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).

| Substance    | Concentration (mg/L) |
|--------------|----------------------|
| NaHCO\(_3\)  | 3176.0               |
| NaCl         | 1597.1               |
| Na\(_2\)CO\(_3\) | 381.6               |
| CaCl\(_2\)   | 112.7                |
| MgCl\(_2\)   | 42.8                 |
| Na\(_2\)SO\(_4\) | 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.
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.

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.

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.

| 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±0.4)×10^{-4}            | (4.1±0.4)×10^{-4}            |
| 2                 | (4.2±0.5)×10^{-4}            | (5.6±0.5)×10^{-4}            |
| 3                 | (4.1±0.3)×10^{-4}            | (4.3±0.3)×10^{-4}            |
| 4                 | (3.8±0.4)×10^{-4}            | (2.5±0.2)×10^{-3}            |
| 5                 | (3.9±0.3)×10^{-4}            | (3.6±0.2)×10^{-3}            |
| 6                 | (5.7±0.6)×10^{-4}            | (2.6±0.3)×10^{-3}            |
| 7                 | (3.2±0.5)×10^{-4}            | (6.7±0.4)×10^{-3}            |
| 8                 | (2.5±0.4)×10^{-4}            | (7.9±0.3)×10^{-4}            |
| 9                 | (5.5±0.5)×10^{-4}            | (3.4±0.2)×10^{-3}            |
10 (1.4±0.3)×10⁻⁴ (3.5±0.4)×10⁻⁴
20 (1.6±0.4)×10⁻⁴ (3.1±0.2)×10⁻⁴
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 IFTmin and IFTeq between crude oil and the aqueous solutions after adsorption (45 °C)

| Days  | 3.0 g/L POAPMB + 1.5 g/L AP-P3 | IFT (mN/m) |
|-------|--------------------------------|------------|
| 1     | (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 Ca²⁺.

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 Ca²⁺ on the viscosity of POAPMB/AP-P3 system (45 °C)

| The concentration of Ca²⁺ (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.

| 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       |

| Solution                          | ZP (mV)    |
|----------------------------------|------------|
| Middle microemulsion             | 50.4±2.4   |

6. Previous result

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

| 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$^5$ |