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Original Paper

The effect of betaine surfactants on the association behavior of associating polymer

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ABSTRACT

The interfacial properties and rheological behavior of surfactant/polymer complex systems were measured to investigate the association behavior of the associating polymer. Compared with the pure surfactant solution, there are two inflection points in the surface tension curve for the surfactant/polymer complex systems. The two inflection points are dependent on the surfactant type and polymer concentration. The effect of surfactant on the rheological behavior of polymer can be divided into two aspects. First, the addition of short-chain betaine surfactant is detrimental to the viscosity of polymer solution due to the electrostatic shielding effect. Second, long-chain betaine surfactant also reduces the viscosity of polymer solutions at low concentrations. However, when the concentration of the long-chain betaine surfactant is relatively high, the long-chain betaine surfactant could form worm-like micelles that promote the intermolecular association and thus increase the number of associating junctions, thereby resulting in the augmentation of viscosity. So it is necessary to apply the long-chain betaine surfactant to build the polymer/surfactant flooding system. The interaction model between surfactant and polymer is proposed, which is different from the traditional 'Three-Region Model'.

1. Introduction

Alkali/surfactant/polymer (A/S/P) flooding is one of the main chemical-enhanced-oil recovery techniques used by PetroChina (Lin et al., 2011; Zhu et al., 2012a). Take the Daqing Oilfield as an example, the A/S/P flooding can enhance oil recovery by 20% OOIP (Wang et al., 1999). With the widespread application of the A/S/P flooding techniques, however, a series of problems have cropped up (Cheng et al., 2014; Guo and Li, 2017; Pal et al., 2018; Xu et al., 2020; Yang et al., 2014). Specifically, the use of alkali leads to clay swelling and mobilization, reservoir permeability reduction, oil well scaling, and the shortening of pump inspection period (Chang, 2006). So the combined surfactant-polymer (S/P) flooding technology gets more and more attention (Dong et al., 2010; Han et al., 2020; Liu et al., 2020; Rousseau et al., 2018; Sun et al., 2020; Wu et al., 2015; Zhang et al., 2014; Zhu et al., 2012b). The introduction of polymer has an impact on the interfacial properties of surfactants: the critical micelle concentration (CMC), surface tension (SFT) and solubilization (Khan et al., 2008). Besides, surfactant affects the rheological properties of polymer, like the viscosity, molecular conformation (Pal et al., 2019). The surfactant/polymer (S/P) flooding technology embodies the advantages of pure polymer flooding and pure surfactant flooding. The interaction between polymer and surfactant has been widely investigated, for example, SDS/PVP (Prasad et al., 2006), CTAB/hydrophobically modified polymers (Panmai et al., 2002), SDS and poly(dimethyl diallyl ammonium chloride) (Staples et al., 2002), SDS/JR400 (Chronakis and Alexandridis, 2001). Moreover, some researchers established the interaction model between polymer and surfactants: 'Three-Region Model' (Biggs et al., 1992; Liang et al., 2019; Wang et al., 1998). However, research on zwitterionic surfactant and hydrophobically associating polymer is in need of a sound understanding.

Besides the excellent temperature tolerance and salt endurance, betaine surfactants have the brilliant ability to reduce O/W interfacial tension. In addition, hydrophobically associating polymers (AP) also have better viscosifying capacity and salt endurance than common polymer. These betaine surfactants and hydrophobically associating polymers (AP) could be used to prepare the S/P flooding system, but the introduction of betaine surfactants may reduce the viscosity of polymer (Zhang, 2014), which is harmful to the oil recovery factor.

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In this work, the interfacial and rheological properties of complex systems of betaine surfactants and hydrophobically associating polymers (AP) are investigated. The purposes are manifold: (1) to investigate the effect of polymer on the interfacial property of surfactant; (2) to investigate the effect of surfactant on the rheological property of polymer; (3) to understand the interaction mechanism between betaine surfactant and associating polymer.

2. Materials and methods

2.1. Materials

Three betaine surfactants with different alkyl chain lengths were used in this study: lauroamide propyl betaine (LAB), oleic amide propyl betaine (OAB), erucic amide propyl betaine (EAB). The chemical structures of three betaine surfactants are shown in Fig. 1. These surfactants were provided by Chengdu Kehongda Technology Co., Ltd, their effective content are claimed as 35%, 35%, and 30%, respectively. The hydrophobically associating polymer (AP), which was obtained from Sichuan Guangya Polymer Chemical Co., Ltd, has a molecular weight of 1.3×10^7 Da and the content of hydrophobe of 2%. The degree of hydrolysis of polymer AP is 25%. NaCl (analytically pure) was used to prepare synthetic formation brine (total salinity: 27700 mg/L). The oil used is the ZND oil from the Shengli Oilfield.

2.2. Methods

2.2.1. Purification and characterization of betaine surfactants and preparation of polymer solution

It is necessary to purify betaine surfactants since the existence of impurities in surfactants would disturb the investigation of the interaction between polymer and surfactant The purification included four steps: (1) Firstly, most of the water and alcohol were removed with the rotary evaporation apparatus. (2) The product of step 1 was dissolved in ethyl acetate to remove the tertiary amine. (3) The product of step 2 was dissolved in ethanol to remove the salts. (4) Finally, the purified betaine surfactants were obtained through recrystallization. Then the Fourier transform infrared spectrum (FTIR) was obtained with a Nicolet 6700 FT-IR spectrometer to identify the functional groups of purified products.

Since carboxy betaine is cationic in glacial acetic acid, the titration with perchloric acid was carried out to determine the effective content of carboxy betaine after purification.

The procedures of preparation of polymer solution were as follows: (1) A container with a known amount of water was vigorously stirred to create a deep vortex. (2) AP was slowly added to the shoulder of the vortex to wet effectively the AP beads. (3) The container was sealed to minimize evaporation and was stirred continuously for 24 h to ensure complete dissolution of AP (Zhang et al., 2015).

2.2.2. Measurements of interfacial property

The surface tension (SFT) was measured by the Kruss K100 tensiometer equipped with a Wilhelmy plate (Metin et al., 2012). The measurements of surface tension were repeated 3 times, so the experimental error was reduced by averaging the testing values of repeated measurements. The relationship between surface tension and surfactant concentration was plotted in the semilogarithmic chart, the inflection point means the critical micelle concentration (CMC) of surfactant. All the experiments were carried out at 76 °C.

2.2.3. Measurements of bulk rheological property

(1) Measurements of zero shear viscosity (η_0)

The viscosity of polymer solution or surfactant/polymer (S/P) complex solution was measured by Anton Paar MCR 92 rheometer equipped with a 25-mm parallel plate geometry (PP25). The experimental data were fitted by the Carreau-Yasuda model to determine the zero shear viscosity (η_0).

As discussed above, betaine surfactants may have an adverse effect on the viscosity of polymer solution, so the retention ratio of viscosity was calculated by the following formula to assess the effect of surfactant on the viscosity.

$$\phi = \frac{\eta_{0S/P}}{\eta_{0P}} \times 100\% \tag{1}$$

where ϕ is the retention ratio of viscosity, η_{0P} is the zero shear viscosity of polymer solution, $\eta_{0S/P}$ is the zero shear viscosity of surfactant/polymer (S/P) complex system.

(2) Measurements of characteristic relaxation time (T_R)

Amplitude sweep tests were conducted to measure storage modulus (G') and loss modulus (G'') at the constant frequency of 1 Hz, and the linear viscoelastic region (LVE) was determined from the relationship between storage modulus (G') and strain.

Dynamic frequency tests were performed to measure the relations of modulus versus shear frequency. The shear strain was set

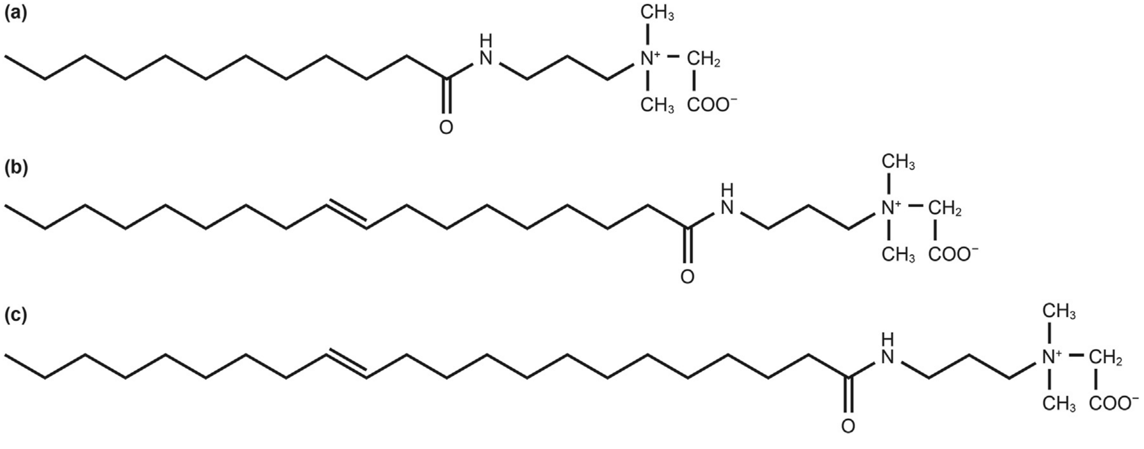

Fig. 1. Molecular formula of betaine surfactants: **(a)** LAB; **(b)** OAB; **(c)** EAB.

according to the linear viscoelastic region (LVE) mentioned above. The characteristic relaxation time (T_R) was determined by the intersection point of G' and G'' curve (T_R is the reciprocal of the frequency of the above intersection point).

(3) The calculation of plateau modulus (G_0)

The plateau modulus (G_0) was related to the zero shear viscosity (η_0) and the characteristic relaxation time (T_R), which could be obtained through the following expression.

$$G_0 = \frac{\eta_0}{T_R} \tag{2}$$

where G_0 is the plateau modulus, η_0 is the zero shear viscosity, T_R is the characteristic relaxation time.

2.2.4. Evaluation of S/P flooding system

(1) Measurements of the interfacial tension

The interfacial tension (IFT) between S/P composite system and oil is measured by using the Texas-500 spinning drop tensiometer at 76 °C. The IFT is determined according to the following equation:

$$\sigma = 1.2336(\rho_w - \rho_o)\omega^2 \left(\frac{D}{n}\right)^3, \quad \frac{L}{D} \geq 4 \tag{3}$$

where σ is the IFT, mN/m; ρ_w and ρ_o are the density of water phase and oil phase, respectively, g/cm^3; ω is the rotational velocity, rpm; D is the width of the measured oil drop, mm; L is the length of the measured oil drop, mm; and n is the refractive index of the water phase.

(2) Measurements of adsorption of surfactants

The steps of the measurement of adsorption of surfactant is as follows: Firstly, the quartz sand is prepared through acid-cleaning and drying. Then, 3 g of quartz sand and 9 mL of surfactant solution are added into a conical flask, and the flask is oscillated for 24 h in a thermostatic water bath. After that, the clear surfactant solution is separated from the flask. Finally, the concentration of surfactant is determined by HPLC. And the adsorption is calculated by the following equation:

$$\Gamma = \frac{(C_0 - C_1)V}{m} \tag{4}$$

where Γ is the adsorption of surfactant per gram of quartz sand, mg/g; C_0 and C_1 are the concentrations of the surfactant solutions before and after the adsorption, mg/mL; V is the volume of the surfactant solution added into the conical flask, mL; and m is the mass of quartz sand, g.

(3) Sandpack flooding test

The displacement characteristics of S/P composite systems are evaluated by sandpack flooding test, which is conducted as follows: (1) The sandpack is prepared with clean quartz sand, and its porosity and permeability are measured. (2) The ZND oil is injected into the sandpack until the water cut is less than 1%. (3) The sandpack is waterflooded until the water cut exceeds 98%. (4) 0.3 pore volume (PV) S/P composite system is injected into the sandpack. (5) The sequent waterflooding is kept until the water cut exceeds 98%. The sandpack flooding test is conducted at 76 °C, and the pressure drop and cumulative oil recovery are recorded during the experiment.

3. Results and discussion

3.1. Purification of betaine surfactants

Following the above methods, three betaine surfactants (LAB, OAB, and EAB) have been firstly purified, and accordingly the FTIR spectra of LAB, OAB, and EAB are shown in Fig. 2. Absorption peaks of LAB at 3336 and 1603 cm^{-1} were attributed to the stretching and bending vibrations of N–H bonds, respectively. The stretching vibrations of C–N and C=O bonds were confirmed by characteristic absorptions at 1391 and 1634 cm^{-1}. The peak at 2918 and 2850 cm^{-1} were assigned to the stretching vibrations of C–H bond in the –CH$_2$CH$_3$ group. Functional groups examined by FTIR analysis coincide with those of LAB, so the purified product could be LAB. The FTIR spectra of OAB and EAB are similar to LAB. According to the results of titration experiments, The effective content of LAB, OAB, and EAB was 99.02%, 98.88%, and 98.67%, respectively, which was measured by the titration. The purity of purified surfactant is high enough to investigate accurately the interaction between surfactant and polymer.

3.2. Effect of polymer on the interfacial property of surfactants

The surface tension-concentration curves of LAB, OAB, and EAB in the absence or presence of polymer are shown in Figs. 3–5. When the polymer was added into the surfactant solution, its concentration was set as 0.05 wt% and 0.15 wt%. We can see there are two inflection points in the surface tension curve after the introduction of polymer, C_1 and C_2, which agrees with some previous studies (Goddard, 1986; Rosen and Kunjappu, 2012). Fig. 6 illustrates the schematic diagram of possible adsorption state between betaine surfactant and polymer. When the concentration of surfactant is blow C_1, the surface tension of surfactant/polymer (S/P) complex system is scarcely decreased with an increase in concentration. This is because the concentration of unassociated surfactant molecules does not increase with a proportional increase in bulk surfactant concentration due to the adsorption of surfactant on the polymer chain (Goswami et al., 2015). Moreover, the surfactant molecules may be combined with polymer in the form of

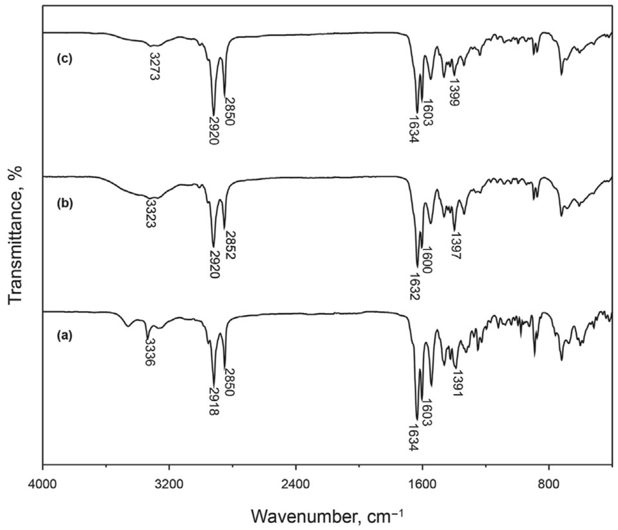

Fig. 2. FTIR spectra of (**a**) LAB, (**b**) OAB, and (**c**) EAB.

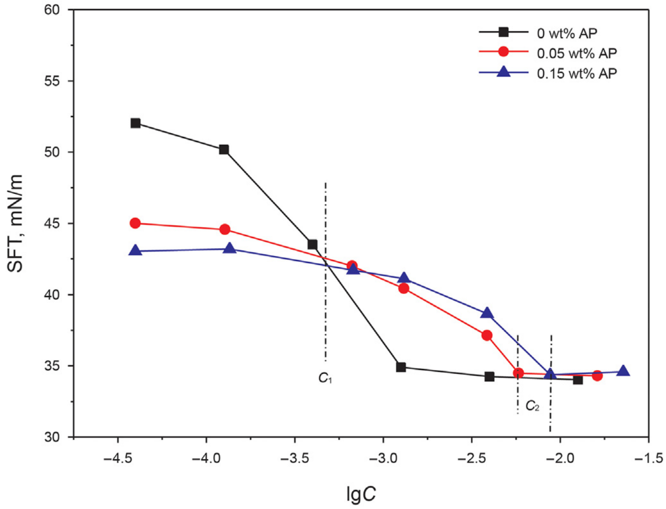

Fig. 3. Effect of polymer on surface tension of LAB (*C* is the surfactant concentration, mol/L).

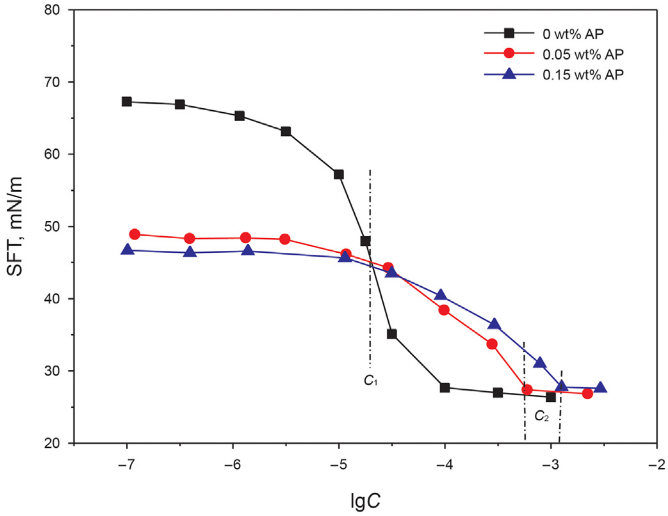

Fig. 4. Effect of polymer on surface tension of OAB.

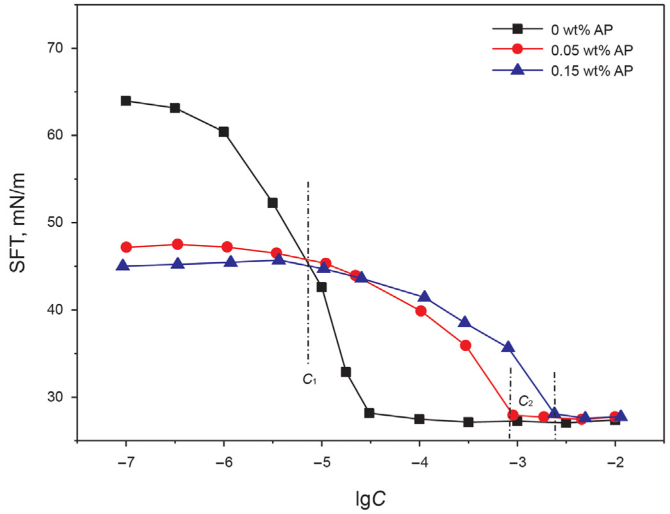

Fig. 5. Effect of polymer on surface tension of EAB.

"cluster" (Cui, 2013). The surface tension of surfactant/polymer (S/P) complex system is less than pure surfactant solution, owing to the adsorption of the hydrophobic polymer and surfactant on the air/water interface (Penfold et al., 2006; Purcell et al., 1995). When the concentration of betaine surfactant reaches C_1, which represents the point at which the polymer tends to be saturated with surfactant, beyond this concentration the surfactant molecules begin to adsorb on the surface and the number of uncomplexed surfactant increases with the increasing of surfactant concentration (Fig. 6), so the surface tension decreases as the surfactant concentration increases. As surfactant concentration increased up to C_2, the surface tension approaches a plateau value which is similar to the pure surfactant. The concentration of C_2 corresponds to normal critical micelle concentration where the excess surfactant molecules begin to form micelles in the solution (Fig. 6).

By comparing the inflection points on the surface tension curve of different complex systems (Figs. 3–5), it can be found that C_1 is dependent on the surfactant type (the alkyl chain length of surfactant molecule), and C_2 is closely related to the concentration of polymer, which is in accordance with the previous study (Cui, 2013). Specifically, C_1 is decreased as the alkyl chain length of surfactant increases. One explanation for this phenomenon could be that surfactants with longer alkyl chain length could form 'clusters' at lower concentrations, which leads to the tendency for polymer to be saturated with long carbon chain surfactant at lower concentrations. This also proves the above hypothesis: the surfactant molecules may be combined with the polymer in the form of "clusters". As to the second inflection point, C_2 is increased with an increase in polymer concentration. The higher the polymer concentration of the complex systems, the larger the adsorption capacity for surfactant. Thus, the C_2 order of systems with different polymer concentrations is 0.15 wt% > 0.05 wt%.

3.3. Effect of surfactant on the rheological property of polymer

The effect of surfactant on the rheological property of polymer was investigated by measuring association parameters of the pure polymer solution and surfactant/polymer (S/P) complex solution, i.e., zero shear viscosity (η_0), characteristic relaxation time (T_R), and plateau modulus (G_0). η_0 shows that the characterization of initial structure strength, T_R represents the strength of associating junctions in network structure, and G_0 could characterize the density and number of associating junctions (Berret, 2003).

3.3.1. The rheological property of pure polymer solution

The viscosity of polymer with different concentrations was measured at different shear rates, and then the zero shear viscosity (η_0) was obtained according to the Carreau-Yasuda model. The results of η_0 are listed in Table 1. The storage modulus (G') and loss modulus (G'') of polymer were measured at different shear rates, and the linear viscoelastic region (LVE) was 50%, so the shear strain of 10% was chosen for the following experiments. The variation of G' and G'' with the shear frequency were measured, and the characteristic relaxation time (T_R) was determined from the intersection point of G' and G'' curve. The plateau modulus (G_0) was calculated according to Eq. (2). The association parameters of polymer are listed in Table 1.

It shows that the viscosity begins to increase significantly with an increase in polymer concentration when the concentration of polymer exceeds 0.15 wt%. Besides, both the plateau modulus (G_0) and the characteristic relaxation time (T_R) are enhanced, indicating that the number of associating junctions and the strength of the associative structure in polymer solutions are enhanced. The reason for the above phenomenon might be that intermolecular association begins to appear in the solution when the polymer

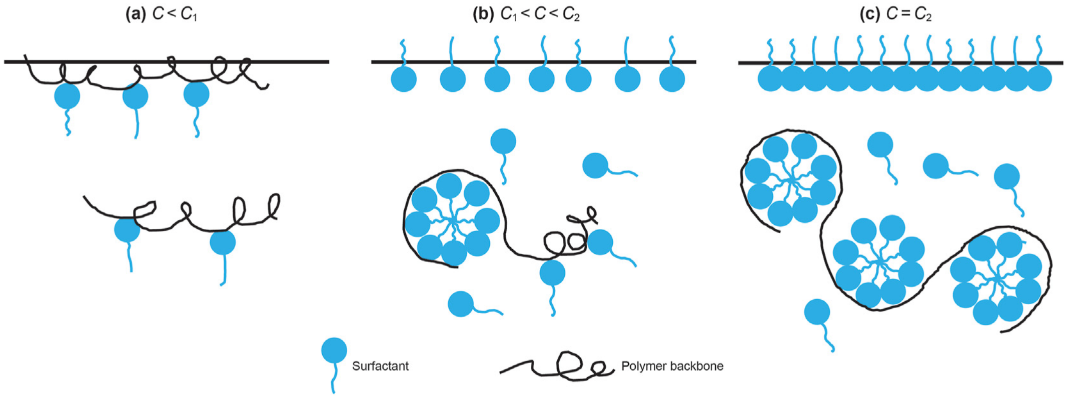

Fig. 6. Adsorption state of betaine surfactant and polymer.

Table 1
Polymer association parameters with different mass fractions.

w(AP), wt%	η_0, Pa·s	T_R, s	G_0, Pa
0.05	0.05	–	–
0.10	0.06	–	–
0.15	0.14	4.52	0.031
0.20	0.27	5.86	0.046
0.25	0.76	16.05	0.047
0.30	1.33	23.15	0.057
0.35	2.53	38.33	0.066

Table 3
Association parameters of 0.15 wt% AP-OAB composite system.

w(OAB), wt%	η_0, Pa·s	T_R, s	G_0, Pa	ϕ, %
0.01	0.08	–	–	57.1
0.03	0.07	–	–	52.9
0.05	0.09	–	–	64.3
0.10	0.10	2.91	0.031	71.4
0.20	0.11	3.33	0.033	78.6
0.30	0.11	3.24	0.034	81.4
0.40	0.12	3.43	0.035	85.7

concentration exceeds 0.15 wt%.

The polymer concentrations were set at 0.15 wt% and 0.25 wt%, for the following experiments in which the rheological properties of surfactant/polymer complex systems were investigated, owing to the fact that the polymer molecules had different association behavior in different concentrations of the polymer.

3.3.2. *Effect of surfactant on the rheological property of polymer solution (0.15 wt% AP)*

When the polymer concentration was 0.15 wt%, LAB, OAB, and EAB were added into the polymer solution, respectively. The rheological parameters (η_0, $T_{R,}$ $G_{0,}$ ϕ) of different systems were measured or calculated and listed in Tables 2–4. One thing to be noticed is that the values of T_R and G_0 cannot be obtained sometimes, owing to the low viscosity (marked as '-' in Tables).

We can see that the effects of surfactants on rheological properties are different for different surfactants. As to LAB (surfactant molecule with short carbon chain), the viscosity decreases slightly when the concentration of LAB is 0.01 wt%, and decreases significantly when the concentration of LAB reaches 0.03 wt%. Figs. 7 and 8 depict the diagram of the adsorption model between polymer and betaine surfactant. The effects of LAB on rheological properties of polymer could be explained according to the adsorption model between polymer and short-chain betaine surfactant (Fig. 7(a)). When the concentration of LAB is 0.01 wt%, below the CMC, free surfactant molecules are relatively less, so the effect of surfactant on polymer viscosity is small, i.e., the value of ϕ is up to 92.9%. When the concentration of LAB is 0.03 wt%, the number of free surfactant molecules increases substantially. Surfactant molecules adsorb on the surrounding of carboxyl groups of polymer, so polymer chains coil due to the electrostatic shielding effect (Fig. 7(a)), thus greatly reducing the viscosity ($\phi = 35.6\%$).

By comparison with LAB, OAB and EAB have different effects on the rheological properties of polymer solutions. The viscosity decreases dramatically as the concentration of OAB or EAB is 0.01 wt%, the number and the strength of associating junctions (G_0 and T_R) are reduced substantially too. When the concentration of OAB or EAB exceeds 0.05 wt%, both G_0 and T_R are increased with the further addition of surfactant, eventually, G_0 returns to the level of polymer solution without surfactants. So the viscosity is increased gradually, and eventually is nearly restored to the original level.

The shape of the micelle is determined by the "packing parameter", $V_H/l_c a_0$, so the longer the hydrophobic chain is, the bigger the packing parameter is (Rosen and Kunjappu, 2012). LAB with small packing parameter tends to form spheroidal micelles, but OAB and EAB can form worm-like micelles. A schematic diagram of the adsorption model of long-chain betaine and polymer is shown in Fig. 8.

Table 2
Association parameters of 0.15 wt% AP-LAB complex system.

w(LAB), wt%	η_0, Pa·s	T_R, s	G_0, Pa	ϕ, %
0.01	0.13	3.64	0.036	92.9
0.03	0.05	–	–	35.6
0.05	0.05	–	–	35.4
0.10	0.05	–	–	35.7
0.20	0.05	–	–	35.6
0.30	0.04	–	–	34.3
0.40	0.04	–	–	34.1

Table 4
Association parameters of 0.15 wt% AP-EAB composite system.

w(EAB), wt%	η_0, Pa·s	T_R, s	G_0, Pa	ϕ, %
0.01	0.08	–	–	60.0
0.03	0.09	–	–	64.3
0.05	0.10	2.70	0.033	71.4
0.10	0.11	3.14	0.035	78.6
0.20	0.12	3.39	0.035	85.7
0.30	0.13	3.48	0.037	92.9
0.40	0.13	3.42	0.038	94.3

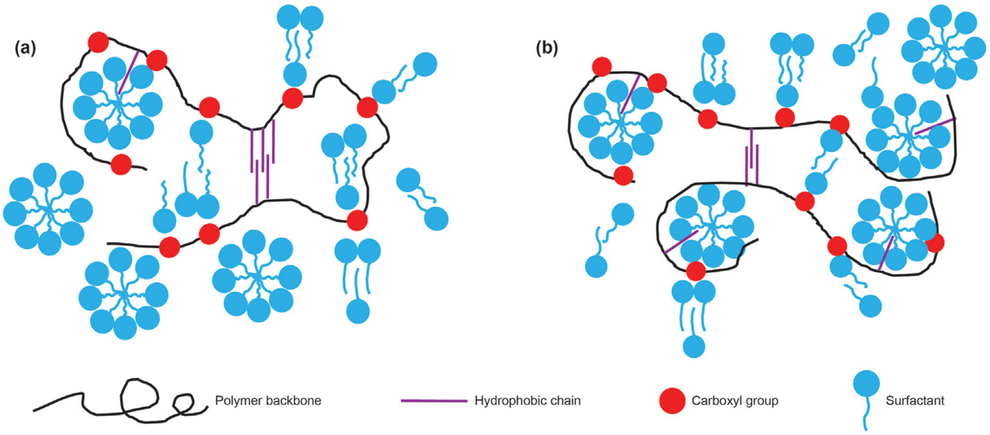

Fig. 7. Adsorption model of short-chain betaine and associating polymer: (**a**) low polymer concentration; (**b**) high polymer concentration.

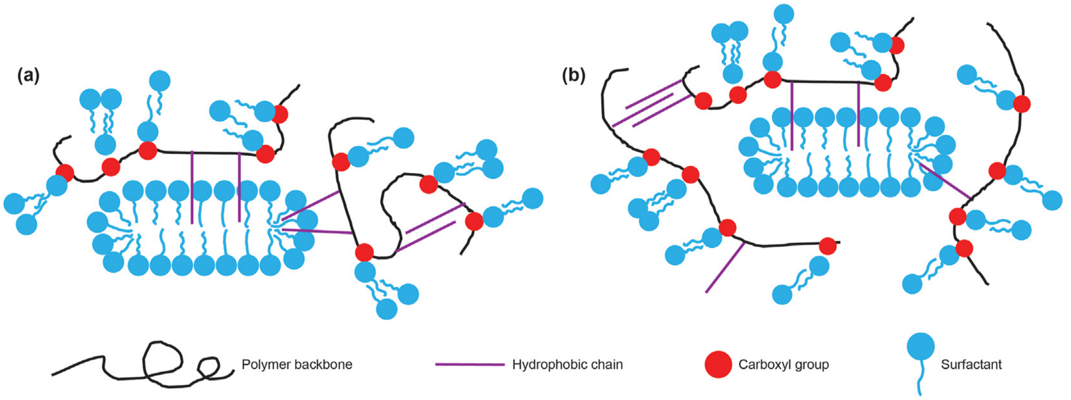

Fig. 8. Adsorption model of long-chain betaine and associating polymer: (**a**) low polymer concentration; (**b**) high polymer concentration.

Take EAB as an example, the effects of EAB on polymer viscosity can be divided into two aspects: (1) The electrostatic shielding effect caused by surfactant molecules leads to an reduction in viscosity of polymer solution. (2) The volume of the worm-like micelle is big enough to incorporate hydrophobic chains from different polymer molecules, forming the complex network. So the formation of the worm-like micelle helps to form an intermolecular association structure and results in an increase in viscosity (Fig. 8(a)). When the concentration of EAB is 0.01 wt%, above the CMC, so there are some free surfactant molecules. In this case, the electrostatic shielding effect is dominant, so the viscosity is decreased with the increase in surfactant concentration. When the concentration of EAB exceeds 0.05 wt%, the number of the worm-like micelles is increased, and thus the effect of intermolecular association is more powerful than the electrostatic shielding effect, so the viscosity is improved again. The augmentation of G_0 with the increase in surfactant concentration, which means an increase in associating junctions, also proves the reliability of the above viewpoint. So it is supposed that the interaction model between EAB and AP is different from the traditional ‘Three-Region Model’.

3.3.3. *Effect of surfactant on the rheological property of polymer solution (0.25 wt% AP)*

When the polymer concentration was 0.25 wt%, LAB, OAB, and EAB were added into the polymer solution, respectively. And the rheological parameters (η_0, T_R, G_0, ϕ) of different systems were measured or calculated and listed in Tables 5–7. Figs. 7(b) and 8(b) depict the diagram of the adsorption model between polymer and betaine surfactant when the polymer concentration is 0.25 wt%.

Generally, the complex system with 0.25 wt% polymer has a higher viscosity (η_0) than the complex system with 0.15 wt% polymer, this is because that intramolecular association is

Table 5
Association parameters of 0.25 wt% AP-LAB composite system.

w(LAB), wt%	η_0, Pa·s	T_R, s	G_0, Pa	ϕ, %
0.01	0.68	14.78	0.046	89.5
0.03	0.23	5.00	0.046	30.8
0.05	0.22	4.89	0.045	29.5
0.10	0.22	4.78	0.046	29.3
0.20	0.22	4.78	0.046	29.5
0.30	0.21	4.67	0.045	28.2
0.40	0.22	4.89	0.045	29.1

Table 6
Association parameters of 0.25 wt% AP-OAB composite system.

w(OAB), wt%	η_0, Pa·s	T_R, s	G_0, Pa	ϕ, %
0.01	0.25	5.68	0.044	33.0
0.03	0.26	5.78	0.045	34.5
0.05	0.34	7.39	0.046	45.0
0.10	0.43	9.35	0.046	56.7
0.20	0.46	9.58	0.048	61.1
0.30	0.54	11.24	0.048	71.6
0.40	0.59	12.06	0.049	78.2

Table 7
Association parameters of 0.25 wt% AP -EAB composite system.

w(EAB), wt%	η_0, Pa·s	T_R, s	G_0, Pa	ϕ, %
0.01	0.46	9.58	0.048	60.5
0.03	0.45	9.38	0.048	59.3
0.05	0.51	10.41	0.049	67.1
0.10	0.62	12.37	0.050	81.6
0.20	0.69	13.69	0.050	90.8
0.30	0.70	13.72	0.051	92.1
0.40	0.71	13.65	0.052	93.4

dominant in the low concentration polymer solutions, and intermolecular association occurs in highly concentrated solutions. The variation of G_0 and T_R with the surfactant (LAB, OAB, EAB) under the polymer concentration of 0.25 wt% is similar to the complex system with 0.15 wt% polymer. When the concentration of surfactant is 0.40 wt%, the value of the retention ratio of viscosity (ϕ) is increased with an increase in alkyl chain length of surfactant, i.e., $\phi_{LAB} < \phi_{OAB} < \phi_{EAB}$. This is because that the volume of the micelle is increased with an increase in the alkyl chain length of surfactant. The existence of a bigger worm-like micelle could promote the intermolecular association, and then a 3D association network was formed, thereby increasing the viscosity of the complex system (Figs. 7(b) and 8(b)).

3.4. Evaluation of S/P flooding systems

In this section, the IFT between A/P composite systems and ZND oil, the adsorption of surfactants and the displacement characteristics of S/P composite systems were measured to check the suitability of the slug for EOR application.

3.4.1. Measurements of the interfacial tension

The IFT between S/P composite systems and oil were measured, and the results are shown in Fig. 9. The S/P complex system containing 0.15 wt% AP and 0.20% wt OAB shows poor capacity in reducing the IFT. However, S/P systems containing AP and EAB show excellent interfacial activity, the IFT value can be reduced to an ultra-low value (10^{-3} mN/m) even at a relatively low concentration (0.10 wt%).

Considering the performance of S/P composite system (in terms of IFT and viscosity) and operating cost, the S/P composite system containing 0.15 wt% AP and 0.10 wt% EAB was chosen for sandpack flooding tests.

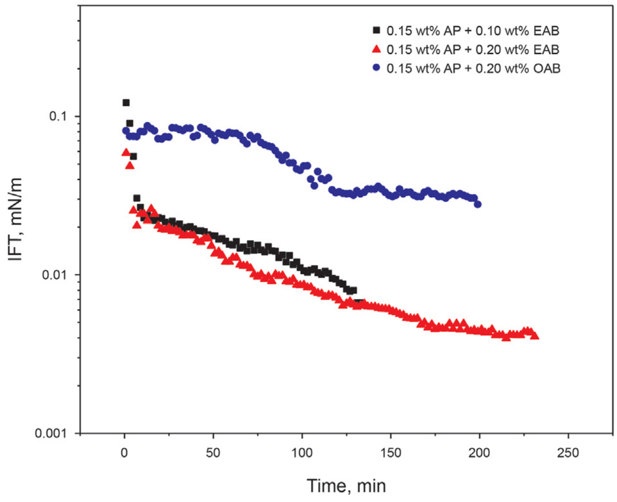

Fig. 9. Dynamic IFT curves of different S/P systems.

Table 8
The adsorption of different composite systems.

No.	Chemical formula	Adsorption, mg/g
1	0.10 wt% EAB +0.15 wt% AP	2.25
2	0.10 wt% EAB +0.15 wt% AP + 0.10 wt% alkali lignin	1.46

3.4.2. Measurements of adsorption of surfactants

It was point out that the adsorption of surfactant is a key parameter for the application of chemical flooding in our previous research (Feng et al., 2012). The adsorption of surfactant on the reservoir rock undoubtedly reduces its concentration in the bulk phase during the process of enhanced oil recovery (EOR). So the adsorption of was measured and shown in Table 8. The adsorption of the selected S/P flooding system is 2.25 mg/g, which is close to the demand of surfactants for oil displacement (2 mg/g). Previous research found that alkali lignin could reduce the adsorption of betaine surfactant (Feng et al., 2012), so 0.10 wt% alkali lignin was added into the S/P composite system, and the adsorption was decreased to 1.46 mg/g, which is acceptable for field application. So the final selected S/P flooding systems is 0.10 wt% EAB +0.15 wt% AP + 0.10 wt% alkali lignin.

3.4.3. Sandpack flooding test

The bench scale displacement tests are often used to evaluate the EOR effectiveness of chemical flooding (Asl et al., 2020; Almahfood and Bai, 2021). In this section, the EOR effectiveness of the selected S/P composite system was evaluated at 76 °C. The porosity and permeability of the sand pack in the displacement experiment was 39.4% and 1567 mD, respectively. The displacement experiment was divided into 3 steps: (1) primary waterflooding; (2) S/P flooding; (3) secondary waterflooding. The displacement results and the picture of the effluent during the subsequent waterflooding are shown in Figs. 10 and 11, respectively.

The results indicate that the recovery is enhanced by 32% after S/P flooding and secondary waterflooding. There are two reasons why the recovery is enhanced: first, the sweep volume is improved owing to the high viscosity of S/P flooding systems, which is in accordance with the increase in pressure drop after S/P flooding

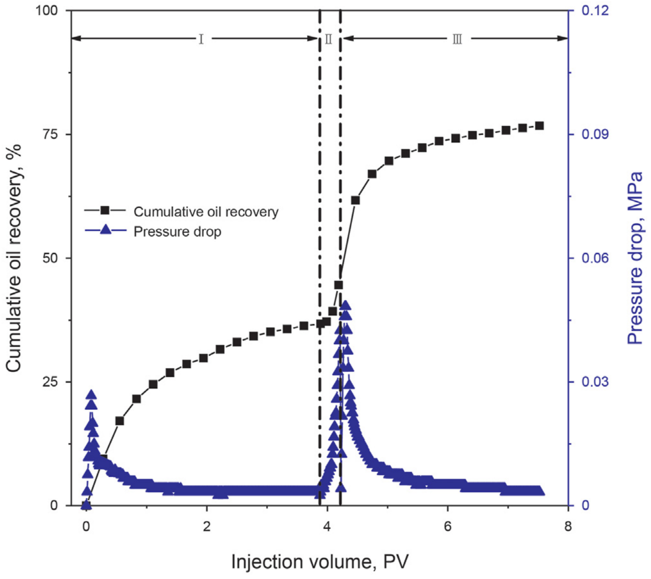

Fig. 10. Displacement results of the S/P flooding system.

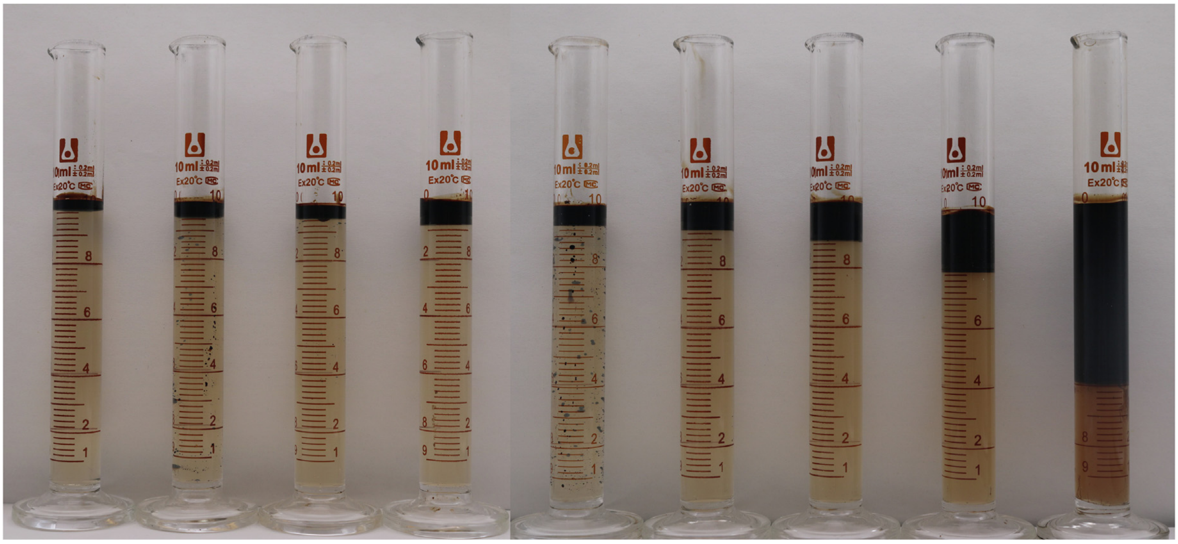

Fig. 11. The effluent during the secondary waterflooding (the effluent was collected from right to left).

and secondary waterflooding; second, the displacement efficiency is enhanced owing to the low IFT. Moreover, the S/P composite system has certain emulsifying power according to the effluent during the subsequent waterflooding (Fig. 11).

4. Conclusions

The interfacial and rheological properties of different S/P complex systems were investigated. The results indicate that the polymer concentration could affect the surface tension (SFT)-surfactant concentration curve, and there are two inflection points in the SFT curve in the presence of polymer, C_1 and C_2. C_1 decreases when the alkyl chain length of surfactant increases, and C_2 increases with the increase in polymer concentration. The impact of betaine surfactant on the rheological properties of polymer could be divided into two aspects. (1) As to short-carbon chain betaine surfactant (LAB), as the concentration of LAB is increased, the values of T_R and G_0 decrease and then tend to be constant. (2) However, in the case of long-carbon chain betaine surfactant (OAB, EAB), the values of T_R and G_0 firstly decrease and then increase with the addition of surfactant. Compared with LAB, OAB and EAB have higher packing parameters, and can form worm-like micelles. These worm-like micelles help to form an intermolecular association structure, which results in the increase in viscosity. According to the effect of different betaine surfactants (short-carbon chain: LAB, long-carbon chain: OAB, EAB) on the rheological properties, the interaction model between surfactant and polymer is proposed, which is different from the traditional 'Three-Region Model'. Long-carbon chain betaine surfactants should be chosen to design the surfactant/polymer (S/P) flooding systems when the associating polymer (AP) is used, which is instructive to the enhanced oil recovery. The sandpack flooding test shows the final selected S/P composite system could improve substantially the recovery through enhancing the sweep efficiency and displacement efficiency.

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