

Research on foaming agents for gas flooding in medium-temperature and high-salinity clastic reservoirs

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Abstract. Anionic surfactants are commonly used as foaming agents in foam-enhanced oil recovery, but their performance is seriously affected by high temperature and high salinity environment. However, there are not many studies on the adsorption pattern and salinity resistance performance of anionic surfactants on solid surfaces. This study evaluated the foaming performance of several anionic surfactants suitable for high-temperature, high-salinity salinity reservoirs. It was found that α -olefin sulfonate (AOS) showed good foaming performance under high temperature and high salt condition. However, the solubility of the foaming agent was low in brine with a salinity of $11 \times 10^4 \text{ mg} \cdot \text{L}^{-1}$. Therefore, a co-solvent (ABS), which is a strong hydrophilic alkyl benzene sulfonate, was chosen to be compounded with AOS in this study. In this study, a foaming agent with excellent foaming performance and solubility at a temperature of 90°C and a salinity of $11 \times 10^4 \text{ mg} \cdot \text{L}^{-1}$ was constructed. The adsorption of the foaming agent was less than 0.3 mg/g on the surface of quartz sand, and its foaming rate and foam decay half-life after three adsorptions maintained more than 85% of the original performance. The results of the study can guide the selection of foaming agents for gas injection and mobility control in medium temperature and high salinity clastic reservoirs.

Keywords: Gas injection; EOR; foaming agent; α -olefin sulfonate; high salinity reservoir

1. Introduction

A clastic reservoir in western China, where the reservoir temperature is between $70\text{-}90^\circ\text{C}$ and the reservoir water salt content is between $7\text{-}11 \times 10^4 \text{ mg} \cdot \text{L}^{-1}$, has adopted a development approach of fluid injection followed by gas injection. The key to implementing this development approach is the development of a temperature and salinity resistant foaming agent. At present, there are two main types of foamers with good temperature and salinity resistance. One type is the foaming agent based on amphoteric surfactants. These surfactants are excellent in solubility and foaming ability, but they exhibit high adsorption on the surface of sandstone [1]. The second category is anionic surfactants. AOS is a more commonly used temperature and salinity resistant foaming agent. The famous foreign foaming agent Chaser CD 1045[2] is mainly composed of AOS, but experimental evaluation showed that AOS was insoluble in water with a salinity of nearly $11 \times 10^4 \text{ mg} \cdot \text{L}^{-1}$. In this paper, the problem of AOS dissolution in high salinity water was solved by the addition of ABS. A salinity-resistant foaming agent based on AOS was constructed.

2. Experimental section

2.1 Materials and apparatus

The industrial surfactants used in this study were carboxymethyl polyoxyethylene alkyl ether (AEC-7, AEC-9, where the number indicates the number of oxyethylene links), sodium fatty alcohol polyoxyethylene ether sulfate (AES0810, where the number of oxyethylene links is about 4), α -olefin sulfonate (AOS) and strong hydrophilic alkyl benzene sulfonate (ABS). In addition, quartz sand with a particle size of 80-100 mesh was used in this paper. The instruments used in the study were a Waring mixer purchased from Qingdao Shengji Instrument Systems Co. and an SP-754 UV-Vis spectrophotometer purchased from Shanghai Spectrum Instruments Co.

The simulated formation water used in the research showed a salinity of $11 \times 10^4 \text{ mg} \cdot \text{L}^{-1}$ and was formulated according to Table 1.

Table 1 Ion compositions in simulated formation water

| Ionic composition/(mg·L ⁻¹) | | | | | Total salinity/(mg·L ⁻¹) |
|--|------------------|------------------|-------------------------------|-----------------|---------------------------------------|
| Na ⁺ | Ca ²⁺ | Mg ²⁺ | HCO ₃ ⁻ | Cl ⁻ | 111901. |
| 36649. | 5636. | 759. | 91.8 | 68764. | 5 |
| 2 | 3 | 4 | | 8 | |

2.2 Experimental methods

2.2.1 Bulk foam test of foaming agents

The experiments used simulated formation water to prepare the foaming agent solution. The experiment first preheated 100 mL of the solution to 90°C, then poured it into the steel cup of the Waring tissue masher, then used the masher to stir at 3000 r/min for 1 min, and finally quickly poured the formed dispersion system into a measuring cylinder placed in a 90°C water bath. In addition, the experiment recorded the changes in foam volume and drainage liquid volume with time in real-time. The foaming rate ψ (equal to $[V/100] \times 100$) indicates the foaming capacity of the foaming agent, and $t_{1/2}$ indicates the stability of the foam.

2.2.2 Solubility evaluation of foaming agents

A spectrophotometer was used to test the absorbance of the standard solution at 680 nm, and the standard curve was plotted based on the absorbance. The surfactant solutions were prepared using simulated formation water, and the solutions were treated at 30°C and 90°C and the absorbance of the solutions was measured. The turbidity of the solutions was found on the standard curve. The solution's preparation method and determination procedure can be referred to as GB13200-91[3].

2.2.3 Determination of the adsorption of foaming agents

The quartz sand was acid washed firstly, then washed and dried. The surfactant solution was prepared using simulated formation water. First, 18g of the prepared solution and 6g of quartz sand were drawn into an ampoule and sealed with an alcohol torch. The sealed ampoules were placed in a constant temperature oven at 90°C for heat treatment, and then the ampoules were removed periodically, and finally, the solutions were carefully removed after cooling and evaluated for content determination and foaming performance.

A two-phase titration method was used for the determination of surfactant content. The indicator used in the two-phase titration method is an imported acidic mixed indicator, and its preparation method and titration procedure can be referred to as GB5173-1995[4].

The sample content is calculated according to equation 1.

$$X = \frac{C \times V \times M_r}{m \times \frac{25}{1000} \times 10} \quad (1)$$

Where X is the content of anionic active substance of the sample (%), C is the actual concentration of cetyltrimethylammonium bromide standard solution (mol/L), V is the volume of cetyltrimethylammonium bromide standard solution consumed in titration(mL), M_r is the molar mass of the sample (g/mol), m is the mass of the sample(g).

The sample adsorption is calculated according to equation 2.

$$A = \frac{(w_1 - w_2) \times m_l}{m_s} \quad (2)$$

Where A is the sample adsorption (mg/g), w_1 w_2 is the content of the anionic active substance in the sample before and after adsorption (%), m_l is the mass of surfactant solution added to the ampoule(g), m_s is the mass of quartz sand added to the ampoule(g).

3. Results and Discussion

3.1 Screening of anionic foaming agents

The current foaming agents with good solubility in high salinity water are mainly anionic and betaine types. Betaine surfactants have good foaming performance, but they exhibit high adsorption on the surface of sandstone [5]. Therefore, in this paper, the foaming performance of anionic foaming agents was mainly evaluated. The evaluation results are shown in Fig. 1.

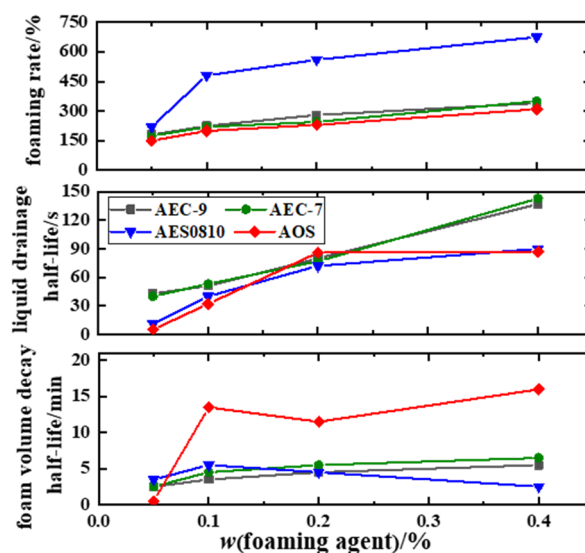


Fig. 1 Evaluation of the foaming performance of different anionic surfactants

It can be seen from Fig. 1 that the foaming rate and half-life of AEC are poor. In addition, AES0810 shows a high foaming rate but a short half-life, while AOS is poor in solubility but exhibits a high foaming rate and half-life. The carbon chain length of AES0810 is mainly 8, and that of AOS is mainly 16-18. Generally speaking, surfactants with short carbon chains are capable of rapid diffusion to the gas-liquid interface. They can easily generate foam.

However, their carbon chain interactions are very weak, so they are poorly stable in foaming. In contrast, surfactants with long carbon chains exhibit slow diffusion rates and strong foam stabilization behavior.

The poor solubility of AOS in simulated brine is due to the formation of reversed micelle between AOS and Ca^{2+} (See Fig.2).

3.2 Evaluation of AOS and co-solvent composite system

ABS can form mixed micelles with AOS agents, (See Fig.2) which effectively resists the electrostatic effect of calcium and magnesium ions on the hydrophilic groups in the micelles. Thus the surfactant solubility in simulated formation water is improved.

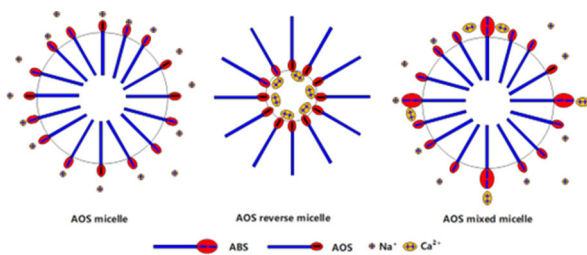
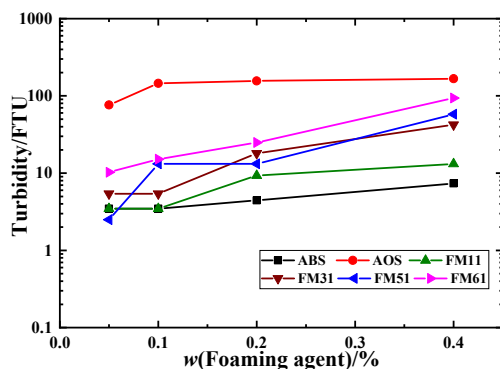
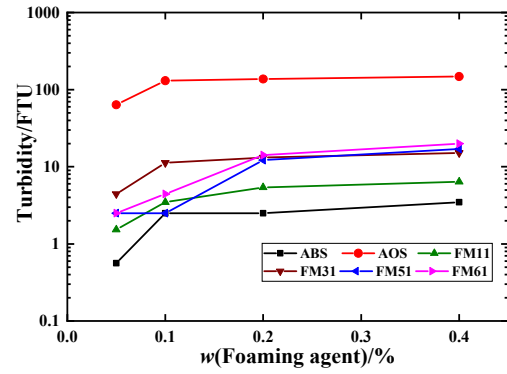


Fig. 2 Micelle and reverse micelle formed by AOS and mixed micelle formed by AOS and ABS

In this paper, AOS and ABS were mixed in a 5:1 ratio to form a system called FM51. FM11, FM31, FM51, and FM61 were composed similarly. The turbidity of the different solutions is shown in Fig. 3. From Fig. 3, it can be seen that the composite system is well soluble at 90°C when the ratio of AOS and ABS is less than 5:1. The dissolution states of AOS and FM51 at different temperatures are shown in Fig. 4.



(a) 30°C



(b) 90°C

Fig. 3 Turbidity of AOS, ABS, and composite systems



0.05%AOS 0.1%AOS 0.2%AOS 0.4%AOS 0.05%FM51
 0.1%FM51 0.2%FM51 0.4%FM51

(a) 30°C



0.05%AOS 0.1%AOS 0.2%AOS 0.4%AOS 0.05%FM51
 0.1%FM51 0.2%FM51 0.4%FM51

(b) 90°C

Fig. 4 Dissolution state of AOS and FM51 at different temperature conditions

The foaming performance of the solution was further measured in this paper, and the results are shown in Fig. 5. It can be seen that high ABS content weakens the foaming performance of the system. so FM51 was selected as the foaming agent in the subsequent study.

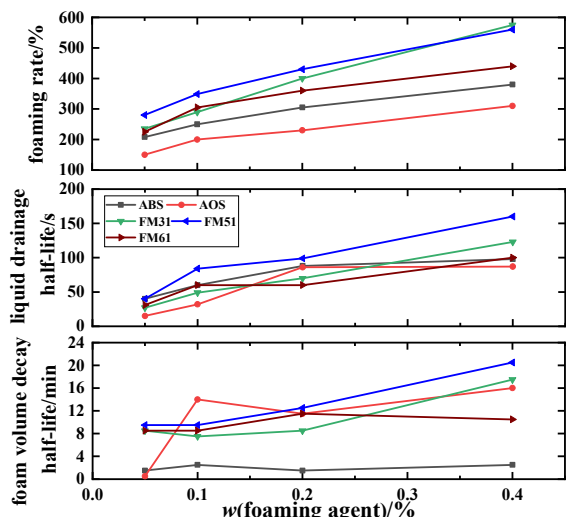


Fig. 5 Foaming performance of different composite systems

3.3 FM51 adsorption performance measurement

Surfactants with strong adsorption have higher losses in the formation process. Zhou Jimin suggested that the static adsorption of the foaming agent should be at least 1mg/g or less [6]. In this paper, the adsorption of FM51 on the surface of quartz sand was measured. The results are shown in Fig. 6.

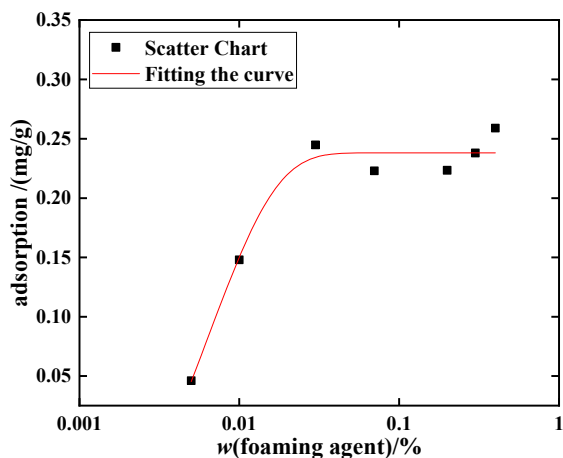


Fig. 6. Adsorption of foaming agent on the surface of quartz sand

It can be seen from Figure 6 that the static adsorption of FM51 is less than 0.3mg/g. FM51 is a complex anionic surfactant, which is negatively charged after ionization in water. It repels each other with the quartz minerals which are negatively charged overall. Therefore, the adsorption of FM51 is low.

3.4 Evaluation of the foaming performance of FM51 after adsorption

Evaluation of foaming performance after adsorption is an important part of the screening of foaming agents [7]. In this paper, the foaming performance of FM51 before and after adsorption was compared. The results are shown in Fig. 7. Although the foaming performance of FM51

decreases after three adsorptions, it can maintain more than 85% of the original performance.

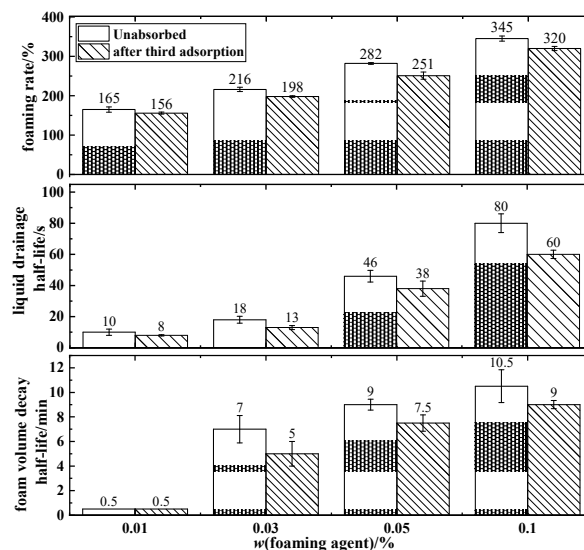


Fig. 7 Foaming performance of FM51 before and after adsorption

4. Summary

(1) At the temperature of 90°C and salinity of $11 \times 10^4 \text{ mg} \cdot \text{L}^{-1}$, the foaming performance and half-life of AEC are worse, the foaming rate of AES0810 is higher and the half-life is shorter, while the solubility of AOS is worse, but it shows higher foaming rate and longer half-life.

(2) The compounding of AOS and ABS can improve the dissolution state of AOS, but the high content of ABS will affect the foaming performance of the system, so the system FM51 is screened as the foaming agent.

(3) The adsorption of FM51 is low, the adsorption is less than 0.3 mg/g. FM51 still keeps good foaming performance after third adsorption, and basically can keep more than 85% of the original performance.

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