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Review of Surfactant Enhanced Oil Recovery in Carbonate Reservoirs

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Abstract

About half of proven conventional oil reserves are in carbonate reservoirs. Due to complex structures, formation heterogeneities and oil-wet/mixed wet conditions, etc., the oil recovery factor in carbonate reservoirs is very low. There is increasing interest in improve oil recovery using surfactants, as the surfactant EOR has the potential after other EOR methods have been tried.

This paper reviews the models of wettability alteration using surfactants and upscaling models related to oil recovery in carbonate reservoirs. Chemicals used in carbonate reservoirs are reviewed. The field cases where surfactants were used to stimulate oil recovery are analyzed.

Key words: Enhanced oil recovery; Carbonate reservoirs; Wettability alteration; Chemical EOR

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NOMENCLATURE

c	ratio of the gravity force to the capillary force, dimensionless
C_{pc}	capillary pressure end-point in Equation 4, m/t^2
C_{surf}	equilibrium surfactant concentration, m/L^3, vol.% or mol/L pore volume
$\hat{C}_{surf}$	adsorbed surfactant concentration, m/L^3, vol.% or mol/L pore volume
g	acceleration of gravity, L/ t^2
k	permeability, L^2, md or m^2
k_r	relative permeability, fraction or %
L_c	characteristic length, L, m or ft
M_e^*	effective mobility at the displacement front (S_{wf}), L^{3}t/m, md/cP
n	exponent to define a relative permeability
N_T	trapping number, dimensionless
P_c	capillary pressure, m/Lt^2, Pa or psi
P_c*	capillary pressure at the displacement front, m/Lt^2, Pa or psi
R	recovery factor (total oil produced/the original oil in place), fraction or %
R*	normalized recovery factor
S	saturation, fraction or %
$\overline{S}$	normalized saturation, fraction or %
S_{wf}	water saturation at the displacement front, fraction or %
S_{wi}	initial water saturation, fraction or %
t	time, t, s or days
t_D	dimensionless time
t_g	gravity reference time, t, s or days
T	trapping parameter, dimensionless
Greek symbols	
Δ	operator that refers to a discrete change
Φ	porosity, fraction or %
ρ	density, m/L^3, g/cm^3
μ	viscosity, m/Lt, mPa·s (cP)
σ	interfacial tension, m/t^2, mN/m
θ	contact angle, degree
w	interpolation scaling factor for p_c and k_r, dimensionless
Superscript	
n	end-point
high	at a high trapping number
low	at a low trapping number
ow	oil-wet
ww	water-wet

Subscript

j	phase j
j’	conjugate phase of phase j
r	residual

INTRODUCTION

Currently, more than 85% of world energy consumption comes from fossil fuels and the World Energy Outlook shows that energy demand could rise by 53% between now and 2030[1]. Although most energy experts agree that the world’s energy resources are adequate to meet this projected growth, more reserves will be needed. This means the petroleum industry will have to increase recovery factors significantly from all types of reservoirs. Schlumberger Market Analysis 2007 shows that more than 60% of the world’s oil and 40% of the world’s gas reserves are held in carbonates[2]. BP Statistical Review 2007 shows that the Middle East has 61% of the world’s proved conventional oil reserves[3]; approximately 70% of these reserves are in carbonate reservoirs[2]. The Middle East also has 41.3% of the world’s proved gas reserves[3]; 90% of these gas reserves lie in carbonate reservoirs[2]. It is clear that the relative importance of carbonate reservoirs compared with other types of reserves will increase dramatically during the first half of the 21st century. The world has 3,000 billion barrels of remaining oil and 3,000 trillion SCF gas in place in carbonates. However, due to complex structures, formation heterogeneities and oil-wet/mixed wet conditions, etc., the oil recovery factor in carbonate reservoirs is very low, probably below 35% on the average, and it is lower than that in sandstone reservoirs. Therefore, there is increasing interest to improve hydrocarbon recovery from carbonate reservoirs, as we are facing challenges to make up depleted reserves.

Although there is a great potential to improve oil recovery in carbonate reservoirs, the research in this area is very limited due to technical and economical challenges. Most of field development schemes in carbonate reservoirs are limited to water flooding and gas flooding with low ultimate recovery factors. A few surfactant-related EOR methods have been tried in carbonate fields, although more polymer flooding projects were carried out before 1990s.

Chemical EOR research in carbonate reservoirs has been focused on using surfactants to change oil-wet to water-wet to enhance water imbibition into matrix blocks. Wettability alteration results in spontaneous imbibition of water into oil containing matrix, thus driving oil out of matrix. These surfactants include cationics, nonionics and anionics. It has been found that anionic function to reduce IFT and associated buoyancy are very important mechanisms[4]. The problem is that such process is slow. Upscaling from laboratory results to field application need more research work to be done. If the process is deemed to be slow, forced imbibition has to be applied. The future research should be on the area to optimize different development schemes and EOR methods in carbonates.

In this paper, we first present the problems with carbonate reservoirs, followed by models of wettability alteration using surfactants. We then discuss the upscaling models related to oil recovery in fractured carbonate reservoirs. Chemicals used in carbonate reservoirs are reviewed. Finally we analyzed several field cases using surfactants to stimulate oil recovery.

1. PROBLEMS IN CARBONATE RESERVOIRS

The average recovery factor in both sandstone and carbonate reservoirs is about 35%. The average recovery factor in sandstone reservoirs is higher than in carbonates. Therefore, the average recovery factor in carbonate reservoirs is below 35%. Carbonate reservoirs present a number of specific characteristics posing complex challenges in reservoir characterization, production and management. Carbonate rocks typically have a complex texture and pore network resulting from their depositional history and later diagenesis.

Heterogeneity may exist at all scales-in pores, grains and textures. The porosities of carbonate rocks can be grouped into three types: connected porosity which is the porosity between the carbonate grains, vugs which are unconnected pores resulting from the dissolution of calcite by water during diagenesis, and fracture porosity which is caused by stresses following deposition. Diagenesis can create stylolite structures which form horizontal flow barriers, sometimes extending over kilometers within the reservoir, having a dramatic effect on field performance. Fractures can be responsible for water breakthrough, gas coning and drilling problems such as heavy mud losses and stuck pipe. Together, these three forms of porosities create a very complex path for fluids and directly affect well productivity.

In addition to the variations in porosity, wettability is a further heterogeneous characteristic in carbonates. The great majority of sandstone reservoirs are probably water-wet. However, the aging of carbonate rocks containing water and oil turns initially water-wet rocks into mixed-wet or even oil-wet. This means that oil can adhere to the surface of carbonate rock and it is therefore harder to produce. Most carbonate reservoirs are believed to be mixed wet or oil-wet.

2. MODELS OF WETTABILITY ALTERATION USING SURFACTANTS

One important mechanism using surfactants in carbonate reservoirs is to change wettability from oil-wet to more water-wet. Wettability alteration has been formulated with surfactant adsorption, and relative permeabilities and capillary curves are modified based on the degree of wettability alteration. Delshad *et al.*[5] used this parameter to modify capillary curve and relative permeability curves:

$$\omega = \frac{\hat{C}_{\mathrm{surf}}}{C_{\mathrm{surf}} + \hat{C}_{\mathrm{surf}}} \tag{1}$$

where w is the interpolation scaling factor, $\hat{C}_{\mathrm{surf}}$ and C_{surf} represent the adsorbed and equilibrium concentrations of surfactant, respectively. The capillary curve and relative permeability curve are then modified:

$$k_r = \omega k_r^{ww} + (1-\omega) k_r^{ow} \tag{2}$$

$$p_C = \omega p_C^{ww} + (1-\omega) p_C^{ow} \tag{3}$$

where the superscript ww and ow denote water-wet and oil-wet conditions, k_r is the relative permeability, and p_c is the capillary pressure. These equations are proposed based on the assumption that surfactant adsorption on calcite rock surfaces increases water-wetness, although this assumption may not be generally valid. The capillary pressure p_c is a scaled with the interfacial tension as follows:

$$p_{cjj'}^{ww} = C_{pc}\sqrt{\frac{\varphi}{k}}\,\frac{\sigma_{jj'}^{ww}}{\sigma_{jj'}^{ow}}\left(1 - \frac{S_j - S_{jr}}{1 - \sum_{j=1}^{3} S_{jr}}\right)^{E_{pc}} \quad j = 1,2,3 \tag{4}$$

where $C_{pc}\sqrt{\varphi / k}$ takes also into account the effect of permeability and porosity using the Leverett-J function[6], φ is the porosity and k is permeability, σ is the interfacial tension, S is the saturation at the water-wet condition, the subscript j and j' denote the phase j and the conjugate phase j', respectively, and E_{pc} is the exponent for capillary pressure. The above model is implemented in UTCHEM version 9.95[7]. In ECLIPSE 2009 version[8], a table of w versus surfactant adsorption is input.

Another model explicitly including wetting angle effect was proposed by Adibhatla *et al.*[9]. In their model, a simple interpolation technique is used to consider the wettability effect on residual saturations and trapping numbers:

$$\frac{S_{rj}^{low} - S_{r,b1}^{low}}{\cos\theta - \cos\theta_0} = \frac{S_{r,b2}^{low} - S_{r,b1}^{low}}{\cos(\pi - \theta_0) - \cos\theta_0} \tag{5}$$

$$\frac{\ln T_j - \ln T_{b1}}{\cos\theta - \cos\theta_0} = \frac{\ln T_{b2} - \ln T_{b1}}{\cos(\pi - \theta_0) - \cos\theta_0} \tag{6}$$

In the above equations, the superscript "low" refers to the parameter value at a low trapping number. To use the above equations, the residual saturation values of S_{rj}^{low} and T_j for a pair of base phases are needed. These base phases are represented with subscripts "b1" and "b2". Without losing the generality, it is assumed the contact angle of the base phase b1 before wettability alteration is θ_0, and the contact angle of the base phase b2 is $(\pi-\theta_0)$. Note that oil and aqueous phases are not distinguished (a dummy phase j is used). The residual saturation at a low trapping number, S_{rj}^{low}, and the trapping parameter, T_j, for phase j are calculated from the above equations, respectively.

Once S_{rj}^{low} and T_j at the altered contact angle q are obtained from the above equations, the residual saturation at a different trapping number N_T is calculated by

$$S_{rj} = S_{rj}^{high} + \frac{S_{rj}^{low} - S_{rj}^{high}}{1 + T_j N_T} \tag{7}$$

where S_{rj} is the residual saturation of phase j at the trapping number N_T. The superscript "high" refers to the parameter value at a high trapping number. The trapping number is the capillary number including gravity effect which is discussed in detail in Sheng[10]. In this equation, S_{rj}^{high} is typically 0. Given the values of S_{rj}^{low} and T_j (the latter can be obtained by fitting experimental data), Equation 7 yields the desaturation curve (S_{rj} versus N_T) that is similar to the capillary desaturation curve (CDC).

Before we present an end-point k_r of a phase at a trapping number, we need to discuss the relationship between the end-point k_r and the conjugate residual saturation first. According to Delshad *et al.*[11],

$$\frac{k_{rj}^{e} - k_{rj}^{e,high}}{k_{rj}^{e,low} - k_{rj}^{e,high}} = \frac{S_{j'r} - S_{j'r}^{high}}{S_{j'r}^{low} - S_{j'r}^{high}} \tag{8}$$

where k_{rj}^{e} denotes the end point relative permeability of phase j, the superscript low and high correspond to low and high capillary (trapping) numbers, respectively, and the subscript j' denotes the conjugate phase of phase j. In Equation 8, it is assumed that the end-point relative permeability enhancements (and the later exponent decreases) are caused by the residual-saturation reduction of the conjugate phase as a function of the trapping number. However, the residual saturation of the conjugate phase may not be a good predictor for the end-point relative permeabilities and exponents, especially when wettability alteration is involved[12-15].

Combining Equations 7 and 8, we have

$$\frac{k_{rj}^{e} - k_{rj}^{e,high}}{k_{rj}^{e,low} - k_{rj}^{e,high}} = \frac{1}{1 + T_{j'} N_{Tj'}} \tag{9}$$

To derive an end-point relative permeability, k_{rj}^{e}, at a trapping number N_T, we have to consider two factors. One is the effect of trapping number; the other is the effect of wettability alteration. According to Equation 9, the effect of trapping number on k_{rj}^{e} at N_T can be considered using the following equation:

$$\frac{k_{rj}^{e,N_T} - k_{rj}^{e,high}}{k_{rj}^{e,N_{T0}} - k_{rj}^{e,high}} = \frac{1+T_{j'}N_{T0j'}}{1+T_{j'}N_{Tj'}} \tag{10}$$

where k_{rj}^{e,N_T}, $k_{rj}^{e,N_{T0}}$, $k_{rj}^{e,high}$ correspond to the end point relative permeabilities at N_T, N_{T0} and a very high trapping number.

To include the effect of wettability, we may have

$$k_{r,b1}^{e,N_{T0}} - k_{rj}^{e,N_{T0}} = \frac{\cos\theta - \cos\theta_0}{\cos(\pi-\theta_0) - \cos\theta_0}\left(k_{r,b1}^{e,N_{T0}} - k_{r,b2}^{e,N_{To}}\right) \tag{11}$$

Here it is assumed that we have the relative permeability curves measured at a certain trapping number N_{T0} for a pair of base phases with the contact angle θ_0 for the phase b1 and π-θ_0 for the phase b2. Putting Equation 11 into Equation 10, we have the relative permeability curves with the trapping number N_T and the contact angle θ:

$$k_{rj}^{e,N_T} = k_{rj}^{e,high} + \left[k_{r,b1}^{e,N_{T0}} + \frac{\cos\theta - \cos\theta_0}{\cos(\pi-\theta_0) - \cos\theta_0}\left(k_{r,b2}^{e,N_{T0}} - k_{r,b1}^{e,N_{To}}\right) - k_{rj}^{e,high}\right]\frac{1+T_{j'}N_{T0}}{1+T_{j'}N_T} \tag{12}$$

Similarly, the exponents of relative permeabilities are

$$n_j^{N_T} = n_j^{high} + \left[n_{b1}^{N_{T0}} + \frac{\cos\theta - \cos\theta_0}{\cos(\pi-\theta_0) - \cos\theta_0}\left(n_{b2}^{N_{T0}} - n_{b1}^{N_{To}}\right) - n_{rj}^{high}\right]\frac{1+T_{j'}N_{T0}}{1+T_{j'}N_T} \tag{13}$$

Equations 12 and 13 are just conceptual models that qualitatively capture the typical trends observed about the effects of trapping number and wettability on relative permeabilities. Note $T_{j'}$ is the trapping parameter of the conjugate phase of phase j and its value is evaluated with Equation 6 using the contact angle π-θ, where θ is the contact angle of phase j. Again, we assume that the end point value, k_{rj}^{e}, and the exponent n_j, for the phase j are correlated to the residual saturation of the conjugate phase j' through linear interpolation. And the Brooks-Corey model is used to describe the relative permeability

$$k_{rj} = k_{rj}^{e}(\overline{S}_j)^{n_j} \tag{14}$$

$$\overline{S}_j = \frac{S_j - S_{jr}}{1 - S_{jr} - S_{j'r}} \tag{15}$$

The effects of IFT and contact angle on capillary pressure are described with the following equation:

$$p_c = p_{c0}\frac{\sigma\cos\theta}{\sigma_0\cos\theta_0} \tag{16}$$

where p_c and p_{c0} are the capillary pressures, and σ and σ_0 are the interfacial tension between oil and aqueous phases at the contact angle θ and θ_0, respectively.

3. UPSCALING

Either surfactant diffusion process or surfactant induced gravity drainage process through wettability alteration and IFT reduction is slow. Therefore, upscaling the laboratory-scale to the field scale becomes very important. Since the pioneering work by Mattax and Kyte[16] who scaled capillary forced imbibition under specific conditions, several modified formulas have been proposed. Basically, the scaling group for capillary imbibitions is defined in terms of the dimensionless time defined as

$$t_D = \frac{\sigma\sqrt{k/\varphi}}{\mu L_c^2}t \tag{17}$$

where k is the rock permeability, φ is the porosity, σ is the interfacial tension between the wetting and the nonwetting phase, μ is the viscosity, t is the actual time, and L_c is the characteristic length. In the above scaling group, different authors defined μ and L_c differently[16-18]. Although they used different equations to define these parameters, they all used the squared characteristic length. In other words, the imibibition rate, thus recovery rate and total recovery, is inversely proportional to the squared characteristic length. Zhang *et al.*[19] verified Equation 17 in different core dimensions experimentally.

Cuiec *et al.*[20] performed experiments in low permeability chalk samples at high IFT and proposed a reference time including the gravity force as the ratio of viscous to gravity forces as

$$t_g = \frac{L_c\mu_o}{k\Delta\rho g} \tag{18}$$

where t_g is the gravity reference time, μ_o is the oil viscosity, and $\Delta\rho$ is the density difference between water and oil. Sheng[4] upscaled a base simulation model into several models by increasing the each dimension size by 2, 5 and 10 times using UTCHEM (version 9.95). The model volumes are increased by 2, 5 and 10 times along each side. According to Equation 18, if we only change the model sizes, the only variable is L_c. Thus we calculate the normalized time by the real time divided by 2 in the case of "Enlarged by 2x2x2", and similarly in the other cases. The results are shown in Figure 1. It shows that the curves of oil recovery factor versus the normalized time for the models of different sizes almost overlap each other. This indicates that the gravity is the dominant mechanism.

Note that corresponding to Equation 18, the dimensionless time can be defined as

$$t_D = \frac{k\Delta\rho g}{L_c\mu_o}t \tag{19}$$

From this equation we can see that the oil recovery rate is inversely proportional to the characteristic length.

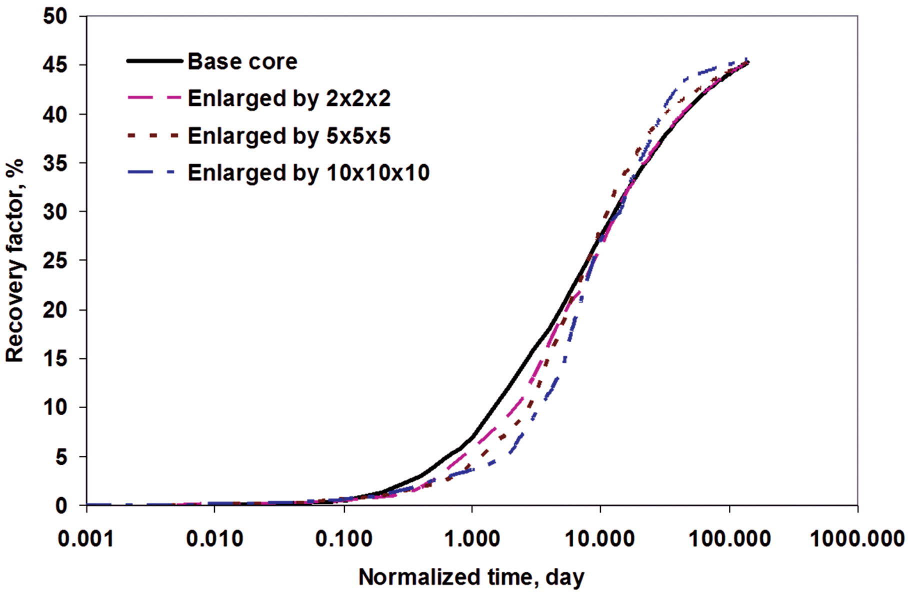

Figure 1
Oil Recovery Factor Versus Normalized Time

Li and Horne[21] derived a scaling model which incorporates both capillary and gravity forces. The model also contained parameters such as mobility and capillary pressure. They tested their scaling model by using the experimental data published by Schechter *et al.*[22], and the fit was surprisingly good when the normalized recovery was plotted versus their defined dimensionless time. Their dimensionless time is

$$t_D = c^2 \left(\frac{M_e^* p_c^* (S_{wf} - S_{wi})}{\varphi L_c^2} \right) t \tag{20}$$

where S_{wf} is the water saturation at the water front, S_{wi} is the initial water saturation, M_e^* is the effective mobility at the water displacement front, p_c^* is the capillary pressure at the water front, φ is the porosity, L_c is the characteristic length, and t is the actual time. The normalized recovery (factor) is

$$R^* = cR \tag{21}$$

where c is the ratio of the gravity force to the capillary force (the Bond number) which is defined as

$$c = \frac{\Delta \rho g L_c}{p_c^* (S_{wf} - S_{wi})} \tag{22}$$

where $\Delta\rho = \rho_w - \rho_o$, (the density difference between water and oil phases), g is the acceleration constant. In Li and Horne's derivation, L_c is the length of the core. Here it is generalized to be the characteristic length. Using these notations, the normalized recovery versus the dimensionless time is

$$R^* \frac{dR^*}{dt_D} = 1 - R^* \tag{23}$$

Høgnesen *et al.*[23] tested the Li and Horne's scaling model using published experimental data for spontaneous imbibitions of aqueous surfactant solution into preferentially oil-wet carbonate reservoirs, which involved wettability alteration. The scaling was performed by plotting the normalized oil recovery versus the dimensionless time. Generally, the experimental data fitted the model surprisingly well. Interestingly, all the tested experimental data scaled well if the heights of the cores were used as the characteristic length in the dimensionless time. That indicates the gravitational force had a very important role in the fluid flow mechanism.

In our simulated cases[4], when the IFT was as low as 0.049 mN/m, the gravitational force alone (without wettability alteration) could not produce oil. In the experiments tested by Høgnesen et al., the IFT ranged 0.3 – 1.0 mN/m. In other words, the IFT's were not at ultralow values. Probably some degree of wettability alteration occurred in those experiments. If the gravitational effect is the dominated mechanism, the oil recovery rate should be scaled with L_c, instead of L_c^2 as in the capillary dominated flow. Further research into the dominating mechanisms and development of correct upscaling models are extremely important to predict field-scale EOR potential.

4. OIL RECOVERY MECHANISMS IN CARBONATES USING CHEMICALS

One mechanism of surfactant stimulation is wettability alteration from oil-wet to mixed-wet or water-wet. Wettability alteration results in spontaneous imbibition of water into oil containing matrix, thus driving oil out of matrix. Cationics and nonionics work based on this mechanism. Cationic surfactants form ion pairs with adsorbed organic carboxylates of crude oil and stabilize them into the oil thereby changing the rock surface to water-wet[24-25]. Austad and his workers used cationics to change wettability from oil-wet to water-wet in carbonate rocks. They found that cationic surfactants of the type R–$N^+(CH_3)_3$ were able to desorb organic carboxylates from the chalk surface in an irreversible way. The mechanism of wettability alteration is supposed to take place by an ion-pair formation by the cationic surfactant and the negatively charged carboxylates in oil. The mechanism of ion-pair formation is schematically described in Figure 2. Due to electrostatic forces, the cationic monomers will interact with adsorbed anionic materials from the crude oil. Some of the adsorbed material at the interface between oil, water, and rock will be desorbed by forming an ion-pair between the cationic surfactant and the negatively charged adsorbed material, mostly carboxylic groups. This ion-pair complex is termed ‘‘cat-anionic surfactant’’, and it is regarded as a stable unit. In addition to electrostatic interactions, the ion-pairs are stabilized by hydrophobic interactions. The ion-pairs are not soluble in the water phase but can be dissolved in the oil phase or in the micelles. As a result, water will penetrate into the pore system, and oil will be expelled from the core through connected pores with high oil saturation in a so-called counter-current flow mode. Thus, once the adsorbed organic material has been released from the surface, the chalk becomes more water-wet, and the imbibition of water is in fact mostly governed by capillary forces in the case of short cores.

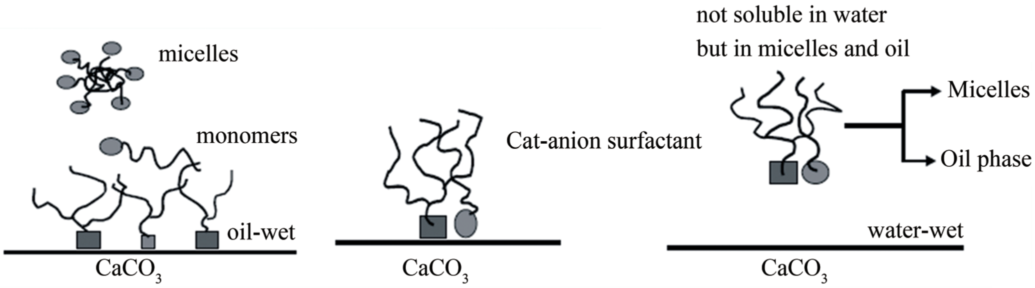

Figure 2
Mechanism of Wettability Alteration from Oil-Wet to Water-Wet. LaRGE SQUIRES REPRESENT CARBOXYLATE GROUps, $-COO^-$, Small Squares Represent Other Polar Components, and Circles Represent Cationic Ammonium Group, $-N^+(CH_3)_3$[24]

Anionic surfactants were not able to desorb anionic organic carboxylates from the crude oil in an irreversible way. Ethoxylated sulfonates with high EO-numbers did, however, displace oil spontaneously in a slow process. The brine imbibed non-uniformly, and the mechanism is suggested to involve the formation of a water-wet bi-layer between the oil and the hydrophobic chalk surface. The mechanism of formation of surfactant double layers is shown schematically in Figure 3. The EO-surfactant is supposed to adsorb with the hydrophobic part onto the hydrophobic surface of the chalk. The water soluble head-group of the surfactant, the EO-group and the anionic sulfonate group, may decrease the contact angle below 90° by forming a small water zone between the organic coated surface and the oil. In this way, a weak capillary force is then created during the imbibition process. The fact that the imbibition of surfactant solution increases with increasing number of EO-groups supports such a model. The formation of the surfactant double layer must not be regarded as a permanent wettability alteration of the chalk. In fact, it will probably be fully reversible due to the weak hydrophobic bond between the surfactant and the hydrophobic surface. The other anionic surfactants tested did not imbibe any significant amount of water into the oil-wet chalk, confirming that the EO-groups play a very important role regarding the imbibition mechanism.

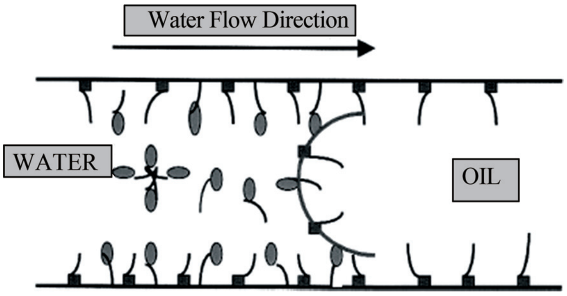

Figure 3
Schematic Illustration of the Mechanism of Bi-Layer Formation in a Pore by EO-Sulfonates. The Eclipses Represent EO-Sulfonates, and the Squares Represent the Carboxylates in the Oil[26]

To reduce anionic surfactant adsorption on carbonate rock surfaces, Hirasaki and Zhang[27] injected Na_2CO_2 with surfactants. The mechanism is that CO_3^{2-} and HCO_3^- change the rock surface to negative surface. The role of anionic surfactants was to reduce the IFT between oil and brine. Once the IFT is reduced, the gravity drive can be enhanced. Gravity plays the role in oil mobilization. For the gravity effect to function, IFT must be reduced to lower capillary pressure so that oil drops can move upwards from the matrix.

Hirasaki and Zhang[27] also explained how adding Na_2CO_3 change wettability of carbonate rock surfaces.

The zeta potential of the crude oil they used was negative for pH greater than 3. This is because of the dissociation of the naphthenic acids in the crude oil with increasing pH. The surface of calcite was positive for pH less than 9 when the only electrolytes were 0.02 M NaCl using NaOH or HCl to adjust pH. The opposite charge between the oil/brine and mineral/brine interfaces results in an electrostatic attraction between the two interfaces, which tends to collapse the brine film and bring the oil in direct contact with the mineral surface. Thus, this system can be expected to be nonwater-wet around neutral pH. However, the zeta potential of calcite was negative even to a neutral pH when the brine was 0.1 N $Na_2CO_3/NaHCO_3$ using HCl to adjust pH. This is because the potential determining ions for the calcite surface are Ca^{2+}, CO_3^{2-} and HCO_3^-. An excess of the carbonate/bicarbonate anions makes the surface negatively charged. If both the crude oil/brine and brine/ calcite interfaces are negatively charged, there will be an electrical repulsion between the two surfaces, which tends to stabilize the brine film between the two surfaces. Therefore, a system with carbonate/bicarbonate ions may be expected to have a preference to be water-wet, compared to that in the absence of carbonate ions.

Xie *et al*.[28] compared the spontaneous imbibition rates using nonionics poly-oxyethylene alcohol (POA) and cationics (CAC). Their results show that the additional recovery from POA was higher and faster with respect to the scaled time than that from CAC. The IFT of POA solution was 19 times higher than of CAC solution (5.7 versus 0.3 mN/m). This observation indicates that, ideally, the wettability should be changed to some optimal water-wet condition with respect to rate and extent of recovery while keeping the IFT relatively high for imbibition.

Acidizing is a common practice in carbonate reservoirs which is used to remove oxidized products of iron (iron sulfide). However, no response to surfactant treatment after acidizing was observed. This is probably because at least an outside layer of rock became strongly water-wet and any remaining oil was trapped[28].

5. CHEMICALS USED IN CARBONATE EOR

For alkalis, sodium tripolyphosphate (STPP) was used in laboratory tests for the Cretaceous Upper Edwards reservoir (Central Texas). STPP was proposed to minimize divalent precipitation, alter wettability and generate emulsions[29]. Sodium carbonate was used in chemical EOR research in carbonate cores[27]. The main function was to reduce surfactant adsorption. Sodium metaborate was also proposed to minimize divalent precipitation[30].

Cationics, anionics and nonionics were all used in research for chemical EOR in carbonate reservoirs. Many cationic surfactants were investigated by the Austad research group[26, 31]. Some of the surfactants they used include dodecyl trimethyl ammonium bromide (DTAB), n-C_8–$N(CH_3)_3Br$ (C8TAB), n-C_{10}–$N(CH_3)_3Br$ (C10TAB), n-C_{12}–$N(CH_3)_3Br$ (C12TAB), n-C_{16}–$N(CH_3)_3Br$ (C16TAB), n-C_8–Ph–$(EO)_2$–$N(CH_3)_2(CH_2$–Ph)Cl (Hyamine), n-(C_8–C_{18})–$N(CH_3)_2(CH_2$–Ph)Cl (ADMBACl), etc. Xie et al.[28] used cocoalkyltrimethyl ammonium chloride (CAC). Tabatabal *et al*.[32] used cetylpyridinium chloride (CPC) and dodecyl pyridinium chloride (DPC).

Some of anionic surfactants used by Seethepalli *et al*.[33] were alkyl aryl ethoxylated sulphonates and propoxylated sulfate. Hirasaki and Zhang[27] used ethoxylated and propoxylated sulfates which were tolerant to divalent ions. These surfactants included CS-330 (sodium dodecyl 3EO sulfate), C12-3PO (sodium dodecyl (Guerbet) 3PO sulfate), TDA-4PO (ammonium iso-tridecyl 4PO sulfate), and ISOFOL14T-4.1PO (sodium tetradecyl (Guerbet) 4PO sulfate).

Stadnes and Austad[26] used n-C_{12}–C_{15})–$(EO)_{15}$–SO_3Na (S-150), n-C_{13} –$(EO)_8$–SO_3Na (B 1317), n-C_8–$(EO)_3$–SO_3Na (S-74), n-(C_{12}–C_{15})–$(PO)_4$–$(EO)_2$–OSO_3Na (APES), (n-C_8O_2CCH2)(n-C_8O_2C)CH–SO_3Na (Cropol), n-C_8–$(EO)_8$–OCH_2–COONa (Akypo), n-C_9–Ph–$(EO)_x$–PO_3Na (Gafac), n-C_{12}–OSO_3Na (SDS). Nonionic surfactants were used by Chen *et al*.[34] and Xie *et al*.[28].

6. CHEMICAL EOR PROJECTS IN CARBONATE RESERVOIRS

According to the Oil & Gas Journal survey in 2004[35], for the total 57 gas injection projects in the United States (WAG or continuous injection), 48 projects were CO_2 injection. Among those CO_2 projects, 67% were in Texas carbonates. There were abundant availability of CO_2 in the Texas Permian Basin, and CO_2 price in Texas was low. Other EOR projects which were active in 2004 include 7 air injection projects, 2 N_2 injection, 1 steam flood, and 1 surfactant stimulation[35, 36]. These data indicate that not many EOR projects were active in carbonate reservoirs.

For chemical EOR, many polymer projects were conducted in 1960s – 1990s. During this period, there were only a few surfactant-polymer (SP) projects. No ASP project was reported. From 1990s – 2000s, no chemical flood projects were reported; only three surfactant stimulations were reported: Mauddud, Cottonwood Creek and Yates projects. These cases are analyzed next.

6.1 The Mauddud Carbonate in Bahrain

The Mauddud carbonate reservoir was the main oil producing reservoir in the Bahrain oilfield. The Mauddud zone was a 100-ft thick, low-dip, and heterogenous limestone reservoir. Its rock was described as moderately soft to hard, fine to medium grained, fossiliferous, detrital, clean, oil-wet limestone with limited fractures and vugs. The acid number of oil was 0.23-0.64.

The Mauddud reservoir had been producing since 1932 and was in a very mature stage. The dominant recovery mechanism was gravity drainage with crestal gas injection that started in 1938. The reservoir energy was supplemented by aquifers. Due to the reservoir rocks wettability characteristics (preferentially oil-wet nature), the residual oil saturation left behind gas and water fronts ranged from 20% to 70%. TDT saturation logs showed residual oil saturations (S_{or}) of about 43%. The water cut was about 98-99%.

Early attempts to reduce water cut in the waterflooded area was made with a pilot trial using conformance chemicals such as cross-linked gels which failed to improve oil production. Later 6 wells were treated with surfactant washes using carrier fluids such as diesel and Xylene. The wells were soaked a few days then produced. S_{or} was reduced by 10-15%. RST/CO logs were used to evaluate S_{or}. Although these jobs were successful, the wells returned to the original water cuts very soon. This gave, however, a positive indication that with chemical treatments it would be possible to strip more oil from the Mauddud rock. It was thereafter decided to study the effectiveness of treating the area with a combination of alkaline and surfactants (AS)[37]. No further report has been published since.

6.2 The Yates Field in Texas

The San Andres reservoir in the Yates field in Texas is a naturally fractured dolomite formation. It was a 400-ft-thick formation with an average matrix porosity and permeability of 15% and 100 md, respectively. The oil viscosity was 6 cP and the reservoir temperature was 28 °C.

A dilute-surfactant-well stimulation pilot test was initiated in the field in the early 1990s. After the surfactant slug was injected, the well was shut-in (soak time) for a brief period of time. When production resumed, the well showed an increase in the recovery of oil owing to reduction in IFT, gravity segregation of oil and water between the fractures and matrix, and wettability alteration (the latter contributed to a lesser extent) [34,38].

The surfactant used in the Yates pilot was 0.3-0.4% nonionic ethoxy alcohol (Shell 91-8) and 0.35% Stepan CS-460 anionic ethoxy sulfate that were well above the critical micelle concentration (CMC) levels. The surfactant solutions injected were prepared with produced water in the concentrations of 3,100 to 3,880 ppm. The field results were reported positive, as evidenced by some pilot wells showing an increase in oil production over 30 bbl per day[38].

6.3 The Cottonwood Creek Field in Wyoming

The Cottonwood Creek field in the Bighom Basin of Wyoming is a dolomitic class II reservoir. The class II reservoirs have low matrix porosities and permeabilities. Oil was produced from the dolomitic Phosphoria formation. The reservoir thickness varied from 20 to 100 ft, and the average porosity and permeability were 10% and 16 md, respectively. The reservoir produced a sour crude oil of 27 °API.

Single-well surfactant stimulation treatments were initiated in Cottonwood Creek in August 1999. 500 to 1,500 bbl of a surfactant solution slug were injected, depending on the perforated interval. Typically, the injection period lasted 3 days with a one-week shut-in period (soak time). Surfactant solutions were prepared using the nonionic POA at a concentration of 750 ppm, almost twice the CMC. Initial well treatments used an acid cleanup with HCl (15%) to remove iron sulfide (FeS) from the wellbore to avoid and/or reduce surfactant adsorption. However, production results were not encouraging. Therefore, acid pretreatment was eliminated later and surfactant concentration was increased of up to 1,500 ppm (to allow for potential losses by adsorption to FeS) in subsequent surfactant stimulations[28,39].

Single-well surfactant soak treatments were made at 23 wells. The general trend was that the oil recovery was increased. However, this increase is not significant. The problem was that 70% of the treated wells failed.

Oil recovery increase in Cottonwood Creek was believed to be due to wettability alteration to less oil-wet and not to a reduction in IFT, because the IFT of POA solutions with oil indicated 5.7 dynes/cm at ambient temperature. The minimum amount of surfactant used for a successful treatment was 60 lbm/ft of perforated internal on the basis of the analysis of 23 well treatments reported in the literature[28,39].

6.4 The Baturaja Formation in the Semoga Field in Indonesia

The Semoga field was discovered in 1996 and is located in the Rimau block in the South Sumatera. The field consists of three prospect formations: Telisa formation (tight sandstone), Baturaja formation (carbonate) and Talang Akar formation (sandstone). The Baturaja formation (BRF) is a carbonate reservoir with a proven volume of about 317,856 acre-ft (77 ft net pay). There were 127 wells: 82 producers, 28 injectors, and 17 shut-in wells.

The production began in 1997 and oil production peaked at 36,200 BOPD in November 2001. Since then the production has declined owing to rising water cut. The average water cut before the surfactant stimulation was 86%, and some wells above 95% or even 100%. A laboratory study showed that the Baturaja formation was oil-wet. Huff and Puff surfactant stimulation was studied for this formation.

In this project, the surfactant was soaked for 7 days to allow a reaction with the hydrocarbon. The radial penetration designed for Well X-1 and Well X-2 was about 21 ft. The injection consisted of three steps:

(1) Preflush. The purpose of the pre-flush was to displace the reservoir brine which contained potassium, sodium, calcium and magnesium ions in the near-wellbore area, therefore avoiding

adverse interactions with the chemical solution. The other purpose was to adjust reservoir salinity to favorable conditions for the surfactant. 100 bbls of produced water was injected in to each well.

(2) Main-flush. 9 bbls of surfactant and 451 bbls of water were injected in to Well X-1; and 9 bbls of surfactant and 536 bbls of water were injected in to Well X-2.

(3) Post-flush. In this phase the formation water was injected to displace the rest of the surfactant away from the wellbores at the end of stimulation. In the post-flush, 3 bbls of surfactant and 127 bbls of water were injected in to Well X-1; and 0.65 bbls of surfactant and 43.35 bbls of water were injected in to Well X-2.

This surfactant stimulation decreased water cut by about 8%, with an increased cumulative oil production of about 5,800 bbls over a period of three months. An extended study was proposed to further investigate the mechanisms[40].

6.5 Cretaceous Upper Edwards Reservoir (Central Texas)

A laboratory study was conducted to study the feasibility of ASP in the Cretaceous Upper Edwards reservoir, located in Central Texas[29]. The field was discovered in 1922. Over 950 development wells had been drilled. The water cut was 99%. The reservoir was preferentially oil-wet. The average permeability was 75 md. The formation water salinity was low (produced TDS = 12,000 ppm). There was no anhydrate or gypsium. The reservoir temperature was 42 ^{o}C, the acid number was 0.34, and the crude oil viscosity was 3 cP. The ASP formula selected was:

- 0.4-0.5% Sodium tripolyphosphate
- 2% sodium carbonate
- 0.2-0.5% Petrostep B100
- 0.12% Pusher 700E

The injection scheme was: 0.1PV fresh water, 0.1 PV ASP, 0.2 PV polymer. The ASP flood recovered approximately 45% of the residual oil after waterflooding. No field trial was reported.

7. CONCLUDING REMARKS

Field application of injecting surfactants in carbonate reservoirs to stimulate oil recovery has been limited to only a few field cases. Field results in general showed positive response to surfactant injection. Surfactant injection is believed to change wettability from oil-wet or more water-wet and to reduce IFT. It is assumed that the wettability alteration is caused by surfactant adsorption on carbonate rock surfaces. The EOR mechanisms are related to capillary imbibitions and gravity drive enhanced by surfactant injection. Capillary imbibitions and gravity drive could be slow processes. Therefore, upscaling from laboratory results to field- scale application is important. Several upscaling models have been proposed. These models and even the drive mechanisms need more research work and field data for validation.

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