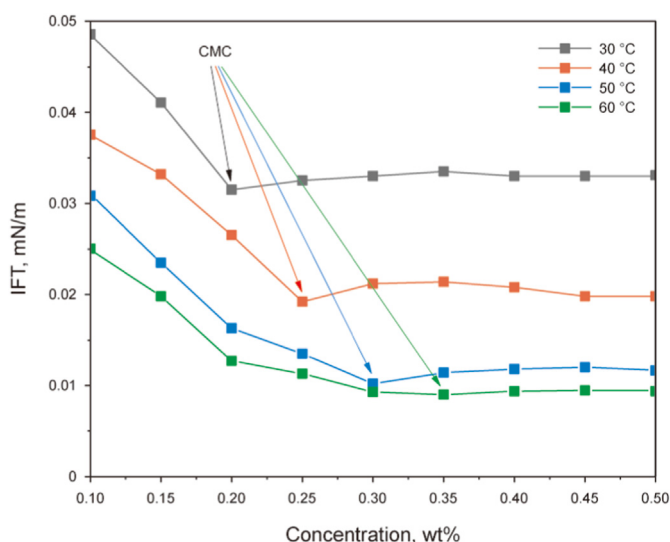

Fig. 6. Critical micelle concentrations of the APGSHS/BS-18 mixed surfactant system at various temperatures.
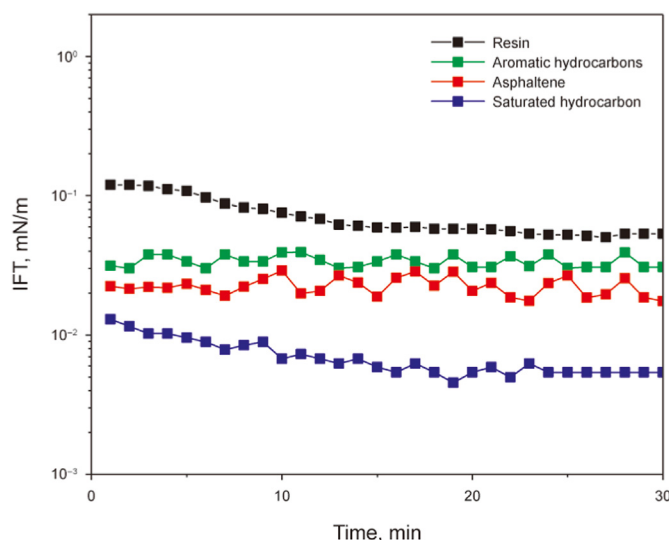

Fig. 7. Interfacial tension reduction effect of APGSHS/BS-18 mixed surfactant system for different crude oil components.

The corresponding rotation speed is the minimum emulsification speed. In this work, the emulsification speed is the rotation speed applied that can realize the emulsion of crude oil.

As shown in Fig. 8, the minimum emulsification speeds for APGSHS aqueous solution and BS-18 aqueous solution alone are 600 and 400 rpm, respectively. Meanwhile, most of the mixed surfactant systems can completely emulsify the crude oil at 300 rpm. When the molar ratio of the system is 4:6, the minimum emulsification speed is 100 rpm, suggesting that this system has the best emulsification ability and can form uniform emulsion under the condition of low energy. Moreover, the minimum emulsification speed of this system is better than that of most surfactant systems, indicating that it has excellent emulsification effect (Hu et al., 2022).

3.2.2. Droplet size and distribution of emulsion

The size of the emulsion droplets can reflect the emulsification ability and stability of the surfactant system. The smaller emulsion

droplets and the narrower droplet size distribution demonstrate that the system has higher emulsification capability and greater the emulsion stability (Hou et al., 2019).

Fig. 9 shows the particle size distribution of the emulsion stabilized by APGSHS/BS-18 mixed surfactant systems with various molar ratios. With the increase in BS-18 concentration, the particle size of the emulsion first decreases and then increases. The smallest average emulsion droplet size of 0.14 μm is obtained when the molar ratio of APGSHS/BS-18 is 4:6. Furthermore, its droplet size distribution range is very narrow, indicating that it can form a stable emulsion. The particle sizes of the mixed surfactant systems are smaller than those of the two surfactants applied alone. The maximum average particle size of the mixed surfactant system is only 0.24 μm, whilst the average particle size of the emulsion stabilized by BS-18 surfactant alone is 0.4 μm. Fig. 10 shows the microscopic morphology of the emulsion. The particle sizes of the emulsion stabilized by APGSHS/BS-18 mixed surfactant systems are evenly distributed and smaller than those stabilized by APGSHS or
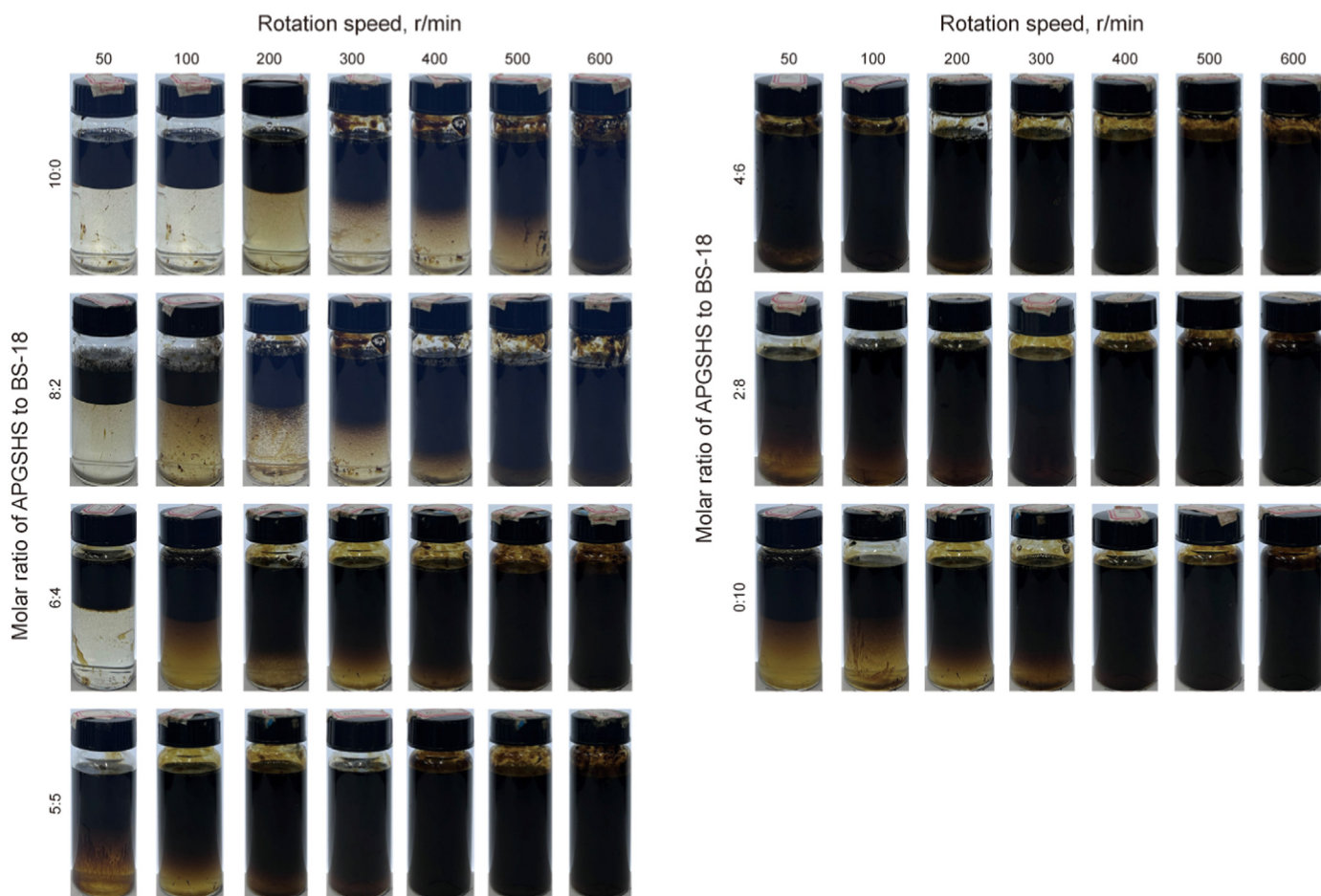
Fig. 8. Emulsification effect of APGSHS/BS-18 mixed surfactant systems with various molar ratios at different rotation speeds.
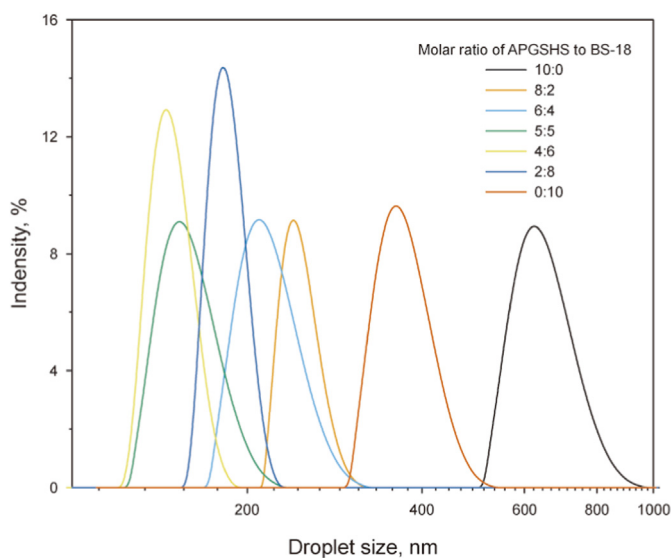

Fig. 9. Particle size distribution of emulsions stabilized by APGSHS/BS-18 mixed surfactant systems with various molar ratios.

BS-18 alone, this is consistent with results depicted in Fig. 9. Meanwhile, emulsion droplets are more uniformly distributed when the molar ratio is 4:6.

The above results indicate that the APGSHS/BS-18 mixed surfactant system has a synergistic effect in achieving ultra-low IFT and stabilizing emulsions. The lowest IFT and the best emulsification effect are achieved at molar ratios of 2:8 and 4:6, respectively. In practice, the emulsification effect is often accompanied by a higher oil recovery (Guo et al., 2018). When the molar ratio is 4:6, the crude oil can be completely emulsified with rotation speed of 100 rpm (see Fig. 8). In addition, the mixed surfactant system with a molar ratio of 4:6 also realizes ultra-low oil–water IFT. Therefore, in the subsequent experiments, the APGSHS/BS-18 mixed surfactant system with a molar ratio of 4:6 was used unless otherwise specified.

3.3. Wettability alternation of rock surface

Changing the surface wettability of oil-wet rock is one of the mechanisms of surfactant flooding to enhance oil recovery, thus it is necessary to determine the wettability alternation ability. Fig. 11 shows the contact angles of water droplets on quartz flakes after treatment by APGSHS/BS-18 mixed surfactant systems with various molar ratios. The quartz flakes treated with simulated formation water were used as a control. The contact angle of the control sample is 115.3°, which indicating a weakly lipophilic surface (see Figs. 11 and 12(a)). It can be seen from Fig. 9, the water contact angle decreases and then increases as the molar ratio of APGSHS/BS-18 changes from 10:0 to 0:10. The contact angles of APGSHS and BS-18 surfactant solutions alone are 101.3° and 102.4°, respectively.
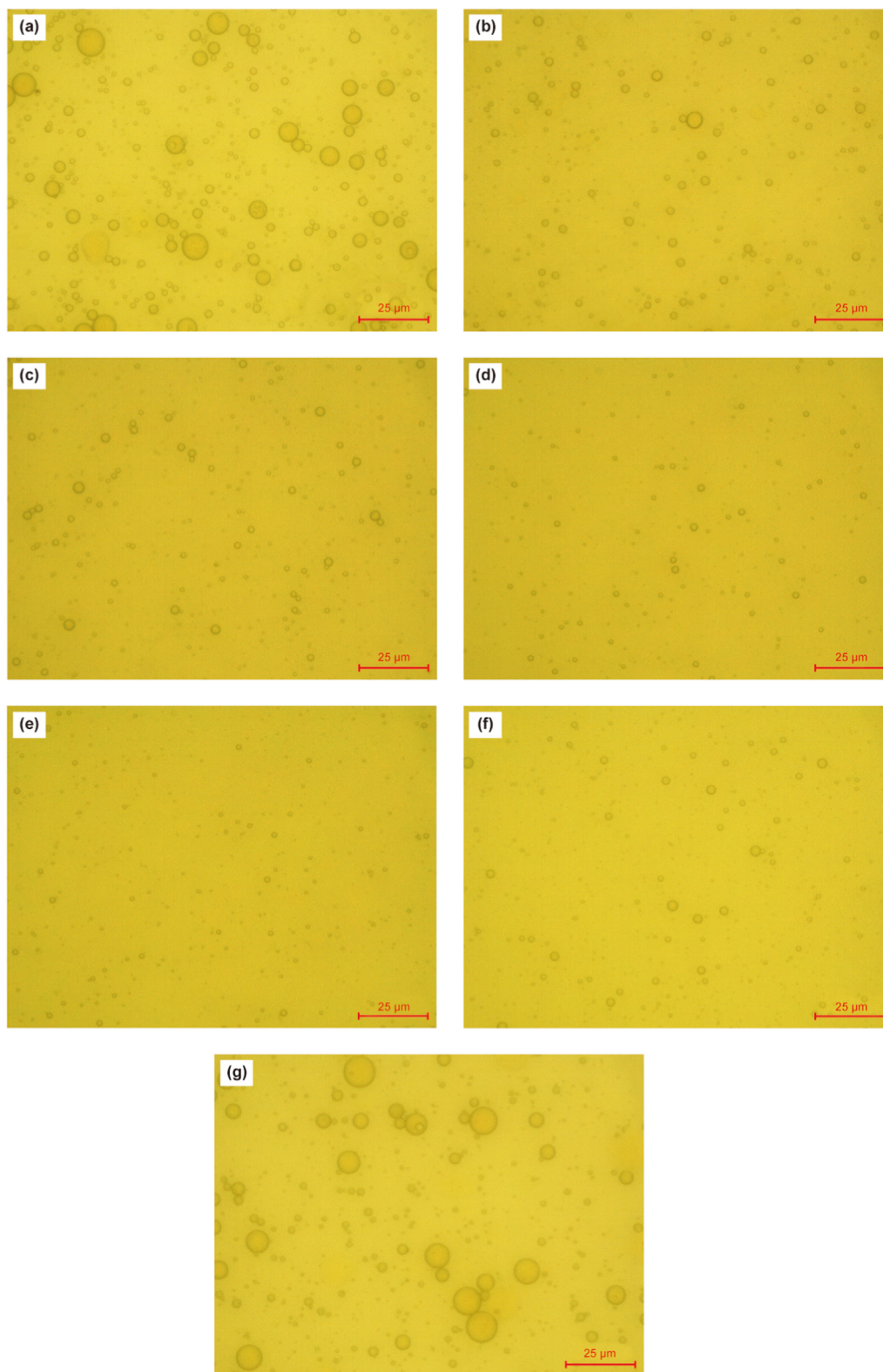
Fig. 10. Microscopic morphology of emulsions stabilized by APGSHS/BS-18 mixed surfactant systems with molar ratios of 10:0 (**a**), 8:2 (**b**), 6:4 (**c**), 5:5 (**d**), 4:6 (**e**), 2:8 (f), and 0:10 (**g**).

In contrast, the mixed surfactant system has a better effect in changing the wettability. When the molar ratio of APGSHS to BS-18 is 4:6 the water contact angle displays the smallest value 67.9° (see Figs. 11 and 12(c)), suggesting that the quartz flakes are hydrophilic.

In this case, the crude oil can be peeled off from the rock surface more easily.

The change of wettability may be attributed to the formation of ionic pairs between the head groups of the mixed surfactant system
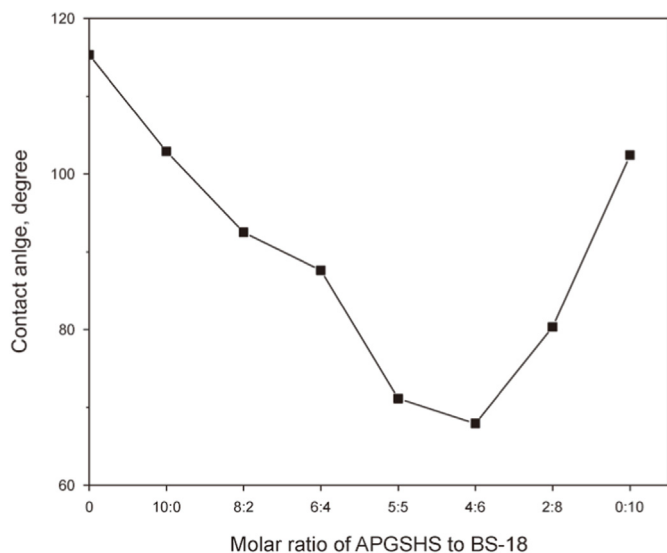
Fig. 11. Water contact angle values treated by APGSHS/BS-18 systems with various molar ratios.

and the charge component of the adsorbed crude oil, for instance, the carboxylic substances (Kumar and Mandal, 2017). The mixed micelles consisting of APGSHS and BS-18 can solubilize the active component of the crude oil adsorbed on the rock surface, thereby restoring the initial wettability of rock surface (Hou et al., 2018);

meanwhile, the hydrophobic interaction of the surfactant tail chain also reduces the lipophilicity of the rock surface (Kesarwani et al., 2021).

3.4. Temperature and salt resistance of mixed surfactant system

Some reservoirs currently being exploited have harsh formation conditions with high salinity or temperature, it is necessary to investigate the effect of temperature and salinity on the IFT reduction of mixed surfactant systems and the emulsions stability. Fig. 13 shows the effects of salinity and temperature on the IFT between the surfactant system solution and crude oil. Fig. 13(a) includes the IFT at different concentrations of monovalent and divalent electrolytes. The results show that the IFT decreases and then increases with the increase in concentrations for both kinds of electrolytes. The lowest IFT values for NaCl and $CaCl_2$ are observed when the salinities are 25,000 and 20,000 mg/L, respectively. This could be attributed to the fact that the addition of NaCl and $CaCl_2$ would affect the charge distribution in the hydrophilic head group of the surfactants. Na^+ and Ca^{2+} would interact with ionic heads of the surfactant molecules, compress the double electric layer, and weaken the electric repulsion between the surfactant ionic head moieties (Sun et al., 2020). Subsequently, the amount of surfactant adsorbed at the interface increases with the increase in salt concentration, leading to a decrease in the IFT. When the inorganic salt content is high, the solubility of the surfactant in water decreases, the surfactant enriched in the oil—water interfacial layer begins to decrease, and the oil—water IFT then increases (Belhaj et al., 2019). As can be seen from Fig. 13(a), when the inorganic salt
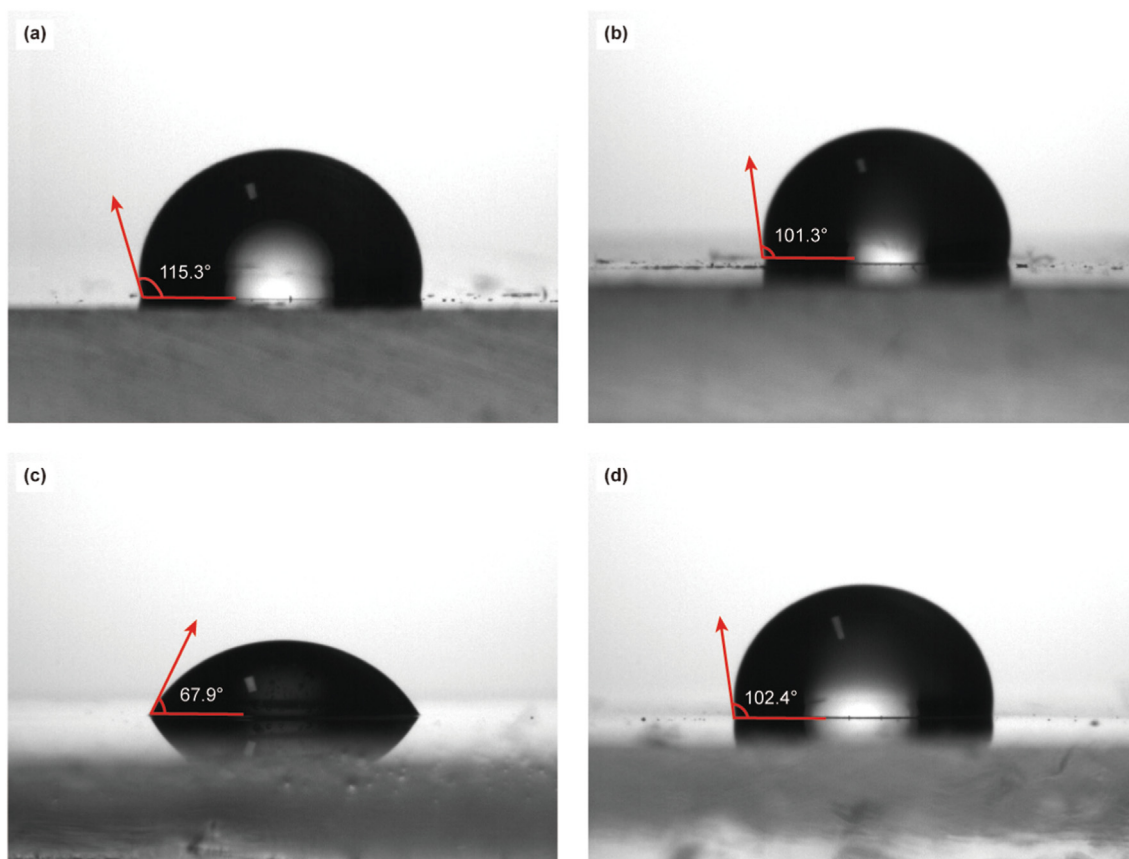

Fig. 12. Contact angles of water droplet on treated by simulated formation water (**a**), APGSHS surfactant solution (**b**), APGSHS/BS-18 mixed surfactant solution with a molar ratio of 4:6 (**c**), and BS-18 surfactant solution (**d**).
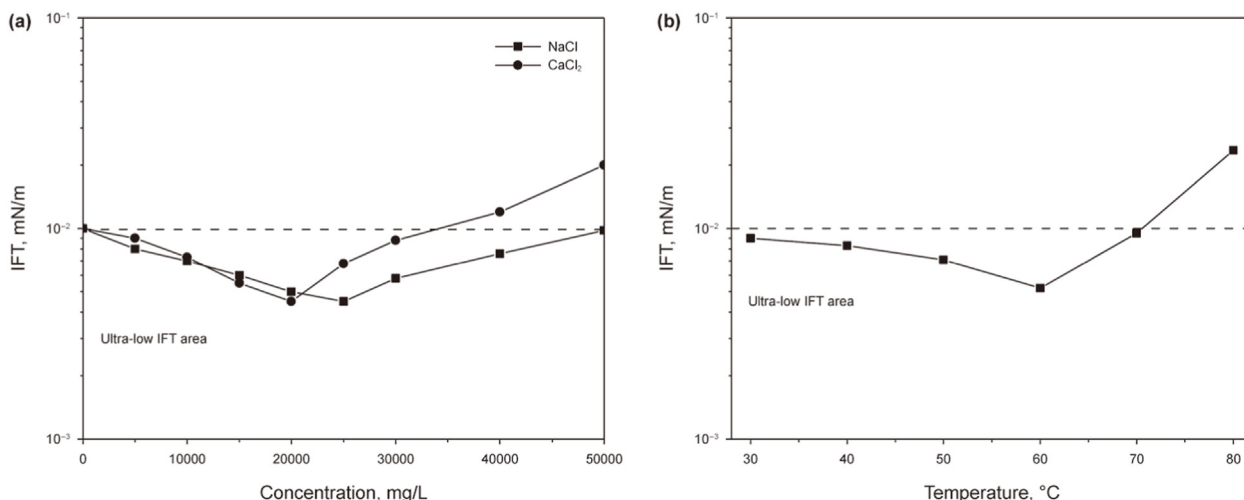
Fig. 13. IFTs between 0.3 wt% APGSHS/BS-18 mixed solution (molar ratio is 4:6) and crude oil at various salinities (**a**) and temperatures (**b**).

concentration increases, the effect of divalent cations on the interfacial activity is greater than that of monovalent cations. When the temperature is higher than 60 °C, the IFT gradually increases as the temperature increases (see Fig. 13(b)), this correlates the increase in the solubility of surfactants at high temperatures. As the temperature elevates, surfactant molecules will leave the oil water interface and dissolve in the aqueous phase, resulting in an increase in IFT value (Hosseini et al., 2020). The high temperature tolerance of the mixed surfactant system shed light on its application for high temperature reservoirs.

Fig. 14 shows the average droplet size of emulsions formed under different salinity and temperature conditions. The results show that the stability of emulsions is greatly affected by salinity and temperature. When the salinity is less than 15,000 mg/L, with the increase in salinity, the particle size of the emulsion gradually decreases, indicating an improved emulsification performance of the system. This may be because betaine type surfactants have anionic and cationic groups, and the positive and negative charges on the molecule can form internal salts, which can chelate with metal ions, forming a more stable surfactant molecular structure (He et al., 2022). When the salinity is 15,000 mg/L, the average particle size of the emulsion reaches the minimum values, which

are 181.1 and 174.4 nm for NaCl and $CaCl_2$ circumstance, respectively. Then, with the increase in salinity, the average particle size gradually increases. When the salinity is 50,000 mg/L, the maximum particle sizes of the emulsion reach 437.3 and 520.7 nm for NaCl and $CaCl_2$ circumstance, respectively. As the salinity increases, more counterions will appear at the interface and shield the double electric layer surrounding the ionic surfactant layer of the emulsion, thereby weakening the electric repulsion between the emulsions. In addition, as the salinity increases, the solubility of the surfactant decreases and the amount of surfactant enriched at the oil−water interface decreases significantly, leading to a decrease in the emulsification capacity (Pal et al., 2019a; Verma et al., 2018). In this situation, the droplets are more likely to aggregate.

Previous studies have shown that aqueous solutions are more likely to form emulsions with crude oil at high temperature conditions (Feng et al., 2017). However, the increase in temperature leads to faster droplet movement and increases the probability of droplet aggregation (Duboué et al., 2019). The droplet size of the emulsion increases from 213 nm at 30 °C to 521 nm at 80 °C. Despite for the harsh conditions, i.e., high temperature or high salinity conditions, the average droplet size of the emulsion is still
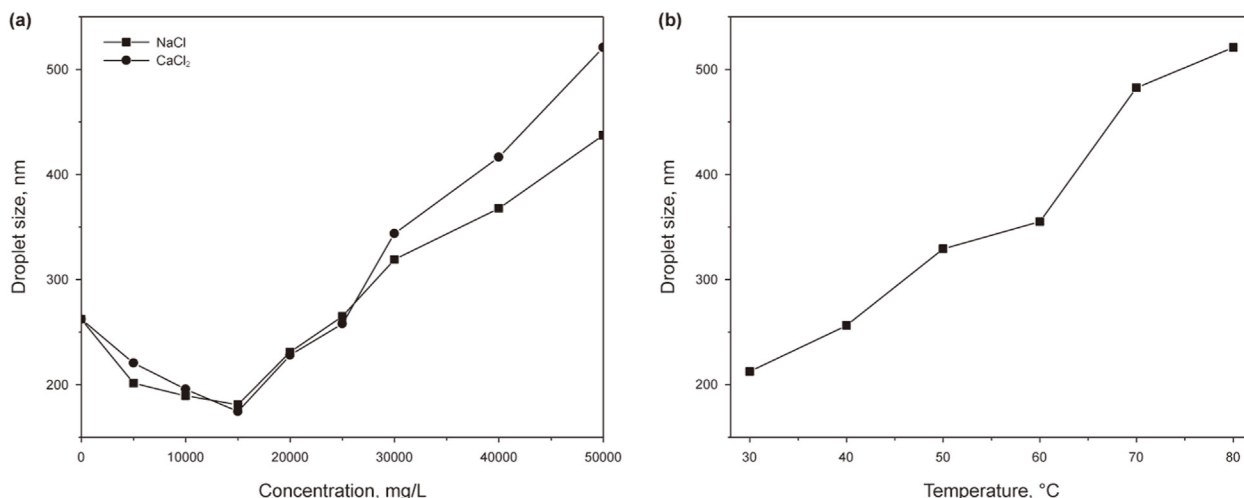

Fig. 14. Average droplet sizes of the formed emulsions at various salinities (**a**) and temperatures (**b**).

less than 600 nm, which indicates that the emulsion is rather stable. Therefore, the surfactant system has good temperature and salt resistance and can be applied in reservoirs with harsh formation conditions.

3.5. Performance of the mixed surfactant system at various pH conditions

Since BS-18 is a zwitterionic surfactant with different charged states at different pH values, thus the pH value of the solution can affect the interfacial tension reduction ability and emulsification ability, thereby affecting its EOR performance.

The isoelectric point and solubility of the APGSHS/BS-18 mixed surfactant system were explored. Fig. 15(a) shows the zeta potential of different systems at various pH values. The potential value of BS-18 increases with the increase in H^+ concentration (see Fig. 15(a)), indicating that BS-18 gradually changes to the cationic form. When the pH is higher than the isoelectric point (8–8.2), BS-18 exhibits zwitterionic surfactant properties, and the potential value of the solution is close to 0. Therefore, BS-18 has different charged properties, and when BS-18 is converted to a cationic surfactant, the opposite charged surfactant will precipitate with BS-18 in aqueous solution due to the strong electrostatic interaction between them. As shown in Fig. 15(b), the initial mixed solution of BS-18 and APGSHS is clear when the pH is 8. With the gradual increase in H^+ concentration, when the pH value is 4.75, the solution becomes cloudy. When the pH value reduces to 2, the solution becomes very turbidity, indicating the appearance of precipitation,

which formed attributing to the strong electrostatic attraction between APGSHS and protonated BS-18 molecules. In addition, the effective concentration and surface activity of the surfactant decrease, showing an obvious pH responsiveness. That is, the APGSHS/BS-18 solution has good stability when the pH value > 4.75, whilst the, the solution begins to precipitate when the pH value < 4.75.

The emulsion stability, emulsification performance and interfacial tension reduction performance of the mixed surfactant system at various pH conditions were investigated by bottle test observation, emulsion size measurement, and determination of IFT. As shown in Fig. 16(a), emulsions formed at pH = 2 and 4 have demulsification rapidly; however, the original mixed surfactant system can form a well-dispersed and stable emulsion with crude oil at pH = 8. Fig. 16(b) shows the emulsion droplet size at various pH values, which shows the same trend as Fig. 16(a). As the pH value decreases, the emulsification ability of the mixed surfactant system decreases, and the sizes of emulsion droplets increase. Fig. 16(c) shows the change of oil–water interfacial tension with pH value. With the increase in pH value, the IFT reduction ability of the mixed surfactant system increases and an ultra-low interfacial tension is achieved at pH = 8. This is mainly due to the highly protonated BS-18 and APGSHS precipitated together, leading to reduced effective concentrations of surfactant molecules in solution. When the pH value is close to the isoelectric point, the weak electrostatic attraction between surfactants can form a relatively dense oil–water interface film, and the emulsion stability, emulsifying ability, and ability to reduce the oil–water interface tension are improved.
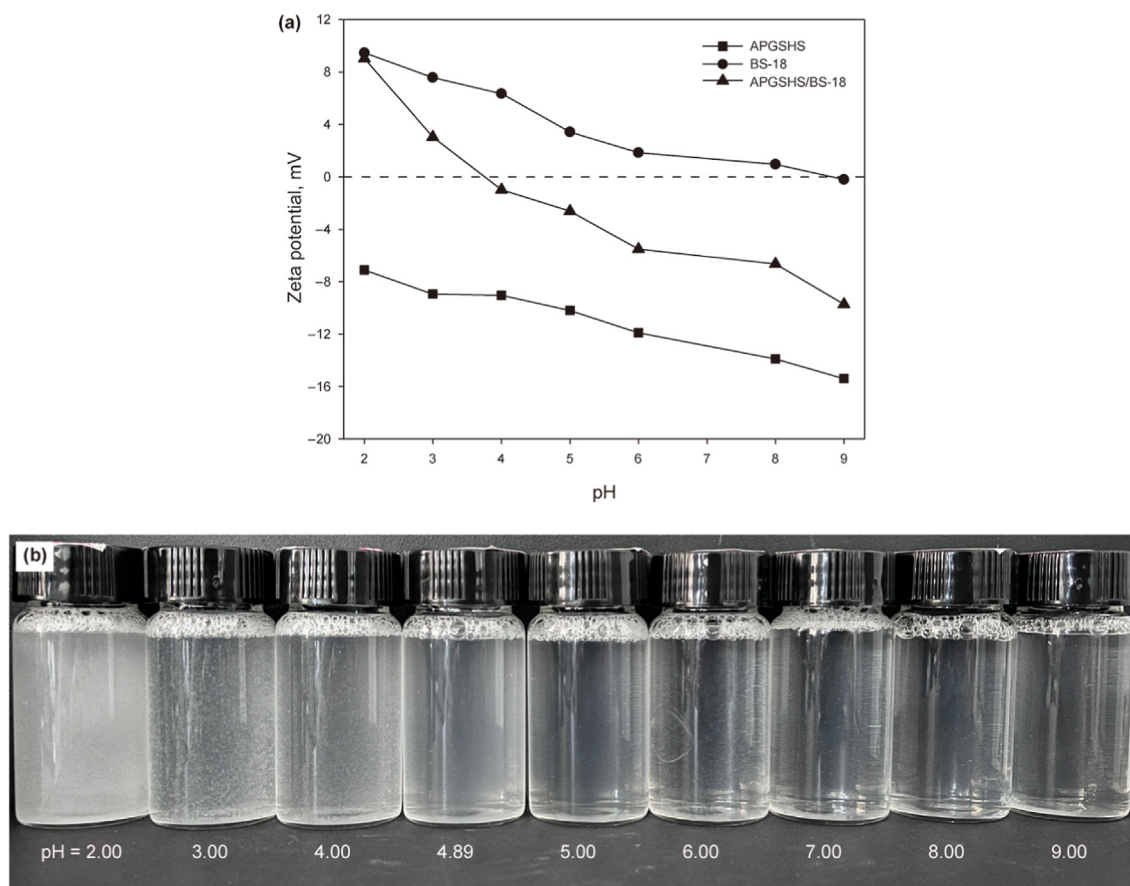

Fig. 15. (**a**) Zeta potential of different systems at various pH values; (**b**) Appearance of mixed surfactant system at different pH values.

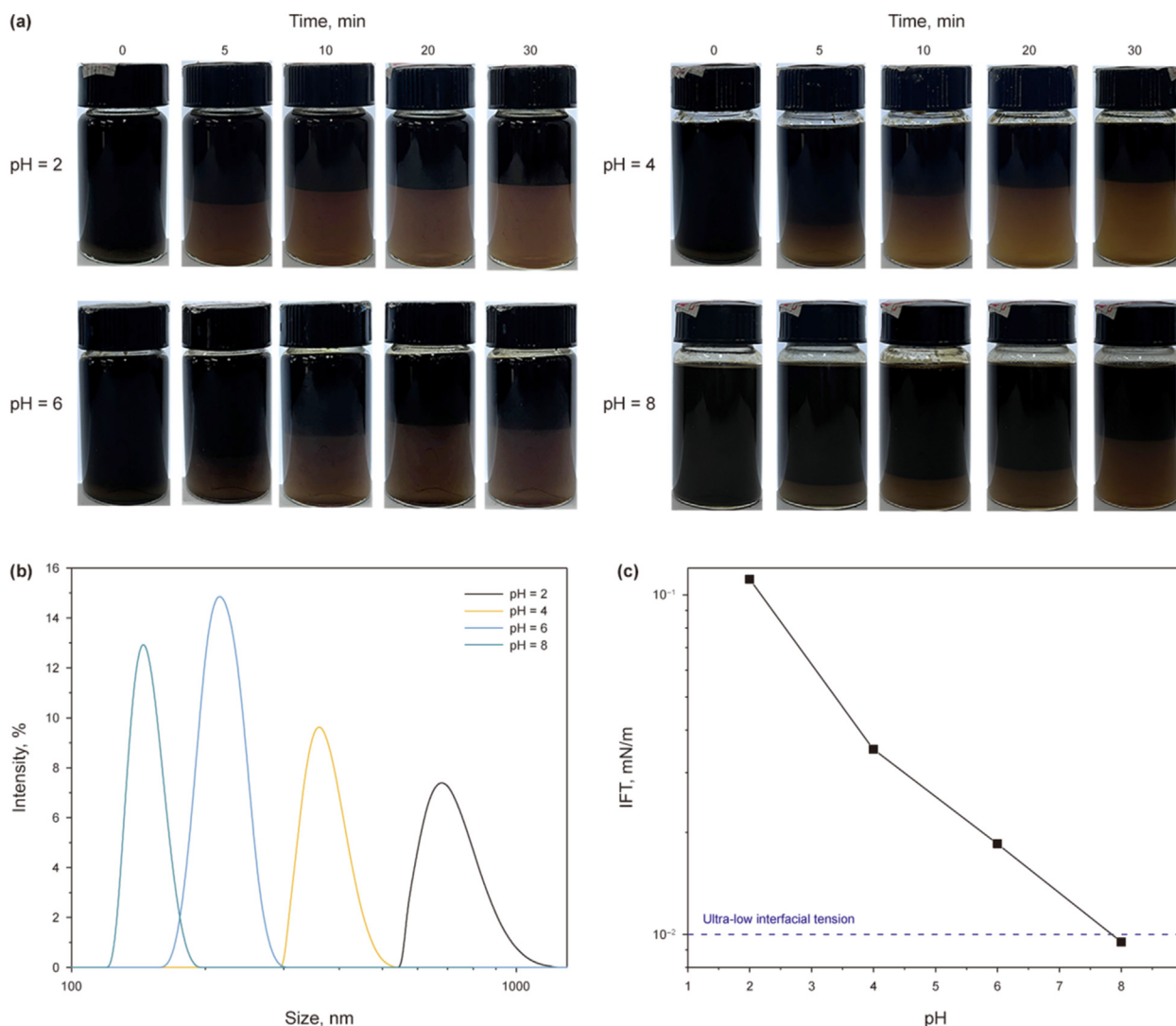**Fig. 16.** (**a**) Appearance of emulsions at various pH values; (**b**) Particle size of emulsions formed by mixed surfactant system at various pH values; (**c**) Interfacial tension recorded at various pH values.

3.6. Core displacement performance

Surfactant flooding is usually performed after the water flooding, aiming at lowering pressure, increasing injection, increasing sweep efficiency, and thus enhancing oil recovery in low permeability reservoirs. To determine the oil displacement efficiency of APGSHS/BS-18 emulsification system in low permeability cores, core displacement experiments were conducted using core samples with permeabilities in the range of 30–50 mD. The chemical flooding systems used in this part including 0.3 wt% APGSHS surfactant system, 0.3 wt% APGSHS/BS-18 with a molar ratio of 4:6, and 0.3 wt% BS-18 surfactant system. The oil recovery, water cut,

and injection pressure changes during the displacing experiment were recorded. The experimental results are shown in Table 3.

From Table 3, after the water flooding, the injection of different surfactant systems can improve the oil recovery by 14%–20%. The final recovery can be improved by 16.00%–25.45% after the subsequent water flooding. The highest oil recovery of 25.45% is achieved by the mixed surfactant system, which is higher than that of the two surfactants alone.

The core displacement performance curves of the three sets of flooding systems are shown in Fig. 17. Surfactant flooding can also be used to reduce the injection pressure when the displacement fluid is injected into the low-permeability core sample (Xiao et al.,

Table 3
Oil displacement performance of various surfactant systems.

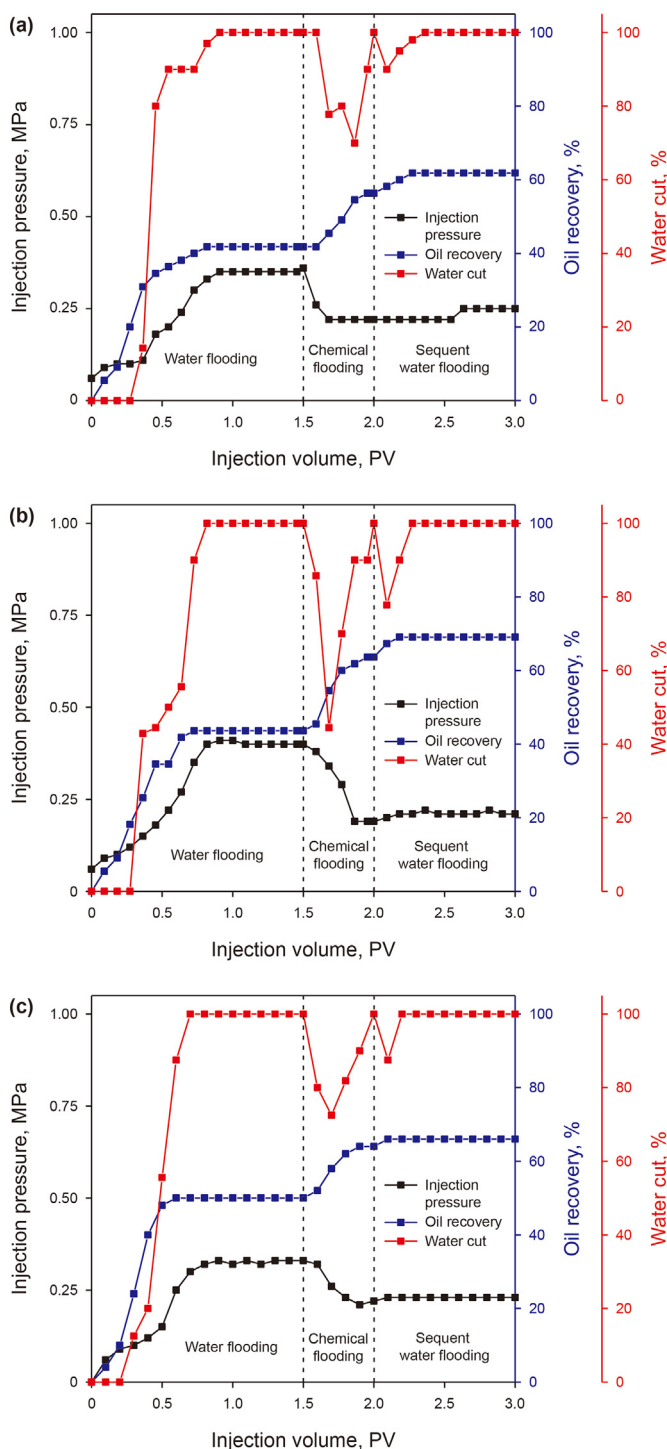| Core sample	System	Oil recovery, %				Pressure reduction rate, %
		Water flooding	Chemical flooding	Post water flooding	Total	
Core-1	0.3 wt% APGSHS	41.82	14.54	5.46	61.82	30.56
Core-2	0.3 wt% APGSHS/BS-18 with a molar ratio of 4:6	43.64	20.00	5.45	69.09	42.00
Core-3	0.3 wt% BS-18	50.00	14.00	2.00	66.00	33.33

Fig. 17. Flooding performance of various chemical flooding systems: (**a**) 0.3 wt% APGSHS; (**b**) 0.3 wt% APGSHS/BS-18 mixed surfactant system with a molar ratio of 4:6; (**c**) 0.3 wt% BS-18.

2021). As shown in Fig. 17, the injection pressure changes in three different stages including primary water flooding, chemical flooding and subsequent water flooding. In the primary water flooding stage, the injection pressure rises rapidly with the increase in water injection volume, then the injection pressure rises slowly and eventually remains constant after the crude oil in the pore space is driven. After this stage, a large amount of residual oil remained in the pore space. After injecting 0.5 PV surfactant systems, the

injection pressure decreases significantly. Different surfactant systems have different ability to reduce pressure, the highest-pressure reduction rate of 42% is achieved by the mixed surfactant system. This is attributed to its high ability in reducing oil–water interfacial tension, changing core wettability, and emulsifying crude oil into tiny droplets which is easy to be transported in porous media. As can be seen from Fig. 17, the injection pressure increases slightly at the beginning of the secondary water flooding and finally reaches stable. Compared to the primary water flooding stage, the injection pressure of the final injection pressure for the secondary water flooding stage is lower.

The recovery enhancement mechanism of the emulsification flooding system includes the following points.

(1) The APGSHS/BS-18 mixed surfactant system can easily emulsify the residual oil film attached to the rock surface under the flow shearing condition, thus producing many small emulsion droplets which will transport more easily in the porous media.

(2) There is usually a lot of residual oil in the small pore channels. APGSHS/BS-18 surfactant molecules can adsorb at the oil–water interface, which significantly reduces the interfacial tension and the oil flooding resistance. Thus, the columnar residual oil blocked to the pore throat can be stretched and repelled out.

(3) APGSHS/BS-18 mixed surfactant system can change the wettability of the rock surface into hydrophilicity, and mobilize the residual crude oil on the rock surface. Meanwhile, alternation of the wettability prevents the crude oil droplets from adhering to the rock surface again during seepage in porous medium, which favors the transportation of the crude oil.

(4) During transportation, the emulsion droplets that flow to the large pore channels can generate the Jamin effect, blocking the flow dominant channels with higher permeability. Accordingly, the subsequent flooding solution will sweep the tiny pores that are not reached.

4. Conclusions

In this study, a highly efficient emulsification oil flooding system consisting of 0.3 wt% APGSHS/BS-18 with a molar ratio of 4:6 was proposed for low permeability reservoir. Its interfacial activity, emulsification performance and oil recovery mechanism were systematically investigated. The main conclusions can be drawn as follows.

(1) The minimum oil–water interfacial tension of the mixed surfactant system is 9×10^{-3} mN/m, which is obtained at 50 °C and salinity of 5000 mg/L.

(2) Crude oil could be emulsified by the mixed surfactant system with low external energy. Emulsion droplets stabilized by mixed surfactant show an average diameter of 0.14 μm as well as a narrow size distribution.

(3) The core flooding experiments for low permeability core samples show that the recovery enhancement performance of the mixed surfactant system is better than those with two surfactants alone. After the subsequent water flooding, the mixed surfactant system can improve the recovery by 25.45% and significantly reduce the injection pressure by 42%.

Therefore, the APGSHS/BS-18 mixed surfactant system has considerable potential for recovery enhancement in low permeability reservoirs.

CRediT authorship contribution statement

Hai-Rong Wu: Writing – review editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Rong Tan:** Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Shi-Ping Hong:** Visualization, Formal analysis, Data curation. **Qiong Zhou:** Writing – review editing, Investigation, Formal analysis. **Bang-Yu Liu:** Writing – review editing, Investigation, Formal analysis. **Jia-Wei Chang:** Writing – review editing, Visualization, Investigation, Formal analysis, Data curation. **Tian-Fang Luan:** Visualization, Investigation, Data curation. **Ning Kang:** Writing – review editing, Investigation, Formal analysis. **Ji-Rui Hou:** Writing – review editing, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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