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Consideration of Application Possibility of Biosurfactant and Alkaline-surfactant-polymer (B-ASP) with Ultra-low Crude Oil/Brine Interfacial Tension for Enhancement of Oil Recovery

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Alkaline-surfactant-polymer (ASP) flooding is one of the leading technologies successfully applied in enhancement of oil recovery over the last few decades. However, it has suffered from high cost and poor environmental compatibility. In this work, a new pseudo-ternary flooding system containing Na_2CO_3 , lipopeptide biosurfactant, petroleum sulfonate, and partially hydrolyzed polyacrylamide was developed, and its possibility in enhancement of oil recovery was evaluated. Compared with the traditional ASP containing only petroleum sulfonate as the surfactant component, the interfacial tension between the new pseudo-ternary flooding system and Daqing crude oil was reduced to a low level in the order of 10^{-4} mN/m, implying positive synergistic effects of the biosurfactant, lipopeptide, and petroleum sulfonate in the new B-ASP system. Meanwhile, the thermal adaptability, interfacial activity, and viscosity stability of the new B-ASP system were significantly improved. The results of this study suggest that B-ASP is a promising and cost-effective flooding system and a developing technology for tertiary oil recovery, particularly amid uncertainties pertaining to oil price fluctuations. To the best of our knowledge, this is the first report on a pseudo-ternary flooding system composed of B-ASP for oil recovery.

Keywords

Alkaline-surfactant-polymer formula, Lipopeptide biosurfactant, Petroleum sulfonate, Synergistic effect, Flooding system

1. Introduction

With the increase in global energy demand and decrease in crude oil reserves, the technology for the enhancement of oil recovery is becoming increasingly important. Even after primary and secondary oil recovery, 60-70 % of the crude oil remains in oil reservoirs^{1),2)}. Chemical flooding technologies, including surfactant flooding^{3),4)}, polymer flooding^{5),6)}, surfactant-polymer flooding^{7),8)}, and alkaline-surfactant-polymer (ASP) flooding^{9),10)}, have been employed in different oil fields over the last few decades. Among these, ASP flooding is one of the leading technologies for tertiary oil recovery from declining oil reservoirs^{11),12)}, and has been successfully applied in several oilfields, including the Daqing, Shengli, and Xinjiang oilfields in China, with a remarkable increase of more than 20 % in

oil recovery from water-flooded oil reservoirs with high water content.

The most important mechanism of ASP flooding for enhancing oil recovery includes two closely correlated aspects: reduction in oil/brine interfacial tension (IFT) to an ultra-low level ($\leq 10^{-3}$ mN/m), and improvement in the swept efficiency of flooding fluids in oil reservoirs^{13)~15)}. Evidently, a key factor for enhancing oil recovery is the decrease in oil/brine IFT to an ultra-low level (10^{-3} mN/m) at low surfactant dosage, and thus at low cost.

In ASP flooding, the surfactant, *i.e.*, petroleum sulfonate (NPS), is widely used owing to its high oil/water interfacial activity^{16)~18)}. However, to some extent, its industrial application is limited by a number of constraints. Commercial NPS is usually a mixture of sulfonates, unsulfonated oil, inorganic salts, and water¹⁹⁾. The performances of sulfonates themselves vary significantly with the raw materials from which they are produced as well as the unpredictable production of polysulfonates²⁰⁾. In field applications, chromatographic

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separation occurred when a surfactant with multiple components was used²¹⁾, resulting in compositional changes²²⁾ and unstable properties. Polysulfonates show strong water solubility and may lead to serious emulsification of the production fluids, thereby exerting a significant negative impact on the test results^{20),23)}. It is difficult to biodegrade NPS and they are toxic to the environment.

Compared with chemical surfactants, biosurfactants produced by microbial metabolism have unique advantages, such as low toxicity, biodegradability, temperature resistance, salt tolerance, and economic efficiency. Joshi *et al.*²⁴⁾ reported that an additional 37.1 % of heavy oil was produced in the Berea sandstone core using a lipopeptide biosurfactant. In addition, the recovery rate increased by 17-31 % with the use of a biosurfactant produced in glucose or molasses medium with *Bacillus subtilis* B30. It was found that the biosurfactant changed the wettability of sandstone to a hydrophilic attribute, which was an important mechanism for scaling on-site application to improve oil recovery²⁵⁾. When the ethoxysulfonate surfactant, S-8B, was mixed with lipopeptide in a ratio of 50 : 50, the saturation of residual oil was reduced to 34 % after hot water flooding²⁶⁾. It is well documented that the use of two or more surfactants can effectively compensate for the deficiencies encountered in the use of a single surfactant, and may additionally improve the flexibility of performance optimization and allow for the combination to be fine-tuned to compensate for any quality changes that may occur in either surfactant²⁰⁾. As a result, the combination of biosurfactants with chemically synthesized surfactants has received increasing attention for potential application in enhancing oil recovery^{25),27)~31)}.

The lipopeptide produced by *B. subtilis* is one of the most effective biosurfactants^{27),32)~37)}. The excellent surface activity of lipopeptide can be attributed to the fact that the interfacial adsorption of surfactin at low solution concentrations results in the depletion of its molecules in solution and that more than 50 mol% of lipopeptide appears in the mixed surfactin-sodium dodecyl benzene sulfonate (SDBS) membrane at the gas-liquid interface even with a 1 : 13 molar ratio of surfactin to SDBS in solution³⁸⁾. There are a few reports on the study of the compounding performance of chemical surfactants and biosurfactants. However, there is only a limited understanding of the interactions between lipopeptide biosurfactants and chemically synthesized surfactants and their roles in ASP flooding systems in applications.

In the present work, a novel flooding system composed of the biosurfactant and alkaline-surfactant-polymer (B-ASP) has been developed. The possibility of the new pseudo-ternary flooding system for enhancement of oil recovery from declining oil reservoirs was

evaluated. To the best of our knowledge, this is the first report on a pseudo-ternary flooding system composed of B-ASP for oil recovery.

2. Materials and Methods

2.1. Materials

Commercial NPS containing 9.7 % water, 63.4 % unsulfonated oil, 16.8 % sulfonate surfactant, and 10.1 % inorganic salts was used.

The crude oil used in this experiment was dehydrated and degassed crude oil produced from the Daqing Xingwuzhong reservoir with an acid value of 0.06 mg KOH/g, density of 0.85 g/cm³, and viscosity of 19.8 mPa s (45 °C).

The lipopeptide biosurfactant sample herein was an original cell-free broth of *B. subtilis* TD-7 cultured in our laboratory (1.8 g/L of lipopeptide) and was directly used without further purification. The main active ingredients in this broth were C14-surfactin and C15-surfactin, which are cyclic lipopeptides formed by connecting β -hydroxy fatty acids with chain lengths of 14 and 15 carbon atoms, respectively, to a seven-amino acid peptide chain *via* lactone bonds³²⁾.

The oil reservoir sand used was collected from the Daqing oilfield and subjected to washing treatment before pulverization to 80-120 mesh.

Partially hydrolyzed polyacrylamide (HPAM) with a molecular weight of 2.5×10^7 Da was obtained from Daqing Refining & Chemical Co. Na₂CO₃ of analytical purity was utilized.

The water used in these experiments was prepared according the composition of real formation brine in Daqing Xingwuzhong reservoir, which contained 1588.3 mg/L of NaCl, 112.2 mg/L of CaCl₂, 42.9 mg/L of MgCl₂, 17.1 mg/L of Na₂SO₄, 3176.0 mg/L of NaHCO₃, and 381.6 mg/L of Na₂CO₃.

2.2. IFT Measurement

The IFT was measured using a spinning drop interfacial tensiometer, TX500C, operated at 4500 rpm at a temperature of 45 °C in this study. The equilibrium IFT value obtained after 2 h was recorded.

2.3. Viscosity Measurement

The viscosity of the ASP or B-ASP solution was determined at a temperature of 45 °C and shear rate of 7.34 s⁻¹ using a Programmable Rheometer DV-III instrument with an accuracy of ± 1 %.

2.4. Evaluation of Emulsification Property

The dehydrated crude oil and the ASP (HPAM, 1400 mg/L; NPS, 0.3 wt%; Na₂CO₃, 1.2 wt%) or B-ASP (HPAM, 1400 mg/L; NPS, 0.15 wt%; lipopeptide, 0.15 wt%; Na₂CO₃, 1.2 wt%) solution were transferred into a 50 mL colorimetric tube in a volume ratio of 1 : 1 and subjected to vigorous shaking for 5 min, and then immediately placed into an oven and maintained at 45 °C. Subsequently, the variation in the

Fig. 1 Dynamic IFT between Crude Oil and ASP Solution or B-ASP Solution with Different NPS/Lipopeptide Ratios

water separated from the emulsion as a function of time was recorded to calculate the water separating rate, which is defined as follows:

Water separating rate = (volume of separated water / volume of total water added) $\times$ 100 %.

Meanwhile, the ASP or B-ASP solution was mixed with dehydrated crude oil in a ratio of 9 : 1 and then stirred at 2000 rpm for 5 min to produce an oil-in-water (O/W) emulsion. The particle size of the emulsion obtained was analyzed *via* scanning electron microscopy (SEM).

Based on the results of the above experiments, the emulsification performance of ASP or B-ASP were evaluated.

2. 5. Evaluation of Dilution Resistance

The ASP or B-ASP solution was mixed with the simulated formation brine in ratios of 1 : 1, 1 : 2, 1 : 3, etc., on which the IFT between the mixture and dehydrated crude oil was determined at 45 °C. The dilution factor, at which the IFT between the diluted ASP or B-ASP solution and crude oil failed to reach an ultra-low value, was considered the dilution resistant factor.

2. 6. Evaluation of Anti-adsorption

The ASP or B-ASP solution was mixed with oil reservoir sand in a mass ratio of 9 : 1. The mixture was shaken and allowed to settle at a constant temperature for 24 h. Thereafter, the mixture was centrifuged to obtain the supernatant for IFT measurements and further mixed with fresh oil reservoir sand. The procedures were continuously repeated until ultra-low IFT between the supernatant and crude oil could not be reached.

2. 7. Temperature Adaptability Analysis

The IFT values between the ASP or B-ASP solution and crude oil were measured at different temperatures in the range 50-90 °C and the temperature adaptability of these two solutions were evaluated.

2. 8. Stability Analysis

A total of 20 mL of ASP or B-ASP solution was

loaded into nine colorimetric tubes with a volume of 25 mL each. The tubes were then sealed and transferred into the oven whose temperature was maintained at a constant value of 45 °C. The viscosity and IFT values of these solutions were recorded on the 1st, 3rd, 5th, 7th, 15th, 30th, 60th, and 90th days. Additionally, the variations in viscosity and IFT with aging time were measured.

2. 9. SEM Analysis

The ASP or B-ASP solution after aging for 1 d and 90 d at 45 °C was dropped on to a Cu block, and then quickly frozen into a solid with the assistance of liquid N₂ to maintain the shape of the polymer molecule. Finally, the Cu block with HPAM solid was transferred into the vacuum environment of the sample chamber of an SEM before the images were recorded.

3. Results and Discussion

3. 1. Composition of B-ASP

A series of B-ASP solutions and an ASP solution were prepared with 0.3 wt% of surfactant, 1400 mg/L of HPAM, and 1.2 wt% of Na₂CO₃. In the B-ASP solutions, the surfactant was a mixture of NPS and lipopeptide broth in mass ratios of 0 : 6, 1 : 5, 2 : 4, 3 : 3, 4 : 2, and 5 : 1. The ASP solution contained only NPS as the surfactant, *i.e.*, the mass ratio of NPS to lipopeptide was 6 : 0. The dynamic IFT values between these solutions and crude oil were determined and are presented in Fig. 1.

The equilibrium IFT between Daqing crude oil and B-ASP solution declined to the order of 10⁻³ mN/m or lower at NPS : lipopeptide ratios of 1 : 5, 3 : 3, 4 : 2, and 5 : 1. Compared with ASP (NPS : lipopeptide = 6 : 0), the IFT values obtained using the B-ASP solutions were even lower, implying their high interfacial activity. In addition, the minimum equilibrium IFT of 4.26 $\times$ 10⁻⁴ mN/m was obtained when the B-ASP solution with an NPS : lipopeptide mass ratio of 3 : 3 was used. Thus, the solution comprising 0.15 wt% of NPS, 0.15 wt% of lipopeptide, 1400 mg/L of HPAM, and 1.2 wt% of Na₂CO₃ was preferably selected for further study.

3. 2. Interfacial Activity Diagrams

A series of B-ASP solutions was prepared with surfactant mixture (NPS + lipopeptide, NPS : lipopeptide = 3 : 3) concentration in the range 0.05-0.3 wt%, Na₂CO₃ concentration in the range 0.6-1.4 wt%, and 1400 mg/L of HPAM. The IFT values between these B-ASP solutions and Daqing crude oil were determined, and the results together with those obtained using ASP with identical composition but only NPS as the surfactant are shown in Fig. 2.

As indicated in Fig. 2, the interfacial activity of the B-ASP solution was significantly improved compared with that of the ASP solution. The regions with

Fig. 2 Interfacial Activity Diagrams of (a) ASP and (b) B-ASP Systems

ultra-low IFT in the order of 10^{-4} mN/m between Daqing crude oil and B-ASP solutions at various Na_2CO_3 concentrations were evidently larger, indicating the favorable synergistic effect between NPS and lipopeptide.

It is noteworthy that the concentration of the surfactant may be lower in practical applications owing to its adsorption on to the oil reservoir matrix. The greater activity range of B-ASP would then be of significant importance to guarantee the performance of the solution and, thereby, its final effect on oil recovery.

Viscous forces and capillary forces are the two major forces acting on the entrapped oil in reservoir pores. It is well established that ultra-low IFT between oil and brine is necessary for overcoming capillary forces and thus allowing the entrapped oil to flow^(39),40). As the capillary number ($N_{ca} = v\mu_w / \sigma_{ow}$, v : interstitial velocity, μ_w : viscosity of displacing phase, σ_{ow} : IFT between oil and brine) is increased, the residual oil saturation is decreased⁽⁴¹⁾. Further, an approximate semi-log relationship between residual oil saturation and capillary number (thus IFT) has been established, based on which, surfactant solutions with oil/brine IFT of 10^{-4} mN/m would significantly recovery more residual oil than that with 10^{-3} mN/m⁽⁴²⁾. On the other hand, it was also reported that higher capillary number is beneficial to mobilize discontinuous oil than continuous oil⁽⁴²⁾. Yuan *et al.* found that surfactant solution (0.05 % AOS + 0.15 % AEC) with initial oil-water IFT of 5.01×10^{-4} mN/m can enhance more oil recovery by a factor of about 4 % compared that with initial oil-water IFT of 6.36×10^{-3} mN/m⁽⁴³⁾. In the present

work, B-ASP (oil/brine IFT = 10^{-4} mN/m) is hoped to enhance more oil recovery than ASP (oil/brine IFT = 10^{-3} mN/m).

Onaizi *et al.*⁽³⁸⁾ proposed that a specific configuration might be formed between surfactin and SDBS molecules, which weakened electrostatic repulsion but enhanced hydrophobic interaction between them. Thus, they were mutually attractive in the monomolecular layer of the mixed interface despite possessing negative charges in their molecules. Al-Wahaibi *et al.*⁽²⁶⁾ prepared a surfactant mixture composed of the lipopeptide produced by *B. subtilis* and a chemical surfactant, *i.e.*, ethoxylated sulfonate, and found significant improvement in the interfacial performance. With their keen observation of the synergy between lipopeptide and ethoxylated sulfonate in the enhancement of oil recovery, the authors concluded that the structure of the bio-surfactant altered when it was adopted in combination with a chemical surfactant. Youssef *et al.*^(44),45) studied the relationships between the hydrophobicity or hydrophilicity of a mixture of different biosurfactants and synthetic surfactants on which the interfacial activity of a mixture of lipopeptide and synthetic surfactants was reasonably regulated to render ultra-low IFT between the mixture and the hexane or decane, resulting in efficient enhancement of oil recovery. Our work revealed that the synergy of lipopeptide and NPS enhanced the interfacial activity. Meanwhile, the B-ASP system was slightly superior to the ASP system in maintaining ultra-low IFT. The present result provides a reference for the construction of a high-performing oil displacement formula containing lipopeptide biosurfactant.

Wettability adjustment was believed to be one of the important mechanisms in the enhancement of oil recovery. A decline in IFT may alter oil-rock contact, contributing to the change in wettability^(46),47). The simulation study carried out by Kowalewski *et al.*⁽⁴⁸⁾ showed that wettability varied with a gradual decrease in IFT, bringing about a decrease in residual oil saturation. Al-Sulaimani *et al.*⁽⁴⁶⁾ reported that the biosurfactant produced by *B. subtilis* W19 at a concentration of 0.25 % reduced the contact angle between distilled water and graphene from 70.6° to 25.32° . In their experiment, 50 % residual oil was exploited using a mixture of biosurfactant and ethoxylated sulfonates (S-8B) in a ratio of 50 : 50 and the change in the wettability characteristic of sandstone from lipophilicity to hydrophilicity was observed. Thus, they considered wettability alteration to be one of the mechanisms by which oil recovery is enhanced. In the present work, the combination of the biosurfactant, *i.e.*, lipopeptide, with NPS in the B-ASP flooding system resulted in a large area of 10^{-4} mN/m in the interfacial activity diagram, which is more helpful in enhancing oil recovery. On the other hand, this significant lowering of IFT would enhance oil recovery further by improving the wettability of the

oil reservoir rock.

3.3. Emulsification and Anti-adsorption Performance

The emulsions were prepared with dehydrated crude oil and the ASP or B-ASP solution in a volumetric ratio of 1 : 1 and maintained at 45 °C. The changes in the volumes of the water and oil phases in the emulsion were recorded periodically and the results are shown in **Table 1**.

Evidently, the emulsion formed using the B-ASP solution outperformed that obtained with the ASP solution in terms of stability. **Figure 3** shows the SEM images of the emulsions formed by stirring the oil/ASP mixture in a ratio of 1 : 9 for 5 min. The size of the oil droplets formed in the ASP system were large and unevenly distributed. However, small and relative evenly distributed oil droplets were formed in the B-ASP system. Emulsification is a critical mechanism for ASP flooding to reinforce oil recovery. The ASP formula usually forms an O/W emulsion by significantly reducing the oil/water IFT, thus remarkably enhancing the flow capacity of oil. In the present work, the lipopeptide-containing B-ASP flooding system showed improved emulsification performance over that of the ASP flooding system with only NPS as the surfactant, indicating its potential improvement in the performance of

oil recovery.

The variation in IFT between Daqing crude oil and the ASP solution containing 1400 mg/L of HPAM, 0.3 wt% of NPS, and 1.2 wt% of Na₂CO₃, or the B-ASP solution containing 1400 mg/L of HPAM, 0.15 wt% of NPS, 0.15 wt% of lipopeptide, and 1.2 wt% of Na₂CO₃, combined with the changes in the viscosity of these solutions are summarized in **Table 2**.

The ASP and B-ASP solutions both maintained ultra-low IFT after the first adsorption by oil reservoir sand at 45 °C. After the secondary adsorption, the IFTs the ASP and B-ASP solutions were $(9.2 \pm 0.2) \times 10^{-3}$ mN/m and $(2.2 \pm 0.1) \times 10^{-2}$ mN/m, respectively, while the viscosity retention rates were 86.1 % and 88.6 %, respectively. Evidently, the anti-adsorption performance of these two solutions were almost identical.

3.4. Anti-dilution Performance

The ASP solution (HPAM, 1400 mg/L; NPS, 0.3 wt%; Na₂CO₃, 1.2 wt%) and B-ASP solution (HPAM, 1400 mg/L; NPS, 0.15 wt%; lipopeptide, 0.15 wt%; Na₂CO₃, 1.2 wt%) were subjected to series dilution with the simulated formation brine. The equilibrium IFTs after each dilution of both the B-ASP and ASP systems were maintained at ultra-low values when the solutions were diluted to one-third of their initial concentrations, and the anti-dilution performances of these two systems showed a slight difference, as shown in **Table 3**.

3.5. Temperature Adaptability

The IFT between the ASP solution (HPAM, 1400 mg/L; NPS, 0.3 wt%; Na₂CO₃, 1.2 wt%) or B-ASP solution (HPAM, 1400 mg/L; NPS, 0.15 wt%; lipopeptide, 0.15 wt%; Na₂CO₃, 1.2 wt%) and crude oil were measured at temperatures in the range 50-90 °C and the results are shown in **Fig. 4**.

Figure 4 shows the dynamic IFT values between crude oil and the ASP or B-ASP solutions at different temperatures. The IFT_{equ} values between crude oil and

Fig. 3 SEM Images of the Emulsions Formed by Stirring the Oil/ASP Mixture (a) and Oil/B-ASP Mixture (b) in a Ratio of 1 : 9 for 5 min

Table 1 Water Separation from Emulsion Prepared with ASP and B-ASP at 45 °C

Time	0.5 h	1 h	2 h	3 h	4 h	8 h
ASP	91 %	93 %	97 %	100 %		
B-ASP	87 %	92 %	95 %	95 %	97 %	100 %

Table 2 IFT_{equ} and Viscosity of ASP Solutions after Adsorption by Oil Reservoir Sand at 45 °C

Adsorption times	ASP IFT _{equ} [mN/m]	ASP viscosity [mPa s]	B-ASP IFT _{equ} [mN/m]	B-ASP viscosity [mPa s]
0	$(1.4 \pm 0.3) \times 10^{-3}$	29.4 ± 0.3	$(4.2 \pm 0.3) \times 10^{-4}$	29.8 ± 0.4
1	$(4.8 \pm 0.4) \times 10^{-3}$	27.2 ± 0.2	$(3.0 \pm 0.3) \times 10^{-3}$	27.6 ± 0.3
2	$(9.2 \pm 0.2) \times 10^{-3}$	25.3 ± 0.3	$(2.2 \pm 0.1) \times 10^{-2}$	26.4 ± 0.3
3	$(4.1 \pm 0.3) \times 10^{-2}$	24.5 ± 0.1	-	-

Viscosity was measured at shear rate of 7.34 s^{-1} .

Table 3 IFT_{equ} between Crude Oil and ASP or B-ASP Solutions at Different Dilution Ratios

Dilution ratios	ASP IFT _{equ} [mN/m]	B-ASP IFT _{equ} [mN/m]
1	$(2.4 \pm 0.2) \times 10^{-3}$	$(4.1 \pm 0.1) \times 10^{-4}$
2	$(2.4 \pm 0.2) \times 10^{-3}$	$(5.1 \pm 0.1) \times 10^{-3}$
3	$(4.2 \pm 0.3) \times 10^{-3}$	$(3.4 \pm 0.3) \times 10^{-3}$
4	$(2.6 \pm 0.3) \times 10^{-2}$	$(3.9 \pm 0.3) \times 10^{-2}$

Fig. 4 Effect of Temperature on IFT between Crude Oil and (a) ASP Solution or (b) B-ASP Solution

ASP and B-ASP were lower than 0.001 mN/m in the temperature ranges 70–90 °C and 50–90 °C, respectively. The IFT_{equ} showed a general downward trend and approximately decreased for both the solutions with increases in temperature. When the temperature was 50–60 °C, it had a weak effect on IFT, while the interface activity of the B-ASP solution was better than that of ASP.

Temperature is believed to be one of the vital factors, which determines the surfactant adsorption at the immiscible liquid/liquid interface, thus the associated interfacial tension. As temperature increases, hydrogen bonds between water molecules and polar group of surfactant decrease, resulting in decrease in the solubility of surfactant molecule in water and increase that in oil. It was reported that the IFT between SDS solution and toluene decreased with increasing temperature⁴⁹⁾. In addition, Goodarzi and Zendehboudi⁵⁰⁾ shown through

(a) ASP aging for 1 day, (b) ASP aging for 90 days, (c) B-ASP aging for 1 day, and (d) B-ASP aging for 90 days.

Fig. 5 Microscopic Morphologies of HPAM after Aging at 45 °C for 1 day and 90 days in Different Solutions

MD simulation that brine/surfactant/oil IFT decreased upon addition of NaCl and CaCl₂ and increasing temperature up to 345 K. Our results were in consistent with that obtained by El-Batanoney *et al.*⁵¹⁾ who found the IFT was decreased with increasing temperature. It is worth noting that IFT dependency on temperature was highly influenced by oil composition. Akstinat⁵²⁾ found that IFT decreased with increasing temperature in crude oils with a high naphthenic content and not changed in aromatic and paraffinic crudes. Meanwhile, the “V” patterns of IFT dependence on temperature were also reported by Aoudia *et al.*⁵³⁾ and Mosayebi *et al.*⁵⁴⁾ for oil/water systems in the presents of anionic and non-ionic surfactants, respectively.

3. 6. Stability

The morphologies of HPAM in the ASP and B-ASP solutions mentioned above after aging at 45 °C for 1 day and 90 days were observed using SEM, as shown in Fig. 5.

The HPAM from both the solutions, *i.e.*, ASP and B-ASP, evidently featured a network texture and similar spatial morphologies at the beginning of aging. After aging for 90 days, the space network structure of the B-ASP HPAM solution remained fluffy and stretched, while that of the ASP solution looked more compact and agglomerated.

The ASP and B-ASP solutions were both capable of achieving ultra-low IFTs after aging for 90 days at 45 °C, as shown in Table 4. The B-ASP solution could maintain IFT in the order of 10⁻⁴ mN/m over 1–15 days, indicating favorable IFT stability. In addition, after 90 days of incubation at 45 °C, the viscosity of the ASP solution decreased from the initial value of 29.4 to 24.5 mPa s with a reduction rate of 16.7 %.

Table 4 Equilibrium IFTs between Crude Oil and ASP or B-ASP Solution and Their Viscosities at Different Aging Times (45 °C)

Days	ASP IFT _{equ} [mN/m]	ASP viscosity [mPa s]	B-ASP IFT _{equ} [mN/m]	B-ASP viscosity [mPa s]
1	$(2.4 \pm 0.4) \times 10^{-3}$	29.4 ± 0.3	$(4.0 \pm 0.3) \times 10^{-4}$	29.8 ± 0.4
3	$(2.4 \pm 0.3) \times 10^{-3}$	29.2 ± 0.2	$(4.0 \pm 0.2) \times 10^{-4}$	29.4 ± 0.3
5	$(2.5 \pm 0.2) \times 10^{-3}$	29.2 ± 0.4	$(4.2 \pm 0.5) \times 10^{-4}$	29.3 ± 0.2
7	$(2.4 \pm 0.3) \times 10^{-3}$	29.2 ± 0.2	$(3.8 \pm 0.4) \times 10^{-4}$	29.2 ± 0.2
15	$(2.4 \pm 0.2) \times 10^{-3}$	28.5 ± 0.5	$(7.8 \pm 0.3) \times 10^{-4}$	29.6 ± 0.4
30	$(2.1 \pm 0.3) \times 10^{-3}$	28.7 ± 0.3	$(1.2 \pm 0.2) \times 10^{-3}$	29.2 ± 0.3
60	$(1.6 \pm 0.3) \times 10^{-3}$	24.0 ± 0.4	$(1.7 \pm 0.3) \times 10^{-3}$	35.1 ± 0.3
90	$(6.6 \pm 0.4) \times 10^{-3}$	24.5 ± 0.3	$(3.0 \pm 0.4) \times 10^{-3}$	38.9 ± 0.4

Viscosity was measured at shear rate of 7.34 s^{-1} .

Under the same conditions, the viscosity of the B-ASP solution increased from the initial value of 29.8 to 38.9 mPa s with a rate of increase of 30.5 %, indicating the perfect performance of B-ASP in the stabilization of viscosity. This characteristic precisely overcame the issue of viscosity loss usually encountered in ASP flooding, which may negatively influence oil recovery. Traditional polymers, such as HPAM, rely on chain extension and physical entanglement of solvated chains for viscosity enhancement⁵⁵. In addition, there are various mechanisms by which metal ions, such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} , influence the viscosity of solutions. For instance, Na^+ may alter the hydration layer around the HPAM molecules by competing for water molecules, and simultaneously compress the electric double layer around the head of the polar region of HPAM with the consequent contraction of its molecular chains, thereby causing viscosity to decrease. The situation is different for divalent metal ions. At low metal ion concentrations, the structural viscosity increases because two $-\text{COO}^-$ groups may share one $\text{Ca}^{2+}/\text{Mg}^{2+}$. An increase in ion concentration in the polymer solution causes some of the original counter ions in the diffusion layer of the polymer chains to be squeezed into the adsorbed layer. This results in decreased thickness of the diffusion layer, correspondingly reducing the electric double layer potential and mutual repulsion between molecular chains. These micro effects additionally reduce the extension of the polymer molecular chains, decreasing the viscosity⁵⁶. The two negatively charged residues of glutamic acid and aspartic acid in lipopeptide molecules form complexes with metal ions^{57,58}, effectively weakening the interaction between metal ions and HPAM. In the present work, the amount of NPS in B-ASP was only half of that in ASP, which effectively reduced the concentration of Na^+ introduced by NPS (inorganic salt, 10.1 %). This was demonstrated by the fact that the initial viscosity of the B-ASP solution was slightly higher than that of the ASP solution. In addition, the seven amino acid residues (mainly amide groups) and the two carboxyl groups in the Glu and Asp residues of the lipopeptide molecules may form hydrogen bonds with the amide

group and carboxyl group from HPAM, reinforcing the network structure of the HPAM chain, as additionally confirmed by the SEM analyses of the B-ASP and ASP solutions. All these contribute to maintaining or even increasing the viscosity of the B-ASP formula⁵⁹.

4. Conclusions

A new flooding system (B-ASP) formed from a biosurfactant and a traditionally recognized ASP with ultra-low IFT between crude oil and formation brine was developed for tertiary oil recovery. The new flooding system was composed of 0.15 wt% of lipopeptide biosurfactant, 0.15 wt% of NPS, 1400 mg/L of HPAM, and 1.2 wt% of Na_2CO_3 . Compared with that of ASP, which contains only NPS as the surfactant component, the IFT between the new flooding system (B-ASP) and Daqing crude oil was reduced to a low level in the order of 10^{-4} mN/m, which is attributed to the positive synergistic effect of the biosurfactant lipopeptide and NPS in the B-ASP system. In addition to the ultra-low IFT, the B-ASP system exhibited a significantly improved performance in terms of thermal adaptability and viscosity stability, which suggests it is a promising and cost-effective flooding system for tertiary oil recovery, particularly amid uncertainties pertaining to oil price fluctuations.

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