

The Effect of Betaine Surfactant on Carbonate Reservoir Wettability in Self-Diverting Acidizing Stimulation

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Abstract

Contact angle alterations of carbonate cores after immersing in spent acid with oleyl amido propyl betaine surfactant were measured to clarify the effect of viscoelastic surfactant on the wettability of carbonate reservoir during self-diverting acidizing. The results showed that spent acid solutions with hydrochloric acid and betaine surfactant induced core wettability to water-wetting for initially oil-wet rocks, and oil-wetting for initially water-wet rocks. Longer immersion time and higher concentration of surfactant enhanced the effects. The adverse wettability reversal for water-wet reservoir was eliminated by mutual solvent or brine postflush. Chemical mechanisms of the wettability alteration were interpreted.

Key words: Carbonate reservoir; Self-diverting acid; Wettability; Contact angle; Postflush

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INTRODUCTION

Self-diverting acid based on viscoelastic surfactant (VES) is a burgeoning system for heterogeneous carbonate reservoir stimulation with large permeability contrasts. Previous study highlighted the diversion agents and in-situ plugging mechanisms of self-diverting acid^[1-2]. However, the effect of wettability alternation induced by self-diverting acid was recognized in the industry for a long time. Generally, neutral-wetting is the preferred wettability for maximum recovery of the spent acid^[3-4]. Additionally, water-wetting and neutral-wetting are required for oil production stimulation after the displacement of spent acid^[5-6]. Wettability and relative permeability highly depend on the reservoir residual fluids. Therefore, numerous retained surfactants on pore surface may alter formation wettability and have uncertain effects on spent acid recovery and the production of hydrocarbons, depending on which direction the change in wettability occurs. In order to clarify the effect of VES on the wettability of carbonate reservoir, contact angle changes after immersing in spent acid were measured by means of a novel drop shape method proposed by Adejare, et al.^[7].

1. MATERIALS AND METHODS

1.1 Materials

Carbonate cores and crude oil were provided by Northwest Oilfield Company of Sinopec, China (Table 1). Petroleum ether, ethanol, decane and several inorganic salts were purchased from Sinopharm Corporation, China. The amphoteric surfactant, oleyl amide propyl betaine (OAPB), was synthesized and purified in our laboratory. Brine was prepared according to Table 2 to simulate the components of formation water.

Table 1
Mineral Compositions of Carbonate Core From Sinopec Northwest Oilfield (wt%)

Quartz	K-feldspar	Plagioclase	Calcite	Dolomite	Siderite	Pyrite	Clay mineral
5	-	-	90	2	-	1	2

Table 2
Ion Compositions of Simulated Formation Water

Ion contents / (mg/L)						Total salinity / (mg/L)	pH value	Water type
Cl ⁻	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺			
137,529.5	183.6	11,272.5	1,518.8	28,732.9	44,565.5	223,802.8	6.8	CaCl ₂

1.2 Carbonate Cores Preparation

Soxhlet extraction method was used to remove the oil, dirt and salts off the natural carbonate cores and the wettability became strongly water-wet after drying^[8]. On this basis, the cores were saturated with oil and aged at 90 °C for 72 hours^[9-10]. The aged cores were oil-wet at room temperature. Finally, both the water-wet and oil-wet cores were cut and polished mechanically to dimensions of 10 mm × 10 mm × 20 mm.

1.3 Spent Acid Preparation

The spent acid was prepared by dissolving 24 wt% calcium chloride (CaCl₂) in deionized water. Then pH was adjusted to 4.4 to match the actual pH value. A certain amount of OAPB was added as required^[11].

1.4 Contact Angle Measurement

Spent acid was used to treat carbonate core samples for some time. Contact angles were measured at 80 °C by sessile drop method with an optical contact angle measuring device, Drop Shape Analyzer 100 (KRUSS, Germany). The oil droplets used in this paper were decane (C₁₀H₂₂) for a good reproducibility of test results.

1.5 Isoelectric Point Measurement

0.5 g OAPB was mixed with 25 mL HCl (0.1 mol/L)

in a 100 mL beaker and stirred for 10 minutes with a magnetic stirrer. The potential changes of the solution with the titration of 0.1 mol/L NaOH standard solution were measured by an automatic potentiometric titrator, 848 Titrino plus (Metrohm, Switzerland). First order differential method was used to process data. The maximum point was the isoelectric point.

2. RESULTS AND DISCUSSION

2.1 Effect of Self-Diverting Acid on Oil-Wet Carbonate Rock Wettability

Reportedly, as many as 80% of world's carbonate reservoirs were oil-wet or mixed-wet^[12]. Therefore our primary object is oil-wet carbonate rock. The contact angle of the aged oil-wet rock surface was 142.5° and after being treated by spent acid without surfactant for 2 h, the contact angle became 138.2° (Figure 1(a), (b)). That meant spent acid by itself did not alter rock wettability. The contact angle changed to 101.5° as the core was immersed in spent acid with 1 wt% OAPB for 2 h (Figure 1 (c)). It indicated that OAPB altered the wettability of carbonate rock from original oil-wetting to neutral wetting^[13].

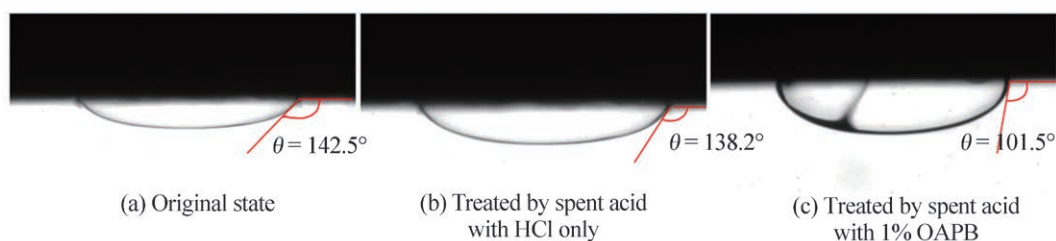


Figure 1
Contact Angle Alterations of Initially Oil-Wet Rocks After Being Treated by Different Spent Acid

Figure 2 showed that with the increase of the immersion time and the OAPB concentration, the contact angles of core samples decreased gradually and induced a more strongly water-wet surface. Given that the values of altered contact angle were almost in the range of 75° to

105°, betaine surfactant offered some advantages in terms of acid clean-up and enhanced oil production by changing the initially oil-wet carbonate rock to intermediate-wetting or weak water-wetting.

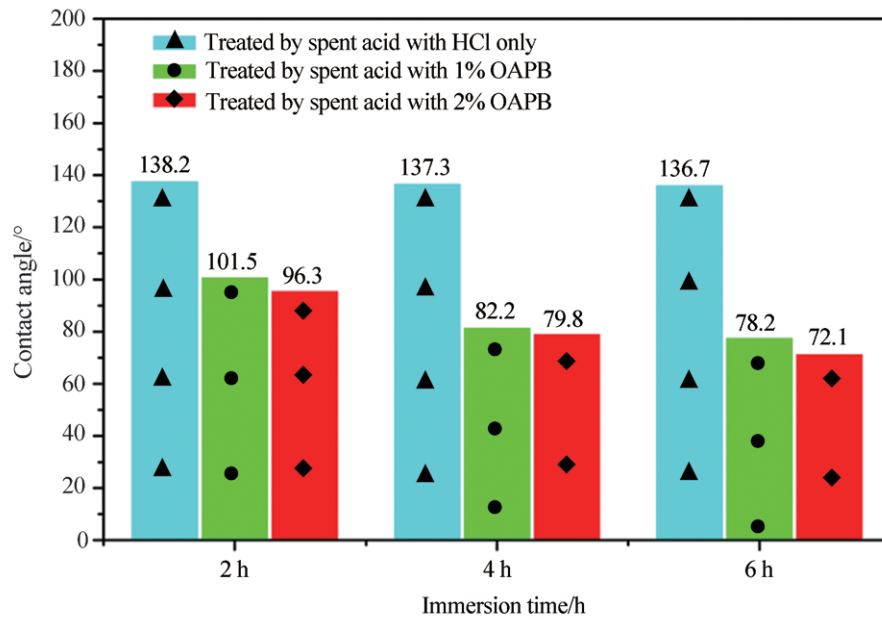


Figure 2
Influence of Immersion Time and Betaine Surfactant Concentration on Oil-Wet Carbonate Rocks Wettability

2.2 Effect of Self-Diverting Acid on Water-Wet Carbonate Rock Wettability

Wettability alteration in oil-wet carbonate reservoir caused by betaine surfactant proves to be positive for acid recovery and production stimulation. For water-wet carbonate reservoir, the situation was more complicated.

The contact angle of a water-wet sample changed from 58.2° to 57.5° after being treated by spent acid with HCl only (Figure 3(a), (b)), and no change occurred in

wettability. The contact angle increased to 120.5° rapidly after 2 h immersion in spent acid with 1% OAPB (Figure 3(c)). Longer immersion time and higher concentration of OAPB increased the contact angles and induced more strongly oil-wet surfaces (Figure 4). Therefore, using betaine surfactant as a diverting agent to treat initially water-wet carbonate leads to an adverse wettability reversal to oil-wetting.

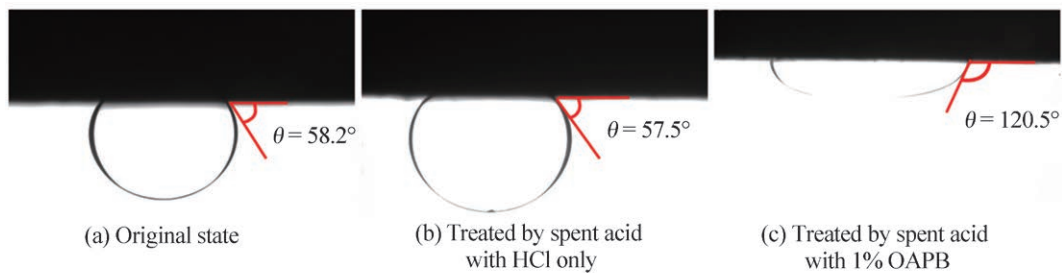


Figure 3
Contact Angle Alterations of Initially Water-Wet Rocks After Being Treated by Different Spent Acid

The mutual solvent, ethylene glycol monobutyl ether (EGMBE), was often utilized to reduce the surface activity of VES^[14]. In this study, 10% EGMBE was used as a postflush to treat carbonate core samples. After being immersed in spent acid with 2% OAPB for 6 h, the core sample was placed into 10% EGMBE for another 0.5 h immersion. Figure 5 showed that contact angle increased to 148.4° after 6 h immersion in spent

acid with 2% OAPB and decreased to 65.9° by 10% EGMBE treatment. Therefore, the EGMBE postflush can recover formation wettability into weak water-wetting and eliminate the secondary damage caused by VES. Further research showed that brine with high concentration of CaCl₂ was a practical alternative to mutual solvent to inverse rock wettability to water-wetting (Figure 5 (c)).

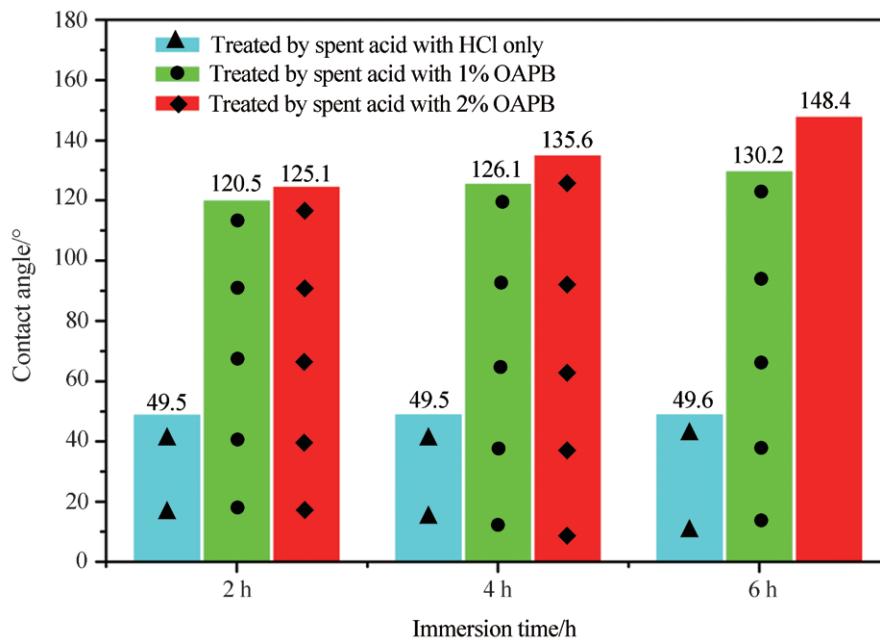


Figure 4
Influence of Immersion Time and Betaine Surfactant Concentration on Water-Wet Carbonate Rocks Wettability

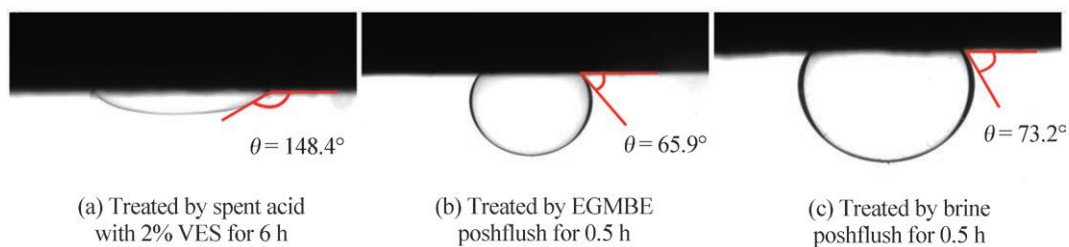


Figure 5
Contact Angle Alterations of Water-Wet Rocks After Being Treated by Mutual Solvent and Brine for 0.5 h

2.3 Chemical Mechanism of the Wettability Alteration Process

2.3.1 Wettability Alteration by Spent Acid With HCl Only

Spent acid with HCl only slightly lowered the contact angle of oil-wet carbonate cores without inducing wettability alteration. This is because polar portions containing carboxylic groups in crude oil are adsorbed strongly onto the surface and nonpolar portions are directed away from the interface and thereby render the surface oil-wet^[15-16]. Numerous Ca^{2+} contained in spent acid can react with some acidic components mainly located in the heavy end fraction of crude oil, i.e., resins and asphaltenes, and make them desorbed from the oil-rock interface, inducing a slight drop of contact angle. This interaction is not strong enough to alter the formations wettability because of the finite exposure duration of acid and rocks, and is not obvious in originally water-wet formations.

2.3.2 Wettability Alteration by Spent Acid With Betaine Surfactant

There is an obvious distinction between oil-wet and water-wet carbonate rock when betaine surfactant was

added into spent acid to treat the rocks. This is attributed to surfactant absorption on the rock surface. It is well known that betaine surfactant has different electrical properties as pH value of solution changes. Charges of betaine surfactant are opposite on the two sides of isoelectric point.

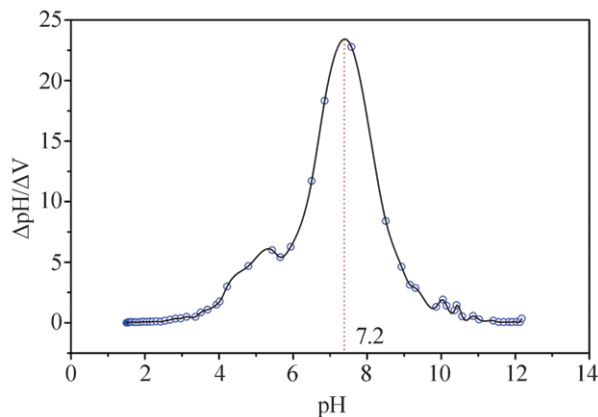


Figure 6
First Order Differential Potential Titration Curve of the OAPB

Figure 6 shows that the isoelectric point of betaine surfactant OAPB is near pH = 7.2. Therefore under spent acid condition with pH lower than the isoelectric point, OAPB molecules are positively charged and similar to cationic surfactant in property.

For oil-wet carbonate rock, ion pairs between the betaine surfactants and carboxylates of polar portions absorbed on rock interface are formed and dissolve into

the spent acid to some extent. On the hand, the partitioning of the reacted surfactant increases as the immersion time and concentration of surfactant increases. On the other hand, the surfactants absorbed on rock surface arrange as that the hydrophobic tails turn towards the rock surface and hydrophilic heads turn towards the liquid phase. These two processes lead to the alteration of oil-wet carbonate rock to intermediate wetting or weak water-wetting (Figure 7 (a)).

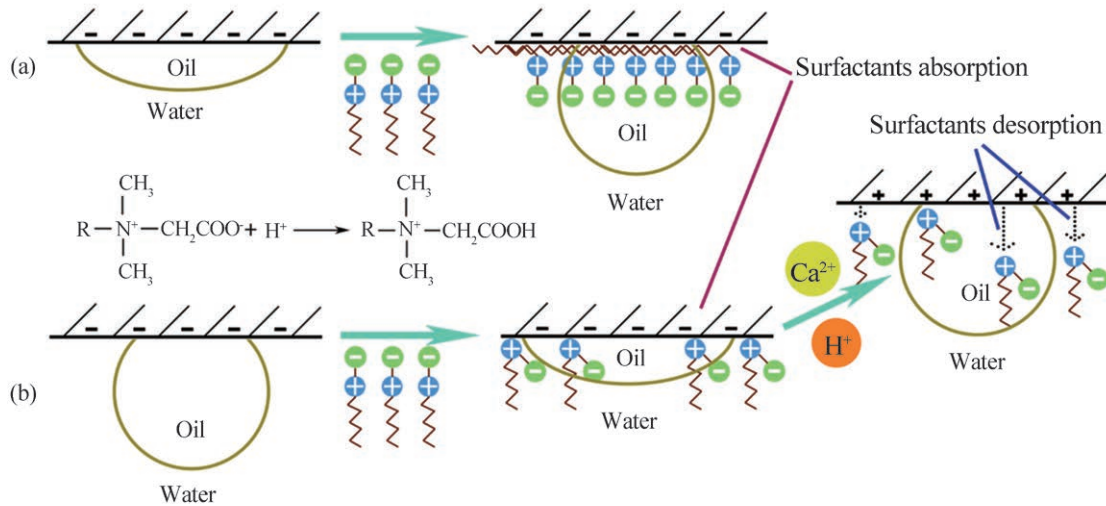


Figure 7
Chemical Mechanisms of the Wettability Alterations Induced by Self-Diverting Acid

For water-wet carbonate rock, as there are not too many asphaltenes on the surface, the change of wettability highly depends on the arrangement of the surfactant molecules on the rock surface. VES molecules are arranged such that the hydrophilic heads turn up towards the rock surface and the hydrophobic tails turn towards the aqueous solution (Figure 7(b)), changing the wettability to oil-wet. Longer immersion time and higher surfactant concentration induce more strongly oil-wet surfaces by improving the adsorbing capacity of betaine surfactant molecules on rock surface.

2.3.3 Wettability Alteration by Postflush

10% EGMBE or brine postflush is essential for water-wet reservoir. Mutual solvent effectively reduces the adsorbing capacity of betaine surfactant on rock surface and recovers the formation to weakly water-wet.

Zeta potentials of carbonate rock powders were determined by laser particle size analyzer, Mastersizer 3000 (Malvin corporation, UK). Figure 8 shows that carbonate rock has high negative electricity in dilute solution. With the increase of salt content, the zeta potential decreases gradually. In comparison to Na⁺, Ca²⁺ has a stronger ability to alter the zeta potential by compressing the diffuse electric double layer on the carbonate surface. When the concentration of Ca²⁺ exceeds 3%, the zeta potential inverts to be positive. Therefore, in spent acid environment with CaCl₂ up to 24

wt%, carbonate surface is positively charged. As both the betaine surfactants and the carbonate rocks are positively charged under spent acid condition, they repel each other and weaken the adsorption of surfactants on rock surface. Therefore the adverse wettability reversal for water-wet reservoir can be recovered by brine postflush.

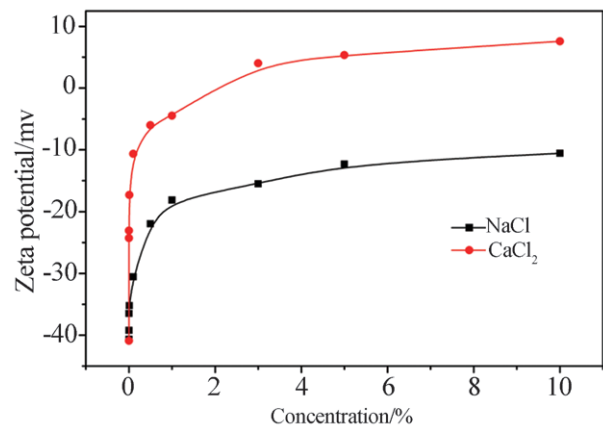


Figure 8
Zeta Potentials of Natural Carbonate Powders Under Different Salt Concentrations

CONCLUSION

Spent acid with HCl only results in no change in wettability. Adsorption of betaine surfactant on the surface

of carbonate rocks can cause wettability reversal in self-diverting acidizing process. Mutual solvent or brine postflush is especially essential for water-wet reservoir to eliminate the adverse wettability reversal.

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