



Dynamic interfacial tension behaviors between Guerbet betaine surfactants solution and Daqing crude oil

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HIGHLIGHTS

- ▶ The effect of ethylene oxide groups was studied.
- ▶ Both of GC16 (3) and GC20 (5) could reduce DIFT to low value.
- ▶ When the mass ratio of GC16 (3)/GC20 (5) was 9:1, the DIFT could reach ultralow value.
- ▶ The GC16 (3)/GC20 (5) compound system showed a certain temperature resistance.

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ABSTRACT

In the surfactant flooding systems for enhanced oil recovery, interfacial tension between surfactant solution and crude oil should be decreased to ultralow value ($<10^{-2}$ mN m⁻¹). Accordingly, in this paper, the dynamic interfacial tension behaviors between Guerbet betaine surfactants solution and Daqing crude oil were studied. The influence factors such as ethylene oxide groups, surfactant concentration, and the mass ratio of compound systems, sodium carbonate concentration and temperature were investigated. It was found that the prepared surfactants used alone cannot reduce the dynamic interfacial tension to ultralow value. In order to meet the demand, the compound systems were taken into account. The results showed that the effect of GC16 (3)/GC20 (5) compound system was better than GC16 (3)/GC18 (5) and GC20 (5)/GC18 (5). When the mass ratio of GC16 (3)/GC20 (5) was 9:1, the dynamic interfacial tension can reach ultralow value. Then the effect of sodium carbonate concentration and temperature were studied for this better compound system (GC16 (3)/GC20 (5) = 9:1), the results showed that this compound system existed an optimum sodium carbonate concentration and exhibited good temperature resistance.

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1. Introduction

With the development of oil fields, more and more tertiary recovery technologies have been put into field tests. Among the technologies used to enhance oil production, surfactant flooding is one of the most appealing methods. It is generally accepted that the strong alkali, which is added into surfactant flooding, plays an important role in reducing interfacial tension, but practice has proved that many problems need to be faced, such as the formation of stable oil-in-water emulsion destroy of the stratum and the corrosion of the oil equipments [1–3]. Accordingly, it is more and more important in the surfactant flooding with weak alkali or alkali-free system for EOR.

Nonionic surfactants, which have high stability and ethylene oxide groups can be adjusted according to the different needs, have

been used in EOR. However, nonionic surfactants have low cloud point which restricts their application scope. Amphoteric betaine surfactants have the advantages of temperature resistance, salt tolerance and biodegradation. With the continuous decrease of oil resources, it is widely accepted by researchers for oil extraction field [4–8]. Introducing ethylene oxide groups into amphoteric betaine surfactants cannot only improve high stability but also obtain the optimum interfacial performance by adjusting the length of hydrophobic chain and the number of ethylene oxide groups.

According to capillary number theory [9,10], the interfacial tension between the displacement fluid and crude oil arrives at an ultralow level, the efficiency of oil recovery will be remarkably enhanced [11–14]. So, many investigators diligently search for systems with ultralow interfacial tension. For surfactant oil-displacement system, dynamic interfacial tension (DIFT) is an important index to evaluate the displacement efficiency of surfactant.

In this paper, the DIFT between Guerbet betaine surfactants with ethylene oxide groups and crude oil of Daqing oil field were

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studied. The effects of various parameters on DIFT, including ethylene oxide groups, surfactant concentration, and mass ratio of compound system, sodium carbonate concentration and temperature were investigated in detail.

2. Experimental

2.1. Materials

Guerbet betaine surfactants with ethylene oxide groups which were synthesized by Guerbet alkyl polyoxyethylene ether surfactants, epichlorohydrin, dimethylamine and sodium chloroacetate in our laboratory [15] were used. They have the following general molecular structure (Fig. 1), namely GC16 (3), GC16 (5), GC16 (7), GC18 (5), GC18 (9), GC20 (5), GC20 (9), respectively. Take GC16 (3) as an example, when m is 6, n is 3 and the total carbon number of Guerbet alkyl polyoxyethylene ether is 16, the Guerbet betaine surfactants is named as GC16 (3). Others can be defined in a similar way. The active matter content of GC16 (3), GC16 (5), GC16 (7), GC18 (5), GC18 (9), GC20 (5), GC20 (9) is 40.99%, 55.94%, 70.36%, 55.21%, 65.65%, 57.52%, 74.33%, respectively. Analytical purity of Na_2CO_3 , NaHCO_3 , CaCl_2 , and KCl were used. The crude oil sample was provided by Daqing oilfield of China, the characteristics of it are shown in Table 1. The inorganic salts were added to the water for preparing the solution to match the Daqing oil field subterranean water. No. 2 factory mineralized water composition: concentrations of Na_2CO_3 , NaHCO_3 , CaCl_2 , and KCl are 233 mg L^{-1} , 2150 mg L^{-1} , 111 mg L^{-1} and 1013 mg L^{-1} , respectively.

2.2. Interfacial tension measurement

The interfacial tensions (IFTs) between the surfactants and crude oil were measured with TX-500C full range tensiometer (Bowling Industry Corporation, USA). The different concentrations of Guerbet betaine surfactants solution were prepared. Before measurement, the surfactant solutions were put in a constant-temperature bath which the temperature is measuring temperature. The centrifuge tube was washed by petroleum ether (1–3 mL), acetone (1–3 mL) deionized water, and the measured solution, respectively. Then the surfactant solution as outer phase was injected into the centrifuge tube by 1 mL syringe, and 1–2 μL crude oil as inner phase was put into the middle of the tube. In all measurements, the rotation speed was sufficiently high (5000 rpm) that the length of the oil drop was larger than four times its diameter. The interfacial tension was obtained from the below equation:

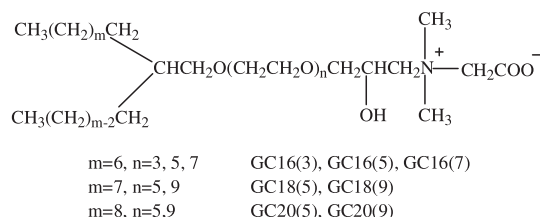


Fig. 1. General molecular structure of Guerbet betaine surfactants (n is an average number of ethylene oxide groups).

$$\gamma = 3.425 \times 10^{-7}(\rho_h - \rho_d)\omega^2 D^3, L/D \geq 4 \quad (1)$$

where γ is the oil–water interfacial tension in mN m^{-1} , ω is angle speed in rad s^{-1} , ρ_h is the density of heavy (outer) phase in g cm^{-3} , ρ_d is the density of light (drop) phase in g cm^{-3} , ω is the rotational velocity in rpm, D is the measured drop width (diameter) in mm and L is the length of the oil drop in mm.

3. Results and discussion

3.1. Effect of ethylene oxide groups on DIFT_{min}

DIFT_{min} is one of major parameters for evaluating the properties of surfactants. Fig. 2 shows the effect of ethylene oxide groups on DIFT_{min} at different betaine surfactants and various surfactant concentrations. As can be seen from that, with the ethylene oxide groups increasing, the DIFT_{min} increase. For surfactants with ethylene oxide groups, the capacity of reducing interfacial tension is related to ethylene oxide groups. The longer the ethylene oxide groups are, the weaker the ability for reducing interfacial tension is. It is due to certain hydrophilicity from the oxygen atom of ethylene oxide groups and water forming intermolecular hydrogen bonds, and certain lipophilicity from ethylene group of ethylene oxide groups. With the ethylene oxide groups increasing, hydrophilicity improves, while the lipophilicity decreases relatively, which causing the decreases of surfactant molecular arrangement in the oil–water interface and a significant rise in the DIFT_{min} .

3.2. Effect of surfactant concentrations on the DIFT

The effect of surfactant concentration on the DIFT was investigated for two surfactants, namely GC16 (3), GC20 (5). Fig. 3 shows the IFT curve between crude oil and GC16 (3) solution at different surfactant concentrations (from 0.005 wt.% to 0.3 wt.%). As is shown that, DIFTs gradually decrease with time first, then increase, finally stabilize. That is due to the surfactant molecules' dynamic equilibrium between adsorption and desorption, and the adsorption and desorption occur at same the time. At the beginning, surfactant molecules diffuse to the interface from bulk solution and then adsorb on the interface, the rate of adsorption of molecules onto the interface is higher than that of desorption of molecules from the interface, so DIFT decreases. As time goes on, the rate of adsorption becomes lower than that of desorption, and DIFT increases. When adsorption and desorption reach a balance finally, the DIFT stabilized accordingly. Furthermore, as the concentration of GC16 (3) increases, the time for the DIFT to reach $10^{-2} \text{ mN m}^{-1}$ becomes short (from 0.005 wt.% to 0.05 wt.%), then long (from 0.1 wt.% to 0.3 wt.%). The reason is as follows: with the surfactant concentration increasing, the adsorption of surfactant molecule at the interface increases; but with the further increase of the surfactant concentration, surfactant molecules forms micelles, resulting in decrease of single surfactant molecule of bulk solution, which is not favorable for the surfactant adsorption onto the interface. Fig. 4 shows the effect of GC20 (5) surfactant concentration on the DIFT at 45°C in the range of 0.01–0.3 wt.%. As shown in the figure, the DIFT can reach $10^{-2} \text{ mN m}^{-1}$ in the range of 0.025–0.2 wt.%.

Table 1
Characteristics of the Daqing No. 2 crude oil sample.

Water content (%)	Saltness (mgNaCl/L)	Density (kg/m ³ 20 °C)	Kinematic viscosity (mm ² /s)		Acid value (mgKOH/g)	Wax (%)	Colloid (%)	Asphalt (%)	Carbon residue (%)
			40 °C	50 °C					
0.15	10	852.6	28.14	21.16	0.005	29.8	7.24	0.54	2.9

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