Electronic Supplementary Information

A novel surfactant-polymer flooding system of the biobased zwitterionic surfactant and hydrophobically associating polymer with ultralow interfacial tensions

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1. Material

Daqing oil sands (specific surface area of 1.43 m^2/g), Daqing crude oil (a density of 0.85 g/cm^3, viscosity of 19.81 mPa at 45 °C). Other materials were all analytical reagents. All of the aqueous solutions used in this study were prepared with simulated formation water (Table 1).

Table 1 The formation of simulate formation water

Substance	Concentration (mg/L)
$NaHCO_3$	3176.0
NaCl	1597.1
Na_2CO_3	381.6
$CaCl_2$	112.7
$MgCl_2$	42.8
Na_2SO_4	17.0

2. Methods

2.1 Interfacial tension measurement

The interfacial tension was measured by a spinning drop interfacial tensiometer, TX500C. The measuring range of TX500C is 100 mN/m -10^{-5} mN/m. A capillary tube filled with surfactant solution and a fresh drop of crude oil, was spun at 4500 rpm. Unless otherwise specified, the temperature was 45 °C in this study. The measure time is one hour for the POAPMB solutions and two hours for POAPMB/AP-P3 system. The interfacial tension between Daqing crude oil and simulated formation water was 9.90 mN/m at 45 °C.

2.2 Dilution resistance measurement

The POAPMB/AP-P3 system was mixed with simulated formation water at the volume ratio of 1:1, 1:2, 1:3…1:8. After mixing, the interfacial tension with crude oil was measured at 45 °C to determine the dilution resistance of the system. The initial concentration of surfactant was 0.50 g/L, and AP-P3 was 1.50 g/L.

2.3 Adsorption resistance measurement

The solutions with a surfactant concentration of 0.50 g/L and with an AP-P3 concentration of 1.50 g/L were prepared. The solutions (8.00 g) and oil sands (0.89 g) were mixed in 10 mL colorimetric tube. Shaking them at 45 °C for 24 h by shaking water bath SW22. The supernatants were collected by centrifuge 3-18 (5000 rpm, 5 min), then measured IFT between Daqing crude oil and the supernatants. If the value of IFT was below 0.01 mN/m, fresh sands were added to the remaining supernatants at the weight fraction radio of 0.1/0.9. Repeat the above operation until the IFT of the solution is above 0.01 mN/m. The resistance of a surfactant formulation against adsorption were evaluated by the total number of times that an ultralow IFT was achieved.

2.4 Viscosity stability measurement

The viscosity stability of SP flooding was determined under the conditions of 45 °C, shear rates 7.34 s^{-1} by Programmable Rheometer DV-III. The accuracy of Programmable Rheometer DV-III is the plus or minus one percent of the result of the measurement.

2.5 Phase behavior study

The solution and crude oil were preheated to 45 °C, then 25 mL of crude oil and 25 mL of POAPMB/AP-P3 system were mixed in a 50 mL colorimetric tube and shaken by hand for 5 minutes. An emulsion was formed and allowed to settle at 45 °C, and equilibrium was assumed when there was no observable change in the phase levels. The final observed levels were recorded.

2.6 Particle size and Zeta potential

Particle size and Zeta potential were measured using Zetasizer procured from Malvern instruments, Model ZEN3690, USA at 45 °C.

3. Results of interfacial properties

3.1 Interfacial tension

Dynamic interfacial tensions (average of three measurements) between Daqing crude oil and different concentrations of surfactant solutions alone and in the presence of 1.50 g/L AP-P3 were showed in Fig.1a and 1b.

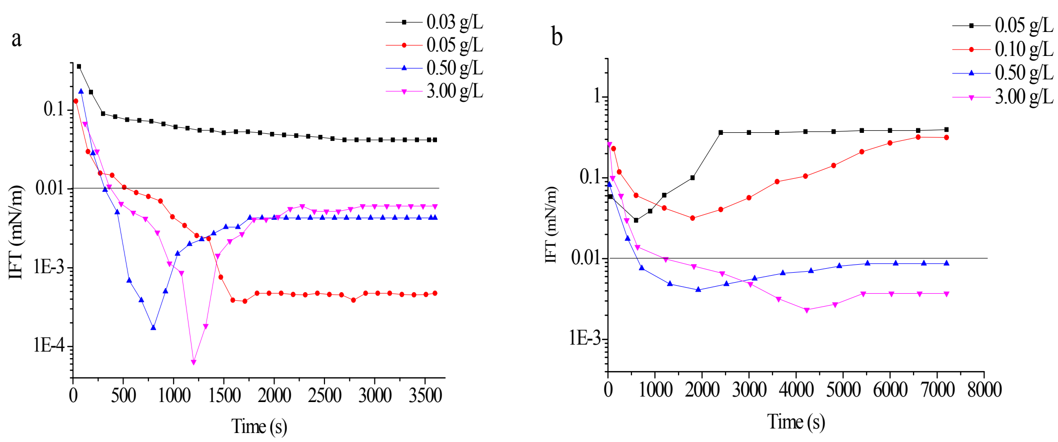

Figure 1. The IFT between crude oil and different concentrations of POAPMB solutions (a) and in the presence of 1.50 g/L AP-P3 (b)

3.2 Effect of temperature

Fig.2 showed IFTs (average of three measurements) of surfactant solution and POAPMB/AP-P3 system at different temperatures. The concentrations of POAPMB and AP-P3 in binary system were 0.50 g/L and 1.50 g/L, respectively.

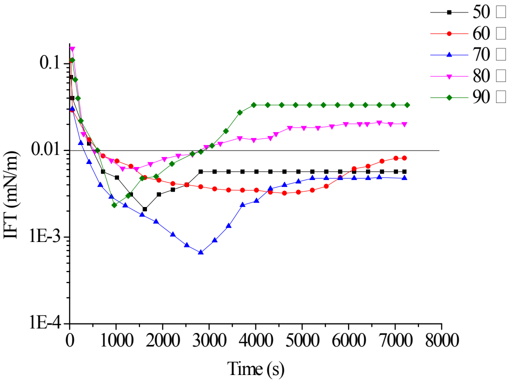

Figure 2. Effect of temperature on the IFTs between crude oil and POAPMB/AP-P3 system

3.3 Effect of salt

The effect of NaCl and Ca^{2+} concentration on IFTs (average of three measurements) was showed in Fig. 3 and Fig. 4. The concentrations of POAPMB and AP-P3 in binary system were 0.50 g/L and 1.50 g/L, respectively.

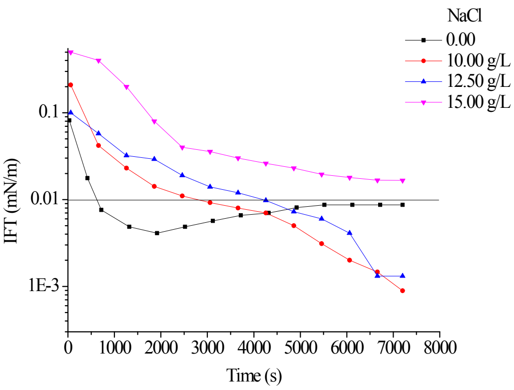

Figure 3. Effect of concentrations of NaCl on the IFTs between crude oil and POAPMB/AP-P3 system

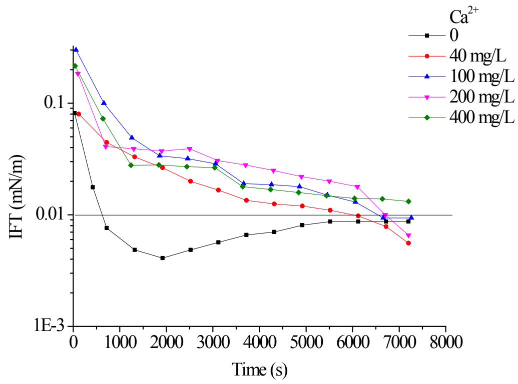

Figure 4. Effect of concentrations of Ca^{2+} on the IFTs between crude oil and POAPMB/AP-P3 system

3.4 Dilution performance

Table 2 showed the IFTs of 3.00 g/L POAPMB solution with 1.50 g/L AP-P3 after dilution against crude oil.

Table 2 The minimum IFTs and the equilibrium IFTs between crude oil and the aqueous solutions after dilution

Dilution multiple	3.0 g/L POAPMB +1.5 g/L AP-P3	3.0 g/L POAPMB +1.5 g/L AP-P3
1	$(2.3\pm0.4)\times10^{-4}$	$(4.1\pm0.4)\times10^{-3}$
2	$(4.2\pm0.5)\times10^{-4}$	$(5.6\pm0.5)\times10^{-3}$
3	$(4.1\pm0.3)\times10^{-4}$	$(4.3\pm0.3)\times10^{-3}$
4	$(3.8\pm0.4)\times10^{-4}$	$(2.5\pm0.2)\times10^{-3}$
5	$(3.9\pm0.3)\times10^{-4}$	$(3.6\pm0.2)\times10^{-3}$
6	$(5.7\pm0.6)\times10^{-4}$	$(2.6\pm0.3)\times10^{-3}$
7	$(3.2\pm0.5)\times10^{-4}$	$(6.7\pm0.4)\times10^{-3}$
8	$(2.5\pm0.4)\times10^{-4}$	$(7.9\pm0.3)\times10^{-4}$
9	$(5.5\pm0.5)\times10^{-4}$	$(3.4\pm0.2)\times10^{-3}$

10	$(1.4±0.3)×10^{-5}$	$(3.5±0.4)×10^{-4}$
20	$(1.6±0.4)×10^{-4}$	$(3.1±0.2)×10^{-3}$
30	$(2.9±0.3)×10^{-4}$	$(2.9±0.3)×10^{-4}$
40	$(4.5±0.6)×10^{-3}$	$(4.5±0.4)×10^{-3}$
50	$(4.3±0.4)×10^{-2}$	$(4.3±0.3)×10^{-2}$

3.5 Resistance against adsorption by Daqing oil sands

Table 3 showed the IFTs of 3.00 g/L POAPMB solution with 1.50 g/L AP-P3 after adsorptions against crude oil.

Table 3 The IFT_{min} and IFT_{equ} between crude oil and the aqueous solutions after adsorption (45 °C)

Days	3.0 g/L POAPMB +1.5 g/L AP-P3 IFT_{min}(mN/m)	3.0 g/L POAPMB +1.5 g/L AP-P3 IFT_{equ}(mN/m)
1	$(4.1±0.4)×10^{-3}$	$(4.1±0.4)×10^{-3}$
2	$(1.0±0.2)×10^{-3}$	$(5.1±0.1)×10^{-3}$
3	$(7.0±0.3)×10^{-3}$	$(7.0±0.3)×10^{-3}$
4	$(5.4±0.4)×10^{-2}$	$(8.8±0.2)×10^{-2}$

4. Results of viscosity properties

4.1 Dilution performance

Table 4 showed the viscosity of 0.50 g/L POAPMB solution with 1.50 g/L AP-P3 after dilution.

Table 4 The viscosity of POAPMB/AP-P3 system diluted (45 °C)

Dilution multiple	1	2	3	4	5	6	7	8	9
Viscosity (mPa·s)	46.8±0.4	15.7±0.2	8.9±0.1	6.5±0.1	5.9±0.1	4.3±0.1	3.9±0.1	3.6±0.1	3.4±0.1

4.2 Resistance against adsorption by Daqing oil sands

Table 5 showed the viscosity of 0.50 g/L POAPMB solution with 1.50 g/L AP-P3 after adsorption.

Table 5 The viscosity of POAPMB/AP-P3 system after adsorption (45 °C)

Adsorption times	0	1	2	3
Viscosity (mPa·s)	46.8±0.4	44.3±0.2	43.7±0.3	42.8±0.2

4.3 Effect of temperature

Table 6 showed the viscosity of 0.50 g/L POAPMB solution with 1.50 g/L at different temperature.

Table 6 Effect of temperature on the viscosity of POAPMB/AP-P3 system

Temperature (℃)	50	60	70	80	90
Viscosity (mPa·s)	39.7±0.3	36.3±0.3	32.8±0.3	29.5±0.2	25.1±0.1

4.4 Effect of salt

Table 7 and Table 8 showed the viscosity of 0.50 g/L POAPMB solution with 1.50 g/L at different concentrations of . NaCl and Ca^{2+}.

Table 7 Effect of the concentration of NaCl on the viscosity of POAPMB/AP-P3 system (45 °C)

The concentration of NaCl (g/L)	0	10	12.5	15
Viscosity (mPa·s)	46.8±0.4	27.5±0.2	25.9±0.2	24.8±0.2

Table 8 Effect of the concentration of Ca^{2+}on the viscosity of POAPMB/AP-P3 system (45 °C)

The concentration of Ca^{2+} (mg/L)	0	40	100	200	400
Viscosity (mPa·s)	46.8±0.4	42.1±0.3	41.5±0.2	35.9±0.2	26.2±0.1

5. Particle size and Zeta potential

Table 9 and Table 10 showed Particle size and Zeta potential results of solutions.

Table 9 Particle size at 45 °C

Solution	Peak 1 (nm)	Intensity%	Peak 2 (nm)	Intensity%
0.5 g/L POAPMB	13.7±0.1	100	-	-
1.5 g/L AP-P3	43.4±6.1	100	-	-
0.5 g/L POAPMB+1.5 g/L AP-P3	14.5±1.5	13.5	100.1±8.9	86.5
Middle microemulsion	144.1±9.5	100	-	-
Bottom phase	40.4±9.3	33.7	212.3±19.9	66.3

Table 10 Particle size at 45 °C

Solution	ZP (mV)
Middle microemulsion	50.4±2.4

6. Previous reslut

The previous results cited in the paper are summarized in Table 11.

Table 11 Previous result

Solution	State
2.5 g/L sugar-based anionic-nonionic surfactant	achieved ultralow IFT[15]
5 mM nonionic + 1.00 g/L polyacrylamide	can't achieve ultralow IFT[10]
0.3~10 mM nonionic surfactant mixed sulfobetaine + 1.00 g/L polyacrylamide	achieved ultralow IFT[10]
gemini-non-ionic mixed surfactant (total 3.00 g/L) + hydrophobically associating polyacrylamide	achieved ultralow IFT after aging for 90 days[5]
nonionic/zwitterionic formulation (total 7.50 mM, mole ratio 1/1) +1.00 g/L polyacrylamide	achieved the ultralow IFT after adsorption four times[2]
0.50 g/L fatty acid disulfonate+1.75 g/L hydrophobically associating polyacrylamide	67% the initial viscosity retention rate.[5]