RELATIVE PERMEABILITY AND WETTABILITY IMPLICATIONS OF DILUTE SURFACTANTS AT RESERVOIR CONDITIONS

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This paper was prepared for presentation at the International Symposium of Society of Core Analysts held in Toronto, Canada, 21-25 August 2005

ABSTRACT
Surfactants have long been considered to enhance oil recovery from petroleum reservoirs through reduction in oil-water interfacial tension. However, the possibility of altering wettability by surfactants for oil recovery enhancement remains largely unexplored. Furthermore, most of the few previous studies conducted to investigate the surfactant-induced wettability alterations were done using stocktank crude oils and at ambient conditions.

Hence, to investigate the influence of surfactants on wettability alteration at realistic reservoir conditions, corefloods were conducted in this study at reservoir conditions (82° F and 700 psi) using Yates reservoir fractured dolomite cores. The fluids used were Yates stocktank crude oil, Yates live oil, synthetic Yates reservoir brine and the nonionic, ethoxy alcohol surfactant. The secondary recovery characteristics of the rock-fluids systems were examined by conducting brine floods at varying surfactant concentrations. The relative permeabilities were computed by history matching the pressure drop and recovery data obtained from the experiments. The relative permeability variations were then used to discern the wettability alterations induced by the surfactant.

Only marginal increments of about 6% OOIP were obtained due to the surfactant in the rock-fluids system consisting of stocktank oil. The gradual shift to the right in the relative permeability ratio (krw/kro) curves indicates the wettability alterations from an initial strongly oil-wet to a weakly oil-wet state. However, in the rock-fluids system consisting of live oil, significant oil recovery enhancements of about 20% OOIP were obtained due to the surfactant. The gradual shift to the right in the relative permeability ratio (krw/kro) curves, steady increase in initial water saturation, very low residual oil saturations, all indicate the development of a special kind of heterogeneous wettability

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known as mixed-wettability. In mixed-wettability state, the smaller pores retain their original water-wet tendency while the larger pores containing oil become oil-wet due to the spreading of a continuous film of oil on the rock surface. This oil film provides a path of least resistance to oil flow, enabling preferential draining of oil-phase resulting in significant oil recovery enhancements. Thus, this study, conducted at in-situ reservoir conditions, offers a new avenue for the use of low-cost surface-active chemicals mainly to alter rock wettability, instead of the conventional approach of relying on interfacial tension reduction, for economically viable field implementations of chemically enhanced oil recovery.

1. INTRODUCTION

Wettability of a reservoir rock is one of the important factors to be considered in the development plans of a new field. Until the early 1980’s, it was assumed that almost all reservoirs are water-wet [1]. However, more recent studies have proven this to be an erroneous assumption [2]. The oil recoveries from oil-wet reservoirs are generally less than those from water-wet reservoirs. This is partly explainable from imbibition phenomenon and the other complex interactions occurring in the reservoir during production [3].

The alteration of reservoir wettability from oil-wet to water-wet appears to be a potential avenue to enhance oil recovery from oil-wet reservoirs. Several different opinions have been expressed in the literature on the most effective means to induce wettability alteration in crude oil reservoirs. Some literature reviewed favored surfactants, while the others favored thermal methods to alter wettability. These experimental studies are briefly discussed below.

Rao et al. [4] demonstrated the strong impact of wettability on water and gas flooding processes at reservoir conditions and observed better recovery rates in intermediate or mixed wetting conditions. Morrow and Jadhunandan [5] made similar observations as Rao et al. [4] and reported that higher oil recoveries are associated with mixed wettability condition. The optimum recovery of hydrocarbon material from oil-bearing reservoirs has been associated with the wetting of the reservoir rock by both water and oil and is usually referred to as mixed wettability.

Tang and Morrow [6] investigated crude oil-brine-rock interactions and observed increase in recovery of crude oil with decrease in brine salinity by conducting numerous laboratory experiments using reservoir sandstone cores. Austad and Standnes [2] reported that the wettability induced by crude oil on chalk surfaces is dependent on the amount of acidic components in the oil and found that crude oils with high acid number have a greater potential to alter the wettability of chalk to oil-wet. Standnes and Austad [7] studied temperature effects in carbonate reservoirs and observed an increase in oil-wetness as the temperature decreases. They further investigated the alteration of wettability in oil-wet carbonate reservoir cores using surfactants. The surfactants were
able to improve spontaneous imbibition into the matrix blocks and hence increased the oil recovery.

Surfactants can be used to alter rock wettability from oil-wet to water-wet and hence can increase oil recovery. The usage of surfactants always favored reduction of oil-water interfacial tension. However, the economics of such a process made it unattractive for field implementation, resulting in the near extinction of chemical EOR field projects [8]. Spinler et al. [9] and Li et al. [10] studied the spontaneous imbibition of aqueous surfactant solutions into preferentially oil-wet carbonate cores at ambient conditions. They reported that the chemical reactions taking place between the rock and the adsorbed polar organic components or carboxylates in the surfactant are responsible for altering wettability. They also concluded that oil recovery can be improved with low concentrations of surfactant for both spontaneous and forced imbibitions and that the surfactant adsorption on rock surface can be reduced by using surfactants at concentrations below the critical micelle concentration (CMC).

The use of surfactants to improve oil recovery in oil industry so far has been largely limited to utilizing the mechanism of only reduction in interfacial tension (IFT). However, the other beneficial aspect, namely the alteration of wettability by the surfactants has received little attention. Furthermore, much of the previous laboratory investigations to study the surfactant-induced wettability alterations have been conducted at ambient conditions using stocktank crude oils. The outcome of such studies has been mostly uncertain for extrapolation to the field. Therefore the objective of this study is to experimentally investigate the wettability altering capability of low-cost surfactants and at low concentrations through oil-water relative permeability measurements at realistic reservoir conditions. For this purpose, coreflooding experiments were conducted in this study at Yates (West Texas) reservoir conditions (82°F and 700 psi) using Yates reservoir fractured dolomite cores and reservoir fluids. The experiments were carried out using the nonionic ethoxy alcohol surfactant in two different reservoir rock-fluids systems: (1) Yates dolomite, Yates stocktank crude oil and Yates synthetic brine and (2) Yates dolomite, Yates live crude oil and Yates synthetic brine. The oil-water relative permeabilities were computed using a coreflood simulator by history matching the oil recovery and pressure drop data obtained during the experiments. The relative permeability variations were then used to infer the surfactant-induced wettability alterations in these reservoir rock-fluids systems.

2. EXPERIMENTAL DETAILS

2.1 Experimental Reagents

Analytical grade reagents were used in the experiments. The cleaning solvents (toluene, acetone, isopropyl alcohol (IPA) and methylene chloride) and the salts used for synthetic brine preparation were from Fisher Scientific having a purity of 99.9%. Deionized water obtained from the Water Quality Laboratory at Louisiana State
University was used. Yates fractured dolomite cores, Yates stocktank crude oil and the nonionic surfactant (ethoxy alcohol) were provided by Marathon Oil Company. The live oil was prepared by adding the lighter components methane to pentane to the Yates stocktank crude oil to match the Yates live oil composition. The measured viscosities of Yates stocktank and Yates live crude oils at Yates reservoir conditions are 15.4 cp and 5.6 cp, respectively.

2.2 Experimental Apparatus

A high-pressure high-temperature coreflood apparatus was assembled to facilitate experimentation in this study. The schematic of the apparatus used is shown in Figure 1. The coreflood apparatus consisted of a Ruska pump for injecting different fluids into the core, two floating-piston transfer vessels to hold the fluids, Hassler-type core holder for placing and pressurizing the core, differential pressure transducer to measure the pressure drop across the core during the floods, back pressure regulator (BPR) to maintain the system pressure at the reservoir pressure, heating tapes to maintain the temperature and a fluid partitioning collector to measure the volume of individual fluids produced.

2.3 Reservoir Core Description

To prevent the coreflooding results being affected by the core-heterogeneities, all the experimental runs were conducted using the same core. This core coded, as 1-17V by Marathon Oil Company was obtained from Yates field unit number 2433. The location of this core was at a top and bottom depths of 1558.6 ft and 1559.4 ft, respectively, providing a core length of 3.5 inches. The reported top and bottom face air permeabilities and porosity were 387 mD, 257 mD, and 20.3%, respectively. The initial measurements of pore volume (PV), porosity and absolute water permeability were 32.70 cc, 32.26% and 768.0 mD, respectively.

2.4 Experimental Procedure

Rapaport and Leas [11] scaling criterion was used to calculate the stable volumetric flow rates to be used in the experiments to ensure independence of oil recovery on injection rate and core length. This scaling criterion ensures a smaller capillary pressure gradient in the flow direction compared to the imposed pressure gradient. From Rapaport and Leas criterion \((L V \mu > 1.0\), where \(L\) is the length in cm, \(V\) is the flow rate per unit cross sectional area in cm/min and \(\mu\) is the displacing phase viscosity in cp), the minimum displacing fluid velocity is determined as 1.389 cc/min (83.32 cc/hr). Hence, all the coreflooding investigations were conducted at a flood rate of 2.75 PV/hr.

The core was installed into the core holder with a 500 psi differential annulus pressure. Core is cleaned by the pressure-flow of alternating Methylene Chloride with Acetone / IPA and Toluene. Pore volume was measured using a Ruska pump. Yates brine was injected to saturate the core under specified reservoir conditions. Absolute permeability of the core to brine was measured at four different flow rates. Yates stocktank crude oil of about 3 pore volumes was injected at 2.75 PV/hr into the core.
End-point effective oil permeability was measured at three different flow rates. The core was then aged for an average time of one week to establish the initial wettability at connate water saturation. Yates reservoir brine flood was then conducted at 2.75 PV/hr for about 3 pore volumes (This is referred to as 0 ppm surfactant flood). End-point effective brine permeability was measured at three different flow rates. Yates stocktank crude oil was again injected into the core at 2.75 PV/hr up to 3 pore volumes. End-point effective oil permeability was measured at three different flow rates. After having restored the initial wettability at connate water saturation, an aging time of about 24 hours was considered sufficient for rest of the floods and hence 24 hour aging time was used for all the oil floods after the 0 ppm surfactant flood. Then, 500 ppm surfactant containing brine at 2.75 PV/hr for about 3 pore volumes was injected and end-point effective permeability measurement at three different flow rates was made. These steps were repeated for brines containing 1500, 3500 and 5000 ppm surfactant concentrations. The core was now cleaned and used for the subsequent investigation using Yates live crude oil following the same procedure as described above.

During each flood, pressure drop and oil and brine productions were continuously monitored. The dead volumes of all the flow lines in the coreflood apparatus were measured and accounted for in the material balance calculations. A coreflood simulator was used to calculate the oil-water relative permeabilities by history matching the pressure drop and oil recovery data obtained during the floods. The relative permeability variations are then used to discern the wettability alterations induced by the surfactant solutions of varying concentrations in the reservoir rock-fluids systems.

2.5 Semi-Analytical Analysis for Oil-Water Relative Permeabilities

A semi-analytical relative permeability model was used to simulate the results of coreflood investigations conducted in this study. This model is applicable mostly to situations where capillary pressure data are negligible. The relative permeabilities were computed in numerical simulation using the JBN technique [12], which assumes stabilized displacement and hence negligible capillary pressure and end effects. The coreflooding experiments in this study were conducted at the volumetric flow rates determined using the Rapaport and Leas scaling criterion [11]. This scaling also causes the capillary pressure gradient in the flow direction to be small, when compared to the total pressure gradient [13]. These enabled the neglect of capillary pressure effects in numerical simulation used. Fractional flow theory is used to calculate the recovery and pressure drop at a given time after the start of displacement. The pressure drop is computed by deriving the saturation profile in the core, thereby calculating the total mobility along the core length. Relative permeabilities are then computed in this model by minimizing the sum-of-squares of the weighted deviations of the experimental pressure and production histories from calculated values. This model generates the relative permeabilities using the following relations,

$$k_{ro} = (1 - S)^c \ k_{rom}$$  \hspace{1cm} (1)
\[ k_{rw} = S_{w}^{e_{w}} k_{rom} \]  
\[ S = (S_{w} - S_{wi}) / (S_{wm} - S_{wi}) \]  

Where \( S_{w} \) is the brine saturation, \( S_{wi} \) is the irreducible brine saturation, \( S_{wm} \) is the maximum brine saturation or \( (1 - S_{or}) \), \( k_{ro} \) is the relative permeability to oil, \( k_{rw} \) is the relative permeability to brine, \( k_{rom} \) is the relative permeability to oil at \( S_{wi} \), \( k_{rw} \) is the relative permeability to brine at \( S_{or} \) and \( e_{o} \) and \( e_{w} \) are saturation exponents.

Fractional water flows were then calculated using,

\[ f_{w} = \frac{1}{1 + \left( \frac{k_{ro}}{k_{rw}} \right) \left( \frac{\mu_{w}}{\mu_{o}} \right)} \]  

Where \( f_{w} \) is the fractional water flow, \( \mu_{w} \) and \( \mu_{o} \) are the viscosities of displacing and displaced phases, respectively.

As an example case, the history match of recovery and pressure drop, and the resulting relative permeability curves obtained from the simulator for 1500 ppm surfactant concentration in Yates dolomite-live oil-brine system are shown in Figure 2.

3. RESULTS AND DISCUSSION

3.1 Yates Dolomite-Stocktank Crude Oil-Brine System

The summary of experimental and simulator results for this rock-fluids system at various surfactant concentrations is shown in Table 1. As can be seen, only minor adjustments were needed in end-point water relative permeabilities to obtain acceptable history match of recovery and pressure drop data during simulation. The initial water saturation (\( S_{wi} \)) gradually increased from 31.2% to 49.4% with the increase of surfactant concentration from 0 ppm to 5000 ppm. The end-point oil relative permeability at initial water saturation (\( k_{ro} \)) gradually decreased from 64.3% to 43.3% as the surfactant concentration is increased from 0 ppm to 5000 ppm. However, no significant change was observed in end-point water relative permeability at residual oil saturation (\( k_{rw} \)) as it varied from 14% to 18% in these floods. Figure 3 shows the effect of surfactant concentration on oil recovery. The effect of surfactant concentration on relative permeability ratios is shown in Figure 4. The effect of surfactant concentration on fractional water flow is depicted in Figure 5.

From the plot of oil recovery against pore volume injected at various surfactant concentrations (Figure 3), it can be seen that the oil recovery gradually increases from 67.5% to 73.3% as the surfactant concentration is increased from 0 ppm to 3500 ppm. Above 3500 ppm, the oil recovery drops back to 65.2% at 5000 ppm, suggesting that
3500 ppm surfactant concentration is the optimum for this rock-fluids system to maximize the oil recovery.

The contact angle measurements conducted for this rock-fluids system at reservoir conditions indicate an advancing contact angle of 155° in the absence of surfactant, which indicates the strong oil-wet nature [14]. The marginal increase in oil recovery from 67.5% to 73.3% observed with the surfactant indicates only a slight wettability alteration from its initial oil-wet state. From Figure 4, it can be seen that the relative permeability ratio \((k_{rw}/k_{ro})\) curves are gradually shifting to the right as the surfactant concentration is increased. Since, the native wettability state of the core is oil-wet, this type of relative shifts to the right in the relative permeability ratio curves [15] as well as the marginal increments of oil recovery observed appear to indicate alteration of wettability to weakly oil-wet state by the surfactant.

### 3.2 Yates Dolomite-Live Crude Oil-Brine System

The summary of experimental results obtained during the corefloods in this rock-fluids system at various surfactant concentrations is shown in Table 2. In this case also, only minor adjustments were needed in the experimental data to obtain acceptable history match of recovery and pressure drop data during simulation. The initial water saturation \((S_{wi})\) gradually increased from 27.6% to 45.8% as the surfactant concentration is increased from 0 ppm to 5000 ppm. The end-point oil relative permeability at initial water saturation \((k_{ro})\) gradually decreased from 51.3% to 35.3% as the surfactant concentration increased from 0 ppm to 5000 ppm. The end-point water relative permeability at residual oil saturation \((k_{rw})\) varied from 13.6% to 21.2% in these floods. Figure 6 shows the effect of surfactant concentration on oil recovery. The effect of surfactant concentration on relative permeability ratios is shown in Figure 7. Figure 8 portrays the effect of surfactant concentration on fractional water flow.

From the plot of oil recovery against injected volume at different surfactant concentrations (Figure 6), it can be seen that the oil recovery gradually increased from 66% at 0 ppm surfactant concentration to a maximum value of 86% at surfactant concentration of 1500 ppm. The oil recovery then gradually declined to 81% at 3500 ppm and to 71% at 5000 ppm surfactant concentration. Hence, 1500 ppm surfactant concentration appears to be the optimum for maximum oil recovery in this reservoir rock-fluids system. The step changes in oil recoveries of Figure 6 at higher surfactant concentrations are due to the accumulation of oil-water emulsion in the flow lines and sudden release of production from the outlet at high injection pressures.

The higher oil recoveries obtained in this system due to the surfactant indicate that the system is neither oil-wet nor water-wet at these surfactant concentrations. Hence, the shifts in relative permeability ratio curves \((k_{rw}/k_{ro})\) were used to infer the wettability alteration. The contact angles measured for this rock-fluids system in the absence of surfactant at reservoir conditions indicated an advancing contact angle of 55°, which corresponds to an initially weakly water-wet native state [14]. The relative permeability
ratio curves are gradually shifting to the right as the surfactant concentration is increased (Figure 7). For an initially water wet system, such type of gradual shift to right in the relative permeability ratio curves indicates development of mixed wettability condition [15 - 17]. This is further substantiated with steady increase in initial water saturation and low residual oil saturations as the surfactant concentration is increased.

The higher surfactant concentrations above the optimum used in Yates stocktank and live oil systems appear to be near critical micelle concentration (cmc) of the surfactants. Therefore, bilayer surfactant adsorption and the consequent wettability reversal to the native wettability state [18] are the possible reasons for the reduction in oil recoveries observed at higher surfactant concentrations above the optimum in both Yates stocktank and live oil systems.

4. CONCLUSIONS

- Coreflooding experiments were conducted using Yates reservoir fractured dolomite core, Yates stocktank and live crude oils, Yates synthetic brine and the nonionic surfactant at Yates reservoir conditions of 82°F and 700 psi.
- Only marginal increments in oil recovery of up to 5 to 6% OOIP were obtained in Yates reservoir rock-fluids system consisting of Yates stocktank crude oil. These increments in oil recovery were due to the surfactant-induced wettability alterations from an initial strongly oil-wet to weakly oil-wet state.
- Significant oil recovery enhancements of about 20% OOIP were obtained due to the surfactant in the reservoir rock-fluids system consisting of Yates live oil. Alteration of wettability to mixed-wet appears to be the principal mechanism for these large enhancements in oil recovery observed.
- 3500 ppm surfactant concentration appears to be the optimum surfactant concentration in stocktank crude oil containing rock-fluids system, while 1500 ppm is the optimum surfactant concentration in live crude oil containing rock-fluids system for obtaining maximum oil recoveries.
- Thus, this study conducted at in-situ reservoir conditions using actual reservoir rock and fluids offers a new avenue for the use of low-cost surfactants to alter rock wettability for significant oil recovery enhancements.

ACKNOWLEDGEMENTS

Financial support of this project by the Louisiana Board of Regents through the Board of Regents Support Fund Contract LEQSF (2000-03)-RD-B-06 and Marathon Oil Company is greatly appreciated. Sincere thanks are due to Eugene Wadleigh, Steve Bourgeois, Brian Policky and Edward Yang of Marathon Oil Company for their support and encouragement and Daryl S. Sequeira of LSU’s Petroleum Engineering Department for preparing the live crude oil used in the experiments.
REFERENCES
Table 1. Comparison between Experimental and Simulator Results for Waterflood of Yates stocktank Crude Oil in Yates Dolomite at Various Surfactant Concentrations

<table>
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<th>Case</th>
<th>Experimental</th>
<th>Simulator</th>
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<td></td>
<td>Recovery (%OOIP)</td>
<td>S_m</td>
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<tr>
<td>Brine</td>
<td>67.5</td>
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<td>500 ppm</td>
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<td>1500 ppm</td>
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<td>3500 ppm</td>
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<td>5000 ppm</td>
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Table 2. Comparison between Experimental and Simulator Results for Waterflood of Yates Live Crude Oil in Yates Dolomite at Various Surfactant Concentrations

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<tr>
<td></td>
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Figure 1. Schematics of Coreflood Apparatus Used
Figure 2. History Match of Recovery and Pressure Drop and the Resulting Relative Permeability Curves Obtained from Simulator at 1500 ppm Surfactant concentration for Yates Live Oil System

Figure 3. Effect of Surfactant Concentration on Oil Recovery in Yates Stocktank Crude Oil System

Figure 4. Effect of Surfactant Concentration on Relative Permeability Ratios in Yates Stocktank Crude Oil System
Figure 5. Effect of Surfactant Concentration on Fractional Water Flow in Yates Stocktank Crude Oil System

Figure 6. Effect of Surfactant Concentration on Oil Recovery in Yates Live Crude Oil System

Figure 7. Effect of Surfactant Concentration on Relative Permeability Ratios in Yates Live Crude Oil System

Figure 8. Effect of Surfactant Concentration on Fractional Water Flow in Yates Live Crude Oil System