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SURFACTANT-ENHANCED ALKALINE FLOODING FOR LIGHT OIL RECOVERY

Contract No. DE-AC22-92BC14883

Illinois Institute of Technology
Chicago, IL

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Principal Investigator:
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**SURFACTANT-ENHANCED ALKALINE FLOODING
FOR LIGHT OIL RECOVERY**

Quarterly Report for the Period
January 1-March 31, 1994

By
Darsh T. Wasan

Work Performed Under Contract No. DE-AC22-92BC14883

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OBJECTIVE

The overall objective of this project is to develop a very cost-effective method for formulating a successful surfactant-enhanced alkaline flood by appropriately choosing mixed alkalis which form inexpensive buffers to obtain the desired pH (between 8.5 and 12.0) for ultimate spontaneous emulsification and ultra-low tension. In addition, the novel concept of pH gradient design to optimize flood water conditions will be tested.

SUMMARY OF TECHNICAL PROGRESS

Last quarter¹ we investigated the phase behavior and the regions where in the middle phase occurs. Middle phase was found to go through a maximum with pH, sodium concentration and surfactant concentration. The optimum pH is about 12.0 to 13.5, the optimum sodium concentration is about 0.513 mol/liter, and the optimum surfactant concentration is about 0.2%. The effect of surfactant type was also investigated. Petrostep B-105 was found to give the most middle phase production.

This quarter, we investigated the contact angle of Long Beach oil, Adena oil, and a model oil on a solid glass surface in contact with an aqueous alkaline solution both with and without added preformed surfactant. The contact angle with Long Beach and Adena oils showed oil-wet conditions, whereas the model oil showed both oil-wet and water-wet conditions depending on the pH of the aqueous phase. The addition of surfactant to the alkaline solution resulted in making the system less oil-wet. Spreading of the oil on the glass surface was observed in all three systems investigated.

MATERIALS AND EXPERIMENTS

In this study, two crude oils containing natural organic acids were contacted with an alkaline pH aqueous solution. One crude oil used in this investigation is a Long Beach crude oil obtained from THUMS Long Beach Company, having an acid number of 1.0, which was determined from ASTM procedure D-664 and an API gravity of 24.9. It was centrifuged at 40,000 G's for 30 minutes to remove water and clays. The viscosity of the crude oil after centrifuging was 52 cp at 25 °C and the interfacial tension against deionized water was 24.5 mN/m. The other crude oil (Adena) used was obtained from SURTEK from Adena field located

in Morgan County, Colorado. The oil is a light oil with an API gravity of 41.95, a viscosity of 3.75 cp at 25 °C, and an acid number less than 0.002. The interfacial tension against deionized water is 39 mN/m. In addition, a model oil of oleic acid (99% pure) in decane (99+% pure) was also used.

The alkaline solutions are a mixture of sodium hydroxide, sodium bicarbonate, and sodium chloride. All alkalis were obtained from Fisher Scientific Co.

Two preformed surfactants, Petrostep B-105 (55% active) and Petrostep B-120, were added to the alkaline solution. The surfactant was obtained from Stepan Chemical Company, and the surfactant solutions were made on a 100% basis.

Throughout this study, the solutions were made by diluting an equimolar ratio of sodium bicarbonate/NaOH (referred to as 20/20) with either the same molarity of sodium bicarbonate plus NaCl to keep the total sodium constant or the same molarity of NaOH plus enough NaCl to keep the total sodium constant. By changing the ratio of sodium bicarbonate/NaOH, the pH is changed. Lower pH is obtained by adding the sodium bicarbonate plus NaCl solution to the 20/20 mixture, or a higher pH is obtained by adding the NaOH plus NaCl solution to the 20/20 mixture. It should be noted that 343 mol/m³ total sodium is about 2.0 wt% sodium bicarbonate/NaOH mixture.

RESULTS AND DISCUSSION

Two sets of experiments were conducted to determine the contact angle of an oil droplet on a glass coverslip. In the first set of experiments, the oil droplet is placed on the coverslip prior to immersion in the alkaline solution. In the second set of experiments, the coverslip is placed in the alkaline solution prior to the oil droplet contacting the coverslip, thus creating an initial aqueous film. The contact angle so measured is that angle taken inside the oil droplet. In all cases, the systems were preequilibrated before measurements were made.

Long Beach oil: alkali only

Figure 1 shows the contact angle as a function of the equilibrium pH of the solution for the Long Beach crude oil with varying sodium concentration. In Figure 1, no initial aqueous film was present. The contact angle goes through a minimum with pH. When the contact angle is

zero spreading of the oil droplet on the glass surface takes place.

Figure 2 shows the contact angle as a function of equilibrium pH when an initial aqueous film is present. When spreading occurs, the initial aqueous film drains, and ruptures. It is the presence of the aqueous film that causes the contact angles in Figure 2 to be greater than in Figure 1.

Figure 3 shows the equilibrium interfacial tension as a function of the equilibrium pH. The pK_a of the system occurs at a pH of 10.6. The spreading which is observed in Figures 1 and 2 takes place at and before the pK_a of the system.

Model oil: alkali only

Decane with 0.013 M oleic acid was investigated against varying NaOH concentrations from 0.001% to 0.5% NaOH. The contact angle was determined were no initial aqueous film was present. The oil spreads, giving zero contact angle, from 0.001% to 0.01% NaOH, and the contact angle is 175° from 0.01% to 0.5% NaOH. The pK_a of the system is approximately 0.01% NaOH (a pH of 10.6). Before the pK_a of the system, the concentration of unionized acid in the oil phase is high, and after this value the concentration of ionized acid in the aqueous phase is high. This means that the aqueous film between the oil droplet and the glass coverslip ruptures before the pK_a of the system because there is no surfactant in the aqueous phase to stabilize it, thus making the system oil-wet. After the pK_a of the system, the aqueous phase has ionized acid in it making the system water-wet.

Long Beach oil: alkali+added surfactant

Figures 4 and 5 are the same as Figures 1 and 2 except 0.1% surfactant was added. The addition of surfactant makes the system less oil-wet, thus no spreading occurs. In both cases, with and without an initial aqueous film, the 0.086 M sodium sample went through a minimum. This minimum may be connected with the minimum in interfacial tension observed in Figure 6.

Adena oil: Alkali+added surfactant

The Adena oil was also investigated against 0.2% Petrostep B-120 at 0.171 and 0.684 M sodium with varying pH from 10.5 to 12.5. In all cases, the oil spreads on the glass coverslip,

making the system totally oil-wet.

REFERENCES

1. Wasan, D.T., Progress Report submitted to DOE for the period October 1-December 31, 1993.

PUBLICATIONS

1. Rudin, J., Bernard, C., and Wasan, D.T. "The Effect of Added Surfactant on Interfacial Tension and Spontaneous Emulsification in Alkali/Acidic Oil Systems," accepted for publication in *Industrial and Engineering Chemistry Research*.

Figure 1. System Possessing no Initial Aqueous Film

Figure 2. System Possessing an Initial Aqueous Film

Figure 3. Equilibrium Interfacial Tension as a Function of Equilibrium pH

Figure 4. System Possessing no Initial Aqueous Film

Figure 5. System Possessing an Initial Aqueous Film

Figure 6. Effect of pH and Sodium on the Equilibrium Interfacial Tension with Petrostep B-105

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