Study on the effect of oligomer silicone surfactant on the properties of drilling fluids

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Abstract. Due to small hole roar, most of low-permeability gas reservoirs are water wetting, and the capillary effect is very prominent, resulting in water blocking damage in the process of exploitation for natural gas. A new kind of oligomer silicone surfactant (OSSF) was developed, and the physical and chemical properties of oligomer silicone surfactant were evaluated. The experimental results indicated that the critical micelle concentration of OSSF was 0.418×10⁻³ mol/L, and the critical surface tension of OSSF was 20.631 mN/m. OSSF could be adsorbed directionally at the water-rock pore interface, and the cores adsorbed with OSSF should reverse from water wetting to oil wetting or gas wetting. OSSF had good compatibility with sulphonated polymer mud. OSSF could play an important role in unlocking water blocking damage to increase production and efficiency.

1. Introduction
During the exploitation of low permeability gas-condensate reservoirs, the mud filtrate, acidizing liquid, and fracturing fluid are easy to invade the reservoir, and severely reduce the permeability of the reservoirs, resulting in severe formation damage [1-3].

Due to small reservoir pores and throats wetted by water, most of low-permeability reservoirs have high capillary pressure. Due to increased capillary pressure and water wettability, severe formation damage is induced by the invasion of working fluid and the subsequent water blocking [4-6]. However, surface modification by surfactant adsorption could change the wettability of rock surface to enhance the removal efficiency of reservoir fluid and reduce the water blocking damage. As a consequence, appropriate surfactants have a good potential applicant in the process of exploitation for natural gas [7-9].

In the current paper, A new kind of oligomer silicone surfactant (OSSF) containing sulfonic acid groups is developed to improve the water locking effect, and the physical and chemical properties of OSSF are evaluated. It is found that the surface tension of OSSF increases with aging temperature but decreases with the increasing of concentration of OSS. OSSF has positive effect on wettability reversal for water-wet reservoir by adsorption on solid-liquid interface. OSSF might hold great promise to address water blocking damage problems in low-permeability reservoirs.

2. Preparation of OSSF
Azobisisobutyronitrile, 2-acrylamide-2-methyl propane sulfonic acid and 100 mL ethanol are added. The mixture is stirred until fully dissolved. The mixture is placed into a three-necked flask equipped
with a stirrer, reflux condenser, and thermometer, and the pH of the mixture was adjusted to 5-6 and stirred at 75 °C for 6 h. The solvent was then removed at reduced pressure. The precipitate was filtered, giving the target compound [10, 11].

3. Results and discussion

3.1. The evaluation of surfactivity

The surface tension of various concentrations of OSSF is tested by surface tension apparatus through Wilhelmy method. Figure 1 shows the curve of surface tension of OSSF, and Table 1 indicates the surface tension of NaOH solution and filtrate of basic mud.

As shown in Figure 1, the critical micelle concentration (cmc) of OSSF is $0.418 \times 10^{-3}$ mol/L, and the critical surface tension of OSSF ($\gamma_{\text{cmc}}$) is 20.631 mN/m, so OSSF has low critical micelle concentration and good surface activity. The surface tension of distilled water could be reduced from 72.8 mN/m to 20.631 mN/m when the concentration of OSSF is more than $0.418 \times 10^{-3}$ mol/L.

![Figure 1. The curve of surface tension of OSSF.](image)

As shown in Table 1, when the dosage is 0.02%~0.04%, the surface tension of solution and filtrate could be reduced gradually with the increase of the dosage of ABSN and OSSF. ABSN could reduce the surface tension of NaOH solution and base mud filtrate from 70.767 mN/m, 41.897 mN/m to 31.578 mN/m, 26.216 mN/m, respectively. OSSF could reduce the surface tension of NaOH solution and base mud filtrate from 70.767 mN/m, 41.897 mN/m to 22.191 mN/m, 23.573 mN/m, respectively. The more the reduction of surface tension, the lower the water blocking damage. So OSSF could improve the water blocking damage of low-permeability gas reservoir better than ABSN.

| Types of surfactant | Dosage (%) | NaOH solution before rolling (mN•m⁻¹) | NaOH solution after rolling (mN•m⁻¹) | base mud filtrate before rolling (mN•m⁻¹) | base mud filtrate after rolling (mN•m⁻¹) |
|--------------------|------------|----------------------------------------|--------------------------------------|------------------------------------------|----------------------------------------|
| Not added          | 0          | 71.254                                 | 70.767                               | 41.697                                   | 41.897                                 |
| ABSN               | 0.20       | 34.269                                 | 34.052                               | 29.074                                   | 28.754                                 |
| ABSN               | 0.40       | 32.852                                 | 31.578                               | 26.160                                   | 26.216                                 |
| OSSF               | 0.20       | 21.436                                 | 22.712                               | 26.492                                   | 23.573                                 |
| OSSF               | 0.40       | 19.986                                 | 22.191                               | 26.584                                   | 23.573                                 |
3.2. The evaluation of high-temperature stability

OSSF solution is rolled at different temperatures for 16 h, and the surface tension of OSSF solution after cooling is tested. Figure 2 shows the relationship between the surface tension of OSSF solution and aging temperature.

![Figure 2](image-url)

**Figure 2.** The relationship between the surface tension of OSSF and aging temperature.

To reduce the water block damage of low-permeability reservoir, the surfactant with good stability at high temperature should be used. As shown in Table 1 at a constant concentration, the surface tension of OSSF can be increased with the increasing of aging temperature, the value added of the surface tension of OSSF can be reduced with the increasing of mass fraction of OSSF. At the same aging temperature, the surface tension of OSSF can be reduced gradually with the increasing of concentration of OSSF. The reason is that the relative molecular mass of OSSF could be increased through mutual polycondensation of silanol groups under high temperature conditions, resulting in the increasing of the surface tension of OSSF. However, when the mass fraction of OSSF is 0.10%~0.50%, the aging temperature is 50 °C~150 °C, the surface tension of OSSF is less than 25mN/m.

3.3. The evaluation of wettability

The cores are soaked in OSSF solution for 16 h, dried for 4 h at 150 °C, and cooled down to room temperature. The contact angle of distilled water and glycol on the surface of cores are tested by contact angle meter. The contact angle of droplets on the surface of cores is calculated by five-point fitting method. As shown in Formula (1) and Formula (2), the surface energy is calculated through Owens method and Wendt method.

\[(1 + \cos \theta) \gamma'_{L} = 2(\gamma'_{S} \gamma'_{L})^{1/2} + 2(\gamma'_{P} \gamma'_{L})^{1/2} \]

\[\gamma'_{S} = \gamma'_{d} + \gamma'_{P} \]

θ is the contact angle of droplets on the surface of rock, \( \gamma_{L} \) is the surface tension of liquid, \( \gamma'_{d} \) is the dispersion force component of rock, \( \gamma'_{P} \) is the polar force component of rock, \( \gamma'_{L} \) is the polar component of fluid. It is water wetting while the contact angle is less 90°, it is neutral wetting while the contact angle is approximately equal to 90°, and it is gas wetting while the contact angle is more than 90°. The contact angle and surface energy of droplets on the surface of core after adsorption equilibrium of OSSF are demonstrated in Table 2.

The surfactant can adsorb on the rock surface, lower the surface energy, change the wettability, and finally affect the microscopic distribution of water, gas, and oil in the porosity of reservoir rock. As shown in Table 2, when the mass fraction of OSSF is more than 0.20%, the cores adsorbed with OSSF should reverse from water wetting to oil wetting or gas wetting, and the surface energy could reduce...
significantly. Given the surface inhomogeneity of artificial cores and reservoir cores, the contact angle of water and ethylene glycol on the surface of artificial cores could be increased greatly with the increase of the concentration of OSSF. When the mass fraction of OSSF is more than 0.20%, the maximum contact angle of distilled water on the surface of artificial cores is 110.12°, the maximum contact angle of ethylene glycol on the surface of artificial cores is 27.14°, and the minimum surface energy is 22.09 mJ/m². Meanwhile, the maximum contact angle of distilled water on the surface of reservoir cores is 114.53°, the maximum contact angle of ethylene glycol on the surface of reservoir cores is 39.58°, and the minimum surface energy is 25.34 mJ/m². Therefore, OSSF could be adsorbed directionally at the water-pore interface, and the formed adsorption film could lower the free energy of pore surface, change the wettability of pores, reduce the capillary force of water phase, and increase the capillary force of oil phase.

| Core type      | Mass fraction of OSSF (%) | Contact angle (°) | Dispersion force (mJ/m²) | Polar force (mJ/m²) | Surface energy (mJ/m²) |
|----------------|----------------------------|-------------------|--------------------------|---------------------|------------------------|
| artificial core | 0                          | 13.47             | /                        | /                   | /                      |
| reservoir core  | 0                          | 13.47             | /                        | /                   | /                      |
| artificial core | 0.1                        | 46.86             | 11.32                    | 16.53               | 35.09                  | 51.63                  |
| artificial core | 0.2                        | 109.35            | 25.28                    | 2.96                | 20.55                  | 23.51                  |
| artificial core | 0.3                        | 108.76            | 24.82                    | 2.30                | 19.80                  | 22.09                  |
| artificial core | 0.4                        | 110.12            | 27.14                    | 3.47                | 20.80                  | 24.27                  |
| artificial core | 0.5                        | 110.01            | 25.37                    | 3.91                | 21.58                  | 25.49                  |
| reservoir core  | 0.1                        | 52.21             | 12.67                    | 21.48               | 26.93                  | 48.42                  |
| reservoir core  | 0.2                        | 114.34            | 39.58                    | 5.87                | 20.98                  | 26.85                  |
| reservoir core  | 0.3                        | 113.61            | 38.72                    | 4.97                | 20.37                  | 25.34                  |
| reservoir core  | 0.4                        | 113.94            | 39.20                    | 5.33                | 20.59                  | 25.92                  |
| reservoir core  | 0.5                        | 114.53            | 39.19                    | 6.44                | 21.52                  | 27.96                  |

3.4. The evaluation of foamability

OSSF is added to 100 mL distilled water, basic mud (4% bentonite mud + 0.2% Na₂CO₃), sulphonated polymer mud (4% bentonite mud + 0.15% NaOH + 0.5% PAC-LV + 0.5% CMC-LVT +2%SMP-I + 2% SMC +2% SPNH +7% KCl), respectively, and then stirred at 1200 r/min for 3 min by high-speed mixer. The mixed solution is poured into measuring cylinder, the volume (V) of mixed solution is read, and the foaming rate (RFV) is calculated. The time is called the foam half-life period (HLP) when the volume is reduced by half.

As shown in Figure 3 and Figure 4, the foaming rate (RFV) of OSSF is first increased and then keep constant with the increase of mass fraction of OSSF, but the foam half-life period (HLP) of OSSF is first increased and then decreased to be stable with the increase of mass fraction of OSSF. The foaming rate (RFV) is very high in distilled water, but the stability of foam is low. The foaming rate (RFV) of OSSF in distilled water is less than 20% when the mass fraction of OSSF is less than
0.5%, and the foaming rate (RFV) of OSSF in NaCl solution is less than 18% when the mass fraction of OSSF is 5%. The foam half-life period (HLP) of OSSF in distilled water is less than 100 s, and the foam half-life period (HLP) of OSSF in 5% NaCl solution is less than 120 s.

Figure 5 indicates the schematic diagram of formation and disappearance process of OSSF foam. The foaming properties is determined by polar group and non-polar group. The sulfonic group in OSSF has a strong hydration capacity, and it can form a stable aqueous layer in air bubble film. But the silicon oxide chain in OSSF is too long, the hydrophilic and lipophilic balance of OSSF is low, and the intermolecular hydrophobic association of siloxane chain will prevent water molecule from filtration, distribution and retention between the chains. It is very difficult for water molecule to be remained between the oriented siloxane chains, and thus it is not easy for bubbles to be generated.

![Figure 3](image1.png)

**Figure 3.** The relationship between the foaming rate (RFV) of OSSF and mass fraction of OSSF in distilled water and NaCl solution.

![Figure 4](image2.png)

**Figure 4.** The relationship between half-life period (HLP) of OSSF and mass fraction of OSSF in distilled water and NaCl solution.
As shown in Table 3, the foaming rate (RFV) of ABSN and OSSF in distilled water, basic mud and sulphonated polymer mud is decreased sequentially when the dosage is the same. When the dosage is 0.2% and 0.4%, the foaming rate (RFV) of OSSF in distilled water, basic mud and sulphonated polymer mud is obviously lower than ABSN. The foaming rate (RFV) of ABSN in distilled water, basic mud and sulphonated polymer mud is 720%, 600%, 28%, respectively, but the foaming rate (RFV) of OSSF in distilled water, basic mud and sulphonated polymer mud is only 20%, 10% and 4%. The half-life period (HLP) of OSSF in distilled water is much lower than ABSN. In the development of low permeability gas reservoirs, it is very important for low foaming rate to maintain the stability of liquid column pressure, the rheological properties of drilling fluid and pump efficiency.
3.5. *The evaluation of compatibility with drilling fluids*

The sulphonated polymer mud (SPM) with a density of 1.07 g/cm³ is prepared, and OSSF and ABSN are added. The rheological properties of drilling fluids before and after rolling at 150°C are tested, as shown in Table 4. Compared with sulphonated polymer mud, the rheological properties of drilling fluid formulas with OSSF and ABSN have changed little. Therefore, OSSF has little effect on the sulphonated polymer mud, and it has good compatibility with drilling fluids.

**Table 4.** The Influence of ABSN and OSSF on the rheological properties of drilling fluids.

| Drilling fluid formulas | Aging condition | AV (mPa) | PV (mPa) | YP (mPa) | YP/PV (Pa·(mPa·s)^{-1}) | G_{10}'' (mPa) | G_{10}' (mPa) | FL (mL) |
|------------------------|-----------------|----------|----------|----------|---------------------------|---------------|-------------|--------|
| SPM                    | before rolling  | 37       | 20       | 17.37    | 0.87                      | 15            | 31          | 2.4    |
|                        | after rolling   | 33       | 27       | 6.13     | 0.23                      | 2             | 3           | 4.4    |
| SPM +0.2%ABSN          | before rolling  | 37       | 20       | 17.37    | 0.87                      | 15            | 31          | 2.4    |
|                        | after rolling   | 33       | 27       | 6.13     | 0.23                      | 2             | 3           | 4.4    |
| SPM +0.4%ABSN          | before rolling  | 37       | 20       | 17.37    | 0.87                      | 14            | 31          | 2.4    |
|                        | after rolling   | 33       | 28       | 5.62     | 0.20                      | 2             | 3           | 4.5    |
| SPM +0.2%OSSF          | before rolling  | 37       | 20       | 17.37    | 0.86                      | 14            | 31          | 2.4    |
|                        | after rolling   | 33       | 28       | 5.62     | 0.20                      | 2             | 3           | 4.5    |
| SPM +0.4%OSSF          | before rolling  | 37       | 20       | 17.37    | 0.86                      | 16            | 31          | 2.4    |
|                        | after rolling   | 33       | 28       | 5.62     | 0.20                      | 2             | 3           | 4.5    |

Formulas for sulphonated polymer mud: 4% bentonite mud + 0.15% NaOH + 0.5% PAC-LV + 0.5% CMC-LVT +2%SMP-I + 2% SMC +2% SPNH +7% KCl.

4. Conclusions

1. Wilhelmy method indicates that the critical micelle concentration of OSSF is 0.418×10^{-3} mol/L, and the critical surface tension of OSSF is 20.631 mN/m. High temperature aging experiments demonstrate that the surface tension of OSSF can be improved with the increasing of aging temperature, and the surface tension of OSSF solution can be reduced gradually with the increasing of concentration of OSSF.

2. Compared with ABSN, OSSF can be adsorbed directionally at the water-rock pore interface, so the contact angle of distilled water on the surface of cores is more than 90°, and the surface energy is reduced to 20–30 mJ/m². The cores adsorbed with OSSF should reverse from water wetting to oil wetting or gas wetting.

3. The foaming rate (RFV) of OSSF in distilled water is higher than that of NaCl solution, but the stability of foam in distilled water is lower than that of NaCl solution. The foaming rate (RFV) and half-life period (HLP) of OSSF in distilled water, basic mud and sulphonated polymer mud is much less than ABSN.

4. OSSF has a relatively small impact on the sulphonated polymer mud before and after rolling at high temperature, so it has good compatibility with sulphonated polymer mud.
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