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The ultra-low interfacial tension behavior of the combined cationic/anionic-nonionic gemini surfactants system for chemical flooding

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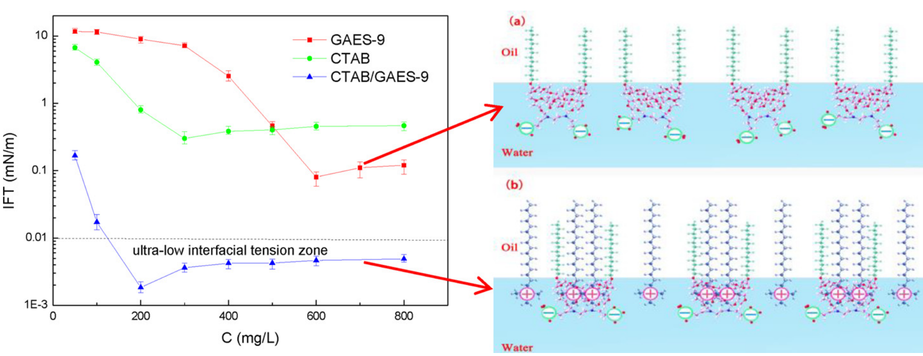
GRAPHICAL ABSTRACT

Schematic representation of the synergistic effect of CTAB/GAES-9 for obtaining ultra-low IFT.



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ABSTRACT

Gemini surfactants have attracted intensive attention owning to their unique physical and chemical properties and have gradually been applied in the field of enhanced oil recovery (EOR). In this work, a combined cationic/anionic-nonionic gemini surfactant system consisting of cetyltrimethyl ammonium bromide (CTAB) and anionic-nonionic gemini surfactants (GAES-9) was proposed for EOR. The surface performance of the combined system was superior to that of either surfactant alone. Critical micelle concentration (CMC) data were used to calculate the molecular interaction parameters according to the regular solution theory. The combined CTAB/GAES-9 surfactant system could greatly affect the interfacial tension (IFT) between water and crude oil, and the strength of this effect depended on the mole fraction and concentration of CTAB/GAES-9. The system could reduce the IFT to an ultra-low level at a total concentration of 200 mg/L, and the system could still maintain ultra-low IFT at a salinity of 10×10^4 mg/L. The mechanism underlying the synergistic effect of CTAB/GAES-9 to obtain ultra-low IFT was systematically investigated. It is most probably related to a large number of anions and cations being adsorbed onto the oil-water interface due to electrostatic attraction. Meanwhile, the spatial structure of the elongated, flexible EO chains in the gemini surfactant entangled at the oil-water interface shields some CTAB cations, enabling the adsorption of more cations. To summarize, the combined surfactants exhibit remarkable abilities and could serve as a candidate for EOR in harsh reservoirs.

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1. Introduction

Surfactant flooding has been a widely used technique in chemical enhanced oil recovery (EOR) for several decades and can greatly enhance the recovery of trapped oil by reducing the water/oil interfacial tension (IFT) to ultra-low values (10^{-3} mN/m) [1]. Increasing attention has been paid to improving and modifying the surfactant structures according to the characteristics of various reservoirs of water (oil or water viscosity, temperature, salinity, and permeability) [2–9]. Traditional single surfactant systems fail to satisfy the operating requirements of unconventional reservoirs under extremely complex conditions. Thus, it is essential to investigate combined surfactant systems with strong synergic effects.

Anionic and cationic surfactant complex systems have shown excellent performance in many fields [10–12]. Due to the strong electrostatic attraction between the hydrophilic groups of anionic and cationic surfactants, surfactant molecules can be closely arranged on an oil-water interface, which is beneficial to obtain ultra-low interfacial tension [13]. At the same time, due to the charge neutralization of anions and cations, the system as a whole is electrically neutral, exhibits good resistance to calcium and magnesium ions and can be used in a high salinity oilfield [14]. However, combined systems have the disadvantage of poor solubility. The high performance and low solubility have become an irreconcilable contradiction. Secondly, the proportions of the combined systems are relatively strict. Finally, due to the complexity of practical oil field applications, as well as the interaction between the different active groups involved, anionic and cationic surfactants are difficulty to implement in practical applications [15].

To solve these problems, a combined cationic/anionic-nonionic gemini surfactant system is proposed to reduce the IFT to ultra-low values at low concentrations, which has seldom been reported. As shown in Fig. 1, gemini surfactants possess a double chains that links two ionic head groups with the same electrical properties, weakening the electrostatic repulsion between the ionic head groups [16–18]. This arrangement effectively enhances the tightly packing of molecules at the adsorbed layer of the solution and enhances the hydrophobic binding force between the hydrocarbon chains; therefore, gemini surfactants exhibit higher surface activity than common surfactants [13]. The interaction between the surfactants is mainly caused by the electrostatic attraction between the ionic head groups such that the synergism between gemini surfactants and conventional ones is much stronger than that among conventional surfactants.

In this study, the surface performance of a combined system was determined. Critical micelle concentration (CMC) data were used to calculate the molecular interaction parameters according to regular solution theory. The effects of the molar ratio, salinity and temperature on the IFT of water/crude oil were systematically investigated. Finally, the mechanism underlying the synergistic effect of CTAB/GAES-9 for obtaining ultra-low IFT was discussed.

2. Experimental

2.1. Materials

The oil was obtained from a low-permeability reservoir in the Dagang Oilfield, China. The viscosity, density, and components analysis of the oil were analyzed and were shown in Table 1. The oil displayed a viscosity of 61.40 m Pa·s and a density of 0.90 g/cm^3 at 20 °C. The GAES-9 was prepared with ethylenediamine, fatty alcohol polyoxyethylene ether and 2-bromoethanesulfonic acid sodium salt in our laboratory and its chemical structure was shown in Fig. 2. Cetyltrimethyl ammonium bromide (CTAB) was purchased from Beijing Chemical Company. In addition, the simulated formation water containing 6726 mg/L salinity was shown in Table 2.

Table 1
Viscosity, density and components of the Dagang crude oil sample.

Parameter	Density (g/cm^3)	Viscosity (mPa·s)	Wax (%)	Resin and asphaltene (%)
Value	0.90	61.40	9.52	13.01

2.2. Measurement of surface tension

Surface tension measurements were conducted on a surface tensiometer (BYZ-1, Shanghai Hengping Instrument Company) using the Wilhelmy method. The samples were equilibrated in the measuring vessel for 15 min to reduce the error caused by the adsorption kinetics. All measurements were repeated at least thrice until the values were reproducible.

2.3. Measurement of interfacial tension

Determination of the interfacial tensions between surfactants aqueous solution and crude oil were measured at 45°C using the spinning drop interfacial tensiometer of TX-500. The solution was injected into the glass tube. Then, a droplet crude oil was injected into the centre of the water phase. Finally, the IFT was measured at a fixed rotating velocity (5000 rpm) at the given temperature.

3. Results and discussion

3.1. The surface activity of combined CTAB/GAES-9 surfactant aqueous solutions

The complexation of cationic and anionic surfactants during surfactant complexation has long been regarded as prohibited. It is generally believed that the interaction between the two in aqueous solution will lead to precipitation, causing the surfactant to lose its surface activity. However, in our study, we found that when the alkyl quaternary ammonium salt CTAB is mixed with GAES-9 containing polyoxyethylene chains, a stable solution is formed. The agents exhibit excellent surface properties due to the strong attraction between their hydrophilic groups. Therefore, surface tension measurements were performed to detect the aggregation behaviors of the combined CTAB/GAES-9 (molar ratio 4:1) surfactants in aqueous solutions at 30 °C (Fig. 3). Initially, the surface tensions gradually decreased with an increase in the concentration of the combined CTAB/GAES-9 surfactants, indicating the prior adsorption of surfactants at the gas/liquid interface [19,20]. At higher concentrations, the surface tension remained nearly constant. The transition between the two behaviors was attributed to the formation of aggregates in the aqueous solutions. The CMC for the combined CTAB/GAES-9 surfactant was 205.48 mg/L, lower than that of the individual GAES-9 (546.45 mg/L) or CTAB (399.74 mg/L) surfactant system (Fig. 3). The surface tension at the CMC was 29.82 mN/m, which was also lower than that for the individual systems. When the concentration was further increased, the surface tension no longer decreased, but instead slowly increased. These micelles in the bulk phase

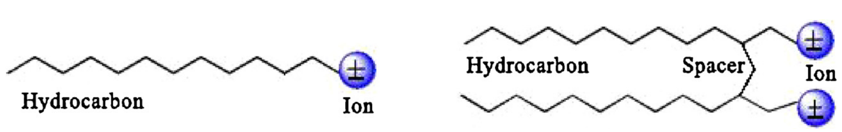

Fig. 1. Schematic representation of conventional and gemini surfactants.