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RESERVOIR ENGINEERING

The optimal salinity concept for oil displacement by oil-external microemulsions and graded salinity slugs

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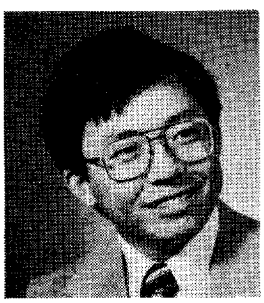

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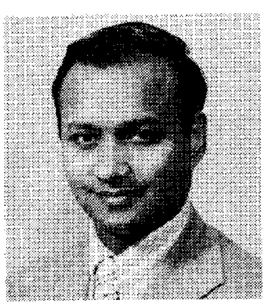

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Kewords: Reservoir engineering, Salinity, Oil displacement, Emulsions, Microemulsions, Flooding, Polymer flooding, Phase behaviour, Interfacial tension, Mobility control, Surfactant loss, Enhanced recover.

Paper reviewed and accepted for publication by the Editorial Board of the Journal of Canadian Petroleum Technology in July 1981.

ABSTRACT

Our laboratory studies showed that the concept of the optimal salinity, as derived from phase behaviour or interfacial tensions of microemulsions, is applicable to oil displacement by soluble oils in porous media. Maximal oil recovery was obtained when the salinity of connate water and polymer solution was at the optimal salinity of the surfactant formulation. In the present study, it is shown that the salinity of polymer solution is far more important than the salinity of connate water. When the salinity of polymer solution was at the optimal salinity of the surfactant formulation, high oil recovery efficiency was obtained over a wide range of connate water salinities. Evidence showed that the phase behaviour of the surfactant slug in porous media is largely determined by the salinity of the polymer solution.

For better mobility control and minimum surfactant loss, a two-slug design of the surfactant formulation was employed. In this design, the first surfactant slug has an optimal salinity close to the connate water salinity and the second surfactant slug has a much lower optimal salinity. The polymer solution salinity is made equal to the optimal salinity of the second surfactant slug. With this design, high oil recovery in Berea cores can be obtained even in the presence of high-salinity (6% NaCl + 1% $CaCl_2$) connate water.

The optimal salinity concept is further extended to include the effects of mobility control and surfactant dispersion and entrapment in porous media. The proposed ***salinity shock*** *design of mobility polymer solutions employs two slugs of polymer solution in which the first polymer slug is at the optimal salinity of the preceding surfactant formulation and the second polymer slug is at a much lower salinity. With this unique design, high oil recovery and high surfactant recovery can be obtained for soluble oil flooding in sand packs, and the polymer consumption can be greatly reduced.*

Introduction

Surfactant-polymer flooding processes for enhanced oil recovery are influenced by a number of parameters. These include reservoir capillary properties (1-4), rock wettability (4-6), reservoir brine and mineralogy (7-14), and rock-fluid interactions (15-19). Connate water salinity and reservoir minerals can affect surfactant flooding through their effects on phase

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behaviour, interfacial tensions with slug and residual oil, and mobility control, as well as on surfactant loss due to adsorption, precipitation and phase entrapment processes. By incorporating small amounts of clays or minerals in sand packs, it was shown [7] that the oil recovery efficiency of soluble oil flooding processes greatly diminishes due to the presence of the clays and minerals. Even when clays or divalent cations are absent or in trace amounts, NaCl alone can effectively deteriorate the performance of oleic [8] and aqueous surfactant flooding processes [11-14]. Such detrimental effects can often be minimized by means of preflush and optimal salinity design [11,20] of the surfactant slug for a given surfactant and cosurfactant system. The design basis is that for a given surfactant formulation and oil; there exists a salinity at which minimum interfacial tensions occur when surfactant, cosurfactant, oil and brine are equilibrated. This salinity was defined as the optimal salinity of the surfactant formulation [20]. It was further shown, for immiscible microemulsion flooding, that maximal oil recovery occurred near the optimal salinity [11]. It is not well established whether or not similar correlation among interfacial tension, optimal salinity and oil recovery efficiency exists for soluble oil flooding.

The salinity of polymer solution can also influence four major parameters of the surfactant-polymer flooding process; namely, interfacial tension, mobility control, surfactant loss and phase behaviour. When polymer solutions of various salinities are equilibrated with surfactant solution in oil, the formation of lower, middle and upper phase microemulsions has been observed [13] to be similar to the effect of increasing the connate water salinity.

Another factor in designing the polymer solution is viscosity. It is well known that the viscosity of partially hydrolyzed polyacrylamide solutions decreases sharply with salinity (in the 0 to 0.5% NaCl range). This factor then favours the use of fresh-water (very low salinity) polymer solution. More recently, it has been shown that fresh polymer solution also gives lowest surfactant loss [21,22]. This is because lower phase microemulsions can be produced in this case, which are miscible with the fresh polymer solution, and because the dispersed and entrapped surfactant slug can be redissolved into the low-salinity polymer solutions. As a result, one may design the salinity of polymer solution at a lower value than the optimal salinity of the surfactant formulation [21] or a contrast salinity design [9,21,23,24] of the preflush-micellar-polymer flooding process.

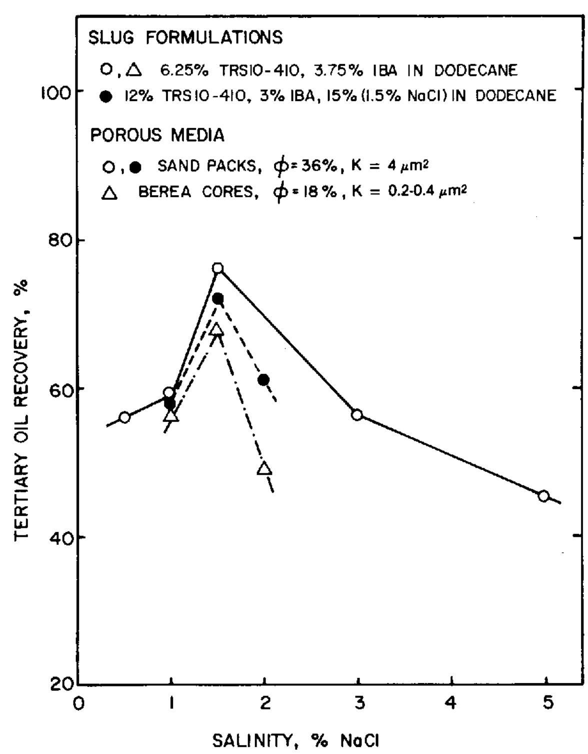

FIGURE 1. The validity of the optimal salinity concept for oil displacement by soluble oils or oil-external microemulsions in sand packs and in Berea cores.

It should be noted, however, that higher surfactant concentrations in the surfactant slug do not necessarily produce lower interfacial tensions [25]. A low-salinity polymer solution capable of dissolving high concentrations of surfactant may not exhibit sufficiently low interfacial tension to mobilize the displacement of the residual oil left behind the surfactant slug.

In this study, the validity of the optimal salinity concept for oil displacement by soluble oils or oil-external microemulsions is examined. The effect of connate water salinity and polymer solution salinity on the phase behaviour and displacement of surfactant slugs *in situ* is explained. The salinity contrast design for soluble oil flooding is examined. A novel concept of salinity shock design of polymer slugs is proposed to maximize oil and surfactant recovery.

Experimental

A commercial petroleum sulfonate, TRS 10-410 (Witco Chemical Company), was used as received. This surfactant has an average molecular weight of 418 and is 62% active. The cosurfactant (isobutanol of 99.9% purity) and the oil (dodecane or hexadecane of 99% purity) were obtained from Chemical Samples Company. The composition of the surfactant formulation will be specified in each section. Pusher-700™ (Dow Chemicals) was used to prepare the polymer solutions. Deionized, distilled water was used to prepare the brine. Short sand packs with a dimension of 33 cm length by 2.5 cm diameter were used as the porous medium for most of the studies. The sand packs had a porosity of 38% and a permeability of about 4.2 μm^2. Rectangular Berea cores with a dimension of 30.5 by 2.5 by 2.5 cm were also employed in oil displacement tests, which had a porosity of 22% and permeabilities of 0.2 to 0.4 μm^2.

Interfacial tensions (IFT) were measured by a spinning-drop tensiometer after phase equilibration for about two months. The samples were vigorously shaken and put on a rotating tumbler for 24 hours, before putting them into a constant-temperature bath to allow phase separation. The equilibration temperature was held at 25 ± 0.1°C. Interfacial tensions between the effluent oil, brine and surfactant phase (microemulsion) were measured immediately after collecting the effluents from porous media. The viscosity was measured by a Brookfield cone and plate microviscometer at a shear rate of 6 sec^{-1}. The readings were taken 30 minutes after starting the rotation. Surfactant concentrations of effluent oil and brine were measured by a two-phase, two-dye titration method [26].

Porous media were conditioned by saturating them with CO_2 at 345 kPa to displace air, then flooded with distilled water (for sand packs) or 1.0% NaCl (for Berea cores) up to 10 pore volumes (PV). Oil displacement experiments were performed by first flooding the porous medium with brine for approximately 5 PV, during which the permeabilities were measured. The porous medium was then saturated with oil at a high flow rate to irreducible brine content (approximately 18% PV for sand packs and 33% PV for Berea cores) and brine flooded to irreducible oil content (approximately 26% PV for sand packs and 34% PV for Berea cores). A surfactant slug was then injected, which was displaced by a polymer solution slug (1 PV) and subsequently by drive water. The linear displacement velocity in the water flooding and the subsequent surfactant slug and polymer solution flooding was 0.85 m/day for sand pack tests and 0.76 m/day for Berea core tests. Oil displacement experiments were performed at room temperature (23 ± 1°C). The salinities of the connate brine, brine for water flooding and polymer solution are specified in each section. The drive water salinity was the same as that of the polymer solution. Oil displacement results were expressed as per cent tertiary oil recovery according to:

$$\text{Tertiary Oil Recovery, \%} = \frac{\text{Oil Produced - Oil Injected}}{\text{Residual Oil}} \times 100\%$$

Results and Discussion

The Validity of the Optimal Salinity Concept for Oil Displacement by Soluble Oils

This section reports on the salinity effects on soluble oil flooding and their correlations with the interfacial tension, solubilization parameter and phase behaviour of soluble oils. To simplify the experimental conditions, the salinities of formation brine (connate water), brine for secondary flooding and of the polymer solution were made equal. Oil displacement tests using a soluble oil slug (6.25% TRS 10-410 and 3.75% IBA in dodecane) were studied in both Berea cores and sand packs. Oil displacement by an oil-external microemulsion (12% TRS 10-410, 3% IBA and 15% brine (1.5% NaCl solution) in dodecane, w/w) was performed in sand packs. The surfactant slug size was 5% PV. Polymer solutions with 500 ppm Pusher-700 in brine were employed. As shown in Figure 1, maximum oil recovery was obtained when the salinity was 1.5% NaCl for soluble oil or oil-external microemulsion flooding in sand packs and in Berea cores.

This salinity for maximal oil recovery correlates well with the optimal salinity obtained from solubilization and interfacial tension behaviour of soluble oil, as shown in Figure 2. When the soluble oil was equilibrated with an equal volume of brine, different phase behaviour appeared, depending on the brine salinity. At low salinities, lower phase ($\ell\phi$) microemulsions were in equilibrium with excess oil; at high salinities, upper phase (uϕ) microemulsions were in equilibrium with excess brine. In the vicinity of 1.5% NaCl, middle phase (mϕ) microemulsions were found in equilibrium with both excess oil and excess brine. Shown in Figure 2, the interfacial tension at the oil/microemulsion interface was denoted as γ_{om} and the interfacial tension at the microemulsion/brine interface as γ_{mw}. The solubilization parameter, V_o or V_w, was the volume of oil or brine solubilized into the microemulsion phase per unit weight of surfactant. The optimal salinity, when defined as the salinity at which V_o equals V_W or γ_{om} equals γ_{mw}[20], was found to be 1.5% NaCl. The data shown here are typical of those sytems having a narrow range of middle phase microemulsions and a sharp minimum of interfacial tension at the optimal salinity. However, the optimal salinity for a given system could vary with the surfactant and alcohol concentrations and with the water-to-oil ratio [25,27]. The correlation of this optimal salinity with that for maximum oil recovery suggests that the initial difference in the water-to-oil ratio in surfactant slug is of minor importance. Therefore, the concept of optimal salinity for maximal oil recovery is valid for oil displacement by soluble oils.

The Importance of the Salinity of Polymer Solution

In the above study, the salinity of connate water and polymer solution was made equal. Such a combination was used only to demonstrate the optimal salinity concept and might not represent the best design for a flooding process. The objective of this study is to show the relative importance of the effects of connate water salinity and polymer solution salinity on oil recovery by soluble oils.

Oil displacement experiments were performed under the following salinity conditions: (1) constant salinity of polymer solution at 1.5% NaCl (i.e., the optimal salinity of the surfactant formulation) and variable connate water salinity; (2) constant connate water salinity at 1.5% NaCl and variable polymer solution salinity; and (3) the salinity of polymer solution was equal to the salinity of connate water and varied simultaneously. Sand packs were chosen as the model porous media in order to avoid the effects of porous medium heterogeneity, clays and excessive surfactant loss. The polymer solution used was 1000 ppm Pusher-700 in brine. For the polymer solution in distilled water, the polymer concentration was reduced to 250 ppm to

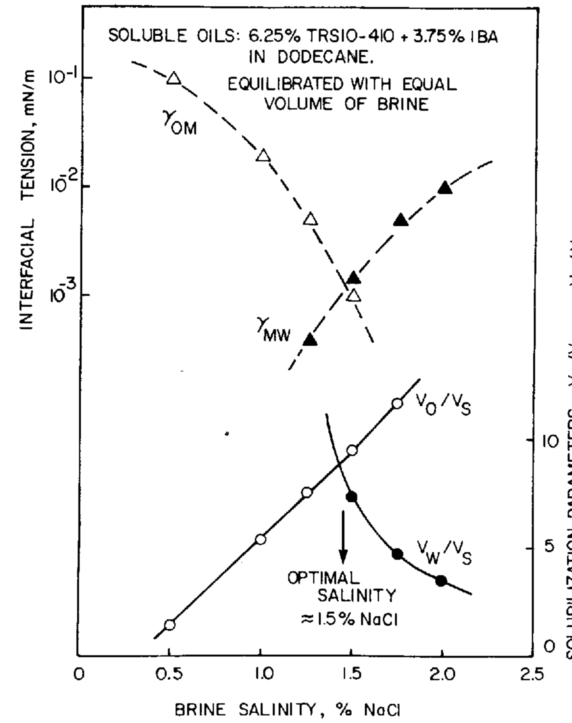

FIGURE 2. The optimal salinity of soluble oils as determined by interfacial tension and solubilization.

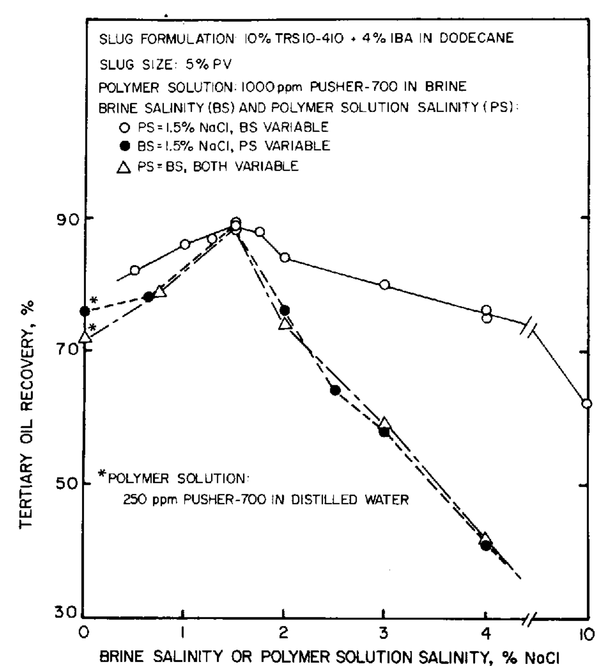

FIGURE 3. The effect of connate water salinity (BS) and polymer solution salinity (PS) on the oil displacement efficiency of soluble oils in sand packs.

avoid excessive viscosity. Several experiments were repeated and the reproducibility was established to be within ± 2% in tertiary oil recovery.

Figure 3 shows the following results:

(1) Maximal oil recovery was obtained when the salinity of both polymer solution and connate water was 1.5% NaCl.

(2) When the salinity of polymer solution was 1.5% NaCl, oil recovery was favorable over a wide range of connate water salinities (0 to 4% NaCl). Oil recovery was 62% when the salinity of connate water was as high as 10% NaCl.

(3) On the other hand, when the salinity of polymer solution was varied from 1.5% NaCl, oil recovery drastically decreased irrespective of connate water salinities.

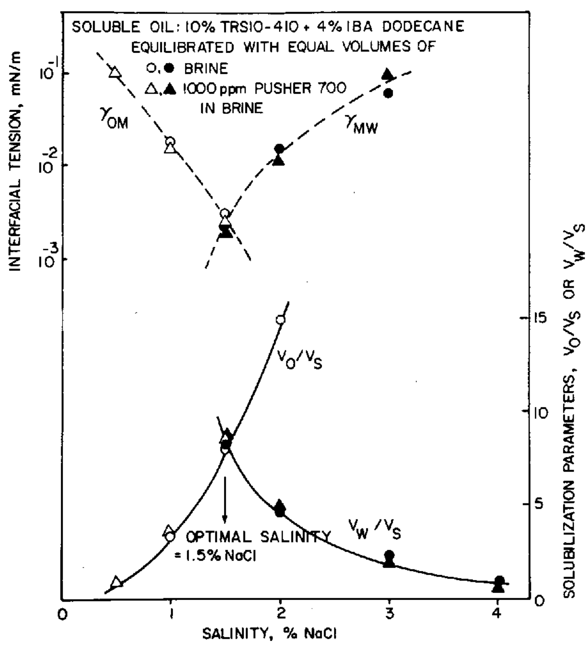

FIGURE 4. The effect of salinity on the solubilization and interfacial tension behaviour of soluble oils equilibrated with brine or polymer solution.

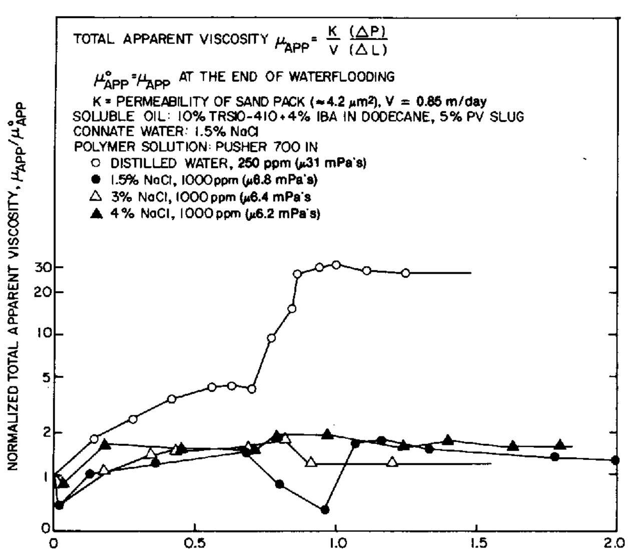

FIGURE 5. The effect of polymer solution salinity on the normalized total apparent viscosity in surfactant-polymer flooding processes in sand packs.

These results suggest, for the present system, that the salinity of polymer solution is far more important than that of connate water in tertiary oil recovery. In other words, the processes occurring at the surfactant slug-polymer solution interface determine the oil recovery efficiency in the systems reported here. Gupta and Trushenski[21] also suggested that the oil recovery process is controlled by the compositions developing in the micellar-polymer mixing zone for aqueous micellar systems with crude oil in Berea core experiments.

When soluble oil was equilibrated with either brine or polymer solution at various salinities, similar phase and interfacial tension behaviours were observed, from which the optimal salinity obtained was the same (1.5% NaCl), as shown in Figure 4. These observations cannot explain why the polymer solution salinity is more critical than the connate water salinity in the present study.

The small changes in the viscosity of polymer solutions cannot account for the drastic differences in oil recovery efficiency when the salinity of polymer solutions is varied. The viscosity decreases from 7 mPa·s to 6 mPa·s when the salinity increases from 1% to 5% NaCl. The maximum decrease in the viscosity of polymer solutions occurs in the 0 to 0.5% NaCl range. The total apparent viscosities* in porous media, as shown in Figure 5, are also nearly the same, with the exception of the fresh polymer solution, which has a Brookfield viscosity of 31 mPa.s. However, tertiary oil recovery using this polymer solution was only 76%, as compared to 89% recovery obtained using the 1.5% NaCl polymer solution. Furthermore, on increasing the viscosity of 4% NaCl polymer solution from 6.2 mPa·s to 15 mPa·s by doubling its polymer concentration and keeping connate water at 1.5% NaCl, oil recovery only increased from 42% to 49%. These observations indicate that the increase in oil recovery due to the increase of the viscosity of polymer solutions (even by four times) is not at all sufficient to offset the decrease in oil recovery due to the high interfacial tensions when polymer solutions at salinities other than 1.5% NaCl are used.

The importance of polymer solution salinity in the present study is related to the phase behaviour of the surfactant slug *in situ,* which is largely determined by the salinity of polymer solution and much less by the salinity of connate water. When a low-salinity polymer solution is used, the rear portion of the surfactant slug is a $\ell\phi$ microemulsion throughout the displacement process. When connate water salinity is high, the front portion of the surfactant slug is an $u\phi$ microemulsion at the initial stage of the displacement process. Due to its high IFT with connate water, the $u\phi$ microemulsion will lag behind the displacement front and is forced to mix with the upcoming $\ell\phi$ microemulsion. On the other hand, the high-salinity connate water is completely displaced by the $\ell\phi$ microemulsion due to the high viscosity ratio and zero IFT between them**. The volume fraction of brine in the $\ell\phi$ microemulsion is usually higher than 75%; that in the $u\phi$ microemulsion is less than 5%. Because of the large difference in water-to-oil ratios, the mixing of $\ell\phi$ and $u\phi$ microemulsions produces a $\ell\phi$ microemulsion (plus some excess oil), irrespective of the salinity of solubilized brine in the $u\phi$ microemulsions. Therefore, in the course of flooding, all the surfactant slugs will eventually become $\ell\phi$ microemulsions when low-salinity polymer solutions are used.

When a high-salinity polymer solution was used, the rear portion of the surfactant slug is an $u\phi$ microemulsion. The front portion of the surfactant slug can be a $\ell\phi$, $m\phi$ or $u\phi$ microemulsion, depending on the connate water salinities. In

*The total apparent viscosity gives a measure of the total resistance to flow (at a constant flow rate) in the surfactant-polymer flooding process and is defined as $\mu_{app.} = (K/v) \times (\Delta P/\Delta L)$, where K is the permeability, v is the displacement velocity and $\Delta P/\Delta L$ is the pressure drop over a length ΔL.

**This is not necessarily true for highly heterogeneous or oil-wet porous media.

TABLE 1. The effect of polymer solution salinity and connate water salinity on soluble oil flooding in sand packs[a,b,c]

Test	Polymer Solution Salinity (% NaCl)	Connate Water Salinity (% NaCl)	Surfactant Recovery (at 1.3 PV, %)	Tertiary Oil Recovery (%)
1-1	0[d]	0	100	73
1-2	0[d]	1.5	99	76
1-3	0[d]	3	92	62
2-1	1.5	0	75	80
2-2	1.5	1.5	67	89
2-3	1.5	3	60	80
3-1	3	0	15	55
3-2	3	1.5	7	58
3-3	3	3	2	59

a. Soluble oil formulation: 10% TRS 10-410 + 4% IBA in dodecane (w/w), 5% PV slug.
b. Sand packs: 33 cm long x 2.5 cm diameter, porosity = 38%, permeability 7 4.2 dm^2.
c. Liner displacement velocity = 0.85 m/day.
d. The polymer concentration used in this case was 250 ppm Pusher-700; in other cases, it was 1000 ppm.

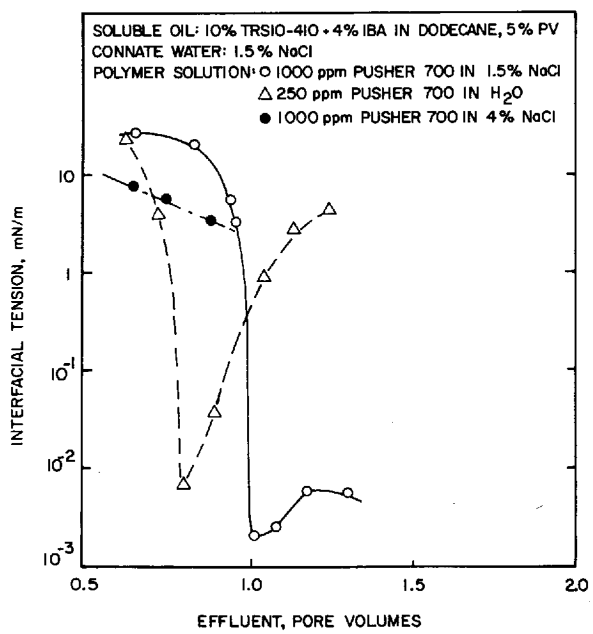

FIGURE 6. Interfacial tension between effluent oil and brine for soluble oil flooding in sand packs using different polymer solutions.

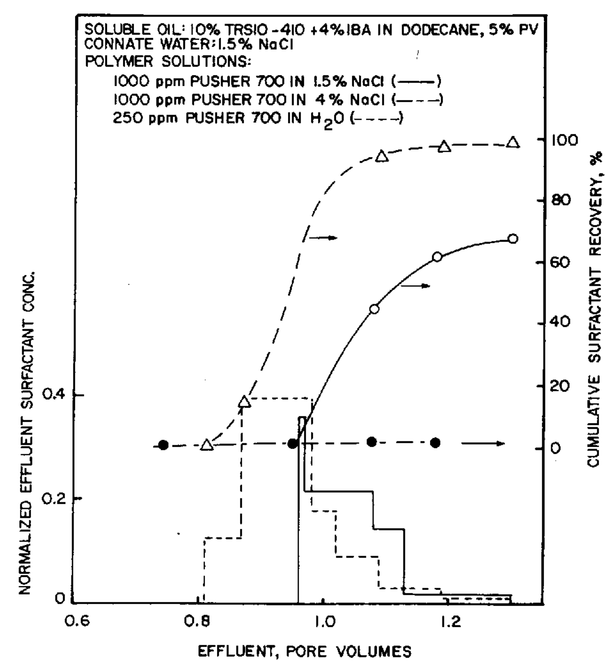

FIGURE 7. Cumulative surfactant recovery and normalized surfactant concentration in effluent oil and brine for soluble oil flooding in sand packs using different polymer solutions.

any event, the uϕ microemulsion will be trapped behind the displacement front due to its high IFT with the polymer solution. As a result, the front portion of the surfactant slug will be immediately invaded by the high-salinity polymer solution. The mϕ or $\ell\phi$ microemulsions, on mixing with the high-salinity polymer solution, will eventually become uϕ microemulsions, which will then be trapped in porous media.

The above discussion is supported by the surfactant recovery results for soluble oil flooding in sand packs under different salinity conditions. As shown in Table 1, the surfactant recovery is largely determined by the salinity of polymer solutions. For fresh-water polymer solutions, the surfactant recovery is higher than 90%, whereas for high-salinity polymer solutions, the surfactant recovery is less than 15%, irrespective of connate water salinities.

Furthermore, the displacement of surfactant slugs in sand packs can be visually observed. It was found that only when the salinity of polymer solution was near the optimal salinity of the surfactant formulation, the slug front migration velocity was very close to the linear displacement velocity. The surfactant slug breakthrough time, as indicated by the first appearance of thick emulsions and a sudden decrease of IFT in effluents, was approximately 0.95 to 0.97 PV. These are shown in Figures 6 and 7. When the polymer solution was made in fresh water, lower phase microemulsions are formed, which exhibit an interfacial tension with oil in the range of 0.5 mN/m. As a result, part of the residual oil was bypassed, leading to a higher slug front migration velocity and an earlier slug breakthrough (0.8 PV, Figs. 6 and 7). For the case of 4% NaCl polymer solution, the surfactant slug disappeared (dispersed) in sand packs after about 0.3 PV injection and no surfactant slug breakthrough was observed. This is because the slug becomes an upper phase microemulsion which is trapped in porous media due to capillary forces similar to residual oil.

The results and discussion of this section can be summarized as follows: The interactions at the surfactant slug-polymer solution mixing zone determine the phase behaviour of the surfactant slug in porous media. Polymer solutions having the optimal salinity of the preceding surfactant formulation assures that the middle phase microemulsion is produced *in situ*, having ultralow interfacial tensions with both residual oil and polymer solution. The low interfacial tensions together with adequate mobility control allow the surfactant slug to be displaced in a piston-like manner. Consequently, favorable oil recovery can be obtained over a wide range of connate water salinities when the polymer solution salinity is maintained near the optimal salinity of the surfactant formulation.

Constant Salinity Design vs. Contrast Salinity Design

For aqueous micellar-polymer flooding with crude oil in Berea cores, it has been shown(9,21,23,24) that a contrast salinity (also called salinity gradient) design of the preflush-micellar-polymer flooding process may produce a better oil recovery than that obtained from a constant salinity process. In the contrast salinity design, the salinity of the preflush water is made higher, and the salinity of polymer solution is made lower than the optimal salinity of the surfactant formulation. The rationale of this design is that the optimal salinity of the surfactant slug may decrease on mixing of the injected fluids in porous media(23,24). In this study, the concept of contrast salinity design is examined by using a surfactant formulation the optimal salinity of which increases with dilution. The increase of optimal salinity with dilution was due to the decrease of the isobutanol concentration in the surfactant formulation. This is shown in Figure 8.

Because anhydrous soluble oil was used in this study, there were only two salinity variables left to be considered; i.e., the salinity of connate water and polymer solution. In this case, the contrast salinity design is such that the average of the connate water and polymer solution salinity is equal to the optimal salinity of the surfactant formulation (i.e., 1.5% NaCl). The results are shown in Table 2.

It is clear from Table 2 that the concept of contrast salinity design should be applied with care. In the present system, only Test 2-2 gave satisfactory oil recovery results, where the salinity of connate water was slightly higher and the salinity of polymer solution was slightly lower than the optimal salinity of the surfactant formulation. In this case, oil recovery was the same as that by the 1.5% NaCl polymer solution while its surfactant recovery was higher. It is also interesting to note that Test 2-2 gave better results than Test 2-3. This indicates that, although the optimal salinity increases with dilution, a decreasing salinity gradient is preferred. Apparently, the optimal salinity profile was not established in Test 2-3, as part of the surfactant slug could be trapped in the initial stage of the displacement process.

As the viscosity of polyacrylamide solutions decreases sharply with the salinity in the 0 to 0.5% NaCl range, it may be beneficial to design a surfactant-formulation with an optimal salinity less than about 0.5% NaCl. However, it is usually not possible to decrease the connate water salinity to below 0.5% NaCl. This difficulty may be overcome by the following two-slug design of the surfactant formulation.

In this design, the first surfactant slug has an optimal salinity close to the connate water salinity and the second surfactant slug has an optimal salinity near the salinity of polymer solution (which is made below 0.5% NaCl), as shown schematically in Figure 9. This design could have the following advantages: (1) middle phase microemulsions with low IFT with residual oil, connate water and polymer solution are produced;

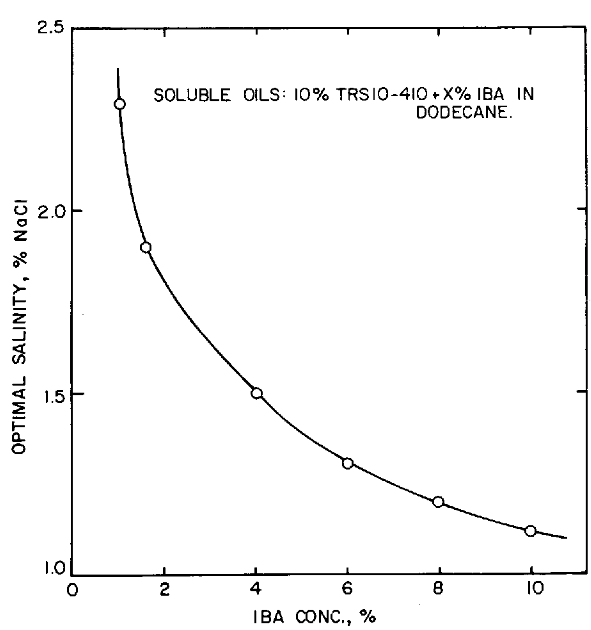

FIGURE 8. The effect of alcohol concentration on the optimal salinity of soluble oils.

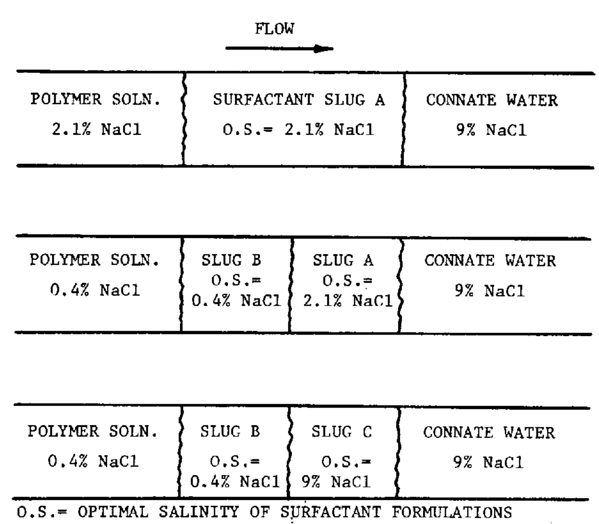

FIGURE 9. A schematic representation of the two-slug design of surfactant formulation for soluble flooding.

TABLE 2. Constant salinity design vs contrast salinity design in soluble oil flooding in sand packs[a,b,c]

Test	Salinity of Connate Water (% NaCl)	Salinity of Polymer Solution (% NaCl)	Tertiary Oil Recovery (%)	Final Oil Saturation (%)	Surfactant Recovery (at 1.3 PV, %)
2-1	3.0	0[d]	62	9.1	92
2-2	2.0	1.0	88	2.9	81
2-3	1.0	2.0	83	4.1	43
2-4	0	3.0	45	13.2	15
2-5	1.5	1.5	89	2.6	67

a. Soluble oil formulation: 10% TRS 10-410 + 4% IBA in dodecane, 5% PV slug.
b. Porous media: 33 cm long by 2.5 cm diameter sand packs, K = 4.2 dm^2.
c. Linear displacement velocity = 0.85 m/day.
d. The polymer concentration used in this case was 250 ppm Pusher-700; in other cases, it was 1000 ppm.

TABLE 3. Two surfactant slug designs for soluble oil flooding in Berea cores[a,b,c]

	Surfactant Formulation[d]	Connate Water	Permeability	Tertiary Oil Recovery	Surfactant Recovery	Final Oil Saturation
3-1	Slug A, 10% PV	3% NaCl + 1% $CaCl_2$	0.458 μm^2	65% (@ 1 PV) 78% (@ 2.6 PV)	4%	7.5%
3-2	Slug A, 5% PV; followed by Slug B, 5% PV	3% NaCl + 1% $CaCl_2$	0.296 μm^2	75% (@ 1 PV) 95% (@ 2.7 PV)	7%	1.7%
3-3	Slug A, 5% PV; followed by Slug B, 5% PV	6% NaCl + 1% $CaCl_2$	0.247 μm^2	64% (@ 1 PV) 84% (@ 2.5 PV)	2%	5.4%
3-4	Slug C, 5% PV: followed by Slug B, 5% PV	6% NaCl + 1% $CaCl_2$	0.144 μm^2	72% (@ 1 PV) 90% (@ 2.4 PV)	7%	3.4%

a. Berea cores: 30.5 cm long x 2.5 cm square. Residual oil = hexadecane.
b. Linear displacement velocity = 0.76 m/day.
c. The polymer solution used in Test 3-1 was 1000 ppm Pusher-700 in 2.1% NaCl; in other cases, it was made in 0.4% NaCl brine.
d. Slug A = 10% TRS 10-410 + 4% IBA in hexadecane (optimal salinity = 2.1% NaCl).
Slug B = 6% TRS 10-410 + 2% IBA + 1.6% PECH in hexadecane (optimal salinity = 0.4% NaCl).
Slug C = 10% TRS 10-410 + 6% EOH + 4% NPA in dodecane (optimal salinity = 9% NaCl).

(2) the viscosity of polymer solution can remain high (due to its very low salinity); and (3) the dispersed and entrapped first surfactant slug can be redissolved into the upcoming low-salinity polymer solution.

In the present study, several alcohols were employed to adjust the optimal salinity of surfactant formulations. A more effective design may require the use of ethoxylated sulfonates[28]. Paraethylcyclohexanol (PECH) was used to decrease the optimal salinity and 2- (2-ethoxy)-ethanol (EOH) was used to increase the optimal salinity of the surfactant formulations. Appropriate amounts of IBA and NPA were also employed to avoid surfactant precipitation. The composition and optimal salinity of each surfactant slug are shown as footnotes in Table 3. Oil displacement experiments were performed in Berea cores under highly hostile connate water salinities (3% NaCl + 1% $CaCl_2$ or 6% NaCl + 1% $CaCl_2$). Because 1% $CaCl_2$ in connate water is equivalent to about 8% NaCl[29], the connate water salinity is higher than the optimal salinity of each surfactant formulation.

As shown in Table 3, tertiary oil recovery can be greatly improved with this design. In Test 3-4, a 90% tertiary oil recovery was obtained even through the connate water salinity was 6% NaCl + 1% $CaCl_2$. However, the surfactant recovery remains below 10%. It is interesting to note that the oil recovery was not complete until about 2.5 PV effluents have been produced. The fractional flows of oil in effluents for Tests 3-1 and 3-2 are shown in Figure 10. The other two tests exhibited similar behaviour. Analysis of Figure 10 reveals that the oil-water bank starts to deteriorate after about 0.7 PV effluents. The pressure drop across the Berea core also showed a sudden decrease near 0.7 PV. The mobility control between the surfactant slug and the polymer solution appeared to be adequate, as the viscosity of produced brine remained below 1.1 mPa·s up to 1 PV total effluent.

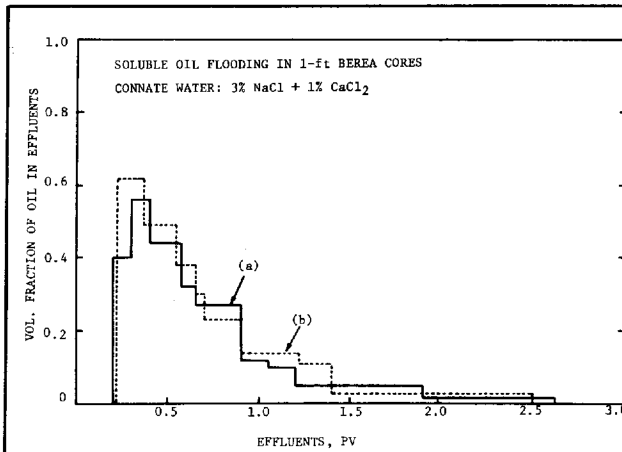

FIGURE 10. Fractional flow of oil for soluble oil flooding in Berea cores. Surfactant formulations: (a) Slug A, 10% PV, (b) Slug A, 5% PV following by Slug B, 5% PV; see Table 3.

The Salinity Shock Design of Mobility Polymer Solutions

It has been shown that there are three factors to consider in designing the salinity of polymer solution; namely, interfacial tension, surfactant loss and viscosity. Instead of making a compromise between these factors, a method is proposed here which can take advantage of all of them. The salinity shock design of mobility polymer solutions employs two polymer slugs in which the first polymer slug is at the optimal salinity of the preceding surfactant formulation and the second polymer slug is in low-salinity brine or fresh water containing a lower concentration of polymer. The design criterion for varying the salinity and concentration of polymer solutions is such that the second polymer slug has a higher viscosity. This is possible because the viscosity of partially hydrolyzed polyacrylamide solution decreases sharply with salinity in the 0 to 0.5% NaCl range.

Oil displacement in sand packs by soluble oil formulation was used to demonstrate the performance of such a design. Some of the previous data were also presented here in order to form a basis for comparison. The results are shown in Table 4. The salinity of connate water was held at the optimal salinity of the surfactant formulation. Test 4-1 was the case without any mobility control; i.e., the surfactant slug was displaced by 1.5% NaCl solution (without polymer). Test 4-2 is the standard experiment, where the salinity of polymer solution was constant at 1.5% NaCl and the polymer concentration was 1000 ppm throughout the displacement process, with which comparison should be made. Tests 4-5 and 4-7 are typical examples of adequate salinity shock design of polymer solutions where the above design criterion was satisfied. A comparison between Tests 4-2 and 4-7 shows that, with this design, tertiary oil recovery can be increased from 89% to 94%, while polymer consumption is reduced by nearly 40%. As the middle phase microemulsions produced *in situ* should not differ too much for these two cases, the increase of oil recovery is probably due to the high viscosity (32 mPa·s) of the second polymer slug. It should be noted, however, that the viscosity of the first polymer slug should also be sufficiently high to provide mobility control.

Conventional graded-concentration designs of polymer solutions always result in unfavorable mobility ratios between successive polymer slugs. When such unfavorable mobility ratios occur, such as those shown in Tests 4-6, 4-8 and 4-9, oil recovery immediately drops from 89% (Test 4-2) to 78%, 83% and 71% respectively. Although, in this report, only two polymer slugs were employed, it can be easily modified to include more slugs of polymer solutions, where necessary, to further decrease the polymer consumption.

Another advantage of this unique design of polymer solutions is that surfactant loss can be reduced. For instance, analysis of the surfactant concentration of effluents in Tests 4-2, 4-5 and 4-7 shows that surfactant recoveries at 1.3 PV are 67%, 84% and 75%, respectively. The reduction of surfactant loss can be attributed to the redissolution of entrapped surfactant into the second polymer slug at a much lower salinity[22]. If the interfacial tension becomes sufficiently low, residual oil left behind the surfactant slug may be mobilized and displaced by the high-viscosity polymer solution. The oil recovered by means of this low-tension mechanism was small in the present sand pack studies because the surfactant loss was not very severe. Oil recovery in Berea cores containing high-salinity connate water can be greatly improved with this design[30].

Conclusions

Based on the results and discussion of this study, it is possible to arrive at the following conclusions:

(1) The optimal salinity concept, as derived from the solubilization or interfacial tension of microemulsions, is applicable to oil displacement by soluble oils or oil-external microemulsions in porous media. Maximal oil recovery was obtained when the salinity of connate water and polymer solution was at the optimal salinity of the surfactant formulation.

(2) The salinity of polymer solution is far more important than the salinity of connate water in the present study. Evidence showed that the phase behaviour of the surfactant slug in porous media is largely determined by the salinity of polymer solution.

(3) The concept of contrast salinity design should be applied with care. For the present system, with an optimal salinity increasing with dilution, a decreasing salinity gradient is still preferred.

(4) A two-slug design of the surfactant formulation is proposed. In this design, the first surfactant slug has an optimal salinity close to the connate water salinity and the second surfactant slug has a much lower optimal salinity (< 0.5% NaCl). The polymer (polyacrylamide) solution salinity is made equal to the optimal salinity of the second surfactant slug. With this design, high oil recovery (90%) can be obtained for soluble oil flooding in Berea cores containing a highly hostile connate water (6% NaCl + 1% $CaCl_2$).

(5) A salinity shock design of mobility polymer solutions is proposed. This design employs two slugs of polymer solution in which the first polymer slug is at the optimal salinity of the surfactant formulation and the second polymer slug is at a much lower salinity (< 0.05% NaCl). With this unique design, high oil recovery and high surfactant recovery can be obtained, and polymer (polyacrylamide) consumption can be greatly reduced.

Acknowledgments

The authors wish to express their sincere thanks and appreciation to the National Science Foundation — RANN, ERDA and the Department of Energy (Grant No. DE-AC1979BC10075) and the consortium of the following industrial associates for their generous support of the University of Florida Enhanced Oil Recovery Research Program during the past seven years: 1) Alberta Research Council, Canada; 2) American Cyanamid Co.; 3) Amoco Production Co.; 4) Atlantic Richfield Co., 5) BASF-Wyandotte Co.; 6) British Petroleum Co., England; 7) Calgon Corp.; 8) Cities Service Oil Co.; 9) Continental Oil Co.; 10) Ethyl Corp.; 11) Exxon Production Research Co.; 12) Getty Oil Co., 13) Gulf Research and Development Co.; 14) Marathon Oil Co.; 15) Mobil Research and Development Co.; 16) Nalco Chemical Co.; 17) Phillips Petroleum Co.; 18) Shell Development Co.; 19) Standard Oil of Ohio; 20) Stepan Chemical Co.; 21) Sun Oil Chemical Co.; 22) Texaco, Inc; 23) Union Carbide Corp.; 24) Union Oil Co.; 25) Westvaco, Inc.; 26) Witco Chemical Co.; and the University of Florida.

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TABLE 4. Salinity shock design of mobility polymer solutions for soluble oil flooding in sand packs[a,b,c]

Test	Polymer Solution	Tertiary Oil Recovery	Surfactant Recovery at 1.3 PV
4-1	0 ppm, 1.5% NaCl, 2 PV	53%	25%
4-2	1000 ppm, 1.5% NaCl, 1 PV	89%	67%
4-3	250 ppm, 0% NaCl, 1 PV	76%	99%
4-4	250 ppm, 1.5% NaCl, 1 PV	69%	—
4-5	1000 ppm, 1.5% NaCl, 0.2 PV followed by 250 ppm, 0% NaCl, 0.8 PV	88%	84%
4-6	1000 ppm, 1.5% NaCl, 0.2 PV followed by 0.8 PV distilled water	78%	—
4-7	1000 ppm, 1.5% NaCl, 0.5 PV followed by 250 ppm, 0% NaCl, 0.5 PV	95%	75%
4-8	1000 ppm, 1.5% NaCl, 0.5 PV followed by distilled water, 0.5 PV	83%	—
4-9	1000 ppm, 1.5% NaCl, 0.2 PV followed by 1.5% NaCl, 0.8 PV	71%	—

a. Soluble oil formulation: 10% TRS 10-410 + 4% IBA in dodecane, 5% PV slug. The salinity of connate water was 1.5% NaCl (optimal of the surfactant formulation) in every case.
b. Porous media: 33 cm long by 2.5 cm diameter sand packs, K = 4.2 μm^2
c. Linear displacement velocity = 0.85 m/day. Tertiary oil recovery was complete within 1.2 PV effluents.

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(Reprinted from The Canadian Mining and Metallurgical Bulletin, July/September, 1981)

Printed in Canada