Study on surface tension and wetting behavior of a novel fluorocarbon surfactant

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Summary

Surfactants have been widely used in the developing process of conventional reservoirs and have achieved many good application results[1-3]. The fluorocarbon surfactants, with its special characteristics, could be applied to unconventional reservoirs[4,5]. In this paper, the surface tension and contact angle of a group of new fluorine-containing low molecular surfactants (CF01, CF03, CF08, CF09) for unconventional rerservoirs were studied, and the CF03 was selected based on the experimental result for the low molecular surfactant containing it has the best surface activity. The CF03 was further studied for better understanding of its composite behavior with the hydrocarbon surfactant (PS). The results show that CF03 can not only greatly reduce the surface tension, but also can change the wettability from water-wetting to neutral-wetting, and its compound system with PS have both these two characteristics. The most important is that a low concentration of fluorocarbon surfactant is sufficient to achieve an obvious change in wettability, greatly reducing the cost of fluorocarbon surfactant, so that it has a broad application prospect in the unconventional reservoirs.

Introduction

In order to enhance oil recovery of unconventional reservoirs, the requirements for surfactants, which is one of the most commonly used chemical flooding methods, are further increased compared with conventional reservoirs[9]. Studies have indicated that the unique advantages of fluorocarbon surfactants (high surface activity, high thermal stability, high chemical stability, oleophobicity and hydrophobicity) show significant potential for unconventional reservoirs[6]. The general oil displacement mechanism of fluorocarbon surfactants is to reduce the oil-water interfacial tension and increase the oil displacement efficiency to improve oil recovery. Besides, as the research progresses, it is found that some fluorocarbon surfactants can effectively change wettability, such as from water-wetting to oil-wetting, neutral wetting or even gas-wetting, which will further enhance the recovery rate[7,8]. In unconventional reservoirs, the capillary pressure is large due to small pore throat radius and low relative permeability, and this high capillary pressure set barrier for water injection and oil production. Fluorocarbon surfactants can reduce capillary forces in two ways, making these problems possible to be solved. Recent studies also have shown that fluorocarbon surfactants can change the wettability of shale reservoirs to gas-wetting and achieve wetting reversal to increase the rate of slick water fracturing fluids [9]. Fluorocarbon surfactants can be used both in oil and gas reservoirs. Therefore, it is of great significance to study the practical application of fluorocarbon surfactants in unconventional reservoirs. In this paper, the surface tension and wettability of the four new fluorocarbon surfactants (CF01, CF03, CF08, CF09) were compared, based on which CF03 are selected for its best surface activity, besides that, hydrocarbon surfactant (PS) has been added to highlight its performance in oil recovery of unconventional reservoir.

Theory

Fluorocarbon surfactants have great potential to enhance recovery of unconventional reservoirs. According to the studies[10-11], the mechanism of fluorocarbon surfactants displacement in unconventional reservoirs can be summarized into two aspects: reducing interfacial tension and changing wettability. Reducing the surface tension means that the molecules of the active agent are directionally arranged at the interface, causing a decrease in the difference in the force between different molecules on both sides of the interface. Fluorocarbon surfactants can greatly reduce the surface tension because F has a strong electronegativity. The C-F bond can be large, and it is difficult to be polarized. The radius of F is larger than H, so the C-F bond force is smaller than the C-H bond. Therefore, the energy required for the molecule of surfactant to move from the inside to the surface of the solution is smaller, leading to the effect of reducing the surface tension is stronger.

The capillary pressure can be expressed as follow [1]:

$$P_c = \frac{2\sigma \cos\theta}{r} \tag{1}$$

where σ is two-phase interfacial tension, mN/m; r is capillary radius, m; θ is contact angle, degree.

Reducing the interfacial tension or increasing the contact angle contributes to enhance recovery. In unconventional reservoirs, the capillary pressure increases when fluids passing through the narrow pore throat, and the Jiamin effect occurs. However, thanks to the influence of the fluorocarbon surfactants, the flow resistance would be much smaller, so the fluids can pass through the pores and throats much more easily.

On the other hand, very different from the hydrocarbon surfactants, which can reduce the contact angle to some extent while they decrease the surface tension, the contact angle increases in the utilization of fluorocarbon surfactants: the fluorocarbon surfactants are characterized by hydrophobicity and oleophobicity， and the contact angle increases with increasing concentration. The strong cohesive energy of the C-F chain leads a lower energy on surface, so the contact angle is significantly higher than that of the hydrocarbon surfactant. This property is important for changing the wettability. In addition, its performance in salt and temperature resistance is good too.

Based on the above principles, in order to evaluate the properties of the four fluorocarbon surfactants(CF01, CF03, CF08, CF09), the surface tension and contact angle of these in pure water and brine were tested first, and the optimum fluorocarbon surfactants was then selected. The surface tension and contact angle of the compound system were then tested by compounding the optimum fluorocarbon surfactants with hydrocarbon surfactant (PS), and obtained an optimum concentration of the fluorocarbon surfactants. Finally, the properties of the best composite system in brine were also evaluated.

Example

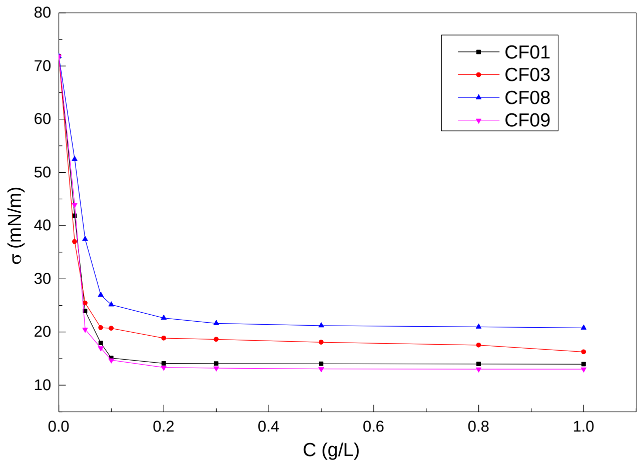
The experimental results were analyzed. The results from Figure 1(a),(b), show that the surface tension decreases significantly with the increase of the concentration of fluorocarbon surfactant, and the inflection point represents for the critical micelle concentration, which remains basically unchanged after the critical micelle concentration. The results in the comparison of pure water and brine show that CF03 can maintain good activity in saline. From Figure 1(c),(d), it can be concluded that the contact angle of the solution on the surface of the silica increases with the increase of the concentration of the fluorocarbon surfactant, and this increase tends to decrease when the concentration exceeds the critical micelle concentration. Based on the experimental results, the increase of CF03 contact angle is the largest of the four, the combined surface tension and contact angle are considered to be optimal. Then we studied the optimal concentration of CF03 in the composite system. From the results of Figure 1(e),(f), it can be concluded that the composite system is also reduced in surface tension with increasing CF03, and the critical micelle concentration is lower than that of the one-component fluorocarbon surfactant. The contact angle of the compound system also showed an increasing trend, indicating that a very low concentration of fluorocarbon surfactant can increase the contact angle and save costs to a certain extent. Thus, for the CF03, adding PS can improve its performance in oil recovery.

Conclusions

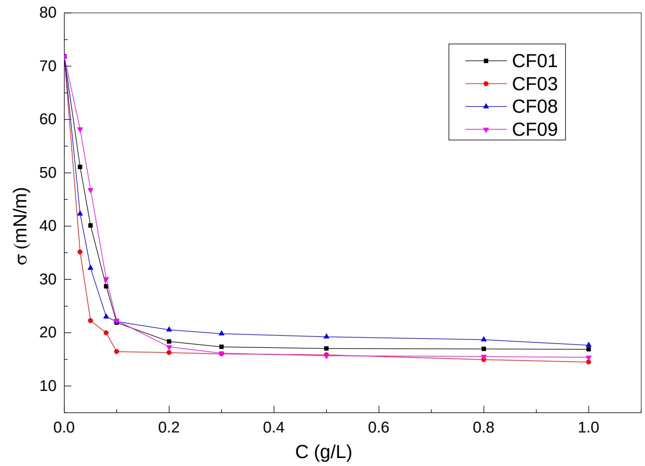
The experimental determination of the surface tension and contact angle of the fluorocarbon surfactant solution suggests that CF03 is the best of the four fluorocarbon surfactants. It can be seen that all the four fluorocarbons can significantly reduce the surface tension, even less than 20 mN/m, which is superior to ordinary hydrocarbon surfactants. These four fluorocarbon surfactants can indeed increase the contact angle as the concentration increases. Among them, CF03 not only maintains a very low surface tension in pure water and brine, but also has a contact angle of 70 degree, even higher than the other three. Neutral-wetting can also be obtained during reservoir development, so CF03 is selected as the primary solution for further study of compound system.

The CF03 was combined with PS to study the optimal concentration of CF03. It can be seen that the compound system can also reduce the surface tension to a great extent and maintain a higher contact angle (greater than 65 degree) as the concentration increases. This is because that when PS works solely, it can reduce the surface tension but also reduce the contact angle. When combined with CFO3, the compound system can increase the contact angle due to the synergistic effect of the two, which only requires a small amount of CF03.

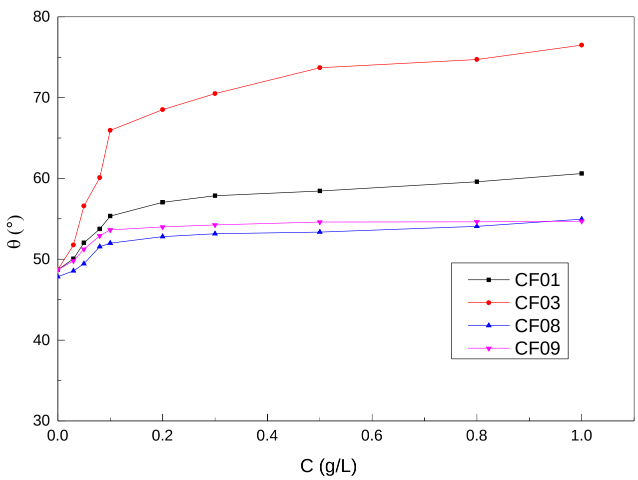
Therefore, we conclude that CF03 is a fluorocarbon surfactant with great potential for unconventional reservoir development because it not only has high surface activity, chemical stability and high thermal stability of general fluorocarbon surfactants, but also the ability to reverse wettability. It could be a new potential option for enhancing oil recovery in unconventional reservoirs.



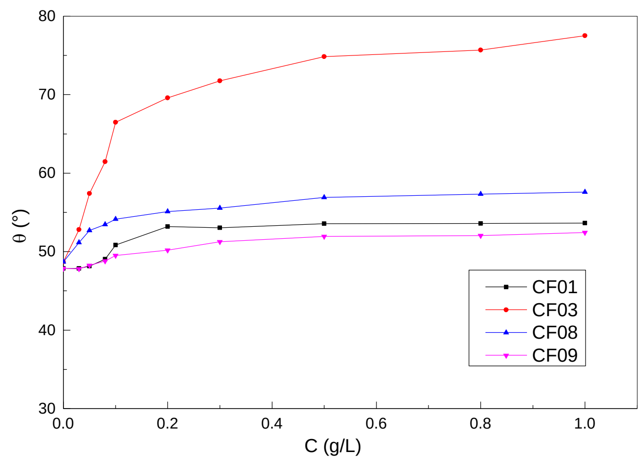
(a) surface tension in pure water



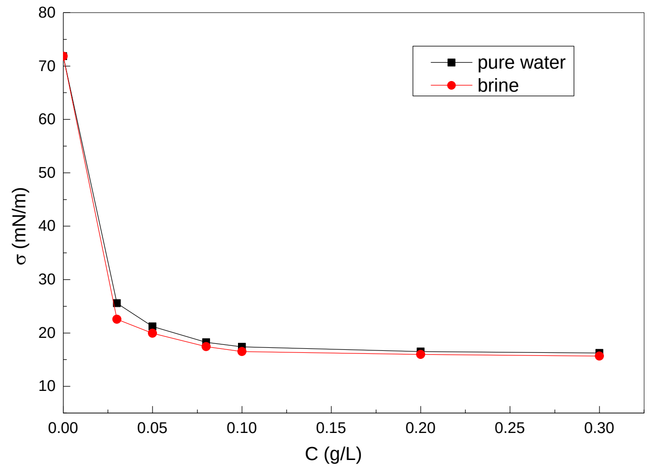
(b) surface tension in brine



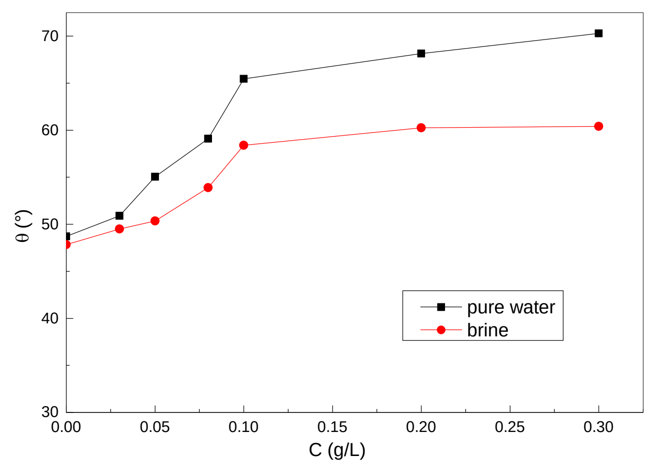
(c) contact angle in pure water



(d) contact angle in brine



(e) surface tension of compound system (CF03&PS)



(f) contact angle of compound system (CF03&PS)

Figure 1. The results of surface tension and wetting contact angle

Novel Information

In this work, a new fluorocarbon surfactant (CF03) for enhanced oil recovery has been selected based on experimental results, which not only has good surface activity, but can also change wettability.

In addition, the compound system of hydrocarbon surfactant and the selected fluorocarbon surfactant was further studied, whose best compound ratio was also determined. Please note that this work is just an exploration of the basic performance of CF03, subsequent related experiments are in progress for better utilization of surfactants in unconventional reservoirs to enhance oil recovery.

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