

Wettability alteration and spontaneous imbibition in oil-wet carbonate formations

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Abstract

Alkaline/surfactant flooding has been widely tested for its ability to improve oil recovery, but little effort has been made toward understanding the controlling mechanisms and variables. This paper investigates the effect of electrolyte concentration, surfactant concentration and water/oil ratio on wettability, phase behavior, and displacement from a narrow gap. Wettability of calcite can be altered to about intermediate-wet to preferentially water-wet with alkaline/surfactant systems. Anionic surfactant adsorption can be significantly reduced in the presence of sodium carbonate.

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1. Introduction

The remaining oil saturation in water invaded regions of fractured, oil-wet, carbonate formations is often high. It may not be possible to apply a large pressure gradient across the matrix, and the oil is retained by capillarity. The recovery of the oil in the matrix thus depends on spontaneous imbibition, which can be enhanced by adding surfactant. The mechanisms involved in surfactant flooding of fractured, oil-wet formations are mainly wettability alteration and interfacial tension reduction.

Cationic surfactants have been used to alter wettability of carbonate formations to more water-wet conditions (Austad and Milter, 1997; Austad et al., 1998; Standnes and Austad, 2000; Standnes et al., 2002; Xie et al., 2004). Standnes and Austad (2000) proposed

the mechanism to be the formation of ion-pairs between surfactant monomers and the adsorbed carboxylates. Their laboratory tests with chalk cores showed that oil recovery can reach 70%.

Xie et al. (2004) applied a cationic surfactant and a nonionic surfactant to over 50 cores from three dolomitic Class II reservoirs. The incremental oil recovery ranged from 5% to 10% OOIP. Wettability alteration was identified as the main factor. They also found that recovery rate with the nonionic surfactant was faster than that with the cationic surfactant because the former had higher interfacial tension.

Alkaline/anionic surfactant flooding has been extensively investigated, and both wettability alteration and interfacial tension reduction have been responsible for the increase in oil recovery (see Further Reading). In our previous work (Hirasaki and Zhang, 2004), three spontaneous imbibition tests in oil-wet dolomite cores were reported. There was no spontaneous imbibition with formation brine for 8 months, while with alkaline/

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Table 1
Surfactant identification

Trade name	Structure name
CS-330	Sodium dodecyl 3EO sulfate
TDA-4PO	Ammonium iso-tridecyl 4PO sulfate
Alfoterra 38	Sodium tetradecyl 8PO sulfate
Blend	Blend of equal weight amount of CS-330 and TDA-4PO

surfactant solution, spontaneous imbibition was initiated within an hour. The scaled oil recovery curves indicated that the process was dominated by gravity. However, no conclusion can be drawn toward what factor contributed most to the differences in oil recovery observed. The current work is dedicated to quantifying the effect of the important factors in alkaline/surfactant enhanced spontaneous imbibition in oil-wet carbonate formations.

2. Surfactant formulations

2.1. Surfactant

The surfactants evaluated are identified in Table 1. Ethoxylated (EO) and propoxylated (PO) sulfates were used because of their known tolerance to divalent ions. These surfactants are limited to reservoir temperatures where sulfate hydrolysis should not be a problem. For high temperature carbonate reservoirs, EO and PO sulfonates may be better choices.

CS-330 is similar to NEODOL 25-3S used previously (Nelson et al., 1984), but is too hydrophilic to use by itself (Hirasaki and Zhang, 2004). TDA-4PO is less hydrophilic, but its solutions at optimal sodium carbonate concentration are turbid and adsorption is anomalously high (Hirasaki and Zhang, 2004). Thus the

two surfactants are blended at equal weight ratio, and the resulting surfactant solution is abbreviated as “Blend”.

2.2. Electrolytes

At the early stage of this research, sodium carbonate was used as the sole electrolyte. But a practical system should have only enough sodium carbonate to saponify the naphthenic acids present in the crude oil and propagate through the formation, and use inexpensive and non-scaling sodium chloride for the remainder of electrolyte strength. Here, sodium chloride is used along with 1% sodium carbonate to adjust the electrolyte strength. Two units of sodium carbonate concentration have been used, and their relationship is: 1% is about 0.1 M.

Mixing with formation brine is a very important issue in alkaline-surfactant flooding. Because of the low solubility product of calcium carbonate, soft water should be used to prepare the solutions for injection. The benefit of using sodium carbonate is that it sequesters calcium ion concentration. For a detailed discussion on mixing with formation brine, refer to our previous work (Hirasaki and Zhang, 2004).

2.3. Surfactant/electrolyte solutions

The appearance of surfactant solutions is very important, because unclear solutions may cause a variety of problems, such as high adsorption (Hirasaki and Zhang, 2004), high viscosity which can occur when gel or liquid crystals are present and result in the prohibition of their application to tertiary oil recovery (Healy and Reed, 1973). The appearance of $y\%$ Blend/ 1% $\text{Na}_2\text{CO}_3/x\%$ NaCl was plotted in Fig. 1. For this

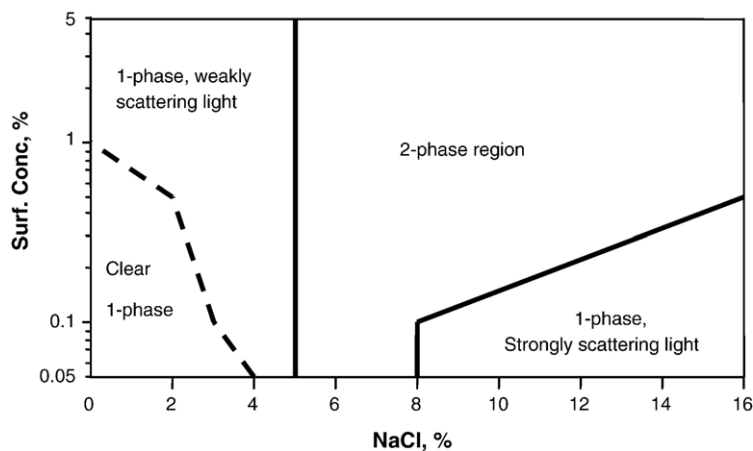


Fig. 1. The appearance of $x\%$ Blend/ 1% $\text{Na}_2\text{CO}_3/y\%$ NaCl (refer to Section 2.3 for the meaning of the legend).

Blend surfactant, phase separation happens at a certain salinity-5% NaCl, which is not affected by surfactant concentration. Solutions in two phase region should not be used, which can result in poor oil recovery as will be shown in Section 5. An external light was applied to solutions in one phase region. If a solution does not scatter light, it is called a “clear” solution. Otherwise, it is labeled “weakly scattering light” or “strongly scattering light” according to the intensity of the light scattered.

3. Wettability alteration on calcite plate

Carbonate surfaces are usually positively charged in neutral pH brine (Hirasaki and Zhang, 2004). This attracts negatively charged compounds in crude oils, such as carboxylic acids. Therefore carbonate formations are usually intermediate-wet to oil-wet. According to Treiber et al. (1972), 84% of carbonate formations are oil-wet, while 8% intermediate-wet, and 8% water-wet. Chilingar and Yen (1983) reported similar results: 80% oil-wet, 12% intermediate-wet, and 8% water-wet.

The wettability of the crude oil MY3 was evaluated by measuring the water advancing contact angle on marble plates. The plates were solvent cleaned, polished on a diamond lap to remove the surface layer, pre-equilibrated with 0.1 M NaCl brine overnight, then aged in the crude oil for 24–48 h at 80 °C. After cooling, the plate was immersed in an optical cell filled with 0.1 M NaCl brine. After all motion had stopped, an oil patch was left on the substrate, as shown in Fig. 2(a). It is clear that the plate is oil-wet since the water advancing contact angle is near 180°.

The effect of alkaline/surfactant solutions on wettability alteration is demonstrated in Figs. 2 and

3. The displacement of oil by reduction of the interfacial tension and the alteration of the wettability upon replacement of the brine with alkaline/surfactant solutions are shown as a function of time. The 0.05% Blend/1% Na₂CO₃/0.5% NaCl system, Fig. 2(b), showed oil streaming off from the surface at early times as a result of the reduction in interfacial tension. Later, the oil left on the plate formed 1 mm oil drops, which were observed with higher magnification. Contact angles were observed to decrease with time, Fig. 2(c)–(e). The final contact angles ranged from 80° to 140°.

Low tension in 0.05% Blend/1% Na₂CO₃/10% NaCl system lasted for a much longer time and only a few tiny drops around 0.05 mm were left on the plate at the end of the experiment, Fig. 3. The wettability of the marble plate was altered to intermediate-wet.

Similar observations were made for 0.05% Blend surfactant at other sodium carbonate and sodium chloride concentrations. The drop configurations after 50 h are illustrated in Fig. 4, and the measured contact angles and drop sizes are summarized in Figs. 5 and 6. When sodium carbonate concentration was increased from 0.45 to 1.2 M, both contact angle and drop size decreased, Figs. 4(a)–(c) and 5. But for 1% Na₂CO₃/x% NaCl system, when sodium chloride concentration was increased from 0.5% to 16%, contact angle changed little, Fig. 4(d)–(g), while the drop size reached a minimum around 10% NaCl, and is un-measurable at 12%, where at the end of the experiment, no drops could be observed with the maximum magnification, Fig. 6. The existence of minimum drop size indicates that at least transient interfacial tension experienced a minimum as sodium carbonate or sodium chloride concentration is increased. For dependence of hydrostatic

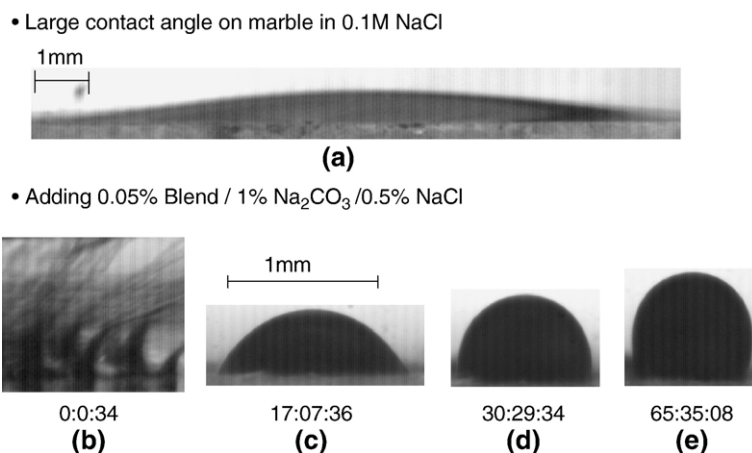


Fig. 2. Wettability alteration of a marble plate with 0.05% Blend/1% Na₂CO₃/0.5% NaCl.

Adding 0.05% blend/ 1% Na_2CO_3 / 10% NaCl.

Oil kept on leaving the marble plate as shown

below:

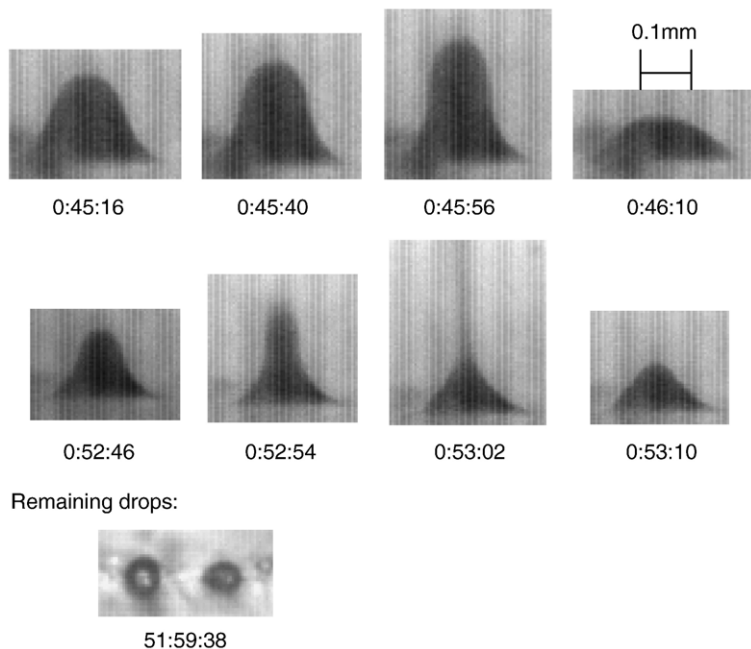


Fig. 3. Wettability alteration of calcite plate with 0.05% Blend/1% Na_2CO_3 /10% NaCl.

configurations of axisymmetric oil drops on interfacial tension and contact angle, see our previous paper (Hirasaki and Zhang, 2004).

Similar to drop size, the amount of oil remaining on the marble plate in 0.05% Blend/1% Na_2CO_3 /NaCl system also went through a minimum at 10–12%, when sodium chloride concentration was increased from 0.5% to 16%, as shown in Fig. 7.

Wettability alteration with several anionic surfactants and sodium carbonate was examined by

Seethepalli et al. (2004). Most of the surfactants were shown to be able to alter wettability of calcite surfaces as well as or better than the cationic surfactant-dodecyltrimethylammonium bromide (DTAB). The best surfactant was Alfoterra 38, with a water RECEDING contact angle of about 32–50°. They reported only the receding contact angle because the drops were smaller than 0.1 mm, and it was difficult to measure an accurate contact angle, so a fresh oil drop was introduced to the plate which was

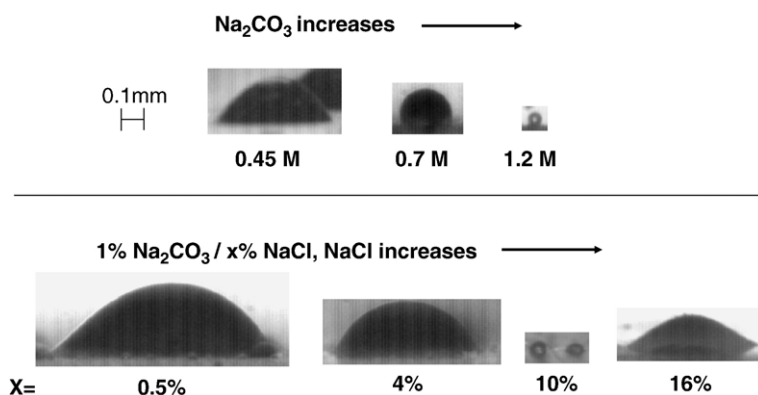


Fig. 4. Final drop configuration after wettability alteration with 0.05% Blend surfactant and Na_2CO_3 or 1% Na_2CO_3 /x% NaCl. Time: greater than 50 h.

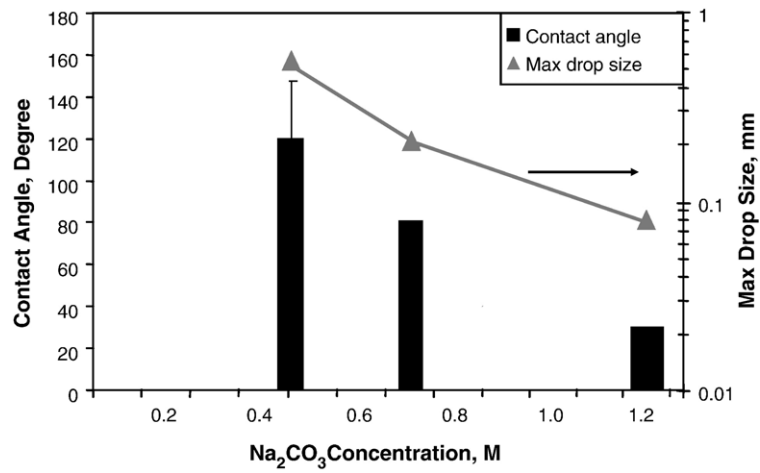
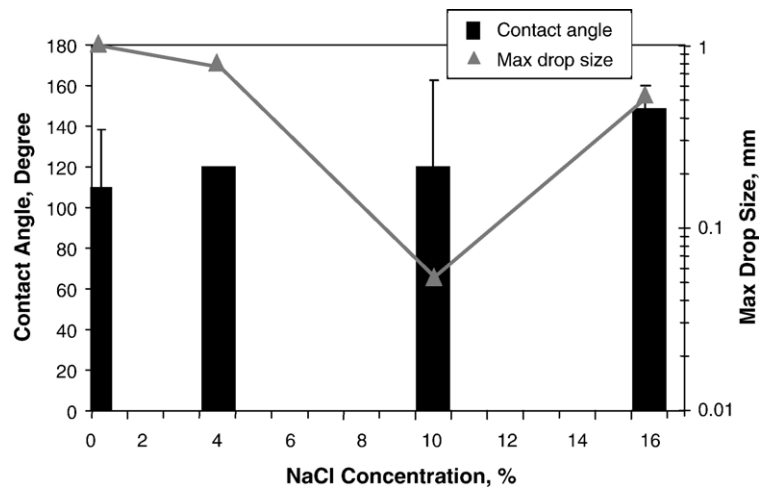
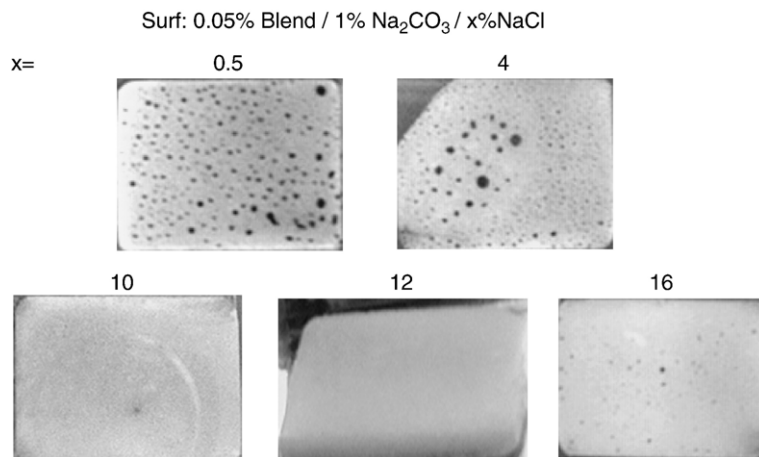
Fig. 5. Wettability alteration with 0.05% Blend/ Na_2CO_3 .Fig. 6. Wettability alteration with 0.05% Blend/1% Na_2CO_3 /x%NaCl.

Fig. 7. Effect of salinity on oil remaining on the marble plate. Time: greater than 50 h.

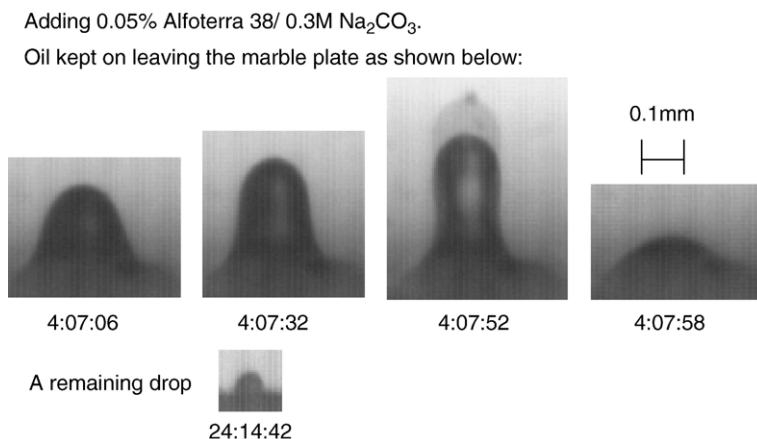


Fig. 8. Wettability alteration of calcite plate with 0.05% Alfoterra 38/0.3 M Na₂CO₃.

washed with brine after the surfactant treatment (the process was called “post-wettability test”).

Wettability alteration with 0.05% Alfoterra 38/0.3 M Na₂CO₃ was also performed in our laboratory, and results are shown in Fig. 8. The phenomena were observed to be similar to those of 0.05% Blend/1% Na₂CO₃/10–12% NaCl. The remaining drop showed a water ADVANCING contact angle of about 90°. Therefore, Alfoterra 38 in 0.3 M Na₂CO₃ can only alter wettability to intermediate-wet, not water-wet.

4. Phase behavior

The objective of studying phase behavior is to determine the optimal salinity from visual observation of the tubes. The optimal salinity could also be determined from interfacial tension between microe-

mulsion and excess phases (Healy et al., 1976). But because the low surfactant concentration results in little microemulsion in the Type III region, measurements are usually either interfacial tension between excess phases, or non-equilibrium measurement at high Water/Oil Ratio (WOR). The problems of both approaches are discussed below.

4.1. Problematic interfacial tension measurements between excess phases

Phase behavior and interfacial tension between excess phases were found to change with separation time. For example, interfacial tension of 0.05% Blend/Na₂CO₃ was first measured after 19 days of settling, with the minimum tension near 10^{−4} mN/m (dyne/cm), Fig. 9. The tension was measured again after 110 days of

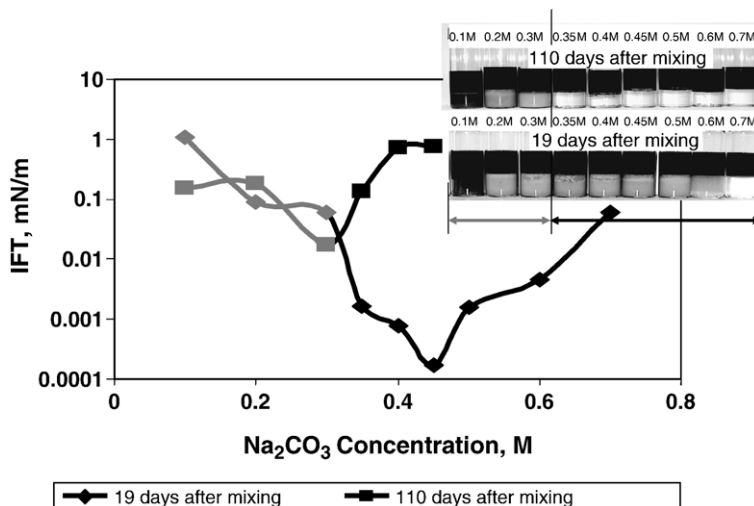


Fig. 9. Phase behavior and IFT of 0.05% Blend surfactant/Na₂CO₃ change with settling time.

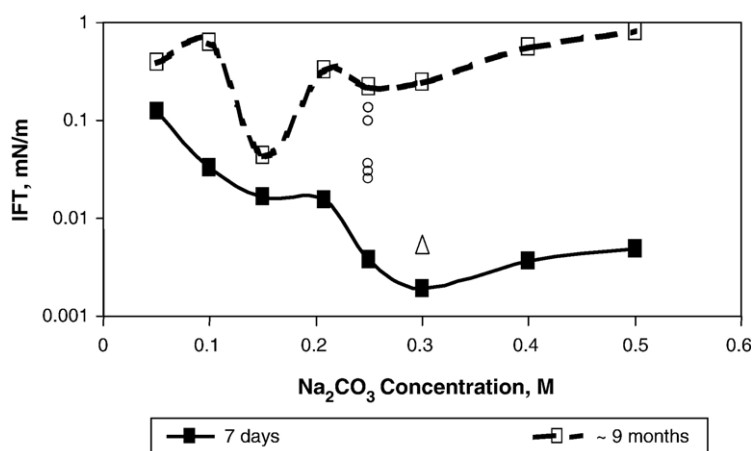


Fig. 10. IFT of 0.05% TDA-4PO/ Na_2CO_3 change with settling time. After long time of settling, interfacial tension went up, but the addition of middle layer lowered it again (represented by unfilled spheres and triangles. Δ : After 9 months settling, added about 0.03 ml of the middle layer in addition to excess aqueous and oil phase. $\circ$: After 9 months settling, added different amount of the middle layer to excess aqueous and oil phases. From top to bottom, 0.001, 0.003, 0.02, 0.05, 0.035 ml middle layer was added.)

settling. It was found that if the lower phase macro-emulsion had not separated, interfacial tension was very close to the first measurement. But if the lower phase had separated, when sampling from the excess phases, because surfactant went to the middle layer, there was little surfactant present to lower the interfacial tension.

Similar phenomena were observed for 0.05% TDA-4PO/ Na_2CO_3 system, Fig. 10. Interfacial tension between excess phases was low after 7 days of settling, but went up significantly after 9 months. But when some of the middle layer was sampled along with excess phases after 9 months, the interfacial tension could be lowered again, especially in the case of 0.3 M Na_2CO_3 , the tension was lowered almost to

the earlier value. But this approach depends on where to sample the middle layer, the middle layer composition (the middle layer could consist of more than one phases) and how much of the middle layer is sampled. Therefore the measurement is usually not reproducible.

4.2. Water/oil ratio

Phase behavior was also found to change with WOR. Fig. 11 illustrates the phase behavior of 0.05% Blend/1% $\text{Na}_2\text{CO}_3/\text{NaCl}$ at WOR of 1:1 and 3:1. At WOR of 1:1, Fig. 11 (a), it is a lower phase emulsion system at 0.5% NaCl, and upper phase emulsion

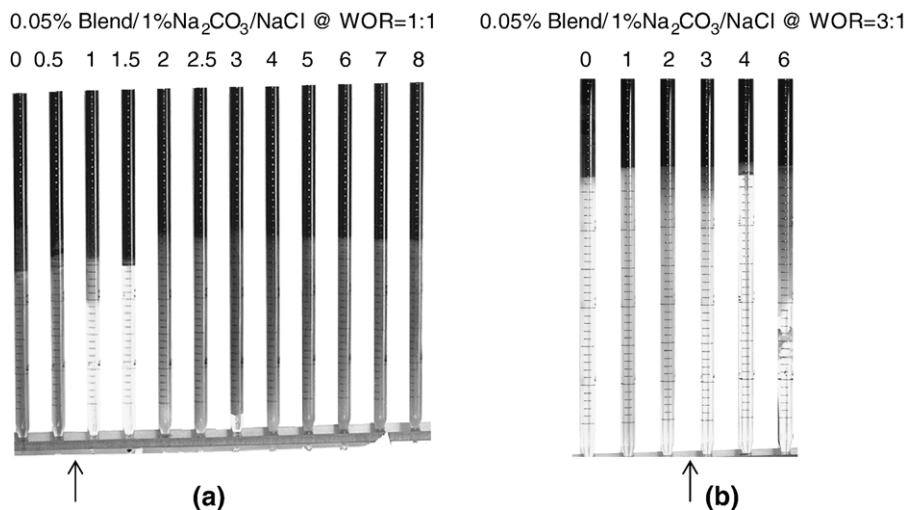


Fig. 11. Phase behavior is a function of WOR. Arrows indicate optimal sodium chloride concentrations.

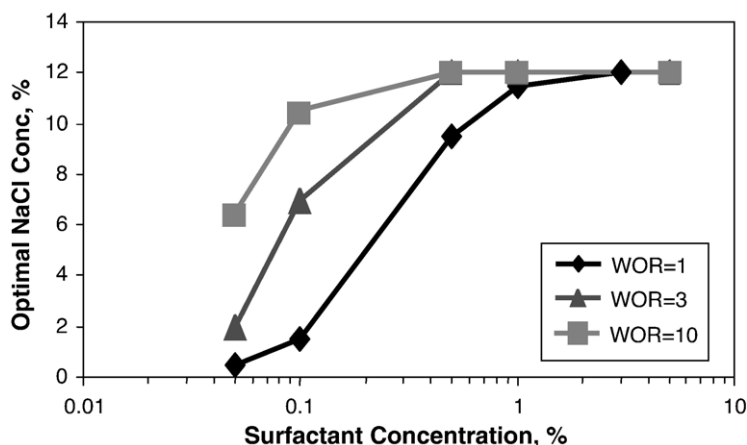


Fig. 12. Optimal sodium chloride concentration as a function of WOR and surfactant concentration for crude oil MY3 and the Blend surfactant (settled for more than 6 months).

system at 1%, therefore the optimal sodium chloride concentration is in between. Similarly, at WOR of 3:1, Fig. 11 (b), optimal sodium chloride concentration is between 2% and 3%. Optimal salinities for other WOR values and surfactant concentrations were similarly determined, and are plotted in Fig. 12.

The non-equilibrium interfacial tension measurement by spinning drop method is at high WOR. In non-equilibrium measurements, low tension is often only a transient phenomenon. The soap is extracted from the oil and is solubilized by the micelles in the surfactant solution. Interfacial tension at different WOR may differ by orders of magnitude (Hirasaki and Zhang, 2004).

The dependence of optimal salinity on WOR also explains why the drop size in wettability alteration experiments depends on electrolyte strength. In

wettability alteration experiment, a small patch of oil is surrounded by a large amount of aqueous solution, so the WOR is very high. When electrolyte concentration is increased, phase behavior gradually changes from under-optimum to optimum to over-optimum. Since IFT is the lowest at optimum, the maximum stable drop size determined by Bond number experiences a minimum at optimal salinity.

Dependence of optimal salinity on surfactant concentration and WOR can be correlated with natural soap/surfactant mole ratio, Fig. 13. The amount of soap was calculated based on the acid number of the crude oil 0.2 mg potassium hydroxide/gram oil. Lower ratios correspond to the dominance by the synthetic surfactant. The curve plateaus at around 12% NaCl, which is close to the optimal salinity of the Blend surfactant.

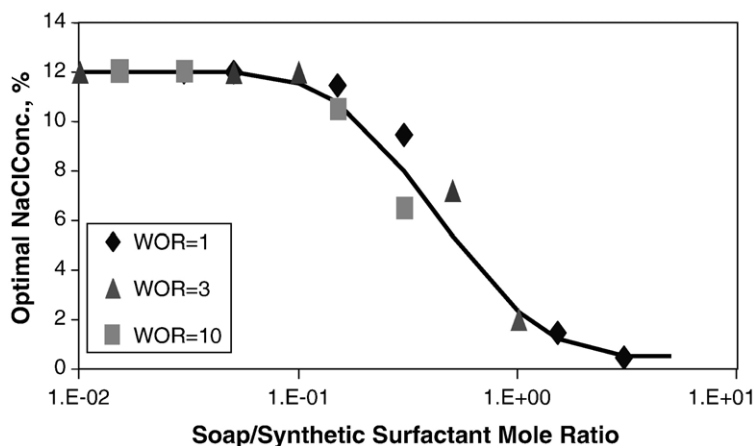


Fig. 13. Optimal sodium chloride concentration as a function of natural soap/synthetic surfactant mole ratio for crude oil MY3 and the Blend surfactant (settled for more than 6 months).

5. Spontaneous imbibition in capillary gap between vertical parallel plates

The schematic set up of the experiment is shown in Fig. 14. A marble plate pre-equilibrated with 0.1 M NaCl brine overnight, then aged in crude oil MY3 at 80 °C for 48 h, is placed in an optical cell with two pieces of plastic film as spacers to create a 13 µm gap between the plate and the front wall of the cell. A bevel is ground at the bottom of the plate to allow the aqueous phase to be present without flow resistance. The front wall of the glass cell has been treated with a dilute solution of hexadecyltrimethylammonium bromide (CTAB) to make it preferentially oil-wet.

Oil in the gap is not displaced when the cell is filled with 0.1 M NaCl brine and left for 20 h, Fig. 15(a). The buoyancy forces cannot overcome the capillary entry pressure to displace the oil from the gap. However, when the brine is replaced with 0.05% Blend/1% Na₂CO₃/1%NaCl, spontaneous imbibition of the aqueous phase occurs, Fig. 15(b). The fraction of oil displaced is plotted against dimensionless time for gravity drainage (refer to Hirasaki and Zhang, 2004, for scaling method) for a range of electrolyte strengths in Fig. 16. Here, the flow is assumed to be plane Poiseuille flow between parallel plates.

$$t_{D,g} = \frac{k\Delta\rho g t}{\mu_o L} \quad (1)$$

$$k = \frac{h^2}{12} \quad (2)$$

where

k	permeability
$\Delta\rho$	density difference between crude oil and aqueous solution;
g	acceleration due to gravity;

t	time elapsed;
μ_o	viscosity of the crude oil;
L	height of the plate;
h	distance between the parallel plates.

Compared with the analytical solution for gravity drainage with linear relative permeability assuming zero capillary pressure, the displacement rate is about an order of magnitude slower. This can be caused by two reasons: 1) the accumulation of a large amount of oil (compared with that in the gap) in the bevel at the time surfactant solution was added; and 2) the plate surfaces being not perfectly flat, and the gap width being less than that of the spacers.

In the 0.05% Blend/1% Na₂CO₃/NaCl systems, oil displacement in the gap peaks at 3% NaCl, which is close to the optimal salinity of WOR of 3:1 (Fig. 12). At 6% NaCl, the oil displaced is the least. It may be caused by the phase separation of the surfactant solution (Fig. 1), after which the surfactant rich phase stayed at the bottom of the cell. Thus the surfactant solution could not propagate in the gap, which resulted in the small displacement fraction.

6. Surfactant adsorption

In previous work (Hirasaki and Zhang, 2004), static adsorption of anionic surfactants on calcite powder was discussed. Because the addition of carbonate/bicarbonate ions changes the charge at calcite/brine interface from positive to negative, the adsorption of anionic surfactants in the presence of sodium carbonate is reduced by an order of magnitude. It also identified that turbid solutions with TDA-4PO and sodium carbonate resulted in high adsorption even in the presence of sodium carbonate. The following sections discuss the static and dynamic adsorption on dolomite.

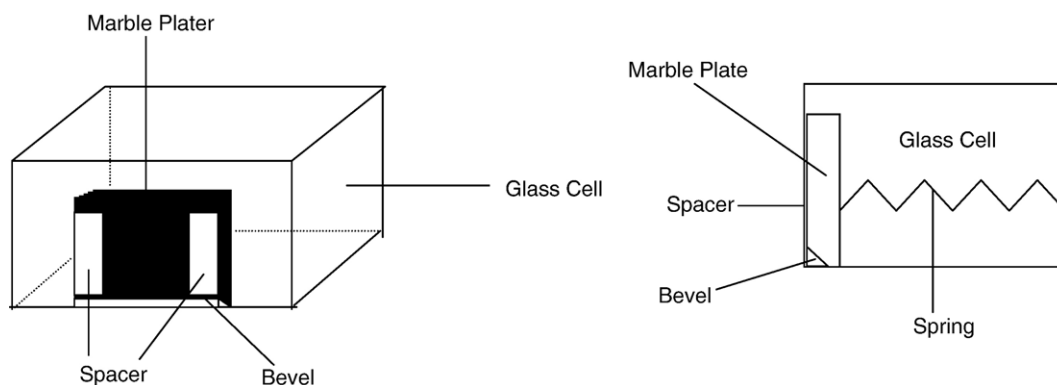


Fig. 14. A calcite (marble) plate has two plastic films to create a 13 µm gap between the plate and the front of an optical cell.

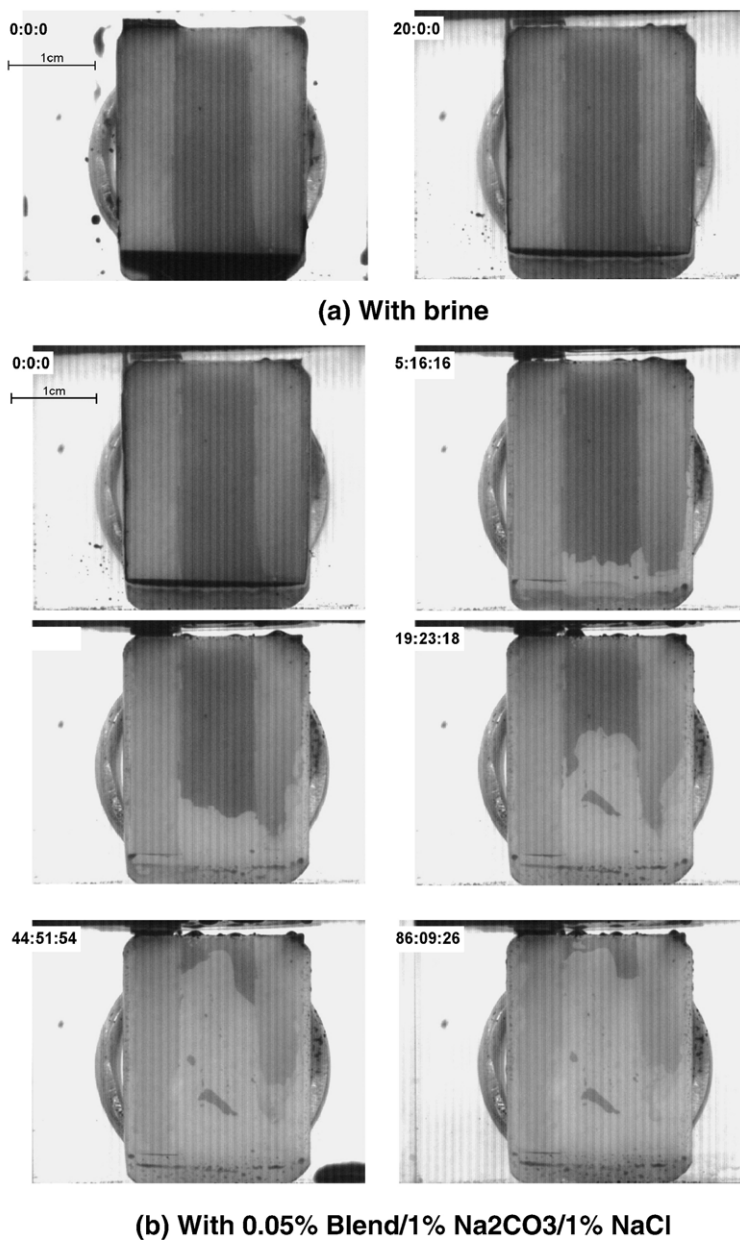


Fig. 15. Displacement of crude oil in a capillary gap between vertical parallel plates with brine (a) or with 0.05% Blend/1% Na₂CO₃/1% NaCl (b).

6.1. Static adsorption on dolomite sand

The adsorption of the Blend surfactant on dolomite sand without and with sodium carbonate is shown in Fig. 17. The adsorption on dolomite sand is similar to that on calcite powder (Hirasaki and Zhang, 2004) in that 1) the plateau adsorption without sodium carbonate in both cases is about 0.002 mmol/m²; and 2) the addition of sodium carbonate reduces the surfactant adsorption by a factor of 10.

6.2. Dynamic adsorption on dolomite sand

A one-foot column packed with dolomite sand was first filled with de-ionized water. Then the surfactant solution containing NaCl as a non-adsorbent tracer was pumped into the column, and effluent collected. The concentration of the anionic surfactant was measured by titration, and NaCl concentration was determined by the solution conductivity.

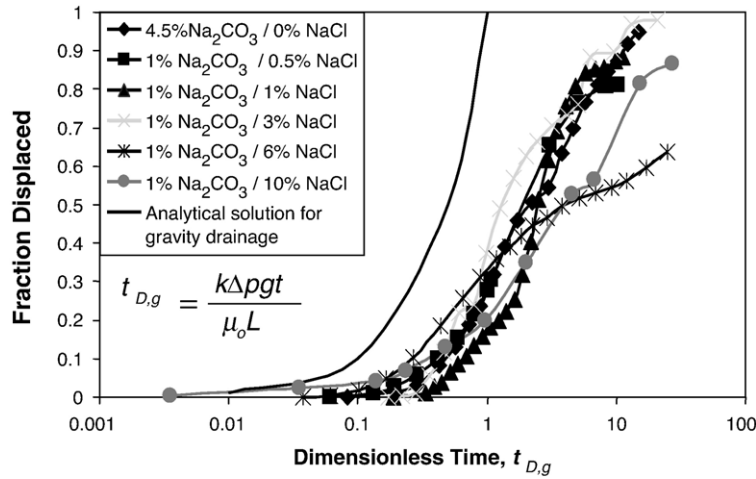


Fig. 16. Spontaneous imbibition in a capillary gap between vertical parallel plates as a function of dimensionless time for gravity drainage (the dimensionless time is listed in Eq. (1)).

The displacement process is fitted with a one-dimensional model. The assumptions made include 1) the adsorption isotherm has a constant slope, i.e. the adsorption is linear with the concentration; and 2) the adsorption process reaches equilibrium immediately.

The dimensionless surfactant concentration C found by solving the mass conservation equation for adsorption is:

$$C = \frac{1}{2} \left[1 - \frac{2}{\sqrt{\pi}} \int_0^\eta e^{-\eta^2} d\eta \right] = \frac{1}{2} \text{erfc}(\eta) \quad (3)$$

$$\eta = \frac{x_D - \frac{t_D}{(1+\beta)}}{2\sqrt{\frac{t_D}{Pe(1+\beta)}}} \quad (4)$$

where

$$t_D = \frac{vt}{L};$$

$$x_D = \frac{x}{L};$$

$\text{erfc}()$: error function;

β : slope of the dimensionless adsorption isotherm;

Pe : Peclet number;

v : interstitial velocity;

L : length of the sand column.

With the measured effluent surfactant concentration and non-adsorbent tracer (Cl^-) concentration, β is

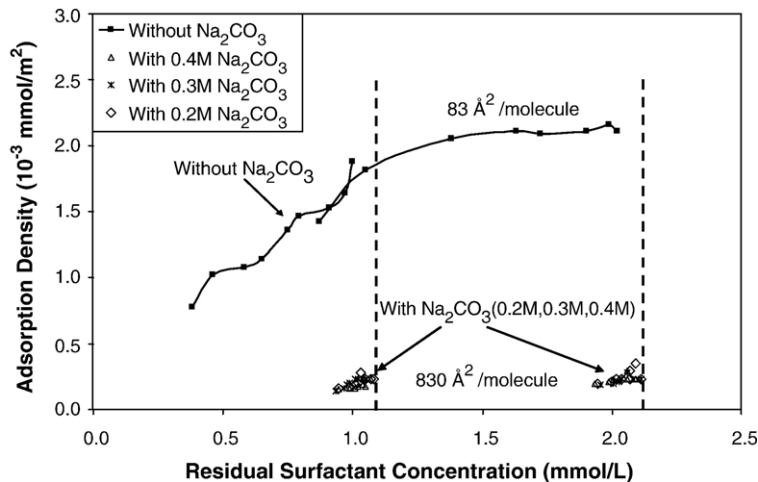


Fig. 17. Static adsorption of the Blend surfactant on dolomite sand (dashed lines indicate original surfactant concentrations).

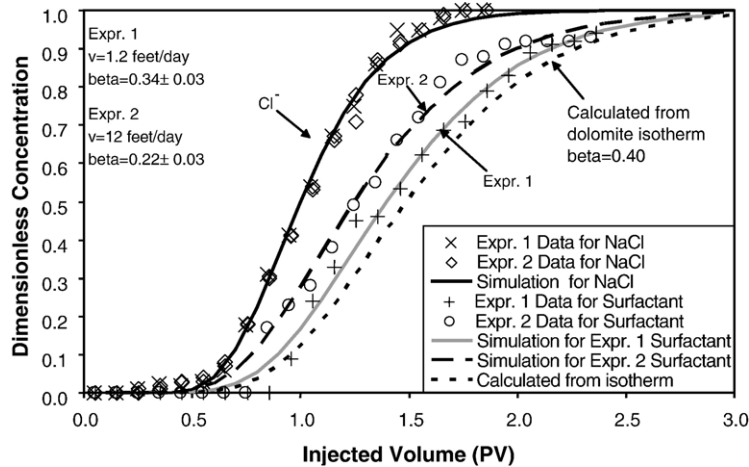


Fig. 18. Dynamic adsorption of 0.2% Blend surfactant on dolomite sand.

calculated from Eqs. (3) and (4). A large β indicates a high surfactant adsorption.

Fig. 18 demonstrates that the adsorption of surfactants is not an instantaneous process and depends on the flow rate. At a high interstitial velocity of 12 ft/day, the retardation is much smaller than that at 1.2 ft/day. Even at the lower flow rate, β is less than that calculated from the static adsorption isotherm (Fig. 17).

The addition of sodium carbonate also significantly reduces dynamic surfactant adsorption, as shown in Fig. 19. β is reduced from 0.34 to 0.07.

7. Conclusions

1) The system of crude oil MY3, brine and marble plate is strongly oil-wet.

- 2) With sodium carbonate/anionic surfactant system, advancing contact angle ranged from intermediate-wet to preferentially water-wet.
- 3) Advancing contact angle and drop size of MY3 crude oil on a marble plate are dependent on electrolyte type and concentration. Drop size experiences a minimum with electrolyte strength. Contact angle decreases with increasing sodium carbonate concentration to the maximum concentration investigated. When sodium carbonate concentration is fixed at 1%, sodium chloride concentration does not seem to affect wettability alteration.
- 4) IFT measurements are problematic for alkali/anionic surfactant systems. At low surfactant concentration, IFT is measured between excess phases, which changes with settling time because of the separation of surfactant from the excess brine phase.

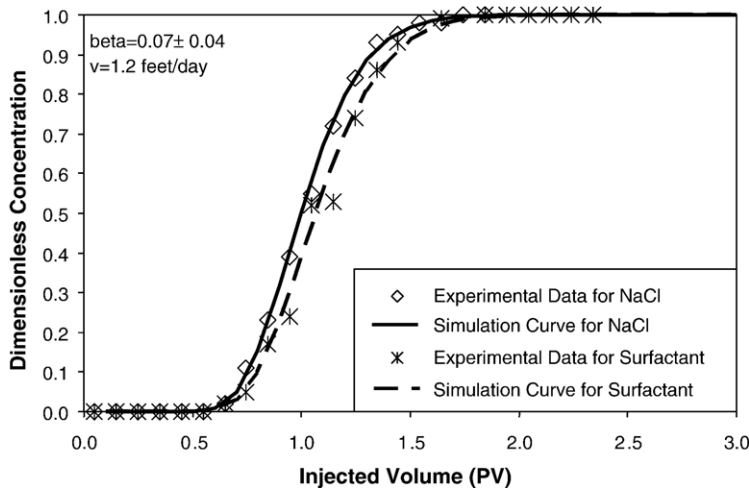


Fig. 19. Dynamic adsorption of 0.2% Blend surfactant on dolomite sand in presence of 0.3 M Na_2CO_3 .

- 5) Alkali/surfactant phase behavior is dependent on salinity, surfactant concentration, and WOR. Dependence of optimal salinity on surfactant concentration and WOR can be correlated with natural soap/surfactant mole ratio.
- 6) Flow rate affects dynamic surfactant adsorption. A relatively low rate is required for the adsorption to reach equilibrium.
- 7) Anionic surfactant adsorption on dolomite is significantly reduced with sodium carbonate.

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