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Impact of Acrylic Acid on ASP Flooding Performance: Interfacial Tension Behaviour

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Abstract: In chemical EOR, interfacial tension plays one of the important roles in carbonate reservoirs. Carbonate reservoirs are composed of calcium and magnesium minerals which affect the performance of alkali and surfactants to reduce interfacial tension. In this study, acrylic acid was used to inhibit precipitation and to create a compatible solution without any precipitations. The impact of acrylic acid on interfacial tension was investigated using various inhibitor concentrations with a hard brine composition of 59, 940 TDS. Sodium metaborate, alpha olefin sulfonate and internal olefin sulfonate were screened as promising chemicals for interfacial tension. Various fluid-fluid compatibility tests were first performed to find the optimum acid-alkali ratio to prevent any precipitations. The optimum acid-alkali ratio was found to be 0.6:1.0. This ratio was then used to keep all solution without any precipitations for 30 days at 80°C. It was also observed that the increase in acid-alkali concentrations can significantly reduce the interfacial tension. Using the optimum concentration for acid, alkali and surfactant, the interfacial tension reduced from 14.9-0.401 mN m⁻¹.

Key words: Acrylic acid, interfacial tension, carbonate reservoirs, acid-alkali ratio, alkali-surfactant-polymer

INTRODUCTION

Achieving low interfacial tension is an important parameter for recovery of oil with respect to Alkali-Surfactant-Polymer (ASP) flooding (Zhao *et al.*, 2007). The purpose of ASP flooding is to enhance oil production by reducing the waterflood residual oil saturation (Al-Mjeni *et al.*, 2010). For the displacement of oil from capillaries and porous media of petroleum reservoir rocks, it is necessary to reduced interfacial tension between oil and ASP slug to an ultra-low interfacial tension (Levitt *et al.*, 2006; Zhao *et al.*, 2006).

Carbonate reservoirs account large quantity of oil reserves. Having been potentially attractive, they exhibit immense variation in properties that include porosity, permeability and flow mechanism. Carbonate reservoirs are found to be naturally fractured and preferentially oil-wet (Akbar *et al.*, 2000; Mahroos and Zubari, 2009; Manrique *et al.*, 2006). The carbonate rocks contain large amounts of calcium and magnesium ions in the form of calcite, dolomite, anhydrite and gypsum (Levitt *et al.*, 2011). The big constraint of Chemical EOR in carbonate reservoirs includes formation of precipitation. Alkali reacts with divalent cationic minerals resulting solids are formed which are insoluble in solution. The precipitates plug effective pore spaces and ultimately cause formation damage near wellbore in the carbonate reservoirs (Levitt *et al.*, 2011).

In the present study, alkaline-surfactant-polymer formulation is developed by incorporating Acrylic Acid (AA) to form *in situ* inhibitor (Sodium Acrylate) to overcome the precipitation problems caused by reservoir minerals and brine compositions. Sodium Acrylate (SA) is generated by the reaction of acrylic acid with sodium ion (Na⁺) and alkali. The *in situ* inhibitor sequesters C⁺⁺ and Mg⁺⁺ ions for preventing the formation of precipitates (Elraies and Tan, 2010). Sodium metaborate was blended with acid to generate acrylate for keeping solutions clear without precipitation.

MATERIALS AND METHODS

Materials: In this study, crude oil was used and was collected from Dulang Oil field, Malaysia. The density and API gravity of the crude oil were 0.799 g cc⁻¹ (80°C) and 35.5°, respectively. Sodium metaborate was supplied by Rio Tinto Minerals. Acrylic acid was supplied by Sigma Aldrich. C₁₄₋₁₆ Alpha Olefin Sufonate was (AOS) supplied by Stepan Chemical Co. C₁₅₋₁₈.

Internal Olefin Sulfonate (IOS) and C₁₆₋₁₇ Alcohol Alkoxy Sulphate (AAS) surfactants were supplied by Shell Chemicals Co. Different synthetic brines were utilized to prepare all solutions and the main compositions for each brine are given in Table 1.

Fluid-fluid compatibility test: In the first part of this test, sodium metaborate was used to evaluate its performance

Table 1: Composition of synthetic hard brine

Components	Softened brine	Hard brine
Sodium (ppm)	20,445	20,445
Calcium (ppm)	-	2523
Magnesium (ppm)	-	239
Chloride (ppm)	31556	36,733
Total salinity	52,001	59,940

with synthetic hard brine. Secondly, acrylic acid and sodium metaborate were blended to mitigate precipitations. In the final stage, compatibility of various surfactants was performed by fluid-fluid evaluation to screen promising surfactants using softened brine and hard brine. All the compatibility tests were performed at 80°C for a period of time and formation of solids in the solutions was indication of incompatibility.

Interfacial tension tests: Spinning drop method was used to measure interfacial tension between Dulang crude oil and various alkali-brine, alkali-surfactant-brine and acid-alkali-surfactant-brine solutions. Model SVT 20 spinning drop tensiometer equipped with video camera was utilized to measure the interfacial activity. All the measurements were conducted at 80°C using softened brine and synthetic hard brine.

RESULTS AND DISCUSSION

Alkali-brine interaction: Sodium metaborate was used as a novel alkali to evaluate its compatibility with the hard brine. Sodium metaborate performed well to sequester divalent cations from precipitating at the ambient temperature. However, precipitations were formed instantly at the elevated temperature of 80°C. Hence, sodium metaborate was found incompatible with the hard brine.

Acrylic acid and alkali interaction tests: In the first part of fluid-fluid compatibility test, sodium metaborate showed incompatibility with the hard brine. Therefore, acrylic acid was combined with alkali to generate sodium acrylate and subsequently to prevent any precipitations within the solutions. The performance of sodium acrylate was investigated using different acrylic acid to sodium metaborate weight ratios. Table 2 summarizes the results for different acid to alkali weight ratio using sodium metaborate.

Sodium acrylate performed very efficiently with sodium metaborate in sequestering calcium and magnesium ions from precipitation over time. Figure 1 shows the compatibility of different acid-alkali weight ratios after 30 days at 80°C. It can be observed from Table 3 that performance of sodium acrylate (*in situ* inhibitor) was enhanced when concentration of acid was increased. It is because when a small concentration (i.e., 0.3%) of acrylic acid was used, the

Table 2: Summary of the acid-alkali compatibility test after 30 days at 80°C

Variables	Values					
Sodium metaborate (1 wt%)						
Acrylic acid (wt%)	0.2	0.3	0.4	0.5	0.6	0.7
pH	9.59	8.94	8.40	7.61	6.81	6.09
Days						
0	clo	-	-	-	-	-
1	-	-	-	-	-	-
5	-	-	-	-	-	-
10	ppt	ppt	ppt	ppt	-	-
15	ppt	ppt	ppt	ppt	-	-
20	ppt	ppt	ppt	ppt	-	-
30	ppt	ppt	ppt	ppt	ppt	-

ppt: Precipitation, -: Clear solution, clo: Cloudy

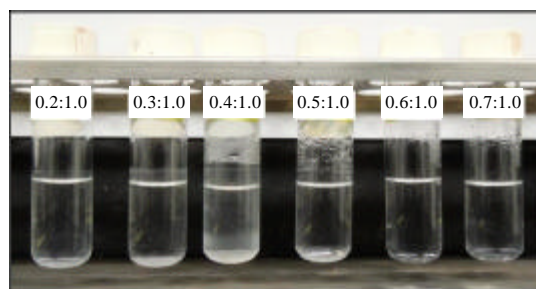


Fig. 1: Performance of the *in situ* inhibitor to prevent divalent ions from precipitating using sodium metaborate after 30 days at 80°C temperature

acid was neutralized by the presence of sodium metaborate (1.0%) and sodium ions within the brine. As a result, *in situ* inhibitor was not sufficiently generated to solubilise precipitates. However, when the concentration of acrylic acid was increased, enough quantity of *in situ* inhibitor was produced which sequestered Ca⁺⁺ and Mg⁺⁺ ions to keep precipitations soluble. Hence, acrylic acid to sodium metaborate weight ratio of 0.6:1.0 was selected as an optimum by considering the pH value into account.

Acid-alkali-surfactants interaction tests: In this test, surfactants were blended with acid-alkali using both softened brine and hard brine. Surfactants included were AOS, IOS and AAS for all the compatibility tests. In case of softened brine, AOS and IOS both showed good stability for 30 days at 80°C temperature whereas AAS was incompatible within the solution. On the other hand, both AOS and IOS vsurfactant were found to be instable with the hard brine at ambient temperature. The blend of acid-alkali with surfactants solutions also resulted cloudiness at the ambient conditions. However, all acid-alkali-surfactant solutions were found clear after few minutes at 80°C. IOS surfactant alone also showed precipitations at 80°C. Yet, homogeneity was examined when AOS was combined with IOS. Hence, two surfactants AOS and IOS were screened as promising surfactants for the

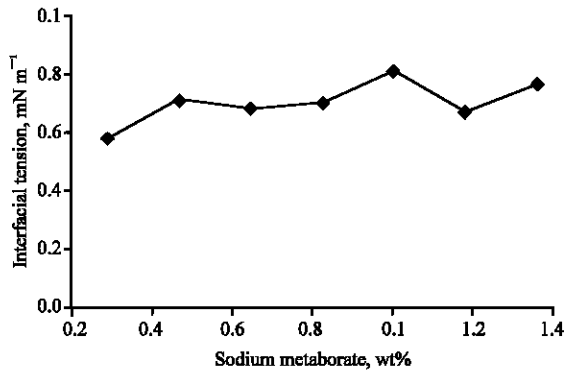


Fig. 2: IFT between crude oil and various alkali concentrations using softened brine

Table 3: Summary of the acid-alkali-surfactant compatibility test after 30 days at 80°C

Variables	Values			
Alpha olefin sulfonate (wt%)	0.6	0.6	0.4	0.6
Internal olefin sulfonate (wt%)	0.0	0.0	0.2	0.2
Acid to alkali concentrations (wt%)	0.0	0.4: 0.7	0.4: 0.7	0.6: 1.0
pH	7.32	7.41	7.67	7.71
Days				
0	-	-	-	-
1	-	-	-	-
1.5	-	-	-	-
30	-	-	-	-

-: Clear solution

next process of experiments. Table 3 summarizes the results of different acid-alkali-surfactant interaction tests.

Interfacial tension measurements: The attainment of a low Interfacial Tension (IFT) is crucial in the immiscible displacement process in the porous media. Extensive IFT measurements were conducted to screen the best chemical formula for the usage of softened water and synthetic hard brine. The IFT measurements were made between alkali-surfactant-water system, acid-alkali-surfactant system and Dulang crude oil.

IFT performance for alkali-brine system, softened brine:

The effect of sodium metaborate on the interfacial tension was investigated using various alkali concentrations. All samples were prepared using softened brine with a total salinity of 52,001 ppm. As can be seen from Fig. 2, sodium metaborate has a significant impact on the interfacial tension. Interfacial tension between the crude oil and 0.2 wt% alkali solution decreased from 10.8-0.579 mN m⁻¹. However, IFT increased slightly when alkali concentration was increased. This increment might be due to high salinity brine which increased concentration of electrolytes and affected alkali to produce *in situ* surfactants to minimize interfacial tension.

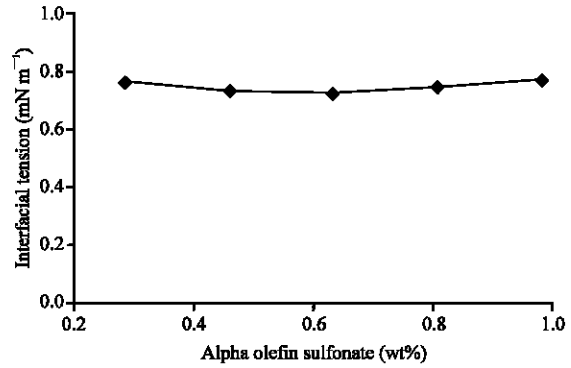


Fig. 3: IFT between crude oil and various alpha olefin sulfonate concentrations in the presence of 0.6% sodium metaborate using softened water

IFT performance for alkali-surfactant-brine system, softened brine:

Figure 3 shows the effect of different surfactant concentrations on interfacial tension performance using softened brine. In this test, concentration of sodium metaborate was kept constant at 0.8% and surfactant concentration was varied from 0.2-1.0%. As can be seen from Fig. 3, the presence of surfactant slightly increased interfacial tension as compared to alkali alone. For example, with 0.4% of surfactant, Interfacial tension was increased from 0.678 mN m⁻¹ for 0.6% alkali to 0.792 mN m⁻¹. This increment is probable due to incompatibility of surfactant with the Dulang crude oil which high wax content. As a result, surfactant would not generate microemulsions to minimize IFT even in the presence of alkali. Hence, at optimum concentrations of alkali and surfactant of 0.6 and 0.8%, respectively, interfacial tension between crude oil and the solutions reduced from 10.8-0.754 mN m⁻¹ with the use of softened brine.

IFT performance for acid-alkali-surfactant-brine system, hard brine:

Various acrylic acid and sodium metaborate concentrations were employed to evaluate the performance of *in situ* inhibitor on interfacial tension in the presence of hard brine. Surfactant concentration was made constant at 0.8% to investigate principally the impact of sodium acrylate on the IFT. As shown in Fig. 4, acrylic acid-alkali has shown significant reduction in interfacial tension between crude oil and aqueous solutions. In the absence of acid-alkali within the system, 0.8% surfactant concentration reduced interfacial tension from about 14.9-0.64 mN m⁻¹. More reduction in the IFT was observed as the acid and alkali concentrations were increased to 0.48 and 0.8%, respectively. However, a slight increment in the IFT was seen when acid-alkali concentrations exceeded from 0.48 and 0.8%. This might

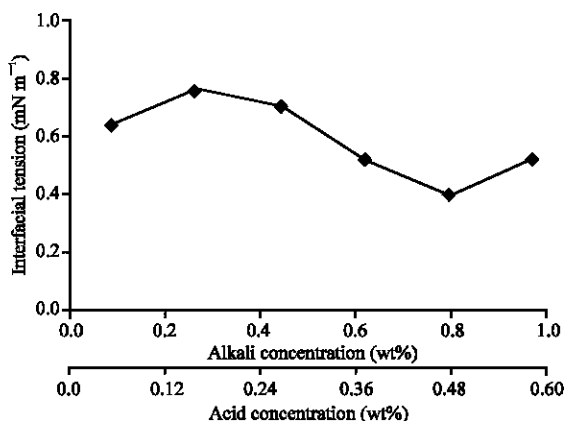


Fig. 4: IFT between crude oil and various acid-alkali concentrations in the presence of 0.8% surfactant using synthetic hard brine

be attributed to excess concentration of generated sodium acrylate which causes salinity to increase. As result, interfacial tension is increased. Hence, with the presence of 0.8% surfactant, optimum concentration for acid and alkali was found as 0.48, 0.8%, respectively. At these optimum concentrations, interfacial tension reduced for the hard brine from 14.9-0.401 mN m⁻¹.

CONCLUSION

The generated sodium acrylate performed effectively to prevent precipitation. The ratio of acrylic acid to sodium metaborate of 0.6:1.0 was found to be optimum for achieving a compatible solution for 30 days at 80°C temperature.

Alpha olefin sulfonate and internal olefin sulfonate were screened as promising surfactants for interfacial tension. Alpha olefin sulfonate clouded immediately in the presence both softened brine and hard brine at ambient temperature. However, all aqueous phases containing acid-alkali-surfactant were found compatible with hard brine for 30 days 80°C.

The combination of acrylic acid and sodium metaborate significantly decreased interfacial tension in the presence of hard brine. Using the optimum acid-alkali-surfactant concentration of 0.48, 0.8, 0.8%, respectively IFT reduced from 14.9-0.401 mN m⁻¹.

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