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MOBILITY CONTROL AND SCALEUP FOR CHEMICAL FLOODING

Annual Report for the Period October 1981—September 1982

By
G. A. Pope

November 1984
Date Published

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The University of Texas at Austin
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FOR CHEMICAL FLOODING

Annual Report
October 1981-September 1982

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1.0 INTRODUCTION

The ongoing objectives of this project are: (1) to determine quantitatively the effects of dispersion, relative permeabilities, apparent viscosity and inaccessible pore volume on micellar/polymer flooding, and (2) to develop numerical simulators which incorporate these and other features of the process, so that mobility control design and scaleup of the micellar/polymer flooding process can be better accomplished. These objectives were discussed fully in our First Annual DOE Report.¹ This same report included discussions of the experimental aspects of the project and the initial experimental results, as well as the progress in the development of both one and two dimensional simulators.

The Second Annual DOE Report² presented a summary and discussion of the results of the work of eight graduate students who completed their degrees during the year. Progress during the third year of the project has been somewhat slower than had been hoped due to the high turnover of graduate students during the second year. This problem was further exacerbated by the premature departure of two graduate students prior to making significant contributions. The progress which has been made, however, is significant in both the experimental and the simulation areas.

Three graduate students contributed to the results given in this year's report. One of these students, Dominic Camilleri, has completed his M.S. thesis,³ while another, Mojdeh Delshad, is a Ph.D. candidate who has not yet graduated. A more detailed discussion of the techniques and results of the simulator advances can be found in Camilleri's thesis. Three papers^{4,5,6}

have been submitted to SPE as well. Senol⁷ completed her thesis on cross-linked polymers and the results were included in a recent SPE paper.⁸

Supporting physical property data for many of the solutions used in these experiments were presented previously as were some results for dispersion and relative permeability experiments.^{1,2} Section 2 of this report includes the results for capillary desaturation experiments for low tension fluids in Berea. These results show that some residual brine remains during microemulsion flooding even at the highest capillary number obtained in this experiment.

Section 2 also includes more extensive results from the dispersion and relative permeability experiments. These experiments include dispersion using both continuous and pulsed tracer data. This section also includes data which extends the dispersion and relative permeability results from the case of two-phase flow to include initial results of three-phase flow at steady state.

One of the difficulties inherent in the three-phase flow experiments has been the problem of appropriate tracers for determination of dispersion of the fluids independently. As discussed by Delshad,⁹ in order to evaluate three-phase flow it is necessary that at least one of the tracers be non-partitioning. Our recent acquisition of a new liquid scintillation counter will enable us to proceed with the three-phase flow experiments under conditions which will allow the accurate evaluation of each flowing phase. This will be accomplished by using tritium-labelled surfactant which acts as a non-partitioning tracer in the middle-phase microemulsion. The previous carbon 14-labelled decane and a new tracer, chlorine 36, will be used as partitioning tracers for the oil and brine phases respectively. Thus, we should be able to resolve the

dispersion and relative permeability results for each of the three flowing phases.

Section 3 is a complete description of our updated simulator. Especially noteworthy are the new phase-behavior model, which approximates the quaternary behavior of mixtures of surfactant, alcohol, oil, and brine, and the cation exchange model, which allows for cation exchange between both clay and micelles. Section 4 describes and gives the results of an oil recovery experiment. The analysis of produced samples is more complete than any previously reported. Section 5 compares the results of this oil recovery experiment with our simulator. The agreement is the best obtained so far. Section 6 compares our simulator with a Sloss experiment reported by Gupta. Again, the agreement is good and demonstrates the capability of the improved simulator to account for the separation of alcohol and surfactant. Section 7 contains the results of several 2-D areal simulations involving new features of the 2-D simulator reported last year. Section 8 is a list of some of the major conclusions of this simulation research. Section 9 is an SPE paper combining the results of Senol with Walsh, a Ph.D. student of Lake and Schechter. Her polymer experiments were interpreted using Walsh's geochemical simulator.

2. EXPERIMENTAL

2.1 Introduction and Background

Previous reports^{1,2} have discussed the results of experiments designed to measure: (1) physical properties of the system under study, (2) rheological behavior of polymer and microemulsion solutions, and (3) dispersion and relative permeability in micellar/polymer flooding. More extensive detailed information regarding procedures and results are to be found in references 9 through 12 inclusive.

The physical property results which had been measured indicated that the system which was selected for use, consisting of 1.5 vol% TRS 10-410: 1.5 vol% isobutanol: 50 vol% normal decane (95% pure): 47% brine (1.1 wt% NaCl), was suitable for our procedures. This composition gave a reasonable viscosity without gel formation and adequate volumes of each of the three phases. A slight modification to this system is detailed in Section 2.2.

Rheologic measurements of this system showed it to exhibit Newtonian behavior at shear rates from 10^{-2} to in excess of 10^3 sec^{-1} in the absence of polymer. The same system prepared using 1000 ppm Xanflood polymer demonstrated a non-Newtonian behavior which was qualitatively the same as the polymer alone.

Although further systematic physical property studies are both in progress and planned, they are as yet incomplete and are not reported here. The physical property data reported in Section 2.2 represents data collected as part of our ongoing evaluation of the surfactant material received to ensure that we maintain our system at the optimum salinity in spite of variations in the batches of surfactants received.

The results of previously reported dispersion experiments demonstrated that the classical single-phase dispersion theory could be generalized to

interpret multiphase dispersion data with the tracer following the error function trend. For multiphase flow the dispersion coefficient at a given flow rate depends on the phase, interfacial tension and phase saturation with a tendency for the dispersivity in a given phase to increase as the phase saturation decreases. An exception to this tendency is observed in cases of microemulsion flowing with either excess oil or excess brine.

The most significant result of the relative permeability experiments reported earlier was the presence of a residual microemulsion even at high capillary number. The capillary desaturation experiment reported in Section 2.3 increases the capillary number to values sufficient to reduce residual microemulsion-phase trapping to zero.

Relative permeability curves were reported to be increased but continued to show significant curvature, even at interfacial tensions of 10^{-3} dynes/cm. Our most recent experiments verify that the curves do not become straight lines at this IFT, but continue to be curved. These results are discussed in Section 2.4.

Section 2.5 of this report presents some results of initial experiments using three-phase flow in Berea. These results, like those reported by us previously for an unconsolidated sandpack, are difficult to adequately interpret because of the lack of a non-partitioning tracer. Consequently, these results should be regarded only as preliminary and tentative. This difficulty has now been overcome and a series of experiments are being planned and conducted using a non-partitioning tracer in the microemulsion phase.

2.2 Physical Properties

As mentioned above, physical property data on the system used for the micellar flooding experiments are collected routinely for each new batch of surfactant received. The overall fluid composition outlined in Section 2.1 is adjusted by the addition of calcium chloride sufficient to produce a calcium concentration in the microemulsion of 15 ppm, based on the assumption that all of the calcium will partition into the microemulsion. The selection of 15 ppm calcium corresponds to values of calcium detected in steady-state floods of microemulsions without calcium, thus injected and produced samples have the same calcium concentration.

The volume fraction diagram which is shown in Figure 2.1 demonstrates the typical transition from Type II(-), through Type III to Type II(+) behavior with increasing salinity. The midpoint of the three-phase region and the salinity at which equal volumes of excess oil and brine are observed do not agree as precisely for this batch of surfactant as results previously reported; however, the differences were not considered significant enough to adjust the salinity of the composition used.

The viscosity of the middle phases was measured over a shear rate range of 0.018 to 128 sec^{-1} . These results, shown in Figure 2.2, do not show any significant viscosity differences when compared with previous results.^{1,2,9-11,13} Viscosity measurements of the microemulsion phase as a function of salinity are shown in Figures 2.3 and 2.4 at constant shear rates of 0.945 and 5.96 sec^{-1} respectively. Again, comparison with previous data shows some differences do exist but are not significant in the conduct of our transport experiments. The appearance of the high viscosity microemulsion at the transition from Type II(-) to Type III behavior has been observed in all of our experiments of this type

to date.

2.3 Capillary Desaturation

Capillary desaturation curves (the relationship between residual phase saturation and the capillary number) is one of the most important physical relations of the micellar-polymer process. Despite this importance, a complete set of experimental capillary desaturation curves for micellar fluids has never been measured. Therefore, the main purpose of experiment CDC-3 was to obtain these data for three-phase micellar fluids as a function of capillary number in a Berea sandstone core.

The porous medium was a two-inch-square by 24-inch-long Berea core (with pressure taps six inches from either end) used in a horizontal configuration. The characteristics of the core are listed in Table 2.1.

A 15 liter batch of micellar fluid with the same total composition as given previously was made up at 1.1 wt% NaCl with 15 ppm Ca^{++} (in the microemulsion phase) and allowed to equilibrate. The equilibration time was about 20 to 30 days.

The composition of the microemulsion phase was determined to be 39.25 v% brine, 55.5 v% n-decane, 1.79 v% IBA, and 3.5 v% TRS 10-410. The physical properties of all the three phases are tabulated in Table 2.2.

The experiment involved the following sequence of floods, starting with a core containing a known residual oil ($S_{or} = 0.30$) from the waterflood.

1. The core was flooded with microemulsion to steady state and material balance calculations were done to determine the saturation state of the core. The core was then flooded with the same microemulsion containing both carbon-14 and tritium as tracers. The latter step enables us to evaluate the saturations by tracer breakthrough data to compare with material balance calculations

and to determine the dispersion coefficients. The residual saturations based on the tracer data were: excess brine $S_{1r} = 0.169$ and excess oil $S_{2r} = 0.0$.

2. The first step of the experiment was to measure the residual microemulsion saturation to excess brine at various capillary numbers. To accomplish this objective, the core was flooded with the excess brine phase at a low flow rate (low capillary number) until the steady-state conditions were achieved. Brine containing tritium was then injected at the same flow rate. Effluent samples were analyzed and dispersion curves and saturations were determined.

3. The capillary number was increased step-wise by repeating step 2 at increasing flow rates for the injection of brine.

Figure 2.5 is the tritium breakthrough curve at the highest capillary number obtained, 0.433 ($q = 51$ cc/min). The curve shows the typical S-shaped trend with the 50% concentration breakthrough at 1.04 P.V.

The same protocol as above was followed for measuring the following data:

- residual brine to microemulsion
- residual microemulsion to excess oil
- residual oil to microemulsion

Figures 2.6-2.8b are the tracer breakthrough curves for the above floods. The experimental results are presented in Table 2.3.

The four different capillary desaturation curves are plotted in Figure 2.9 showing the residual phase saturation as a function of capillary numbers. The definition of capillary number used in this study is

$$N_c = \frac{k \Delta \phi}{L \sigma}$$

where k is the absolute permeability to brine

$\Delta\phi$ is the potential drop,

L is the porous sample length,

and σ is the interfacial tension.

Figure 2.9 shows the phase saturations calculated from the dispersion measurements as a function of capillary number. The most significant feature of these capillary desaturation curves is that the residual saturation of microemulsion to brine does not go to zero until a capillary number of approximately 0.4 is reached. At this same capillary number a residual saturation of brine to microemulsion remains. The dispersion data, therefore, suggests that the brine phase is more wetting than the microemulsion phase. Material balance calculations for residual microemulsion to brine gives a residual saturation of approximately 0.025 which is slightly higher than the residual brine saturation. Further experiments are planned for high capillary numbers in order to determine which fluid is acting as the wetting phase at high capillary numbers.

It can also be noted from Figure 2.9 that the residual oil to microemulsion is already zero at the lowest capillary number measured, 3.8×10^{-3} , while residual microemulsion to oil is about 10% at about the same capillary numbers.

The endpoint relative permeabilities were calculated using the measured pressure drop and Darcy's equation. Figure 2.10 shows the endpoint relative permeabilities for the injected fluids as a function of capillary number. The endpoint relative permeability for oil and microemulsion is already at a plateau value at a capillary number of 10^{-3} , while the relative permeability to brine does not approach a plateau until the capillary number exceeds 10^{-1} .

The single-phase dispersion coefficients for carbon-14 in the excess oil, both carbon-14 and tritium in the microemulsion, and tritium in the excess brine are plotted as a function of phase frontal velocity ($q_j/A\phi S_j$) in Figures 2.11 to 2.13. All curves show an increase in dispersion coefficient with increasing velocity similar to that observed by many others for single-phase flow. A straight line on a log-log scale is obtained for the data for each phase with a reasonable value for the slope. The slope corresponds to the exponent β in equation 2.1 and is about 1.05 for the oil phase, 1.11 for the microemulsion phase, and 1.21 for the brine phase. These values are typical for single-phase flow reported in the literature.¹⁴⁻¹⁹ No values for microemulsions have been previously reported.

$$K_{lij} = \frac{D_{ij}}{F\phi} + \alpha_{lij} v_j^\beta \quad (2.1)$$

where K_{lij} = longitudinal dispersion coefficient of component i
in phase j

D_{ij} = molecular diffusion coefficient of component i
in phase j

F = formation resistivity factor

ϕ = porosity

α_{lij} = longitudinal dispersivity of component i in phase j

v_j = frontal velocity of phase j

2.4 Dispersion and Relative Permeability

A. Experiment No. SMO.- Oil and Microemulsion in Berea core

This experiment was conducted in the same core as used in experiment CDC-3 at 30°C (see Table 2.1) but in the vertical configuration to prevent fluid segregation. The purpose of this experiment was the evaluation of

relative permeability and dispersion at a constant capillary number of 10^{-2} for the upper phase excess oil and middle phase microemulsion of the three-phase micellar solution previously discussed.

The main difference between this experiment and those previously reported^{1,2,9,11,13} is that at each cut the flow rate was adjusted to obtain a constant potential drop and thus a constant capillary number.

A new batch of micellar solution with the same composition was made and the properties of this solution are presented in Table 2.4. Comparisons of Tables 2.2 and 2.4 illustrate the minor variations between stock solutions which are prepared.

The procedure followed in this experiment was to:

- (1) Saturate the core with microemulsion at 0.955 cc/min (potential drop of 1.97 psi/ft) until the produced samples showed single-phase microemulsion, and the pressure drop was constant.
- (2) Inject the microemulsion containing both carbon-14 and tritium at the same velocity. The residual saturations at this point were $S_{1r} = 0.117$ and $S_{2r} = 0.0$.
- (3) Flood the core with excess oil to steady state at 0.647 cc/min (or potential drop of 0.22 psi/ft) and then
- (4) Inject oil containing carbon-14 at the same velocity. The residual saturations at this point from the dispersion data were determined to be $S_{1r} = 0.117$ and $S_{3r} = 0.0$.
- (5) Inject microemulsion cuts of 4.7%, 9.9%, 22%, 57.2%, and 100%. At steady state for each cut, tritium and carbon-14 were used in the microemulsion to measure dispersion of the microemulsion phase. Similarly, carbon-14 was used in the oil phase to measure oleic dispersion.

In this experiment, because of the residual brine ($S_{1r} = 0.0117$), both

- to evaluate the dispersion coefficients for both of these phases using continuous and slug displacements of tracers.
- The same batch of micellar solution was used as in experiment No. SMO. (See Table 2.4.)

The procedure for the experiment was to:

- Flood the core (which is at the known saturations of $S_{1r} = 0.117$, $S_{2r} = 0.033$, $S_3 = 0.849$ from carbon 14 data) with 22.5% brine and 77.5% microemulsion to steady state,
- Flood the core with tritium and carbon 14-labelled microemulsion and tritium-labelled brine at the same cut and rate,
- Inject 67.5% and 83.4% brine cuts. At each cut, after reaching the steady state, inject a 15.6% pore volume slug of tracers.
- Inject 93.3% brine cut to steady state followed by continuous injection of tritium-labelled brine at steady state.

There were four tasks involved in running a slug type experiment. The tasks were: the establishment of steady state at the specific cut; the measurement of pressure drop across the core to allow phase permeability calculation; the injection of a certain size (15.6% P.V.'s) of radioactive tracers in both phases; and, finally, displacement of the slug with the same fluid (without tracers) at the same flow rate. Raimoni and Torcaso²⁰ were among the first of several investigators^{20,21} to have run similar experiments for single-phase flow with unit saturation or one flowing phase and an immobile phase. However, this is the first time that slug-type runs have been done for two-phase, low-tension flow.

Figures 2.19 through 2.24 are the breakthrough curves for carbon 14 and

carbon-14 and tritium are partitioning tracers. The values of the partition coefficients were 0.407 and 0.555 (see Table 2.4) for tritium and carbon-14 respectively.

Figures 2.14 to 2.16 show the normalized tracer concentration versus injected pore volumes for two-phase flow of microemulsion and oil at 78% oil and 22% microemulsion cut. These dispersion curves are the normal sigmoid curves which are expected.

The relative permeabilities were calculated by the use of Darcy's law taking into consideration the effect of the gravity head. The calculated saturations (from material balance and breakthrough curves), relative permeabilities and potential drops are shown in Table 2.5.

The relative permeability curves for excess oil and microemulsion based on both material balance calculations and dispersion data are presented in Figure 2.17. The relative permeabilities are plotted as a function of both oil and microemulsion saturations. The endpoint of the curves, based on material balance calculations, are at $S_{1r} = 0.117$, $S_{2r} = 0.096$, and $S_{3r} = 0.0436$. The relative permeabilities show less curvature at this high capillary number ($N_c = 10^{-2}$) than at low capillary number, but still differ from straight lines.

The oil-phase fractional flow is plotted as a function of oil saturation in Figure 2.18.

B. Experiment No. SMW - Brine and Microemulsion in Berea Core

The core from experiment No. SMO was used once again for this experiment. The objectives of this experiment were:

- to measure the relative permeability curves for middle-phase microemulsion and lower-phase brine at a constant capillary number of 6.6×10^{-3} .

tritium in brine at 67.5% and 83.4% brine cuts. All the dispersion curves are very asymmetric and have long tails. This is more pronounced for tritium than for carbon-14.

In the case of continuous injection of tracers in two-phase flow, at some of the cuts the concentration increases rapidly to a 50% concentration, after which the effluent concentration rises only slowly to that of the injected fluid. Thus, it was thought that the slug-type run might decrease the time required and the quantity of fluid injected to do the dispersion run. As was pointed out earlier, the slug concentration profiles have long tails. Therefore, it takes nearly as long to produce the entire slug as the complete profile using continuous injection. The advantage of this type of run was found to be that the concentration profiles for tracers are readily distinguishable (Figures 2.20 and 2.24).

The values for potential drop, relative permeabilities, and saturations for both material balance calculations and tracer data are presented in Table 2.6.

The procedure for calculating saturations from the tracer breakthrough curves for the slug-type runs are discussed later.

Two sets of relative permeability curves versus saturation are plotted in Figure 2.25. One set of curves is based on the material balance calculations, and the other one is based on the dispersion data. The relative permeabilities are plotted as a function of both brine and microemulsion saturations in Figure 2.25. A constant residual oil saturation of 0.033 was present during the experiment. These results, like those previously reported,² demonstrate the persistent curvature of the relative permeability curves.

Last, the brine fractional flow curve from material balance calculation is plotted in Figure 2.26.

2.5 Three-Phase Flow

It was initially anticipated that the sequence of floods conducted would follow the saturation pathway shown in Figure 2.27. From previous experiments, the residual saturations (shown as dashed lines) and relative permeabilities were used to calculate the fractional flow rates necessary to give the saturations shown in Figure 2.26. These same data were used to calculate the total flow rate necessary to maintain a constant capillary number. These values were then used as the nominal flow rates injected.

The three-phase flow experiments, using the calculated fractional flow rates were begun and run for the predicted saturations identified as 1 and 2 in the figure. The experimental protocol remained unchanged from previous experiments. The fluids were injected at the pre-selected nominal flow rates until steady state was reached. This was followed by the injection of tritium- and carbon-14-labelled phases. The effluent samples were analyzed by liquid scintillation counting techniques to determine the dispersion curve characteristics. The actual phase fractional flows were calculated from the effluent sample volume measurements.

The dispersion and dispersivity results of these two experiments are shown in Figures 2.28 through 2.35, inclusive. For reasons discussed below, the dispersion curves for the microemulsion phases in these experiments are not available.

The actual fractional flow rates for experiment BM01-2 were:

brine 0.772, oil 0.185, and microemulsion 0.043. Figures 2.28 and 2.30 show the dispersion curves for tritium in the brine phase and carbon-14 in the oil phase respectively. The corresponding lambda plots are shown in Figures 2.29 and 2.31. Experiment BM01-4 had fractional flow rates of: brine 0.51, oil 0.455, and microemulsion 0.035. Dispersion and lambda plots for tritium in the aqueous phase and carbon-14 in the oleic phase may be found in Figures 2.32 through 2.35.

Comparison of Figures 2.28 and 2.32, showing dispersion of tritium in the brine phase for these two experiments, shows that the breakthrough in both cases occurred at 0.77 pore volumes. Furthermore, the lambda plots for these two experiments are virtually identical. This result showing virtually no change in brine dispersion in spite of a change in fraction flow of 0.262 is as yet unexplained. As pointed out earlier, however, these results are preliminary and hence any conclusions would be premature.

The results of the carbon-14 tracers in these two experiments would appear to indicate that phase saturation changes are, in fact, taking place. Calculations of phase saturations based on the breakthrough of the two tracers, however, give results indicating that the phase saturation for each phase is in excess of unity. Resolution of this anomaly depends upon further experiments in which all three phase dispersions can be measured.

Analysis of the middle phase for these experiments could not be accomplished due to the extremely low microemulsion-phase cut used in the experiments (0.045 and 0.035). The produced volumes of microemulsion were not large enough to allow removal of a sufficient volume for analysis without contamination by an adjacent phase. These experiments will be repeated at a later date using new tracer materials. As mentioned previously, we now have

the capacity to conduct experiments using three radioisotopes. By using a non-partitioning surfactant tracer in the microemulsion phase, its dispersion can be measured even in the presence of contamination from the other phases. Therefore, we anticipate that later experiments, using the three tracers will enable us to resolve these results.

The relative permeability of each phase is shown as a function of the fractional flow of that phase in Figure 2.36. The limited data available indicate three distinct relative permeability curves exist as shown. It must, however, be emphasized that these results are tentative and further data are needed before definitive conclusions can be made and we are in the process of conducting the experiments needed to provide these data.

2.6 Procedure for Calculating Saturations and Dispersion Coefficient Using the Slug Concentration Profile

Consider the flow of an ideal, non-interacting tracer through a one-dimensional homogeneous permeable medium. The convection-diffusion (C-D) equation in dimensionless terms which describes the conservation of the tracer in single-phase flow is (for more details see references 9,11, and 13):

$$\frac{\partial C_D}{\partial x_D} + \frac{\partial C_D}{\partial t_D} = \frac{K_\ell}{Lv} \frac{\partial^2 C_D}{\partial x_D^2}$$

where $C_D = C_T/C_0$ is normalized tracer concentration
 K_ℓ is longitudinal dispersion coefficient
 v is frontal velocity.

The exact analytic solution to the above equation with the following boundary conditions has been derived by Naiki⁵⁴ using a Laplace Transform.

$$\begin{aligned}
C_D(x_D, 0) &= 0 & x_D &\geq 0 \\
C_D(x_D \rightarrow \infty, t_D) &= 0 & t_D &\geq 0 \\
C_D(0, t_D) &= 1 & t_D &\geq 0
\end{aligned}$$

The exact solution to the C-D equation is as follows:

$$C_D = \frac{1}{2} \operatorname{erfc} \left(\frac{x_D - t_D}{\sqrt{4t_D N_{pe}^{-1}}} \right) + \frac{e^{x_D N_{pe}}}{2} \operatorname{erfc} \left(\frac{x_D - t_D}{\sqrt{4t_D N_{pe}^{-1}}} \right)$$

where N_{pe} is a macroscopic Peclet number ($N_{pe} = \frac{vL}{K}$).

Returning to the case of the slug, the boundary conditions are

$$\begin{aligned}
C_D(x_D, 0) &= 0 \\
C_D(0, t_D) &= 1 & 0 < t_D < t_{DS} \\
C_D(0, t_D) &= 0 & t_D > t_{DS} \\
C_D(x_D \rightarrow \infty, t_D) &= 0 & t_D > 0
\end{aligned}$$

where t_{DS} is the size of slug in pore volumes.

By the principle of superposition, the solution for the dispersion of the slug for $t_D \geq t_{DS}$ and at $x_D = 1.0$, is

$$\begin{aligned}
C_D &= \frac{1}{2} \operatorname{erfc} \left(\frac{1 - t_D}{\sqrt{4N_{pe}^{-1} t_D}} \right) + \frac{e^{N_{pe}}}{2} \operatorname{erfc} \left(\frac{1 + t_D}{\sqrt{4N_{pe}^{-1} t_D}} \right) \\
&- \frac{1}{2} \operatorname{erfc} \left(\frac{1 - (t_D - t_{DS})}{\sqrt{4N_{pe}^{-1} (t_D - t_{DS})}} \right) - \frac{e^{N_{pe}}}{2} \operatorname{erfc} \left(\frac{1 + (t_D - t_{DS})}{\sqrt{4N_{pe}^{-1} (t_D - t_{DS})}} \right)
\end{aligned}$$

For large times (t_D), the above is approximated by the following equation

$$C_D = \frac{1}{2} \left[\operatorname{erf} \left(\frac{1.0 - (t_D - t_{DS})}{\sqrt{4N_{pe}^{-1}(t_D - t_{DS})}} \right) - \operatorname{erf} \left(\frac{1 - t_D}{\sqrt{4N_{pe}^{-1}t_D}} \right) \right]$$

The convection-diffusion equation for two-phase flow with a partitioning tracer has been derived by Delshad et al.,¹³ which is a generalization of single-phase flow. The C-D equation for two-phase flow at steady state for brine phase ($j = 1$) and microemulsion phase ($j = 3$) with a partitioning tritium tracer ($i = 1$) is as follows:

$$\frac{\partial C_{D1}}{\partial t_{DT}} + \frac{\partial C_{D1}}{\partial x_D} = \frac{\bar{K}}{v_T L} \frac{\partial^2 C_{D1}}{\partial x_D^2}$$

where

$$v_T = \frac{q}{A\phi} \frac{f_1 + f_3 K_{T1}}{S_1 + S_3 K_{T1}}$$

$$t_{DT} = \frac{tv_T}{L} = \frac{t_D}{t_{DBT}}$$

$$\bar{K} = \frac{S_1 K_{11} + S_3 K_{13} K_{T1}}{S_1 + S_3 K_{T1}}$$

where K_{13} and K_{11} are the longitudinal dispersion coefficients of tritium in the microemulsion and brine phases, respectively. K_{T1} is the partition coefficient of tritium ($K_{T1} = \frac{C_{T3}}{C_{T1}}$).

By analogy the solution to the above equation for the case of slug is:

$$C_{D1} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{1 - t_{DT}}{\sqrt{4\bar{N}_{pe}^{-1} t_{DT}}} \right) + e^{\bar{N}_{pe}} \operatorname{erfc} \left(\frac{1 + t_{Dr}}{\sqrt{4\bar{N}_{pe}^{-1} t_{DT}}} \right) \right] \\ - \frac{1}{2} \left[\operatorname{erfc} \left(\frac{1 - (t_{DT} - t_{DTS})}{\sqrt{4\bar{N}_{pe}^{-1} (t_{DT} - t_{DTS})}} \right) + e^{\bar{N}_{pe}} \operatorname{erfc} \left(\frac{1 + (t_{DT} - t_{DTS})}{\sqrt{4\bar{N}_{pe}^{-1} (t_{DT} - t_{DTS})}} \right) \right]$$

where

$$\bar{N}_{pe} = \frac{\bar{K}}{Lv_T} \\ t_{DTS} = \frac{t_{DS}}{t_{DBT}}$$

It should be noted that there are two unknowns, t_{DBT} and $\bar{N}_{pe}$, in the solution equation. Therefore, a computer program was written to generate slug concentration profiles (C_{D1} vs t_D) for arbitrary values of $\bar{N}_{pe}$ and t_{DBT} . Then the experimental curve was compared to the computer-generated curves and the t_{DBT} and $\bar{N}_{pe}$ for the best matches were determined. Figures 2.37 to 2.40 show the experimental pulse and the best computed match for the dispersion of tritium in brine and carbon-14 in microemulsion at 67.5% brine and 32.5% microemulsion cut consecutively.

The phase saturations were then calculated using the value of t_{DBT} in the following equation

$$t_{DBT} = \frac{S_1 + S_3 K_{T1}}{f_1 + f_3 K_{T1}}$$

with $S_1 + S_3 + S_{2r} = 1.0$, S_{2r} the known residual oil saturation present during the experiment, and f_1 and f_3 are the steady-state experimental values for brine and microemulsion cuts.

The average dispersion coefficient and dispersivity were calculated from

$$\bar{\alpha} = \frac{L}{\bar{N}_{pe}}$$

$$\bar{K} = v_T \bar{\alpha}$$

There are two average dispersivity equations and three unknowns, K_{11} , K_{13} , and K_{23} , where K_{23} is the dispersion coefficient of carbon-14 ($i = 2$) in the microemulsion phase. The value of K_{23} can be calculated using the average dispersion coefficient for carbon-14. The calculation of the dispersion coefficient of tritium in brine and microemulsion is not possible with only these data.

TABLE 2.1
Characteristics of Berea Core

Length	24 in. (60.96 cm)
Cross-section area	3.95 in ² (25.5 cm ²)
Bulk volume	1554.5 cc
Pore volume	330 cc.
Porosity	0.212
100% brine permeability	0.739 Darcy
Residual brine (S_{wr})	0.35
Residual oil (S_{or})	0.30
Dispersivity at $S_w = 1$	0.224 cm

TABLE 2.2
Physical Properties of Fluids
(Experiment No. CDC-3)

	<u>Lower Phase</u>	<u>Middle Phase</u>	<u>Upper Phase</u>
Volume fraction	0.279	0.451	0.268
Density, g/cc	1.0008	0.8508	0.7275
Viscosity, cp	0.84	4.0	0.780
Calcium content, ppm	0.86	21.9	0.0
Brine content, v%	97.87	39.25	0.0
N-decane content, v%	0.0	55.46	99.65
Alcohol (IBA) content, v%	2.1	1.79	0.30
TRS10-410 content, v%	0.03	3.5	0.05
Interfacial tension dvne/cm	7.6×10^{-4} 4×10^{-4}		

TABLE 2.3
Experimental Results

Fluid Injected	Potential drop psi/ft	IFT dyne/cm	N_c	Endpoint Relative Permeability	Brine Saturation	Microemulsion Saturation	Oil Saturation
excess brine	0.095	7.6×10^{-4}	2.06×10^{-3}	0.470	0.774	0.226	0.0
excess brine	1.20	7.6×10^{-4}	2.6×10^{-2}	0.793	0.931	0.069	0.0
excess brine	20.0	7.6×10^{-4}	0.433	0.849	1.0	0.0	0.0
microemulsion	0.055	7.6×10^{-4}	1.19×10^{-3}	0.922	0.140	0.860	0.0
microemulsion	0.425	7.6×10^{-4}	9.2×10^{-3}	0.969	0.04	0.960	0.0
microemulsion	4.8	7.6×10^{-4}	0.104	0.944	0.02	0.980	0.0
microemulsion	20.0	7.6×10^{-4}	0.433	0.927	0.01	0.99	0.0
excess oil	0.0575	4×10^{-4}	2.36×10^{-3}	1.0	0.07	0.119	0.811
excess oil	0.295	4×10^{-4}	1.2×10^{-2}	0.916	0.07	0.0	0.930
excess oil	15.65	4×10^{-4}	0.644	0.938	0.07	0.0	0.930
microemulsion	0.09	4×10^{-4}	3.7×10^{-3}	0.986	0.07	0.93	0.0
microemulsion	1.60	4×10^{-4}	0.066	0.931	0.07	0.93	0.0
microemulsion	22.0	4×10^{-4}	0.906	0.923	0.07	0.93	0.0

TABLE 2.4
Physical Properties of Fluids
(Experiment No. SMO)

	<u>Lower Phase</u>	<u>Middle Phase</u>	<u>Upper Phase</u>
Volume fraction	0.277	0.483	0.240
Density, g/cc	1.0018	0.8637	0.7247
Viscosity, cp	0.897	4.50	0.824
Calcium content, ppm	2.10	10.00	—
Magnesium content, ppm	0.45	5.52	—
Brine content, v%	97.87	40.7	0.0
Oil content, v%	0.0	54.3	99.65
Alcohol (IBA) content, v%	2.1	1.50	0.30
TRS10-410 content, v%	0.03	3.5	0.05
Interfacial tension, dyne/cm	7.4×10^{-3}	3×10^{-4}	
Partition coefficient	0.407	0.555	

TABLE 2.5

Oil/Microemulsion Relative Permeabilities

(Experiment No. SMO)

oil cut (f_2)	oil phase potential drop psi/ft	microemulsion relative permeability k_{r3}	oil relative permeability k_{r2}	Material Balance		Carbon 14		Tritium	
				microemulsion saturation S_3	oil saturation S_2	microemulsion saturation S_3	oil saturation S_2	microemulsion saturation S_3	oil saturation S_2
0.0	—	0.864	—	0.883	0.0	0.883	0.0	0.883	0.0
1.0	0.22	—	0.955	0.0435	0.839	0.0	0.883	—	—
0.953	0.25	0.194	0.908	0.115	0.768	—	—	—	—
0.901	0.27	0.361	0.727	0.248	0.635	0.287	0.596	—	—
0.78	0.27	0.606	0.476	0.321	0.562	0.343	0.54	0.243	0.640
0.428	0.26	0.821	0.137	0.590	0.293	0.82	0.063	0.680	0.203
0.0	—	1.0	—	0.787	0.096	0.849	0.033	0.872	0.010

* $S_{1r} = 0.117$ = constant during the experiment

TABLE 2.6
Brine/Microemulsion Relative Permeabilities
(Experiment No. SMW)

microemulsion cut (f_3)	microemulsion potential drop psi/ft	microemulsion relative permeability k_{r3}	brine relative permeability k_{r1}	Material Balance		- Carbon 14		Tritium	
				microemulsion saturation S_3	brine saturation S_1	microemulsion saturation S_3	brine saturation S_1	microemulsion saturation S_3	brine saturation S_1
0.775	0.250	0.978	0.045	0.687	0.280	0.754	0.213	0.678	0.288
0.325	0.250	0.718	0.237	0.430	0.537	0.519	0.447	0.734	0.233
0.166	0.250	0.536	0.428	0.205	0.702	0.357	0.610	0.581	0.385
0.067	0.240	0.295	0.648	0.136	0.831	0.210	0.756	0.465	0.502

$S_{2r} = 0.033 = \text{constant during the experiment}$

FIGURE 2.1 Volume Fraction Diagram

FIGURE 2.2 Viscosity of TRS 10-410/IBA/Brine Micellar Middle Phase

FIGURE 2.3 Viscosity of Micellar Middle Phase at Shear Rate of 0.945 sec⁻¹

FIGURE 2.4 Viscosity of Micellar Middle Phase at Shear Rate of 5.96 sec⁻¹

EXP. NO.	CDC9-16
PORE VOL. (CC)	930.00
FRACTIONAL FLOW	100% BRINE
TRACER AND PHASE	TRITIUM 1
MAX. COUNTS PER 0.25CC (DPM)	15300.
BREAK THROUGH (P.V.) $C/C_0=0.5$	1.04
FLOW RATE (CC/MIN)	51.0000

FIGURE 2.5 Dispersion of Tritium in Brine Phase at 100% Brine Cut

EXP. NO.	CDC3-20
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	100% M.E.
TRACER AND PHASE	CARBON-14 3
MAX. COUNTS PER 0.25CC (DPM)	1080.
BREAK THROUGH (P.V.) C/CO-0.5	0.88
FLOW RATE (CC/MIN)	0.0910

FIGURE 2.6 Dispersion of Carbon-14 in Microemulsion Phase
at 100% Microemulsion Cut

EXP. NO.	CDC9-20
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	100% M.E.
TRACER AND PHASE	TRITIUM 3
MAX. COUNTS PER 0.25CC (DPM)	5340.
BREAK THROUGH (P.V.) C/CO=0.5	1.27
FLOW RATE (CC/MIN)	0.0310

FIGURE 2.7 Dispersion of Tritium in Microemulsion
at 100% Microemulsion Cut

EXP. NO.	CDC3-90
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	100% OIL
TRACER AND PHASE	CARBON-14 2
MAX. COUNTS PER 0.25CC (DPM)	2050.
BREAK THROUGH (P.V.) C/CO=0.5	0.93
FLOW RATE (CC/MIN)	0.8750

FIGURE 2.8 Dispersion of Carbon-14 in Oil Phase
at 100% Oil Out

EXP. NO.	CDC9-98
PORE VOL. (CC)	990.00
FRACTIONAL FLOW	100% H.E.
TRACER AND PHASE	CARBON-14 3
MAX. COUNTS PER 0.25CC (DPM)	990.
BREAK THROUGH (P.V.) C/CO=0.5	0.96
FLOW RATE (CC/MIN)	12.8100

FIGURE 2.8a The Dispersion of Carbon 14 in Microemulsion Phase at 100% Microemulsion Cut

EXP. NO.	CDC3-38
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	100% M.E.
TRACER AND PHASE	TRITIUM 3
MAX. COUNTS PER 0.25CC (OPM)	5100.
BREAK THROUGH (P.V.) C/CO=0.5	1.14
FLOW RATE (CC/MIN)	12.8100

FIGURE 2.8b The Dispersion of Tritium in Microemulsion Phase
at 100% Microemulsion Cut

FIGURE 2.9 Residual Saturation as a Function of Capillary Number in Berea Core

FIGURE 2.10 Endpoint Relative Permeability for Microemulsion/Oil/Brine as a Function of Capillary Number

FIGURE 2.11 Dispersion Coefficient of Carbon-14 in Oil Phase Versus Oil Phase Frontal Velocity

FIGURE 2.12 Dispersion Coefficient of Carbon-14 and Tritium in Microemulsion Phase as a Function of Frontal Velocity

FIGURE 2.13 Dispersion Coefficient of Tritium in Water Phase as a Function of Water Frontal Velocity

EXP. NO.	SMO-10
PORE VOL. (CC)	930.00
FRACTIONAL FLOW	78% OIL, 22% M..
TRACER AND PHASE	CARBON-14 2
MAX. COUNTS PER 0.25CC (DPM)	2120.
BREAK THROUGH (P.V.) C/CO=0.5	0.83
FLOW RATE (CC/MIN)	0.5070

FIGURE 2.14 Dispersion of C-14 in Oleic Phase at
78% Oil Cut and 22% Microemulsion Cut

EXP. NO.	SMO-10
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	78% OIL, 22% M.E.
TRACER AND PHASE	TRITIUM 3
MAX. COUNTS PER 0.25CC (DPM)	3850.
BREAK THROUGH (P.V.) $C/C_0=0.5$	2.41
FLOW RATE (CC/MIN)	0.5070

FIGURE 2.15 Dispersion of Tritium in Microemulsion Phase
at 78% Oil Cut and 22% Microemulsion Cut

EXP. NO.	SMO-10
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	78% OIL, 22% M.E
TRACER AND PHASE	CARBON-14 3
MAX. COUNTS PER 0.25CC (DPM)	700.
BREAK THROUGH (P.V.) $C/C_0=0.5$	0.90
FLOW RATE (CC/MIN)	0.5070

FIGURE 2.16 Dispersion of Carbon-14 in Microemulsion Phase
at 78% Oil Cut and 22% Microemulsion Cut

EXPERIMENT # SMO

$$N_{cap} = 0.010$$

FIGURE 2.17 Relative Permeability Curves for Microemulsion and Oil Flow in Berea Core

EXPERIMENT NUMBER SMO
MATERIAL BALANCE RESULTS

FIGURE 2.18 Fractional Flow Curve for Microemulsion and Oil in Berea Core

EXP. NO.	SMW-4
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	67.5% BR, 32.5% M.E
TRACER AND PHASE	TRITIUM I
MAX. COUNTS PER 0.50CC (DPM)	26073
SLUG SIZE (P.V.)	0.1560
FLOW RATE (CC/MIN)	0.3070

FIGURE 2.19 The Dispersion of Tritium in Brine Phase
at 67.5% Brine and 32.5% Microemulsion Cut

EXP. NO.	SMW-4
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	67.5% BR, 32.5% M.E
TRACER AND PHASE	TRITIUM 3
MAX. COUNTS PER 0.50CC (DPM)	8912.
SLUG SIZE (P.V.)	0.1560
FLOW RATE (CC/MIN)	0.3070

FIGURE 2.20 The Dispersion of Tritium in Microemulsion Phase at 67.5% Brine and 32.5% Microemulsion Cut

EXP. NO.	9MW-4
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	67.5% Brine 32.5% Microemulsion
TRACER AND PHASE	CARBON-14 3
MAX. COUNTS PER 0.50CC (DPM)	1107.
SLUG SIZE (P.V.)	0.1560
FLOW RATE (CC/MIN)	0.3070

FIGURE 2.21 The Dispersion of Carbon-14 in Microemulsion Phase
at 67.5% Brine and 32.5% Microemulsion Cut

EXP. NO.	SMW-6
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	83.4% Brine 16.6% Microemulsion
TRACER AND PHASE	TRITIUM 1
MAX. COUNTS PER 0.50CC (DPH)	25498.
SLUG SIZE (P.V.)	0.1560
FLOW RATE (CC/MIN)	0.4530

FIGURE 2.22 The Dispersion of Tritium in Brine Phase
at 83.4% Brine and 16.6% Microemulsion Cut

EXP. NO.	SMW-6
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	83.4% Brine 16.6% Microemulsion
TRACER AND PHASE	TRITIUM 3
MAX. COUNTS PER 0.50CC (DPM)	9376.
SLUG SIZE (P.V.)	0.1560
FLOW RATE (CC/MIN)	0.4530

FIGURE 2.23 The Dispersion of Tritium in Microemulsion Phase at 83.4% Brine and 16.6% Microemulsion Cut

EXP. NO.	SMW-6
PORE VOL. (CC)	930.00
FRACTIONAL FLOW	83.4% Brine 16.6% Microemulsion
TRACER AND PHASE	CARBON-14 3
MAX. COUNTS PER 0.50CC (DPM)	1229.
SLUG SIZE (P.V.)	0.1560
FLOW RATE (CC/MIN)	0.4530

FIGURE 2.24 The Dispersion of Carbon 14 in Microemulsion Phase at 83.4% Brine and 16.6% Microemulsion Cut

EXPERIMENT # SMW

$N_{cap} = 0.0066$

☒ C-14 TRACER

* MATERIAL BALANCE

MICROEMULSION SATURATION (S_3)

FIGURE 2.25 Relative Permeability Curves for Microemulsion and Brine Flow in Berea Core

EXPERIMENT NUMBER SMW

MATERIAL BALANCE RESULTS

$$N_{cap} = 6.6 \times 10^{-3}$$

FIGURE 2.26 Fractional Flow Curve for Microemulsion and Brine in Berea Core

FIGURE 2.27 Phase Saturation Diagram and Flow Chart for Two- and Three-Phase Flow Experiments

EXP. NO.	BM01-2
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	1: 0.772, 2: 0.185, 3: 0.043
TRACER AND PHASE	TRITIUM 1
MAX. COUNTS PER 0.25CC (DPM)	19000.
BREAK THROUGH (P.V.) C/CO=0.5	0.77
FLOW RATE (CC/MIN)	0.7080

FIGURE 2.28 The Dispersion of Tritium in Brine Phase
at 0.772 Brine, 0.185 Oil, and 0.043 Microemulsion Cut

EXP. NO.	8M01-2
FRACTIONAL FLOW	1: 0.772, 2: 0.185, 3: 0.043
TRACER AND PHASE	TRITIUM 1
MAX. COUNTS PER 0.25CC (OPM)	19000.
LAMBDA1 (10)	-0.22
LAMBDA1 (90)	0.22
DISPERSIVITY (CM)	0.895
FLOW RATE (CC/MIN)	0.7060

FIGURE 2.29 Dispersivity of Tritium in the Brine Phase
at 0.772 Brine, 0.185 Oil, and 0.043 Microemulsion Cut

EXP. NO.	BM01-2
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	1: 0.772, 2: 0.185, 3: 0.043
TRACER AND PHASE	CARBON-14 2
MAX. COUNTS PER 0.25CC (DPM)	3550.
BREAK THROUGH (P.V.) C/CO=0.5	1.18
FLOW RATE (CC/MIN)	0.7060

FIGURE 2.30 The Dispersion of Carbon-14 in Oil Phase
at 0.772 Brine, 0.185 Oil, and 0.043 Microemulsion Cut

EXP. NO.
 FRACTIONAL FLOW
 TRACER AND PHASE
 MAX. COUNTS PER 0.25CC (DPM)
 LAMBDA1 (10)
 LAMBDA1 (90)
 DISPERSIVITY (CM)
 FLOW RATE (CC/MIN)

BH01-2
 1: 0.772, 2: 0.185, 3: 0.043
 CARBON-14 2
 3550.
 -0.49
 0.64
 5.940
 0.7060

FIGURE 2.31 Dispersivity of Carbon 14 in Oil Phase
 at 0.772 Brine, 0.185 Oil, and 0.043 Microemulsion Cut

EXP. NO.	BM01-4
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	1: 0.51, 2: 0.455, 3: 0.035
TRACER AND PHASE	TRITIUM 1
MAX. COUNTS PER 0.25CC (DPM)	20500.
BREAK THROUGH (P.V.) $C/C_0=0.5$	0.77
FLOW RATE (CC/MIN)	0.6890

FIGURE 2.32 The Dispersion of Tritium in Brine Phase
at 0.51 Brine, 0.455 Oil, and 0.035 Microemulsion Cut

EXP. NO.	BH01-4
FRACTIONAL FLOW	1: 0.51, 2: 0.455, 3: 0.035
TRACER AND PHASE	TRITIUM 1
MAX. COUNTS PER 0.25CC (DPM)	20500.
LAMBDA1 (10)	-0.22
LAMBDA1 (90)	0.23
DISPERSIVITY (CM)	0.963
FLOW RATE (CC/MIN)	0.6890

FIGURE 2.33 Dispersivity of Tritium in Brine Phase
at 0.51 Brine, 0.455 Oil, and 0.035 Microemulsion Cut

EXP. NO.	BM01-4
PORE VOL. (CC)	990.00
FRACTIONAL FLOW	1.51, 2.455, 3.035
TRACER AND PHASE	CARBON-14 2
MAX. COUNTS PER 0.25CC (OPM)	2900.
BREAK THROUGH (P.V.) C/CO=0.5	0.87
FLOW RATE (CC/MIN)	0.6890

FIGURE 2.34 The Dispersion of Carbon-14 in Oil Phase
at 0.51 Brine, 0.455 Oil, and 0.035 Microemulsion Cut

EXP. NO.	BM01-4
FRACTIONAL FLOW	1: 0.51, 2: 0.455, 3: 0.035
TRACER AND PHASE	CARBON-14 2
MAX. COUNTS PER 0.25CC (DPM)	2900.
LAMBDA1 (10)	-0.15
LAMBDA1 (90)	0.16
DISPENSIVITY (CM)	0.447
FLOW RATE (CC/MIN)	0.6890

FIGURE 2.35 Dispersivity of Carbon-14 in Oil Phase
at 0.51 Brine, 0.455 Oil, and 0.035 Microemulsion Cut

RELATIVE PERMEABILITY VERSUS FRACTIONAL FLOW

$$N_{cap} = 0.01$$

FIGURE 2.36 The Relative Permeability of Brine, Oil, and Microemulsion Phases Versus Fractional Flow in Berea Core

EXP. NO.	9MM-4
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	67.5% Brine 32.5% Microemulsion
TRACER AND PHASE	TRITIUM 1
MAX. COUNTS PER 0.50CC (DPM)	26073.
SLUG SIZE (P.V.)	0.1560
FLOW RATE (CC/MIN)	0.3070

FIGURE 2.37 The Dispersion of Tritium in Brine Phase
at 67.5% Brine and 32.5% Microemulsion Cut

ARBITRARY VALUES FOR COMPUTATION

PORE VOL. (CC)

FRACTIONAL FLOW

TRACER AND PHASE

MAX. COUNTS PER 0.50CC (OPM)

SLUG SIZE (P.V.)

FLOW RATE (CC/MIN)

PECN=45, TDBT=0.66

330.00

67.5 Brine 32.5% Microemulsion

TRITIUM 1

26073.

0.1560

0.3070

FIGURE 2.38 Computed Pulse Concentration Profile for Dispersion of Tritium in Brine Phase at Peclet Number of 45 and Breakthrough of 0.66

EXP. NO.	SMH-4
PORE VOL. (CC)	330.00
FRACTIONAL FLOW	67.5% Brine 32.5% Microemulsion
TRACER AND PHASE	CARBON-14 3
MAX. COUNTS PER 0.50CC (DPM)	1107.
SLUG SIZE (P.V.)	0.1560
FLOW RATE (CC/MIN)	0.3070

FIGURE 2.39 The Dispersion of Carbon-14 in Microemulsion Phase at 67.5% Brine and 32.5% Microemulsion Cut

ARBITRARY VALUES FOR COMPUTATION

PORE VOL. (CC)

FRACTIONAL FLOW

TRACER AND PHASE

MAX. COUNTS PER 0.50CC (DPM)

SLUG SIZE (P.V.)

FLOW RATE (CC/MIN)

PECN=105, TOBT=1.78

330.00

67.5% Brine 32.5% Microemulsion

CARBON-14 3

1107.

0.1580

0.3070

FIGURE 2.40 Computed Pulse Concentration Profile for Dispersion of Carbon-14 in Microemulsion Phase at Peclet Number of 105 and Breakthrough of 1.78

3. PHYSICAL PROPERTY RELATIONSHIPS

3.1 Introduction

The modeling of the Physical Properties for a micellar/polymer process is very important in attempting to match experimental results. A good match also depends on the numerical techniques employed. Since the numerics are general in the field of engineering, the numerical aspects have been addressed and advanced upon enormously in comparison to the physics of the process. Ohno²² studied the 1-D process using semi-discrete methods in conjunction with four different ordinary differential equations integrators. His study concluded that these advanced techniques help little in reducing the time step when low interfacial tensions are encountered. They do have other advantages such as automatic time and step selection and truncation error control. However, a rather primitive fully explicit differencing scheme (Euler's method) was used in this study, which emphasizes the physical process description. Okano is doing more research on semi-discrete techniques as part of this same DOE project. This will be reported next year.

The main process properties discussed here include a review on polymer-inaccessible pore volume, permeability reduction, viscosity, adsorption, interfacial tensions, residual saturations, relative permeabilities and ion exchange. A new definition of effective salinity, and a new phase-behavior concept which allows the alcohol to be treated as a separate component in a pseudoquaternary representation are added. Also included is a way of treating the dispersivities in the continuity equation

to make them saturation dependent. A modification in the interfacial tension relations makes it possible to have zero IFT at the plait point.

Other properties such as capillary pressure are not important in 1-D studies. They are, however, important in two and three dimensions⁷⁴.

Components are referred to by the following convention: (1) water, (2) oil, (3) surfactant, (4) polymer, (5) chloride ions, (6) calcium ions, (7) alcohol, (9) sodium ions. Sodium ions are sometimes required such as in the cation exchange routine or in calculating the effective salinity for the polymer viscosity. They are obtained from an electrical balance using the relation

$$C_{9j} = C_{5j} - C_{6j} \quad (3.1)$$

and are not calculated from the continuity equations (subroutine SOLVE). Thus the maximum number of components calculated by material balance is seven.

The total number of mobile phases considered is three and they are referred to by the following convention: (1) aqueous, (2) oleic and (3) microemulsion. The last one is defined as the phase containing the highest concentration of surfactant. The number and type of phases present depend on the total composition. Three basic types of phase behavior are considered depending on the effective salinity. They are shown in Figure 3.1 together with the phase numbering convention used. In the limit as C_1 or C_2 tends to unity, the phase number takes the value of the richest component. Compositions with $C_2 = 0$, become phase one when C_3 is less than 0.0001.

In the most common of situations, electrolyte and polymer concentrations are very small, often less than 1% and for this reason it is assumed that they occupy no volume. It is also assumed that the adsorbed polymer, sodium and calcium occupy no volume. No adsorption of water, oil and alcohol is considered, though the alcohol can be associated with the adsorbed surfactant, but further studies are needed to test the importance of this property. The polymer is assumed to be entirely in the most water-rich phase. This assumption is in accordance with static experimental observations and is explained by a phenomenon known as polymer-surfactant incompatibility. Trushenski²³ associated his experimental results with this effect and Shah²⁴ explained the effect thermodynamically due to a polymer-deficient layer around the micelles. The free electrolytes are assumed to be uniformly distributed in the water component. They can, however, exchange due to electrical forces with the clays and the micelles. This latter property is treated using Hirasaki's⁶⁰ theoretical description.

3.2 Inaccessible Pore Volume

It has been observed experimentally,^{23, 25-30} that for flow in porous media, polymer solutions usually flow faster than the solvent or smaller non-interacting components such as chloride in the solution. This effect can be explained by assuming that the area of flow for the polymer is smaller than that for the solvent, hence the so-called inaccessible pore volume (IPV) name.

In general the inaccessible pore volume phenomena strongly depends on the characteristics of the porous medium, especially its permeability.

It also depends on the polymer and electrolyte type, concentrations, saturations, temperature, and velocity. Lower permeabilities cause larger inaccessible pore volumes. Other factors such as polymer gels, trapped phases, surfactant/polymer interactions, and emulsions may be significant and sometimes may completely dominate. Dawson and Lantz²⁸ observed that as much as 30% of the pore volume may be inaccessible to polymer. This effect can be accounted for by reducing the porosity for the polymer in the component mass balance equation.³¹ Such observations, though modelled as if the polymer is inaccessible to a fraction of the pores, do not imply that the polymer actually by-passes certain pore spaces, but rather that the polymer velocity is larger than for a reference tracer. Although several studies have been done, the detailed mechanisms involved are not completely understood. It should be pointed out, however, that whatever is the microscopic cause should not be of much concern since any practical model must involve a finite averaging which would be equivalent to the IPV concept. It seems likely that the effect is mostly caused by pore wall exclusion of the polymer molecule relative to the very small molecules such as water which makes up the polymer solvent. It could be also caused by rheological properties. The shear rate is considerably different in different parts of a given pore and also from pore to pore. Another cause can be due to the amount and type of retention. An adsorbed polymer coil effectively excludes a certain volume of the pore to further penetration by a mobile polymer coil. Whatever the cause, a porosity correction factor is used to model the lumped effect.

The form of the continuity equation used in this study is:

$$\frac{\partial}{\partial t_D} (\tilde{C}_i) + \sum_j \frac{\partial}{\partial x_D} (f_j C_{ij}) - \sum_j \frac{\partial}{\partial x_D} (\alpha_{Dij} f_j \frac{\partial C_{ij}}{\partial x_D}) = 0 \quad (3.2)$$

An effective porosity for polymer is defined by Lin⁽³¹⁾ as:

$$\phi_{4,eff} = \frac{\phi_4}{\phi} \quad (3.3)$$

where ϕ_4 is the apparent porosity for the polymer and ϕ is the actual porosity. $\phi_{4,eff}$ is then used in calculating the polymer concentrations from the continuity equations as follows:

$$\frac{\partial \tilde{C}_4}{\partial t_D} + \frac{1}{\phi_{4,eff}} \frac{\partial}{\partial x_D} \left\{ \sum_j (f_j C_{4j} - \alpha_{D4j} f_j \frac{\partial C_{4j}}{\partial x_D}) \right\} = 0 \quad (3.4)$$

For a typical Berea core, the polymer IPV is approximately 0.2 RV.²⁵ However, other mechanisms can counteract the IPV effect. For the experiments conducted, polymer breakthrough was always at the same time as the surfactant and the tracer injected in the same slug, and, thus, the IPV effect was not used in matching the experiments of this study. Lin³¹ tested the effect as modelled above for a single-phase flow run and the results were as expected. He further used this model for surfactant, but since there is little evidence of IPV for surfactant, this was removed from the current version of the simulator.

3.3 Permeability Reduction

Certain polymers can adsorb on the porous media and reduce its mobility beyond what could be expected from the increase in viscosity

alone. This effect is called permeability reduction. They also can cause a reduction in the mobility of a brine following the polymer, a phenomenon described by a residual resistance factor. Permeability reduction and residual resistance are defined as:

Permeability reduction factor (R_k),

$$R_k = \frac{\text{Effective permeability of brine}}{\text{Effective permeability of polymer solution}}$$

Residual resistance factor (R_{rf}),

$$R_{rf} = \frac{\text{Brine mobility before polymer flood}}{\text{Brine mobility after polymer flood}}$$

These phenomena have been observed and investigated by many authors.^{15,32-52}

The model used to simulate the reduction assumes³¹ that

- R_k is a function of polymer concentration only for a given set of rock and fluid properties,
- Only the polymer-rich phase is affected by this reduction in permeability,
- the reduction is irreversible.

Partially hydrolyzed polyacrylamide polymers mostly demonstrate this reduction which is modelled by:

$$R_k = 1.0 + \frac{(R_{k,\max} - 1.0)b_p C_{4j}}{1.0 + b_p C_{4j}} \quad (3.5)$$

where C_{4j} refers to the polymer concentration in the polymer-rich phase. These effects are modeled by equation 3.13.

This equation is similar to that of the polymer adsorption isotherm which is Langmuir-type.⁵³ However, the parameters are made independent because permeability reduction can depend on factors other than adsorption. When the polymer concentration C_{4j} approaches zero, the value of R_k approaches one, and when C_{4j} approaches infinity, R_k approaches $R_{k,max}$. The reduction effect is usually small for xanthan gum, but the same equation could be used. In general the dependence of other variables such as permeability would be required, but for 1-D homogeneous runs these effects are fixed, thus, input parameters $R_{k,max}$ and b_p are constant for a given run. Naiki⁵⁴ described how these other variables can be handled in more complex simulations. Both Hong⁷⁴ and Wang⁷³ used Naiki's more complex 2-D description.

3.4 Polymer Viscosity

Dilute polymer solutions have non-Newtonian viscosity properties -- that is, viscosity is a function of shear rate. The most common behavior encountered, described as shear thinning, can be modelled by a power-law equation.⁴⁶ Other viscosity models include Ellis's, Oldroyd's, Bogue's and Meter's^{41,46}. The shear rate dependence of the polymer viscosity is modelled by Meter's equation which is written as:

$$\mu_p = \mu_\infty + \frac{\mu_0 - \mu_\infty}{1 + (\dot{\gamma}/\dot{\gamma}_H)^\alpha} \quad (3.6)$$

Using the assumption that μ_∞ is small compared to μ_0 , the above equation reduces to:

$$\mu_p = \mu_\infty + \frac{\mu_0}{1 + (\dot{\gamma}/\dot{\gamma}_c)^{p_\alpha - 1}} \quad (3.7)$$

Lin³¹ used equation (3.6) to simulate viscosity vs. shear rate data, (Fig. 3.2).

An equivalent shear rate, $\dot{\gamma}$, for flow in porous media must be calculated in order to obtain the apparent viscosity, given by (3.7). For single phase, one-dimensional flow of a power-law fluid³⁷:

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right)^{\frac{n}{n-1}} \left(\frac{4V}{R_{eq}} \right) \quad (3.8)$$

where $V = \frac{q}{A\phi}$, $R_{eq} = \sqrt{(8k/\phi)}$

For one-dimensional, multi-phase flow, Lin³¹ generalized the above by setting $v_j = \frac{q_j}{A\phi S_j}$, where j is the phase number.

By definition, $\frac{q_j}{A} = u_j = u_T f_j$ thus $v_j = \frac{u_T f_j}{\phi S_j}$

Similarly $R_{eq,j} = \sqrt{(8k_j/\phi S_j)}$, $j = 1, 2, 3$

Using phase values for V and R_{eq} in (3.8) we get

$$\dot{\gamma}_j = \left(\frac{3n+1}{4n} \right)^{\frac{n}{n+1}} \left(\frac{4v_j}{R_{eq,j}} \right) \quad (3.9)$$

dividing equation (3.9) by equation (3.8)

$$\dot{\gamma}_j = \dot{\gamma} \frac{R_{eq}}{R_{eq,j}} \frac{v_j}{V} = \dot{\gamma} f_j / \sqrt{(k_{rj} S_j)} \quad (3.10)$$

where $k_{rj} = \frac{k_j}{k}$

The polymer viscosity at zero shear rate (μ_0 in equation 3.6) is a function of polymer and electrolyte concentration. Figure 3.3 shows the dependence of viscosity on polymer concentration, the salinity and shear rate being constant. This curve is approximated by a third order polynomial which is similar to Huggin's⁵⁶ equation for dilute polymer solutions. The dependence of polymer viscosity on electrolyte concentration is shown in Figures 3.4 and 3.5. Hydrolyzed polyacrylamides (HPAM) are very sensitive to salinity, especially at low salinity.^{55,56} On a log-log plot of polymer viscosity versus salinity a linear relationship is often obtained in the range of interest.

The equation used to model polymer viscosity at a fixed shear rate as a function of polymer concentration and salinity is as follows:

$$\mu_p = \mu_w \{ 1 + (A_{p1} C_{4j} + A_{p2} C_{4j}^2 + A_{p3} C_{4j}^3) C_{SEP}^{S_p} \} \quad (3.11)$$

where C_{SEP} is the effective salinity for the polymer and is calculated from

$$C_{SEP} = C_{9j} + \beta_p C_{6j} \quad (3.12)$$

j = polymer rich phase.

S_p is a constant (input variable) corresponding to the slope of μ_p versus C_{SEP} on a log-log plot. As noticed in Figures 3.4 and 3.5 the slope is large and negative for HPAM, and small and positive for xanthan gum. Equation (3.11) is used for any polymer concentration but only for salinities greater than 0.001 meq/ml, since small values of C_{SEP} will produce unrealistic viscosities. Cases where C_{SEP} is less than some input cut-off value (CSE1 in simulator) are treated as if their value was equal to the cut-off value.

The effect of permeability reduction discussed earlier is to reduce the mobility of the polymer phase. This is equivalent to increasing the viscosity in equation (3.11) by a factor R_k , thus

$$\mu_p^* = \mu_p R_k \quad (3.13)$$

3.5 Phase Viscosity

This viscosity of any phase j is calculated from

$$\begin{aligned} \mu_j = & C_{1j} \mu_w e^{\alpha_1(C_{2j} + C_{3j})} + C_{2j} \mu_0 e^{\alpha_2(C_{1j} + C_{3j})} \\ & + C_{3j} \alpha_3 e^{(\alpha_4 C_{1j} + \alpha_5 C_{2j})} \end{aligned} \quad (3.14)$$

For polymer phases, μ_w in equation (3.14) is replaced by the polymer viscosity, μ_p^* , calculated from equations (3.6), (3.11) and (3.13). The α parameters are constants and should be determined from laboratory viscosity

data. For a given overall composition, the viscosity of the surfactant rich phase approaches the brine viscosity when in Type II(-) phase environment and the oil viscosity when in Type II(+) phase environment. The viscosity in a Type III phase environment attains a maximum. Engelsen⁵⁷ attempted to improve the salinity dependence by making α_3 in equation (3.14) salinity dependent. He showed one case where the viscosity versus salinity data match reasonably well. However, it is still difficult to get a good match in some cases. In this study, α_3 was taken to be a constant. Although equation (3.14) is quite complex, it is felt that this equation needs to be improved by including the effect of the alcohol to get better results.

3.6 Effective Salinity

The phase behavior of a four-pure-component mixture, pure oil, surfactant, water and NaCl, can be represented on a series of ternaries with pure oil, pure surfactant and brine at the apexes. Each ternary represents a fixed brine composition and is equivalent to a slice through a tetrahedron with pure components at the apexes. The slices will all pass through the pure oil, surfactant edge of the tetrahedron. Hirasaki⁵⁹ used Gibbs phase rule to show that for such a mixture, the optimal salinity, which is defined as that salinity (plane) at which a microemulsion is in equilibrium with excess brine and excess oil phases such that the concentrations of oil and water in the microemulsion are equal, is a constant. The pseudoternary representation, when coupled with salinity as used for the four component mixture, is in effect a transformation of the tetrahedron into a triangular prism, see Figure 3.6(a). A similar method is

used for a mixture of five pure components, namely surfactant, oil, water, alcohol and NaCl. Tetrahedrons at fixed brine salinities are used to represent a mixture on a pseudoquaternary where the water and the NaCl are taken to be one component. Planes through these tetrahedrons are then considered such that mixtures of the three pseudocomponents defined by ternaries thus formed, satisfy an alcohol material balance according to some fixed partition coefficients as discussed in section 3.7. A variable is then defined such that it is a constant for all mixtures in any particular one of these planes. When such planes are stacked on top of each other in an order dictated by the so-defined variable, then the tetrahedron is transformed into a triangular prism, see Figure 3.6(b). This variable is often referred to as the effective salinity.

Engelsen⁵⁷ represents the phase behavior as a pseudoternary where all the alcohol is lumped with the surfactant. For such a representation, the optimal salinity is not constant as would be expected of a pure four-component mixture. Rather, it is observed to be a function of surfactant, alcohol, and electrolyte concentrations. On this observation he empirically defined an effective salinity as follows:

$$C_{SE} = \left(\frac{C_9}{C_1} + \beta_1 \frac{C_6}{C_9} + \beta_2 C_3 \right) \exp^{\beta_3 C_7} \quad (3.15)$$

This definition is replaced by one which is more consistent with the theoretical notion of effective salinity as discussed above.

Hirasaki⁵⁹ uses the following empirical relation to define the optimal salinity as a function of, (1) the fraction of alcohol associated with the surfactant + alcohol pseudo phase f_7^S , and (2) the fraction of

calcium of the associated counter ions f_6^S .

$$C_{51\text{opt}} = C_{51\text{opt}}^* (1 + \beta_7 f_7^S) (1 + \beta_6 f_6^S) \quad (3.16)$$

where $C_{51\text{opt}}^*$, β_6 and β_7 are constant for a particular surfactant/oil formulation. Equations for f_7^S and f_6^S are given in sections 3.7 and 3.12 below. $C_{51\text{opt}}^*$ is equal to the optimal salinity in the absence of alcohol and divalent ions, that is

$$f_7^S = f_6^S = 0 \quad \text{implies} \quad C_{51\text{opt}} = C_{51\text{opt}}^*$$

Using the same relation over the whole salinity space, we write

$$C_{51} = C_{51}^* (1 + \beta_7 f_7^S) (1 + \beta_6 f_6^S) \quad (3.17)$$

again $C_{51} = C_{51}^*$ when $f_7^S = f_6^S = 0$

C_{51}^* is defined to be the effective salinity, and it is the intercept of a plane surface defined by equation (3.17) with the C_{51} axis in a 3-D space with C_{51} , f_6^S and f_7^S as orthogonal co-ordinates and as illustrated in Figure 3.7. Thus for any (C_{51}, f_6^S, f_7^S) there exists a point C_{51}^* on the C_{51} axis defined by the intersection of a plane through (C_{51}, f_6^S, f_7^S) , parallel to the plane defining optimal salinity, and the C_{51} axis. This point, C_{51}^* is defined as the effective salinity (C_{SE}) thus

$$C_{SE} = C_{51}^* = \frac{C_{51}}{(1 + \beta_7 f_7^S)(1 + \beta_6 f_6^S)} \quad (3.18)$$

3.7 Phase Behavior

Phase behavior and the associated phase properties are very important in micellar/polymer flooding. The phase behavior is represented by ternary diagrams using pseudocomponents brine/alcohol, oil/alcohol, surfactant/alcohol. The actual compositions of the pseudocomponents are a function of the overall composition and are assumed independent of salinity. Modified Hand equations^{58, 98} are used to represent the two-phase envelopes and tie lines. Three types of phase environments (Type II (-), Type III and Type II (+)) are considered where, for each situation, the Hand parameters, plait points, and invariant point, are a function of the normalized effective salinity which is the effective salinity divided by the effective optimal salinity. The effective salinity is defined in the previous section.

Micellar slugs of interest in enhanced oil recovery usually consist of at least five components. These are a surfactant, a co-surfactant, (usually an alcohol), water, an electrolyte, and a hydrocarbon. Since the surfactant, hydrocarbon and electrolyte may also be mixtures of molecular species, the number of individual components can become large. With aqueous slugs, polymer is often used.

Graphical representations of mixtures of N components require an $N-1$ dimensional space, thus the maximum number of components which can be represented in a 3-D space is four. Because of this graphical limitation, various techniques have been developed⁶¹⁻⁶⁴ whereby the definition of pseudocomponents is used to reduce the degrees of freedom (components), thus being able to represent a chemical mixture in 3-D space. Even after this reduction, it is difficult to mathematically

represent the phase behavior which is a surface enclosed in a tetrahedron. The representation is further simplified by using pseudoternary diagrams to display portions of the quaternary phase data. These pseudoternary diagrams are slices through the tetrahedron and most commonly are chosen to pass through an edge of the tetrahedron.⁶⁴

Pseudoternary phase diagrams, particularly with surfactant/alcohol (S/A) as a pseudocomponent, have been used by many authors⁶⁸⁻⁷¹ to describe the phase behavior of microemulsions. As noted by Wlickerl et al.⁶⁴ and Salter⁶³, an arbitrary way of choosing the pseudocomponents can cause problems. Fleming⁶² cites Francis's⁶⁵ example of the types of problems that can arise when pseudo-components are selected using linear algebraic techniques. For any selected pseudoternary plane, the phase envelopes can be represented accurately because each point on the pseudo-diagram is the total composition of the mixture, which is known if the titration method used by Dominguez⁹⁶ is used for phase behavior studies. However, the tie lines and tie triangles that are found on the true quaternary diagram in the multiphase regions do not necessarily exist on the same pseudoternary plane. The tie lines and tie triangles will exist in the plane of the pseudoternary diagram if the equilibrium phases are composed of mixtures of the pseudocomponents. Vinatieri et al.¹¹⁴ discuss a criteria for the choice of the pseudocomponents based on regression analysis. It will be shown later how from the composition of the equilibrium phases, pseudocomponents are calculated such that phase boundaries, tie lines or tie triangle, all lie in the same plane.

The pseudoternary approach has been used previously in a different form by lumping the surfactant and alcohol, and did not require a major

change in the simulator. Once the pseudocompounds have been calculated, the same phase behavior routine used by Pope,^{75, 76} Wang,^{72, 73} Lin,³¹ Ohno,²² Engelsen⁵⁷ and Hong,⁷⁴ is used. Engelsen allowed the alcohol to partition between the oil and water phase according to Salter's⁶⁶ relation, but the alcohol was lumped with the surfactant in performing the phase behavior calculations.

Recently Kilpatrick et al.⁶⁷ extended Rossen's et al.¹¹³ model for pseudoternary phase behavior to develop a thermodynamic model for quaternary systems based on Gibb's free energy rule. They use a modified version of the Flory-Higgins equation of state to describe the phase behavior surface which is referred to as the spinodal. This method is however still in an experimental stage and needs more development before it can be confidently used. Development of this method would eliminate the need to use the Hand method of determining the phase behavior surface and would also make it possible to make flash calculations in 3-D space thus eliminating the need to reduce a multi-component mixture to a three pseudocomponent mixture. The method is unfortunately complicated, and since it has not yet been compared to experimental results, nothing can be said about its accuracy or superiority over the method used here.

In this study, a theoretical basis which makes use of the pseudophase equilibrium idea^{59, 96, 115-119} is used to define three pseudocomponents. The pseudophase model assumes that the microemulsion phase consists of three pseudophases. These are: an oil phase, a brine phase and a surfactant phase as depicted in Figure 3.8(b-c). It is also assumed that the brine and oil pseudophases have the same compositions as the excess

brine and excess oil phases respectively.

The phase behavior is characterized by four pseudocomponents, surfactant, alcohol, oil and brine. The brine is assumed to contain all of the polymer and electrolytes. The alcohol is assumed to partition into the brine, the oil, and the surfactant according to some fixed partition coefficients K_a^0 and K_a^s defined later, such that a mixture of the four pseudocomponents can now be represented by three pseudocomponents. Each of the pseudocomponents can be represented on the edges of a tetrahedron opposite the surfactant, brine, oil surface, see Fig. 3.8(a). The composition of the pseudocomponents are calculated as follows: ^{59, 96}

Let (C_1, C_2, C_3, C_7) define a composition point inside the tetrahedron, where C_i = overall volume fraction of component i . Then

$$C_1 + C_2 + C_3 + C_7 = 1$$

define $C_7^1 = \frac{\text{Total volume of component 7 associated with component 1}}{\text{Total volume of component 1}}$

$C_7^2 = \frac{\text{Total volume of component 7 associated with component 2}}{\text{Total volume of component 2}}$

$C_7^3 = \frac{\text{Total volume of component 7 associated with component 3}}{\text{Total volume of component 3}}$

$$K_a^0 = \frac{C_7^2}{C_7^1} \quad K_a^s = \frac{C_7^3}{C_7^1} \quad (3.19)$$

Then from an alcohol material balance, assuming that all the alcohol (C_7) is distributed between the three pseudocomponents,

$$C_7 = C_1 C_7^1 + C_2 C_7^2 + C_3 C_7^3 \quad (3.20)$$

Assuming the partition coefficients (K) to be constant, then we can write

$$C_7 = C_1 C_7^1 + C_2 C_7^1 K_a^0 + C_3 C_7^1 K_a^S \quad (3.21)$$

from which

$$C_7^1 = C_7 (C_1 + C_2 K_a^0 + C_3 K_a^S)^{-1} \quad (3.22)$$

Hence for an overall composition (C_1, C_2, C_3, C_7) and partition coefficients K_a^0 and K_a^S , C_7^1 can be calculated from equation (3.22). C_7^2 and C_7^3 are then calculated from equation (3.19).

The idea is to transform overall compositions from 3-D space to 2-D space. Let C_{p1}, C_{p2}, C_{p3} be the transformed overall composition relative to the 2-D space. C_{p1} reads concentration of pseudocomponent 1.

$$C_{p1} = \frac{\text{Total volume of 1 + volume of 7 associated with 1}}{\text{Total volume of 1 + Total volume of 2 + Total volume of 3 + Total volume of 7}}$$

(numbers refer to components represented on the tetrahedron)

$$\begin{aligned} &= \frac{\text{Total volume of 1} + C_7^1 \times (\text{Total volume of 1})}{\text{Total volume}} \\ &= C_1 (1 + C_7^1) \end{aligned} \quad (3.23)$$

Similarly:

$$C_{p2} = C_2(C_1 + C_7^2) \quad (3.24)$$

$$C_{p3} = C_3(C_1 + C_7^3) \quad (3.25)$$

These pseudocomponent concentrations C_{p1} , C_{p2} , C_{p3} are used in the flash calculations to get phase compositions which are also in terms of the pseudocomponents.

3.7(a) Conversion of Concentrations from Pseudoternary to Pseudoquaternary

At the end of the flash calculations, we have C_{pij}

where i = component index = 1, 2, 3

j = phase index = 1, 2, 3

Note: C_p - concentrations relative to pseudoternary

C - concentrations relative to pseudoquaternary.

$$C_{ij} = \frac{\text{Volume of } i \text{ in } j}{\text{Volume of } j}$$

$$= \frac{\text{Volume of } i \text{ in } j + \text{volume of } 7 \text{ associated with } i \text{ in } j}{\text{Volume of } j}$$

$$= C_{pij} - \frac{C_7^i \times \text{Total volume of } i \text{ in } j}{\text{Volume of } j}$$

$$= C_{pij} - C_7^i \times C_{ij} \quad (3.26)$$

Note: equations (3.26) are the same as equations (3.23, 3.24, 3.25).

$$\begin{aligned}
 C_{7j} &= \frac{\text{Volume of 7 in } j}{\text{Volume of } j} \\
 &= \frac{\text{Total volume of 1 in } j \times C_7^1 + \text{total volume of 2 in } j \times C_7^2}{\text{Volume of } j} \\
 &\quad + \text{total volume of 3 in } j \times C_7^3 \\
 &= C_7^1 C_{1j} + C_7^2 C_{2j} + C_7^3 C_{3j} \\
 &= \sum_i C_7^i C_{ij} \quad (3.27)
 \end{aligned}$$

Note: equations (3.27) are the same as the alcohol material balance equation (3.20) applied to individual phases.

Equation (3.18) makes use of a quantity f_7^s defined as:

$$\begin{aligned}
 f_7^s &= \frac{\text{Total volume of alcohol associated with surfactant}}{\text{Total volume of the (surfactant + alcohol) pseudocomponent}} \\
 &= \frac{\text{Total volume of alcohol associated with surfactant}}{\text{Total volume of alcohol associated with surfactant} + \text{total volume of surfactant}} \\
 &= \frac{1}{1 + \frac{\text{Total volume of surfactant}}{\text{Total volume of alcohol associated with surfactant}}}
 \end{aligned}$$

which from the definition of C_7^3 ,

$$f_7^s = \frac{1}{1 + (C_7^3)^{-1}} \quad (3.28)$$

3.7(b) Application of the Pseudocomponent Theory to Static Phase Behavior Experiments---Comments

The partitioning coefficients K_a^0 and K_a^s were determined from a three phase sample with TRS10-410, IBA, water, n-decane and NaCl as components, (section 4.3). Equations (3.19) and (3.22) were then used to calculate the pseudocomponent composition. Samples at fixed surfactant to alcohol ratios and at constant salinities were then prepared. The overall composition of each sample was calculated such that each has the same pseudocomponent composition (C_7^1). Equation (3.20) and the condition

$$C_1 + C_2 + C_3 + C_7 = 1 \quad (3.29)$$

were used to calculate the overall compositions of each sample.

$$C_7 = C_1 C_7^1 + C_7^2 - C_1 C_7^2 - C_3 C_7^2 - C_7 C_7^2 + C_3 C_7^3$$

$$C_7 = \frac{C_1(C_7^1 - C_7^2) + C_7^2}{(1 + C_7^2) - \frac{C_3}{C_7}(C_7^3 - C_7^2)} \quad (3.30)$$

Each sample prepared, thus, had identical C_7^3 and hence f_7^s (equation (3.28)). Samples with a fixed brine salinity also had the same effective salinity (equation (3.18)). The invariant points calculated from the different samples with the same brine salinity should be ideally identical if the definition of effective salinity and the pseudocomponent theory were both exact. The results shown in Figures (4.5-4.13) do support the

theory somewhat. For fixed surfactant to alcohol ratios, the invariant points calculated from samples of different compositions agree within experimental error. The invariant point does however shift with surfactant/alcohol ratios at constant brine salinities. It is however noted that for samples with a brine salinity of 1.1 wt % NaCl, the invariant point is fairly constant with variations in the surfactant-to-alcohol ratio. The partition coefficients K_a^0 and K_a^s were calculated from a sample with a brine salinity of 1.1 wt % NaCl, and this may be the reason why the composition of the invariant point agrees best with the theory for samples at a brine salinity of 1.1 wt % NaCl.

Salter⁶⁶ shows that the partition-coefficient K_a^0 is a function of salinity. Since the calculation of samples with salinities different than 1.1 wt % NaCl were done using partition coefficients derived from a sample at 1.1 wt % NaCl, this may be a reason why the invariant point for samples other than the ones at 1.1 wt % NaCl drifted with surfactant to alcohol ratio. Another possible cause may be in the definition of effective salinity. Further experiments are needed to determine if the effective salinity as defined by equation (3.18) is adequate.

3.8 Adsorption

Polymer and surfactant are allowed to adsorb in a Langmuir⁵⁵ type fashion

$$\bar{C}_i = \frac{a_i C_{ij}^*}{1 + b_i C_{ij}^*} \quad i = 3 \text{ or } 4 \quad (3.31)$$

where $\bar{C}_i$ = adsorbed concentration and $C_{ij}^* = \text{Max}(C_{ij})$
 $i = 3 \text{ or } 4, \quad j = 1, 3$

Parameters a_i and b_i are determined from experimental data. b_i is a constant, while a_i is a function of salinity, porosity and permeability.^{36, 77, 83} In 1-D simulations, porosity and permeability are constant, and a_i is taken to be a linear function of salinity.

$$a_i = a_{i1} + a_{i2} C_{SE}, \quad i = 3 \text{ or } 4 \quad (3.32)$$

For the cases of varying porosities and permeability refer to Hong,⁷⁴ Wang.⁷³ In the simulator a_{42} is taken to be zero thus making polymer adsorption independent of salinity. Also surfactant adsorption is made reversible with salinity. Both surfactant and polymer adsorption are irreversible with concentration.

3.9 Interfacial Tensions

The interfacial tensions are calculated using the empirical relations of Reed and Healy¹⁸ which can be briefly stated as: the interfacial tension between two phases is a function of the relative amount of solubilized water or oil to surfactant in the microemulsion phase. For three phase compositions two interfaces are present and the tensions are computed using the following equations:

$$\log \gamma_{wm} = G_{12} + \frac{G_{11}}{G_{13} \left(\frac{C_{13}}{C_{33}} \right) + 1} \quad (3.33)$$

$$\log \gamma_{om} = G_{22} + \frac{G_{21}}{G_{23}(\frac{C_{23}}{C_{33}}) + 1} \quad (3.34)$$

Equations (3.33 and 3.34) fail to approach the proper limits for compositions at the plait points where the IFT should be zero and for compositions with (C_{13}/C_{33}) and (C_{23}/C_{33}) close to zero where the IFT should be equal to the water-oil value. Hirasaki's²⁰ method is adopted, where a factor is used to reduce the interfacial tension to zero as the composition approaches the plait point. This factor is expressed as follows:

$$F_Y = (1 - \exp\{-C_{RMS}\}) / (1.0 - \exp(-2)^{1/2}) \quad (3.35)$$

where $C_{RMS} = [(C_{11}-C_{12})^2 + (C_{21}-C_{22})^2 + (C_{31}-C_{32})^2]^{1/2}$

the second subscript differentiates between phases.

The interfacial tensions are then calculated using the following equations:

$$\begin{aligned} \log \gamma_{wm} = & \log F_Y + (\log \gamma_{wo})(1 - C_{13}/C_{33}) \\ & + [G_{12} + G_{11}/(G_{13} + 1)]C_{13}/C_{33}, \\ & C_{13}/C_{33} < 1.0 \end{aligned} \quad (3.36)$$

$$\begin{aligned} \log \gamma_{wm} = & \log F_Y + G_{12} + G_{11}/(G_{13}C_{13}/C_{33} + 1) \\ & C_{13}/C_{33} > 1.0 \end{aligned} \quad (3.37)$$

$$\begin{aligned}\log \gamma_{om} &= \log F_{\gamma} + (\log \gamma_{wo})(1 - C_{23}/C_{33}) \\ &+ [G_{22} + G_{21}/(G_{23} + 1)]C_{23}/C_{33}, \\ C_{23}/C_{33} &< 1.0\end{aligned}\tag{3.38}$$

$$\begin{aligned}\log \gamma_{om} &= \log F_{\gamma} + G_{22} + G_{21}/(G_{23}C_{12}/C_{32} + 1), \\ C_{23}/C_{32} &> 1.0\end{aligned}\tag{3.39}$$

When only two phases exist, either equation (3.36) or (3.37) or (3.38) or (3.39) is used depending on which phases are present. The other interfacial tension is set to zero, which physically means that no surface exists. Interfacial tension is used in the calculation of a capillary number. The residual saturations are then calculated from a capillary desaturation correlation. For the case of three coexisting phases, two interfacial tensions and capillary numbers are calculated.

3.10 Residual Saturations

Residual saturations are calculated from capillary desaturation curves similar to Figure 2.2. The definition of capillary number which is used in the simulator is

$$N_c = \frac{u_T}{\lambda_{rt} \gamma} \tag{3.40}$$

where λ_{rt} is total mobility defined by

$$\lambda_{rt} = \sum_j \frac{k_{rj}}{\mu_j} \quad (3.41)$$

The capillary desaturation data are modelled using the following equations:⁵⁷

$$S_{jr}/S_{jrw} = T_{j1}(\log N_C + T_{j2}) \quad (3.42)$$

$$0.0 \leq S_{jr}/S_{jrw} \leq 1$$

Since N_C is dimensionless, care must be used with the units of u_T , λ_{rt} , γ .

Consistent units are

$$u_T - \text{cm/sec.}$$

$$\lambda_{rt} - 1/\text{poise}$$

$$\gamma - \text{dynes/cm}$$

The units for λ_{rt} in the program are cp^{-1} . This discrepancy is absorbed in parameter T_{j2} . The parameters T_{ij} in equations (3.42) depend on fluid/rock properties such as contact angle, pore size distribution and other rock properties, and to a lesser degree on viscosity (neglected here).

These parameters are obtained by fitting equation (3.42) to experimental data for two-phase flow. Since the definition of N_C used by some authors in reporting experimental data is different than the one used here (equation (3.40)), conversion of the capillary number reported to the equivalent value when defined by equation (3.40) is necessary. Unfortunately since not all the information necessary for the conversion is always known, some values for relative permeability have to be estimated. An example of the conversion from a commonly used definition of N_C to the

one used here is illustrated below.

Example Conversion of $N_c = \frac{u\mu}{\gamma}$ to $N_c = \frac{u_T}{\lambda r t \gamma}$

$$\text{Define } N'_c = \frac{u\mu}{\gamma}$$

$$\text{Then } N_c = \frac{u\mu}{k_r \gamma} = \frac{N'_c}{k_r} \quad (3.40a)$$

Equation (3.40a) is equivalent to equation (3.40) for a flowing and a residual phase situation. When k_r is not known it can be either estimated from similar experimental data such as plots of k_r versus saturation,⁹⁵ or else from linearly extrapolating the value of k_r^0 at a low capillary number to a value of unity at zero residual saturation. The first method was used to convert the non-wetting phase data, and the second method was used to convert the wetting phase data reported in reference 94. The results are plotted in Figure 4.31.

The capillary desaturation curves as conceptualized for two-phase flow are further extended to three-phase flow with little theoretical or experimental basis. The reasoning used assumes that for three phase flow, where the third phase has intermediate wettability between the other two, then a third curve can be drawn such that for any capillary number the residual saturation of the third phase is between the residual saturation of the other two. In the original model of Pope^{75, 97} this third curve was defined by an equation similar to (3.42) which required T_{31} and T_{32} as parameters. The capillary number used was the largest one. Lake⁹⁸ defines an interpolating function of the wetting phase and non-wetting phase saturations and used it to interpolate the residual saturation of the

third phase between the residual of the wetting and non-wetting phases. Hirasaki⁹⁹ uses a physical idea that lumps the residual saturation of the third phase with either the wetting or non-wetting phase residual saturations. He then calculates residual wetting and non-wetting phase saturation. From a combination of his equations two possible residual saturations can be calculated for each phase. The biggest residual of each phase is then chosen. The equations used are given in section (3.11-B). Ohno²² describes each of the methods mentioned here in more detail. He also compares the effects of each model on the oil recovery of various chemical floods.

The understanding of three-phase trapping in porous media is very important in chemical flood studies. The interfacial tensions of most surfactant formulations are lowest when at optimum salinity. This favors the formation of three phases. As a consequence, surfactant floods are designed to generate three phases at some stage of the oil recovery process in order to be effective and efficient. A serious attempt to understand the mechanisms involved should originate from laboratory experiments. Three-phase residual saturation data should be used to develop a sound theoretical model for simulation use.

3.11 Relative Permeabilities

A - Two-Phase Flow

The relative permeabilities for two-phase flow are modelled using the following relations.

$$k_{rj} = k_{rj}^0 \left(\frac{S_j - S_{jr}}{1 - S_{jr} - S_{j'r}} \right)^{e_j} \quad j \neq j' \quad (3.43)$$

The basic requirement is to have the k_{rj} approach its proper limit as the capillary number and hence S_{jr} change. That is:

(1) k_{rj} should approach the water-oil (no surfactant) value as the capillary number decreases

(2) k_{rj} should approach the phase saturation as the capillary number increases (straight line relative permeabilities where $S_{jr} = 0$)

In equation (3.43) phase j can be defined to be either wetting or non-wetting. When phase j is the wetting phase, phase j' is the non-wetting phase (and vice-versa). The S_j are calculated with the phase behavior routine, see appendix B. The S_{jr} are calculated from equations (3.42).

The reservoir rock is assumed to be preferentially water wet. The microemulsion phase can be either the wetting or non-wetting phase, depending on the phase environment. When Type II (-), that is when the surfactant is predominantly in the water-rich phase, then the microemulsion is considered to be the wetting phase. When Type II (+), that is when the surfactant is predominantly in the oil-rich phase, then the microemulsion is considered to be the non-wetting phase.

In order to make the relative permeabilities approach the proper limits, linear interpolation of end points and curvatures of equation (3.43) are performed based on the change in the residual phase saturations as follows.

$$k_{rj}^0 = k_{rjw}^0 + \frac{S_{j'rw} - S_{j'r}}{S_{j'rw}} (k_{rjc}^0 - k_{rjw}^0) \quad j \neq j' \quad (3.44)$$

$$e_j = e_{jw} + \frac{S_{j'rw} - S_{j'r}}{S_{j'rw}} (e_{jc} - e_{jw}) \quad j \neq j' \quad (3.45)$$

where subscript w designates a water-oil (no surfactant), low capillary number quantity, and subscript c the large capillary number value. Values with subscript c and w are specified as input data in the simulator and usually values with subscript c are assigned values of unity, which corresponds to high capillary number and zero residual saturations.

B - Three-Phase Flow

The basic requirement that k_{rj} approaches the proper limit as in two-phase flow is also used for three-phase flow. The relative permeabilities for three-phase flow are modelled using relations similar to equations (3.43), namely:

$$k_{rj} = k_{rj}^0 S_{nj}^{ej}, \quad j = 1, 2, 3 \quad (3.46)$$

S_{nj} is a normalized saturation which requires the values of the residual saturation of each phase. As discussed in section (3.10), three different empirical models have been used to quantify the residual saturations. These models were developed by Pope, Lake, and Hirasaki. Each model is discussed below.

Pope's model

The original model used by Pope²⁵ assumes that the third phase is trapped according to a function similar to the one used for two-phase flow, that is

$$S_{3r} = T_{31} + T_{32} \log(N_c) \quad (3.47)$$

The residual saturation for the oil and the water are calculated as for the two-phase flow situation. Parameters T_{31} and T_{32} are adjusted to give a residual saturation S_{3r} between that of the water and oil for a given capillary number (N_c). In this model the residual saturation of the third phase is independent of the other two phases and is only a function of the capillary number. The capillary number used in equation (3.47) is the largest one of the two possible for the three phase case. S_{nj} in equations (3.46) are then calculated using

$$S_{nj} = \frac{S_j - S_{jr}}{1 - \sum_{j'=1}^3 S_{jr}} \quad j = 1, 2, 3 \quad (3.48)$$

The relative permeabilities are then calculated from equations (3.46), where k_{r1}^0 and k_{r2}^0 are calculated from equations (3.44). For the version used here k_{r3}^0 , e_1 and e_2 are taken to be equal to 1.0, while e_3 is a specified constant. In the original model e_1 and e_2 were input variables.

Lake's model ⁹⁸

The basic idea is to make the residual saturation of the third phase a function of the saturations of the other two in such a way that for a given capillary number,

$$S_{1r} > S_{3r} > S_{2r} \quad (3.49)$$

where phase 1 is the wetting and phase 2 the non-wetting phase. And that, $S_{3r} = S_{1r}$ when $S_1 = 0$, $S_3 > 0$ (Type II -)

$$S_{3r} = S_{2r} \text{ when } S_2 = 0, S_3 > 0 \text{ (Type II +)} \quad (3.50)$$

S_{1r} and S_{2r} are calculated as for two-phase flow using equations (3.42). Conditions (3.49) and (3.50) are satisfied by defining a simple interpolating function

$$G(S_1, S_2) = \frac{S_2(1 - S_1)}{S_1 + S_2} \quad (3.51)$$

$$\text{Function } G = \begin{cases} 0, & \text{when } S_2 = 0 \\ 1, & \text{when } S_1 = 0 \end{cases}$$

S_{3r} is then calculated from the relation:

$$S_{3r} = S_{2r} + G(S_{1r} - S_{2r}) \quad (3.52)$$

Relations similar to equation (3.52) are used to calculate k_{r3}^0 and e_3 which are used in equations (3.46) for the calculation of the relative permeabilities.

$$k_{r3}^0 = k_{r2}^0 + G(k_{r1}^0 - k_{r2}^0) \quad (3.53)$$

$$e_3 = e_2 + G(e_1 - e_2) \quad (3.54)$$

k_{r1}^0 and k_{r2}^0 in equation (3.53) are calculated from equations (3.44) while, e_1 and e_2 in equation (3.54) are calculated from equations (3.45).

S_{nj} in equations (3.46) are calculated from equations (3.48) as in Pope's model.

Because of phase behavior, saturations can become less than the calculated value for immiscible displacement, and the residual saturation of each phase is defined as

$$S_{jr} = \min(S_j, S_{jr}) \quad j = 1, 2, 3 \quad (3.55)$$

Equations (3.55) are used in all the equations above involving residual saturations.

Hirasaki's model

Hirasaki⁹⁹ defines the residual saturations for three phases based on a physical idea, which is shown in Figure (3.11). In describing the model, an assumption is made that the reservoir is preferentially water-wet. This assumption is made in order to make the explanation easier and does not affect the generality of the model.

Figure 3.11(a) leads to equation (3.56), which describes the trapping of the oil and microemulsion phases by the water phase.

$$S_{3r} + S_{2r} = f(\gamma_{wm}) \quad (3.56)$$

where $f(\gamma)$ is the non-wetting phase trapping function, which is identical to equation (3.42).

Figure 3.11b shows the trapping of the water and microemulsion phases by the water phase.

$$S_{3r} + S_{1r} = g(\gamma_{mo}) \quad (3.57)$$

where $g(\gamma)$ is the wetting-phase trapping function which is given by equation (3.42).

From figures 3.11c and 3.11d

$$S_{2r} = f(\gamma_{mo}) \quad (3.58)$$

$$S_{1r} = g(\gamma_{wm}) \quad (3.59)$$

After evaluating equations (3.56) through (3.59) the residual saturation of each phase is determined as follows:

$$S_{1r} = \max \begin{cases} g(\gamma_{wm}) \\ g(\gamma_{mo}) - S_3 \end{cases} \quad (3.60a)$$

$$S_{2r} = \max \begin{cases} f(\gamma_{mo}) \\ f(\gamma_{wm}) - S_3 \end{cases} \quad (3.60b)$$

$$S_{3r} = \max \begin{cases} f(\gamma_{wm}) - S_2 \\ 0 \\ g(\gamma_{mo}) - S_1 \end{cases} \quad (3.60c)$$

The relative permeabilities are again calculated by equation (3.46).

$$k_{rj} = k_{rj}^0 S_{nj}^{e_j} \quad (j = 1, 2, 3). \quad (3.46)$$

Where, S_{nj} are calculated as in Pope's and Lake's models from equations (3.48),

$$k_{r1}^0 = k_{r1c}^0 - (k_{r1c}^0 - k_{r1w}^0)f(\gamma_{wm})/S_{2rw} \quad (3.61a)$$

$$k_{r2}^0 = k_{r2c}^0 - (k_{r2c}^0 - k_{r2w}^0)g(\gamma_{mo})/S_{1rw} \quad (3.61b)$$

$$k_{r3}^0 = k_{r2}^0 + \omega(k_{r1}^0 - k_{r2}^0) \quad (3.61c)$$

$$\omega = S_{2r}/(S_{1r} + S_{2r}) \quad (3.62)$$

$$e_1 = 1.0 + (e_{1w} - 1.0)f(\gamma_{wm})/S_{2rw} \quad (3.63a)$$

$$e_2 = 1.0 + (e_{2w} - 1.0)g(\gamma_{mo})/S_{1rw} \quad (3.63b)$$

$$e_3 = e_2 + \omega(e_1 - e_2) \quad (3.63c)$$

Equations (3.55) are also used in conjunction with the above equations.

3.12 Cation Exchange

The cation exchange model reported by Hirasaki⁶⁰ was extended to multiphase flow by Fil^{79, 107} and used in this study. This model calculates the transport of sodium and calcium through porous media in the presence of both clays and surfactant. The cations are allowed to exchange between both the clays and surfactant according to electrostatic association.

The model is as follows:

Calcium (C_6) and sodium (C_9) exchange by mass action.

$$\frac{(\bar{C}_9)^2}{\bar{C}_6} = \beta^c Q_v \frac{(C_{9j}^o)^2}{(C_{6j}^o)} \quad \text{for clay} \quad (3.64)$$

$$\frac{(C_{9j}^s)^2}{C_{6j}^s} = \beta^s C_{3j} \frac{(C_{9j}^o)^2}{C_{6j}^o} \quad \text{for micelles} \quad (3.65)$$

where Q_v is the cation exchange capacity of the clays and is expressed in meq/ml pore volumes. Superscripts o and s represent free ions and ions associated with the micelles. It is assumed that the adsorbed surfactant ($\bar{C}_3$) associates sodium ($\bar{C}_9^s$) and calcium ($\bar{C}_6^s$) in the same way as the micelles and that the adsorbed surfactant does not interfere with the cation exchange between the clays and the free ions in solution. Then,

$$\frac{\bar{C}_9^s}{\bar{C}_6^s} = \frac{C_{9j}}{C_{6j}^s} \quad (3.66)$$

From electrical neutrality, the following equations must hold:

$$C_{6j}^s + C_{9j}^s = C_{3j} \quad (3.67)$$

$$C_{6j}^o + C_{9j}^o = C_{5j} \quad (3.68)$$

$$\bar{C}_6^s + \bar{C}_9^s = C_3 \quad (3.69)$$

$$\bar{C}_6 + \bar{C}_9 = Q_v \quad (3.70)$$

$$j = 1, 2, 3$$

From a calcium material balance we get

$$\tilde{C}_6 = \sum_{j=1}^3 S_j \bar{C}_{6j} + C_6 + \bar{C}_6^s \quad (3.71)$$

$$= \sum_{j=1}^3 S_j (C_{6j}^0 + C_{6j}^s) + \bar{C}_6 + \bar{C}_6^s \quad (3.72)$$

we also assume

$$C_{53} = (C_5/C_1)C_{13} \quad (3.73)$$

$$C_{61}^0 = (C_{63}^0/C_{13})C_{11} \quad (3.74)$$

$$C_{62}^0 = (C_{63}^0/C_{13})C_{12} \quad (3.75)$$

$$C_{61}^s = (C_{63}^s/C_{33})C_{31} \quad (3.76)$$

$$C_{62}^s = (C_{63}^s/C_{33})C_{32} \quad (3.77)$$

$$\bar{C}_6^s = (C_{63}^s/C_{33})\bar{C}_3 \quad (3.78)$$

Old values of S_j , C_{53} , C_{1j} , C_{3j} and C_3 are used to calculate C_{63}^0 , $\bar{C}_6$, $\bar{C}_{63}^s$, C_{63}^s for the new time step as follows.

Define a function of C_{63}^0

$$F(C_{63}^0) = \sum_{j=1}^3 S_j (C_{6j}^0 + C_{6j}^s) + \bar{C}_6 + \bar{C}_6^s - \tilde{C}_{6N} \quad (3.79)$$

where C_{6N} is the new time-step value just calculated by the differenced material balance equation (A-22). $\bar{C}_6$ and C_6^s are calculated by equations (3.64) through (3.70)

$$\bar{C}_6 = \frac{1}{2}(2Q_v + R_{96}^C - \sqrt{(R_{96}^C)^2 + 4R_{96}^C Q_v}) \quad (3.80)$$

$$\text{where } R_{96}^C = \beta^C Q_v \frac{(C_{93}^0)^2}{C_{63}^0} \quad (3.81)$$

$$C_{63}^s = \frac{1}{2}(2C_{33} + R_{96}^s - \sqrt{(R_{96}^s)^2 + 4R_{96}^s C_{33}}) \quad (3.82)$$

$$\text{where } R_{96}^s = \beta^s C_{33} \frac{(C_{93})^2}{C_{63}^0} \quad (3.83)$$

equation (3.79) is solved for C_{63}^0 using the Newton-Raphson iteration method until $|F(C_{63}^0)| < \epsilon$, where ϵ is a specified tolerance (input as EPS). Equation (3.18) makes use of a quantity f_6^s defined as:

$$f_6^s = \frac{\text{concentration of calcium associated with surfactant}}{\text{concentration of total ions associated with the surfactant.}}$$

$$= \frac{C_{63}^s}{C_{33}} \quad (3.84)$$

For the case of Type II (-) phase behavior, the microemulsion is the wetting phase, and cation exchange is considered between the microemul-

sion and the clays. For Types III and II(+), the aqueous phase is considered to be the wetting phase, and cation exchange is considered between the aqueous phase and the clays. For this latter case

$$R_{96}^C = \beta^C Q_v \frac{(C_{91}^o)^2}{C_{61}^o} \quad (3.85)$$

As mentioned by Hong,⁷⁴ Wang,⁷³ and Fil⁷⁹ an inaccuracy is involved by using old time step saturations and some concentrations. This is due to the explicit nature of the time integration. Fil⁷⁹ made the calculation of C_6 more implicit by doing the phase behavior and cation exchange calculations alternately until the calculated values converged, but as he pointed out, the benefits obtained are not worth the extra computer time.

As already pointed out, this problem is inherent in the explicit nature of the finite-differencing scheme used and a similar problem appears in the calculation of relative permeabilities when old values of relative mobility are used in the calculation of residual saturations. Ohno,²² implemented an iteration on the calculation of mobilities by looping to recalculate the residual saturation using the new values of mobility. This iteration was removed from the program since sometimes the total mobility was converging to zero, and, as with the iteration on cation exchange, no significant improvement was observed.

3.13 Dispersivity

Experimental results^{27, 80-82, 100-103} show that the dispersivity for multiphase flow is a function of saturation. The experimental data of

Figure 3.10 suggests a logarithmic relationship which is modelled by:

$$\alpha_{Dij}^1 = \alpha_{Dij}^1 e^{\delta_{ij}(1-S_j)} \quad i = 1, 2, 3, 4, 5, 6, 7$$

$$\alpha_{Dij}^1 = \frac{\phi S_j K_{ij}}{u_j L} \quad j = 1, 2, 3 \quad (3.86)$$

where α_{Dij}^1 is the dispersivity when $S_j = 1$, that is for single-phase flow, and δ_{ij} is the rate of change of the natural logarithm of dispersivity with saturation.

The finite-differencing used to solve the continuity equation inherently includes some numerical dispersion. According to Lantz⁸⁶, for single-phase flow:

$$\alpha_{NUM} = \frac{\Delta x_D - \Delta t_D}{2}$$

$$= \frac{\Delta x_D}{2} \left(1 - \frac{\Delta t_D}{\Delta x_D}\right) \quad (3.87)$$

which for small values of $\frac{\Delta t_D}{\Delta x_D}$, can be approximated by

$$\alpha_{NUM} = \frac{\Delta x_D}{2} \quad (3.88)$$

When physical dispersion is included in the calculations, then the total dispersion is equal to the sum of the numerical and the physical. That is

$$\alpha_{TOT} = \alpha_{NUM} + \alpha_{physical}$$

$$= -\frac{\Delta x_D}{2} + \alpha_{Dij}^1 e^{\delta_{ij}(1-S_j)} \quad (3.89)$$

α_{Dij}^1 is then calculated by setting $S_j = 1$, thus

$$\alpha_{Dij}^1 = \alpha_{TOT} - \frac{\Delta x_D}{2} \quad (3.90)$$

Figure 3.1 Phase number convention.

FIGURE 3.2 EXPERIMENTAL AND SIMULATED XANFLOOD VISCOSITIES VERSUS SHEAR RATE AT VARIOUS CONCENTRATIONS

Figure 3.3 VISCOSITY VERSUS POLYMER CONCENTRATION

Figure 3.4 Viscosity of 1000 ppm XANFLOOD Versus Salinity (Tsaur) 56

FIGURE 3.5 COMPARISON OF HI-VIS, CYANATROL WF 950S AND
PUSHER 700 VISCOSITIES VERSUS SALINITY

Figure 3.6 Transformation of tetrahedron to triangular prism,
 (A) for four component mixture,
 (B) for five component mixture.

Figure 3.7 PLANES OF CONSTANT EFFECTIVE SALINITY.
(SALINITY REQUIREMENT DIAGRAM)

Figure 3.8a Slice through tetrahedron described by the pseudocomponents.

Figure 3.8 (b) Actual Phase Behavior
 (c) Pseudophase Representation

Longitudinal dispersion coefficient as a function of saturation and pore velocity (82)

Mixing in the wetting and nonwetting phases during simultaneous flow in 243.8 cm long Berea core (103)

Figure 3.9 Dispersion as a function of saturation

FIGURE 3.10 DISPERSIVITY OF N-DECANE AND BRINE
IN BEAER SANDSTONE (80)

Figure 3.11 Basic Idea of Phase Trapping Employed in Hirasaki's Model (99)

4. OIL RECOVERY EXPERIMENT

A tertiary oil recovery experiment was conducted to gather physical property data for comparison with the improved simulator. The physical properties of the core and the experimental conditions for the chemical flood are summarized in Table 4.1. The slug contained 4.8 vol % Witco TRS 10-410, a petroleum sulfonate (3 vol % active surfactant), 3 vol % isobutanol (IBA), and 92.2 vol % brine containing 0.04 wt % NaCl and 0.1 wt % Xanflood polymer, a xanthan gum. The polymer drive consisted of the same polymer brine. The initial salinity of 1.7 wt % NaCl gave the desired salinity gradient (see below) relative to optimal salinity of 1.1 wt % NaCl for this slug mixed with 50% decane. More data are given in references 3, 4, and 5. All floods were performed with the core in a horizontal position. The core was dried in an oven at 75°C before being coated with epoxy. The epoxy was applied with the core at room temperature. Five pressure taps were fitted as shown in Figure 4.1. The sectional pressure drops were recorded continuously on a chart recorder. The pressure transducers and demodulators were Validyne type. The fluid injection sequence is listed in Table 4.2.

The viscosities of the chemical slug and polymer drive were measured by a Contraves low shear couette viscometer (Figure 4.2). The shear rate at a frontal velocity of 1 ft/day is on the order of 1 sec⁻¹. The viscosities at such a low shear rate correspond to the plateau values of the curves in Figure 4. 2. This polymer viscosity was designed to provide a favorable mobility ratio. Pressure data

recorded continuously during the experiment (Figure 4.3) show that favorable displacement did take place. The injection pressure increased gradually until it leveled out at 0.8 PV, thus indicating that no face plugging occurred. Sudden increases and decreases in the differential pressures for all sections between 0.0 and 0.5 PV are attributed to capillary pressures which are of the same order of magnitude as the viscous pressure drops. Similar pressure behavior was observed by Willhite et al.¹⁰⁵ and the effect was further investigated by McCool et al.¹⁴

Microemulsion viscosity data for the mixtures used in our experiment with and without polymer and comparisons with the apparent viscosity of the mixtures in permeable media can be found in Jones.¹⁰ A comparison of the microemulsion data with our viscosity model is in the second of these papers.⁵

4.1 Production History

The upper phase cut and oil recovery calculated from carbon-14 tagged decane and from gas chromatographic analysis of the produced fluid are shown in Figure 4.4. The carbon-14 analysis gave 100% oil recovery and is considered to be the most accurate. Only one sample formed more than two phases after three weeks in a 30°C air bath. This sample was produced at 0.96 P.V. It consisted of a large clear bottom phase (80% vol) and a turbid upper region which consisted of three separate layers. An attempt to separate these layers for

analysis disturbed the equilibrium and the upper layers mixed into one turbid phase.

Oil breakthrough occurred at 0.17 P.V. and a clean n-decane bank was produced up to 0.67 P.V., by which time more than 74% of the residual oil was recovered. The oil cut reached a maximum value of 0.64 just before surfactant breakthrough. The surfactant, polymer and tritium present in the chemical slug were all detected simultaneously at 0.67 P.V.

4.2 Effluent Analysis

All the phases of the produced effluent were analyzed for polymer, surfactant, alcohol, oil, and calcium. Sodium was only analyzed in the lower phases. Figure 4.5 is a plot of the analyzed polymer in all the phases. The polymer concentration increased from zero to 200 ppm in the lower phase over the interval from 0.67 to 0.79 P.V. while no polymer was detected in the upper phase. Analysis showed (Figure 4.6) that the upper phase was almost 100% oil up to 0.73 P.V. As the water concentration in the upper phase increased, so did the polymer concentration. The polymer concentration of the upper phase remained constant at a low value of 50 ppm, while the concentration of the lower phase increased rapidly from 200 ppm to a peak of 1300 ppm before leveling to a constant average of 1000 ppm, the concentration of the injected solution. The peak polymer concentration of 1300 ppm occurred at 0.98 P.V. and was accompanied by a polymer peak in the upper phase (340 ppm).

The IBA concentration of each phase was measured using gas chromatography. The results are plotted in Figure 4.7. Alcohol was first detected in the lower phase of the same sample which contained the first surfactant (0.67 P.V.). No alcohol was measured in the upper phase until 0.79 P.V. which coincides with the detection of water in the upper phase. A peak IBA concentration in the upper phase also coincides with a peak in the upper phase cut at 0.98 P.V. A peak in the polymer concentration in both phases was measured for the same sample. No peak IBA concentration was detected in the lower phase at this point. The IBA concentration in the lower phase reached a maximum of 0.53 vol % at 1.2 P.V.

Figure 4.8 is a plot of the surfactant in the lower and upper phases. The surfactant was analyzed using a sulphur analyzer which burns the sample and analyses the produced SO_2 with an iodine titrant. The surfactant concentration in the upper phase increased rapidly after breakthrough and reached a maximum value of 2.72 wt % at 0.93 P.V. This is only slightly less than the 3 vol % in the injected slug. Surfactant in the lower phase was first measured at 0.98 P.V. This sample had a peak in the upper phase cut and was followed by only one other two-phase sample. The surfactant in the lower phase gave a spike for the first one-phase sample produced after the two-phase samples. This could also be the first Type II(-) sample. The concentration of the spike was measured to be 1.6 wt %. The surfactant concentration following the spike remained at a constant level of 0.72 wt % up to 1.24 P.V., after which it decreased almost linearly to 0.35 wt % at 1.4 P.V. Surfactant concentration then decreased rapidly and

only trace amounts were measured in the next samples up to 1.6 P.V. Later samples had no surfactant. A total of 1.3 cc of surfactant was injected and analysis showed 1.33 cc of produced surfactant, (volume and weight concentrations were assumed equal). This indicates that within experimental error all the surfactant was produced. We attribute this lack of surfactant retention to the favorable alcohol/surfactant transport (see below), a salinity gradient resulting in Type II(-) phase behavior upstream, and to good mobility control.

The water of the injected chemical slug was labeled with tritium. Scintillation counts of the tritium in the effluent were measured and the normalized values plotted on Figure 4.9. Overall concentrations of the surfactant and alcohol, also normalized by the injected values are plotted on Figure 4.9. Tritium counts are a measure of the water initially in the slug. Figure 4.9 shows that the water, surfactant and alcohol of the injected slug transported at the same rate. An interesting feature in Figure 4.9 is the relatively smooth IBA and tritium histories compared to a spike in the surfactant.

The n-decane recovered from the core was labeled with carbon-14. Scintillation counts of the effluent samples were used to calculate the concentration of water and n-decane in each phase. The results are plotted in Figure 4.6. The high water concentration in the upper phase towards the end of the two-phase region indicates Type II(+) phase behavior. Other considerations suggest Type III phase behavior with the overall composition in the Type II(+) mode. Also the surfactant and oil compositions for the two phases at 1.0 P.V. strongly

indicates that the overall composition was close to a plait point. It is interesting to note that 100% oil recovery was obtained at the end of 1.0 P.V. injection, by which time about one-third of the surfactant was produced.

Figure 4.10 is a plot of the calcium concentration in the upper and lower phases together with the sodium in the lower phase. The decrease in the calcium concentration of the lower phase can be caused by two mechanisms. First, a low salinity in the slug will reverse the cation exchange process thus causing calcium pickup by the clays. Second, the surfactant in the slug is competing for the calcium. Observe that the calcium peaks during the front of the surfactant slug, indicating calcium depletion by the surfactant.

Table 4.1

Summary of Oil Recovery Experiment B6

Physical Property

Temperature °C	30.0
CORE DATA	
Dimensions (inches)	2.0 X 2.0 X 24.0
Total Pore Volume (ml)	333.0
Porosity (fraction)	0.236
Absolute Brine Permeability (md)	500.0
Residual Brine Saturation (Swr)	0.37
Residual Oil Saturation (Sor)	0.35
End-Point Perm. at Swr (md)	477.0
End-Point Perm. at Sor (md)	57.0
Initial Salinity (wt % NaCl)	1.7

CHEMICAL SLUG	
Pore Volumes Injected	0.13
Composition:	3.0 vol % TRS 10-410 (active)
	3.0 vol % IBA
	92.2 vol % 1000 ppm Xanflood soln.
Salinity (wt % NaCl)	0.04
Viscosity (cp at 1.0 sec ⁻¹)	28.0

POLYMER DRIVE	
Polymer	Xanflood
Concentration (ppm)	1000.0
Viscosity (cp at 1.0 sec ⁻¹)	37.0
Salinity (wt % NaCl)	0.04

Injection Rate (cc/hr)	6.98
Frontal Velocity (ft/day)	1.0
Oil	n-Decane
Oil Breakthrough (PV injected)	0.17
Final Oil Recovery (% of Sor)	100

Table 4.2

Fluid Injection Sequence for Tertiary Oil Recovery Experiment B6

1. Saturate core with 1.7 wt % NaCl brine.
2. Inject 10 P.V. of 1.7 wt % NaCl brine.
3. Inject 1.5 P.V. of T_2O (tritium) labeled 1.7 wt % NaCl brine.
4. Inject 1.5 P.V. of 1.7 wt % NaCl brine.
5. Inject n-decane at 40 psig injection pressure until residual water saturation was reached (10 P.V. oil injected)
6. Inject 1.0 P.V. of carbon-14 labeled n-decane.
7. Waterflood core to residual oil saturation with a frontal velocity of 6 ft/day.
8. Inject 0.13 P.V. of chemical slug tagged with T_2O .
9. Inject 2.0 P.V. of polymer solution.
10. Inject 1.5 P.V. of T_2O tagged polymer solution.

FIGURE 4.1 Schematic illustration of the positioning of the pressure taps and the setup used for recording pressure drops

FIGURE 4.2 VISCOSITY VS. SHEAR RATE FOR THE SLUG AND POLYMER DRIVE

FIGURE 4.3 NORMALIZED PRESSURE DROPS ACROSS SECTIONS 1, 2, 3 & 4

FIGURE 4.4 PHASE-CUT AND OIL RECOVERY VERSUS PORE VOLUMES

FIGURE 4.5 POLYMER CONC. IN THE UPPER AND LOWER PHASES

FIGURE 4.6 PHASE DISTRIBUTION OF WATER AND OIL IN THE EFFLUENT

FIGURE 4.7. IBA CONC. IN THE UPPER AND LOWER PHASES

FIGURE 4.8 SURFACTANT CONC. IN THE UPPER AND LOWER PHASES

FIGURE 4.9

TOTAL TRITIUM, SURF. OR ALCOHOL CONC. (NORM.)

FIGURE 4.10 PHASE CONCENTRATIONS OF CALCIUM AND SODIUM

5. COMPARISON OF EXPERIMENTAL DATA AND SIMULATION RESULTS

The experiment described above was simulated with the improved simulator. The input physical properties and a discussion of the simulation results follows.

A list of the input parameters is shown on Table 5.1. The relations used to model the physical properties are discussed in section 3. It should be noted that the height of the binodal curve is appropriately small because the new phase behavior model distributes the alcohol among the three pseudocomponents. The relative permeability exponents used were calculated using fractional flow theory so as to match the oil breakthrough and cut. The capillary desaturation parameters were adjusted to match the data of Gupta et al.⁹⁴

The alcohol partition coefficients used were $K_a^O=0.25$ and $K_a^S=10.0$. The parameter which controls the effect of the alcohol on effective salinity, β_7 , was input as -1.65. The parameter which controls the effect of the calcium on effective salinity, β_6 , was input as 1.5. The model used is described in reference 5 and is based on Hirasaki's equation⁵⁹ for optimal salinity.

Figure 5.1 shows the simulated total concentration profiles at 0.5 pore volumes. The shape of the surfactant profile is produced by the shift of phase behavior from Type II(+) to Type III and Type II(-) from the downstream to the upstream direction. This shift complicates

the transport of the surfactant which is effected by changes in phase viscosities, saturations and relative permeabilities.

Figure 5.2 compares the simulated and experimental oil and polymer. A polymer inaccessible pore volume of 0.08 was used. The polymer is usually assumed to be entirely in the most water-rich phase. However, with this assumption it was difficult to match the polymer front. A very high viscosity polymer phase resulted when the phase behavior was of Type III, and as a consequence, the polymer was delayed too much. For this reason, the polymer was assumed to be distributed in proportion to the water concentration in each phase. This gives a reasonably good match of the produced polymer (Figure 5.2). Better understanding of the distribution of polymer among phases would help in modelling polymer transport.

Figure 5.3 is a superposition of the experimental and simulated total surfactant and alcohol. The difference in the surfactant tail can be explained by the lack of adsorption in the simulator. Although no surfactant adsorption was measured experimentally, the salinity gradient may have caused desorption of earlier adsorbed surfactant. Experimental results showed the same trend as the simulated one. However, 100% alcohol recovery was simulated, while less than 60% was recovered experimentally. The experimental values were subsequently determined to be too low due to a systematic error in our alcohol measurements caused by loss of alcohol from the samples which has since been corrected. The alcohol data in Figure 5.5 has been corrected by 50%. The remarkable agreement between the very sharp

surfactant peak and the simulated peak is one of the most interesting and convincing features of this comparison between experiment and simulation. The peak is due to a focusing effect caused by the salinity gradient. The salinity gradient required to accomplish this desirable feature was designed by simulation before the experimental coreflood was conducted taking into account not only the actual salinity, but the expected calcium changes and the dilution effect caused by alcohol partitioning to excess phases. These effects and their consequences on salinity gradient design and the process generally have been carefully and systematically investigated by Nelson¹²² and Hirasaki and Nelson.⁹⁹

Figure 5.4 shows a comparison between the simulated and experimental sodium in the lower phases. The close agreement indicates that both the cation exchange model and the amount of dispersion were correct. The dispersion for this run was contributed numerically with 40 grid blocks. A physical dispersion coefficient could have been included but was not. Additional investigation of this factor, especially the saturation dependence of dispersion which we¹³ and others have found experimentally would be interesting. However, the extreme self-focusing nature of this displacement helps reduce mixing by dispersion and its importance in the simulation. Others⁹⁹ have noted this previously. We did test the sensitivity of the results to the number of grid blocks used. Both 20 and 80 were tried. Although there were noticeable differences, the essential features remained the same and with adjustment for dispersion probably could have been made very close to the 40 block results shown in this

paper. Slight oscillations in the 20 block case indicated that there is a minimum number of grid blocks for a particular problem below which the quality of the results becomes poor. One should not, however, be tempted to scale this number to field dimensions proportionately. Our experience with 2-D simulations^{3,6,7} to date indicate this is far too pessimistic a procedure. Figure 5.5 compares the simulated and experimental total calcium. The agreement, further supports the cation exchange model, which is described in references 5 and 60. This is a new and very important feature of micellar/polymer simulations.

Figure 5.6 compares the simulated and experimental normalized pressure drop across the downstream quarter of the core. Close agreement was obtained for the oil bank and again following polymer breakthrough. As mentioned earlier, capillary pressures are suspected to have had an effect on the measured pressure drops and this may be part of the reason for the small difference corresponding to the surfactant transport period. However, the primary reason is likely to be due to the inadequacy of the three-phase relative permeability model used. Still another possibility is the phase viscosity model.

To further test the simulator, an experiment reported in the literature has been studied. The experiment of Gupta²⁶ was chosen because it shows a very clearly defined separation of alcohol and surfactant; it is also a good example of cation exchange and is one of the best reported experiments in the literature based on the completeness of the data. Gupta's experiment was part of an extensive

study reported in connection with the Sloss field pilot. 26,94,103,127

A discussion of the simulation results follows. in section 6.

Conclusions for both comparisons are given at the end of section 6.

TABLE 5.1
SIMULATION PARAMETERS FOR OUR EXPERIMENT*

$\Delta t_D / \Delta x_D$	0.04	T_{31}	0.0	C_{3min}	0.0001
N	7	T_{32}	0.0	C_{3max0}	0.1
K	40	α_1	0.0	C_{3max1}	0.05
u_T	8.33E-3	α_2	0.0	C_{3max2}	0.1
k	0.5	α_3	20.0	C_{2PL}^*	0.1
ϕ	0.236	α_4	0.0	C_{2PR}^*	0.9
$\phi_{4,eff}$	0.92	α_5	0.0	a_{31}	0.0
C_{5I}	0.29	μ_1	0.86	a_{32}	0.0
C_{6I}	0.0012	μ_2	0.83	a_4	0.0
S_1	0.65	A_{p1}	52.0	b_3	0.0
S_2	0.35	A_{p2}	2430.0	b_4	0.0
S_{1rw}	0.35	A_{p3}	40000.0	β^c	0.20
S_{2rw}	0.35	S_p	0.1695	β^s	0.45
α_{Dij}^1	0.0	$\dot{\gamma}_{1/2}$	10.0	Q_v	0.044
δ_{ij}	0.0	P_α	1.8	β_p	10.0
$\log(\gamma_{wo})$	1.3	$R_{k,max}$	1.0	W_s	419.0
G_{11}	13.0	b_p	1000.0	β_6	1.5
G_{12}	-14.0	k_{r1w}^0	0.05	β_7	-1.65
G_{13}	0.0221	k_{r2w}^0	0.98	f_{6I}^s	0.0
G_{21}	13.5	k_{r3w}^0	1.0	f_{7I}^s	0.163
G_{22}	-14.0	e_1	1.0	K_a^o	0.25
G_{23}	0.0221	e_2	3.17	K_a^s	10.0
T_{11}	-0.428	e_3	1.0	C_{5L}	0.154
T_{12}	-0.415	k_{r1c}^0	1.0	C_{5U}	0.222
T_{21}	-0.422	k_{r2c}^0	1.0		
T_{22}	0.155				

TABLE 5.1 (cont.)

	t_D	C_{11}	C_{21}	C_{31}	C_{41}	C_{51}	C_{61}	C_{71}
Chemical Slug:	0.13	0.94	0.0	0.03	0.1	0.0068	0.0	0.03
Polymer Drive:	1.5	1.0	0.0	0.0	0.1	0.0068	0.0	0.0

FIGURE 5.1 Simulated total concentration profiles at 0.5 pore volumes

FIGURE 5.2

COMPARISON BETWEEN SIMULATED AND EXPERIMENTAL
TOTAL OIL AND TOTAL POLYMER HISTORIES

FIGURE 5.3 COMPARISON OF EXPERIMENTAL AND SIMULATED HISTORIES

FIGURE 5.4 COMPARISON OF SIMULATED AND EXPERIMENTAL SODIUM IN THE LOWER PHASES

FIGURE 5.5 COMPARISON OF SIMULATED AND EXPERIMENTAL TOTAL CALCIUM

FIGURE 5.6 SIMULATED AND EXPERIMENTAL NORMALIZED PRESSURE DROP ACROSS THE LAST QUARTER OF THE CORE

6. SIMULATION OF SLOSS EXPERIMENT

Table 6.1 is a list of the input parameters used for simulating the Sloss experiment. The capillary desaturation parameters were the same as those used to simulate our experiment. The end point relative permeabilities used are those reported by Gupta,²⁶ while the curvature exponents used were such as to match the oil breakthrough and oil cut.

The isopropyl alcohol (IPA) was considered to be absent from the oil pseudocomponent, and only associated with the surfactant and water pseudocomponents. This was modeled by use of Hirasaki's⁵⁹ values for the partition coefficients of IPA, namely $K_a^S=4.0$ and $K_a^O=0.0$. The effect of IPA on the phase behavior effective salinity was calculated using Hirasaki's value of $\beta_7=6.2$, while the effect of calcium was calculated with a value of $\beta_6=0.5$.

The Sloss experiment produced a large upper phase microemulsion (Type II(+)). Considering the salinity of the initial and injected fluids, this could only be explained by a cation exchange mechanism which results in calcium pick up by the surfactant from the clays. The cation exchange capacity of the clays was measured by Gupta and his value (0.044 eq/l P.V.) for Berea rock was used in the simulations. The values used for the cation exchange coefficients for the clays and surfactant are those of Hirasaki,⁶⁰ $\beta^C=0.25 \text{ (eq/l)}^{-1}$ and $\beta^S=0.45 \text{ (eq/l)}^{-1}$.

Figure 6.1 shows the simulated total concentration profiles at 0.5 P.V. The calcium pick up by the surfactant is clearly demonstrated. This produces a Type II(+) phase behavior and thus the surfactant partitions into the tail of the oil bank producing an upper-phase microemulsion. This microemulsion contains solubilized water which together with the surfactant accounts for the presence of the alcohol. For this particular formulation the alcohol associates with both the water and the surfactant. The saturation of the swollen oil phase is thus slightly increased, which in turn increases its fractional flow. This situation results in the separation of the surfactant and the alcohol. The surfactant being totally in the microemulsion phase is transported at a faster rate than the alcohol which is distributed amongst the aqueous and microemulsion phases.

Figure 6.2 is a plot of the simulated oil and microemulsion cuts. Superimposed on this plot are the experimental data points reported by Gupta. The oil bank breakthrough time and size are matched very well, and so is the front of the microemulsion. The tail of the microemulsion is not matched and no lower phase microemulsion is predicted. However, this represents an insignificant part of the oil displacement in this experiment. A three-phase region was simulated following the Type II(+) region. As observed experimentally, the size of this region is also small and due to low oil concentrations. The excess oil cut is negligible in this three-phase region of production.

Figure 6.3 compares the simulated and experimental oil saturation profiles at the termination of the recovery process. The simulator

predicted a slightly lower oil saturation for the upstream half of the core but matched that at the downstream half almost exactly. Although it is not known what exactly produced the particular residual saturation profile for the experimental situation, the simulated profile was produced by a change in phase behavior. As the slug is injected, cation exchange between the surfactant and the clays occurs. The electrolyte concentration is such that initially the slug is mostly in a Type III phase behavior environment. As the slug is transported in the core, calcium is picked up by the slug and the phase behavior shifts to Type II(+). This process results in the first section of the core to be in a Type III phase behavior for a longer time than the downstream section, and thus the lower oil saturations.

The simulated and experimental surfactant and alcohol histories are plotted on Figures 6.4 and 6.5 for comparison. For both, the peak is matched accurately. The simulated surfactant pulse is sharper than the experimental, while the simulated alcohol pulse is more diffuse than the experimental. The exact shape of the pulses is sensitive to the relative phase transport. In consideration of the many assumptions and approximate models employed by the simulator, the results are satisfactory. The results are a great improvement over previous attempts which modeled the alcohol and surfactant as one pseudocomponent in the phase behavior calculations. Fil and Pope¹⁰⁴ reported difficulties in matching surfactant breakthrough and its lead over the alcohol for Gupta's experiment. Others^{16,84,103} have consistently failed to match the surfactant pulse for this and other similar experiments. Their predictions show a later surfactant production

compared to the actual measurements. Thus, our new phase behavior model represents a significant advance in the capability to simulate micellar displacements.

The ability of the simulator to model cation exchange is shown in Figures 6.6 to 6.8. Figure 6.6 compares the simulated and experimental normalized chloride ion concentration in the aqueous phase. The close match indicates that the level of numerical dispersion is about equal to that which physically occurred in the experiment, and that transport of the aqueous phase is simulated correctly. Figure 6.7 compares the calcium concentration in the oleic phase. The simulated peak concentration is higher than the experiment value. However, the overall match can still be considered good. Figure 6.8 compares the calcium concentration in the aqueous phase. In this case the simulated calcium is slightly less and the peaks do not coincide. In spite of this difference, the trend is very well matched, particularly with reference to the second peak. This and other features of this experiment could probably be matched more precisely if we had fine tuned the input. Even as complete as this experiment was, there are still significant physical property and coreflood data missing. These missing data actually make it more difficult for us to match displacement experiments because more possibilities have to be considered. When only oil recovery is matched, simulation are practically meaningless since merely adjusting the relative permeability curves suffices. However, we have found that adjusting relative permeability curves among several other factors is not sufficient to match composition histories.

The Sloss experiment is one in which phase behavior properties caused a separation of the surfactant and alcohol such that the surfactant transported at a faster rate than the alcohol. This was promoted in part by the strong preference the IPA has for the water. We next simulate a situation where the alcohol also prefers the water, however the interfacial properties of the surfactant are not good enough to reduce the residual saturation. This results in the surfactant being trapped with the residual oil while the alcohol is transported in the aqueous phase. Profiles at 0.5 pore volumes are shown in Figure 6.9. The conditions for this simulation were purposely chosen to exaggerate the separation. Examples of other types of separation are given in Camilleri's thesis.³ These types of simulations form the basis for chemical selection (especially of the alcohol), as well as process performance studies.

Conclusions

Simulation results from an improved micellar/polymer simulator have been compared with experimental data. The conclusions derived from these comparisons are summarized below.

1. The new phase behavior model gives satisfactory results. It can distinguish between the alcohol and surfactant and provides for their independent transport. Most important is the simplicity of the model, which computes quaternary phase behavior with a negligible increase in computer time as compared to the old ternary phase behavior calculations.

2. Hirasaki's⁵⁹ optimal salinity concept, which states that optimal salinity is a function of the associated alcohol and divalent cations with the surfactant, produced satisfactory results for the two chemical formulations simulated. Other types of micellar formulations need to be investigated and studies of alternatives involving co-surfactants other than alcohol or more than one co-surfactant are currently under way.
3. Hirasaki's⁶⁰ cation exchange model, which considers exchange between surfactant, clays and solution, has also proved to produce results consistent with experimental observations.
4. The success of closely matching experimental phase concentration histories indicates that the physical property models used together with the simplifying assumptions provide a good description of the physical processes occurring during the displacement of oil by surfactant. The notion of chemical equilibrium in particular seems to be valid for the experiments considered. We do not expect this to always be the case. Significant progress has been made on the common problem of matching the surfactant pulse. For the cases considered, both the surfactant and alcohol histories have been approximately matched.
5. Cation exchange can and should be taken into account in designing the effective salinity gradient of a surfactant flood. Calcium pick up by the surfactant often results in Type II(+) phase behavior at the leading front of the surfactant slug. Its effect

can place a large part of the surfactant in a Type II(+) region and reduce the size of the Type III region thus reducing the oil recovery efficiency. Cation exchange also increases the possibility of microemulsion trapping. Simulation can be used effectively to cope with this feature of the process and improve design.

6. Application of this improved simulator should be useful for field studies and design. It would be desirable to first simulate 2-D laboratory experiments, then pilots. Some nominally 1-D laboratory experiments involving significant gravity effects, heterogeneity, etc. should also be investigated with a compositional 2-D simulator. Remarkably, the extra computing time required to include more complete process physics is small. The benefits regarding scaleup, optimization, risk and cost reductions, etc. should be significant for field applications.

TABLE 6.1
SIMULATION PARAMETERS FOR SLOSS*

$\Delta t_D / \Delta x_D$	0.04	T_{31}	0.0	C_{3min}	0.0001
N	7	T_{32}	0.0	C_{3max0}	0.2
K	40	α_1	0.0	C_{3max1}	0.1
u_T	2.37E-2	α_2	0.0	C_{3max2}	0.2
k	0.66	α_3	0.1	C_{2PL}^*	0.1
ϕ	0.21	α_4	0.0	C_{2PR}^*	0.9
$\phi_{4,eff}$	1.0	α_5	0.0	a_{31}	0.1
C_{5I}	0.209	μ_1	0.305	a_{32}	0.0
C_{6I}	0.00296	μ_2	0.8	a_4	2.0
S_1	0.641	A_{p1}	7.4	b_3	10.0
S_2	0.359	A_{p2}	46.3	b_4	100.0
S_{1rw}	0.47	A_{p3}	89.4	β^c	0.24
S_{2rw}	0.359	S_p	-0.52	β^s	0.45
α_{D1j}^1	0.0	γ_{12}	200.0	Q_v	0.044
δ_{1j}	0.0	P_α	1.6	β_p	20.0
$\log(\gamma_{wo})$	1.2	$R_{k,max}$	1.2	w_s	430.0
G_{11}	13.2	b_p	1000.0	β_6	0.5
G_{12}	-14.0	k_{r1w}^0	0.2	β_7	6.2
G_{13}	0.0221	k_{r2w}^0	1.0	f_{6I}^s	0.0
G_{21}	13.2	k_{r3w}^0	1.0	f_{7I}^s	0.0
G_{22}	-14.0	e_1	1.0	K_a^o	0.0
G_{23}	0.0221	e_2	2.2	K_a^s	4.0
T_{11}	-0.428	e_3	1.0	C_{5L}	0.065
T_{12}	-0.415	k_{r1c}^0	0.8	C_{5U}	0.2
T_{21}	-0.422	k_{r2c}^0	1.0		
T_{22}	0.155				

TABLE 6.1 (cont.)

	t_D	C_{11}	C_{21}	C_{31}	C_{41}	C_{51}	C_{61}	C_{71}
Chemical Slug:	0.1	0.9489	0.0	0.0386	0.16	0.198	0.0028	0.0125
Polymer Drive:	1.5	1.0	0.0	0.0	0.09	0.0036	0.003	0.0

TOTAL CONCENTRATION VS. FRACTIONAL DISTANCE

FIGURE 6.1 Simulated total concentration Sloss profiles at 0.5 PV.

FIGURE 6.2 Simulated and Experimental Oil Cuts for Sloss

FIGURE 5.3 COMPARISON OF SIMULATED AND MEASURED RESIDUAL OIL SATURATION

FIGURE 6.4 COMPARISON OF EXPERIMENTAL AND SIMULATED SLOSS HISTORIES

FIGURE 6.5 COMPARISON OF EXPERIMENTAL AND SIMULATED SLOSS HISTORIES

FIGURE 6.6 COMPARISON OF EXPERIMENTAL AND SIMULATED SLOSS HISTORIES

FIGURE 6.7 COMPARISON OF EXPERIMENTAL AND SIMULATED SLOSS HISTORIES

FIGURE 6.8 COMPARISON OF EXPERIMENTAL AND SIMULATED SLOSS HISTORIES

FIGURE 6.9 O11, Surfactant and alcohol profiles at 0.5 PV.
for a hypothetical case.

7. 2-D SIMULATION RUNS

7.1 Introduction

One of the objectives of this project is the understanding of the physical properties, mainly phase behavior, as related to the micellar/polymer oil recovery process. 1-D core experiments and 1-D simulations are sufficient for the purpose of developing and testing most theoretical property models. However, field studies require use of 2-D or 3-D models. A 2-D finite-difference micellar/polymer simulator developed by Hong et al.^{74, 76} was used to simulate a 2-D oil recovery experiment reported by Putz et al.¹¹² These should be considered preliminary simulations. The phase behavior model used by the 2-D simulator considers the surfactant and the alcohol as one pseudocomponent. The only modification to Hong's simulator was the addition of an optional three-phase relative permeability model. Hong used Pope's three-phase relative permeability model; Lake's model was added as an option. A description of the three-phase relative permeability models can be found in Section 3.11.

The experiment studied in this chapter was previously simulated by Fil⁷⁹, who also used a streamline simulator developed by Wang et al.^{73, 128} in addition to Hong's simulator. The purpose of the runs discussed here is to test certain features of the simulator such as cation exchange, and to serve as a limited sensitivity study. Only areal simulations are considered.

7.2 Discussion

The experiment consisted of a quarter five-spot sand pack. A rubber cell was packed with reservoir sand and put under pressure as in a Hassler cell. Waterflood residual oil was then recovered by the injection of 0.06 PV microemulsion slug, followed by 1.9 PV of polymer solution. 92% oil recovery was achieved.

Table 7.1 is a list of the general fluid and reservoir data. These data are the same for all the runs considered here. Table 7.2 lists the different runs, and identifies the slug, drive and physical property data used for each run. The oil recovery of each run after the injection of 1.65 pore volumes is tabulated for comparison. Tables 7.3 and 7.4 list the nonzero parameters for the slugs and drive used. Table 7.5 lists the physical property parameters PBCOT2, the base case. The perturbations of the physical property parameters are listed in Table 7.6. IPERM is a parameter added to Hong's simulator; its function is to select the three-phase relative permeability model. A value of 0 selects Pope's model while a value of 3 selects Lake's model.

Production histories, including phase cuts, oil recovery and total concentrations for each run are shown on Figures 7.1 - 7.22.

Run BCOT2 is a fixed salinity Type II(-) run. The physical property parameters used equate to effective lower and upper salinity limits of 0.0845 and 0.0967 eq/l respectively, while the calculated effective salinity is 0.04615 eq/l.

Hong's simulator uses a dilution effect in the phase behavior model as given below:

$$C_{SE} = \frac{C_9}{C_1} + \beta_1 \frac{C_6}{C_1} + \beta_2 \frac{C_3}{C_1} \quad (7.1)$$

The effective salinity limits are calculated from the experimental salinity limits from the following

$$C_{SEL} = C_{SELI} + \beta_1 \frac{C_{6I}}{C_{1I}} + \beta_2 \frac{C_{3I}}{C_{1I}} \quad (7.2)$$

$$C_{SEU} = C_{SEUI} + \beta_1 \frac{C_{6I}}{C_{1I}} + \beta_2 \frac{C_{3I}}{C_{1I}} \quad (7.3)$$

7.2.1 Example Calculation of C_{SEL} for Run BCOT2

With reference to Table 7.5, $C_{SELI} = 0.0522$, $\beta_1 = 10$, $\beta_2 = 0.0$

$$C_{6I} = 0.001157, C_{1I} = 0.26$$

Substituting these values in equation (7.2) we obtain:

$$C_{SEL} = 0.04 + 10 \times 0.001157/0.26 = 0.0845$$

As is normally expected, the salinity values for run BCOT2 give low oil recovery since the interfacial tension is not reduced sufficiently. The surfactant is, however, always in the aqueous phase, and, thus, loss by trapping in the microemulsion or oleic phase does not occur. The results for Run BCOT2 are plotted in Figures 7.1 - 7.2. Surfactant breakthrough is somewhat early and is basically a result of dispersion and pattern or effects. Simulated oil breakthrough is late, 0.82 PV, compared to 0.63 PV experimentally. The shape of the oil-bank is similar to the experimental

one which was characterized by a sharp front followed by an exponentially decaying tail.

Run BCOT3 is different from BCOT2 in the effective lower and upper salinity limits, which were changed to 0.04 and 0.0522, respectively. This change now makes the phase behavior Type III throughout the whole displacement. The results of this run are plotted in Figures 7.3 - 7.4. As expected, this type of phase behavior is very efficient in displacing the residual oil (98.5% oil recovery). Simulated oil breakthrough was 0.74 PV, which although earlier than for BCOT2, is still later than the experimentally observed time of 0.63. The results of this run show some undesirable numerical features which include oscillation in the oil bank, and high oil cuts (100%). Conditions stabilize for the oil-bank tail, where the oil cut resembles the experimental results.

In an effort to eliminate the oil-bank oscillations obtained in Run BCOT3, the relative permeability exponent for the microemulsion phase was changed in Run BCOT4. History results for Run BCOT4 are plotted in Figures 7.5 - 7.6. This change did help in eliminating the oscillations, however, the oil-bank breakthrough time and oil-cut did not change. The total oil recovery for Run BCOT4 is also substantially lower than for Run BCOT3.

The effect of using a different relative permeability model is demonstrated by Run BCOT4A, which is similar to BCOT4 except that Lake's model was used instead of Pope's model. The effect is a drastic reduction of the oil recovery (Figures 7.7 - 7.8). It should be noted that for both Runs BCOT4 and BCOT4A no surfactant was produced. The difference in oil recovery is because the surfactant in Run BCOT4A did

not propagate as much as in Run BCOT4.

For all the runs considered so far, the alcohol was lumped with the surfactant and given the same properties. Also, no cation exchange was considered, and the salinity was kept constant. For the following runs, the alcohol was treated as water, and cation exchange was included.

Run BCOT5 also uses Lake's relative permeability model. Together with the changes above, Run BCOT5 differs from Run BCOT4A in the capillary desaturation parameters which slightly increase trapping. The slug salinity was increased from .001586 to 0.2696 eq/l. Histories for BCOT5 are plotted in Figures 7.9 - 7.10. The calcium and anion histories demonstrate the effect of cation exchange on the salinity. The overall changes did not improve the oil recovery, in fact, the opposite happened. The lower oil recovery is attributed to the capillary desaturation parameters and the different way of treating the alcohol, which is equivalent to reducing the slug size. As with the previous two runs, no surfactant was produced during Run BCOT5.

Run BCOT8 reduces the multi-phase region in an effort to increase the oil-recovery. The slug salinity is again reduced to the level of the previous runs. The reason for high salinities in slug SBCOT5 was to include the salt introduced by the surfactant, but it was later realized that this is not necessary. The results of Run BCOT8 are plotted in Figures 7.11 - 7.12. A slight improvement in the oil recovered is achieved, possibly due to the smaller multi-phase region, but the improvement is negligible.

The low oil recovery from runs with Lake's relative permeability model prompted use of Pope's model for the remainder of the runs. Run

BCOT9 differs from BCOT8 only in the relative permeability model. The results for BCOT9 are plotted in Figures 7.13 - 7.14. The close resemblance of BCOT8 and BCOT9 suggest that only a small three-phase region exists, if at all.

The absence of any produced surfactant prompted setting the surfactant adsorption to zero for Run BCOT12, which also had slight changes in the capillary desaturation parameters, and no cation exchange. The results of Run BCOT12 are plotted in Figures 7.15 - 7.16. The shape of the oil history, oil bank, oil cut, and the oil recovered match the experimental results much better than before (see experimental curve on Figure 7.16). BCOT12 gives the best match of all the runs.

Cation exchange is again included in Run BCOT13, which also has higher effective salinity limits, and reduced calcium effect on salinity (BETA1) in an effort to keep the phase behavior Type III when the calcium concentration increases because of cation exchange. The results of Run BCOT13 are plotted in Figures 7.17 - 7.18. The calcium history shows an increase coincident with the surfactant which would be expected for this type of environment. The changes in input produced a Type II(-) phase behavior because the effects mentioned above were overcompensated. As a result of the Type II(-) phase behavior, the oil recovery was very low.

Runs BCOT15 and BCOT16 are very similar. Both include surfactant adsorption and the same cation exchange parameters. Also, both are Type II(-) phase behavior runs. However, the oil recovery is much larger than for BCOT13. Further investigation is required to understand the cause of such a difference. The histories of the above two runs are plotted in Figures 7.19 - 7.22. It should be noted that although the effective salinity

limits for BCOT16 were made too high to ensure Type II(-) phase behavior, the effect produces minor differences.

7.3 Conclusions

The results of this study show a preliminary simulation of a five-spot sandpack experiment with a 2-D areal simulator. Laboratory data available were limited to oil cut and oil recovery. Run BCOT12 roughly matched the available data (Figure 7.16), but a high degree of uncertainty exists in the input parameters due to a lack of reported property data at the time this work was being done.

Table 7.1

General Information¹ for 2-D (areal) Simulation RunsReservoir Dimensions

X-Length (ft)	5.577
Y-Breadth (ft)	5.577
h-Thickness (ft)	0.656
# x-nodes	11
# y-nodes	11

Reservoir Data

Porosity (fraction)	0.365
X-Permeability (Darcy)	7.0
Y-Permeability (Darcy)	7.0
Initial Oil Saturation	0.2

Fluid Data

Oil viscosity (cp)	40.0
Water viscosity (cp)	0.8
Initial anion conc.(N)	0.0061
Initial calcium conc.(N)	0.00445
Longitudinal disp. (ft)	0.3944
Transverse disp.(ft)	0.01315
Molecular diff.	0.0

Injection Data

Surfactant slug (%P.V.)	6.0
Polymer drive (%P.V.)	160.0
Injection rate (ft ³ /D)	0.8476
Flux (ft ³ /D at 0.5 ft)	1.645

¹ See reference (112) for more detail

Table 7.2
Comparisons of 2-D (Areal) Simulation Runs

Run Number	BCOT2	BCOT3	BCOT4	BCOT4A	BCOT5	BCOT8	BCOT9	BCOT12	BCOT13	BCOT15	BCOT16
Slug code	SBCOT1				SBCOT5	SBCOT8					
Drive code	DBCOT1										
Physical Prop. code	PBCOT2	PBCOT3	PECOT4	PBCOT4A	PBCOT5	PBCOT8	PBCOT9	PBCOT12	PBCOT13	PBCOT15	PBCOT16
% Oil Recovery (at 1.65 PV.)	42.8	98.52	78.5	28.19	18.97	21.46	23.21	87.87	25.22	65.52	65.43
Time Step = 0.000625 PV.											

Table 7.3
Slugs Specified in Table 7.2

Slug code	SBCOT1	SBCOT5	SBCOT8
Parameter * (FORTRAN)			
N	6		
P(1,J,1)	0.0		
C50	0.0061		
C60	0.00445		
QT(1)	0.8476		
CI(1,1)	0.26	0.343	
CI(2,1)	0.523		
CI(3,1)	0.217	0.134	
CI(4,1)	0.0		
CI(5,1)	0.001586	0.269586	0.0021
CI(6,1)	0.001157		0.00153
CI(7,1)	0.0		
TINJ	0.5272		

Table 7.4

Drive Specified in Table 7.2

Drive code	DBCOT1
Parameter * (FORTRAN)	
QT(1)	0.8476
CI(1,1)	1.0
CI(2,1)	0.0
CI(3,1)	0.0
CI(4,1)	0.17
CI(5,1)	0.0061
CI(6,1)	0.004455
CI(7,1)	0.0
TINJ	15.0

* All other input parameters not listed have zero values

Table 7.5

Simulation Physical Property Parameters PBCOT2

→IPERM	= 0	→T11	= -0.37	→GAMHF	= 13.0
→CSELI	= 0.04	T12	= 2.582	SSLOPE	= -0.4
CSEUI	= 0.0522	T21	= -0.37	POWN	= 1.6
C1I	= 0.26	T22	= 6.553	CSE1	= 0.0005
C3I	= 0.217	T31	= 0.0	→ALPHA1	= 2.0
C6I	= 0.001157	T32	= 0.0	ALPHA2	= 2.5
→C2PLC	= 0.0	→S1RW	= 0.25	ALPHA3	= 0.0
C2PRC	= 1.0	S2RW	= 0.2	ALPHA4	= 0.0
→C3MAX0	± 0.2	→P1RW	= 0.075	ALPHA5	= 0.0
C3MAX1	= 0.2	P2RW	= 1.0	→DEN1	= 0.433
C3MAX2	= 0.2	→E1	= 1.0	→DEN2	= 0.3681
→B1	= -1.0	E2	= 3.0	DEN3	= 0.42
B2	= -1.0	E3	= 1.0	DEN7	= 0.0
B3	= -1.0	→P1RC	= 1.0	IDEN	= 1
→F1	= 1.0	P2RC	= 1.0	→CPC	= 0.0
F2	= 1.0	→RKMAX	= 1.2	IPC	= 2
F3	= 1.0	BRK	= 1000.0	→D(K,L)	= 0.0
→BETA1	= 10.0	→VIS1	= 0.8	→ALPHAL	= 0.3944
BETA2	= 0.0	VIS2	= 40.0	→ALPHAT	= 0.01315
BETAP	= 10.0	→AP1	= 220.0	→AD31	= 6.2
→G11	= 13.13	AP2	= 0.0	AD32	= 6.2
G12	= -14.0	AP3	= 0.0	B3D	= 1000.0
G13	= 0.0221	→P3RW	= 1.0	→A4D	= 2.0
G21	= 13.13	GAMMAC	= 4.0	B4D	= 100.0
G22	= -14.0	EPHI4	= 1.0	→QV	= 0.0
G23	= 0.0221	EPHI3	= 1.0	XK96	= 0.0
→XIFTW	= 1.2			XKS	= 0.0

→ Represents a new line on input file

Table 7.6

Changes in Physical Properties for the 2-D (areal) Simulations

Input Parameter *	PHYSICAL PROPERTY CODE										
	PBCOT2	PBCOT3	PBCOT4	PECOT4A	PBCOT5	PBCOT8	PBCOT9	PBCOT12	PBCOT13	PBCOT15	PBCOT16
IPERM	0			3			0				
CSEL1	0.04								0.08		2.0
CSEU1	0.0522								0.1		2.01
C11	0.26								0.343		
C31	0.217	0.0									
C61	0.001157	0.0									
C3MAX0	0.2					0.15					
C3MAX1	0.2					0.08					
C3MAX2	0.2					0.15					
BETA1	10.0					9.74			5.0		
T11	-0.37				-0.428			-0.605			
T12	2.582				3.921			4.699			
T21	-0.37				-0.422			-0.605			
T22	6.553				4.525			4.699			
E3	1.0		1.5							3.1	
AD31	6.2							0.0		3.1	
AD32	6.2							0.0			
QV	0.0				0.044	0.02		0.0	0.01		
XK96	0.0				0.011			0.0	0.01	0.25	
XKS	0.0				0.45			0.0	0.45		

* Parameters not listed are constant for all runs; see Table 7.5

FIGURE 7.1

RUN: BCOT2

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.2

RUN: BC0T2

HISTORIES UP TO 1.50 PV. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.3

RUN: BC0T3

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.4

RUN: BCOT3

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.5

RUN: BCOT4

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.6

RUN: BCOT4

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.7

RUN: BCOT4A

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.8

RUN: BC0T4R

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.9

RUN: BC0T5

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.10

RUN: BC0T5

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.11

RUN: BCOT8

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.12

RUN: BCOT8

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.13

RUN: BC0T9

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.14

RUN: BCOT9

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.15

RUN: BCOT12

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.16

RUN: BCOT12

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.17

RUN: BCOT13

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.18

RUN: BCOT13

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.19

RUN: BCOT15

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.20

RUN: BCOT15

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

FIGURE 7.21

RUN: BCOT16

HISTORIES UP TO 1.50 P.V. INJECTED

TOTAL CONCENTRATIONS VS. P.V. INJECTED

FIGURE 7.22

RUN: BCOT16

HISTORIES UP TO 1.50 P.V. INJECTED

PHASE CUT OR OIL REC. VS. P.V. INJECTED

8. SUMMARY, ADDITIONAL CONCLUSIONS AND RECOMMENDATIONS (SECTIONS 4-7)

8.1 Summary

Our simulation-related research can be classified into three parts. The first part deals with the improvement of the physical properties used in the modelling of the chemical flood oil recovery process. This mainly involves the application of the pseudophase theory to the phase behavior model. Other changes include recoding of the cation exchange routine, and implementation of a saturation-dependent dispersion coefficient. These changes are discussed in Section 3.

The second part deals with conducting core flood experiments with the aim of collecting as much data as possible for testing of the simulator. Static experiments were also performed to obtain data for the calculation of several input parameters needed by the new phase behavior model. These experiments were also used to partially test the pseudophase theory. Section 4 describes one of the coreflood experiments.

The last part, which includes Sections 5 and 6, deals with the testing of the new simulator using data obtained from the experiments and the literature.

8.2 Conclusions in Addition to Those of Section 6

Experience gained from the runs of Section 5 and others from Camilleri³ lead to the following conclusions: The difficulty in matching the oil-bank breakthrough time and oil cut is not entirely a cause of the relative permeability endpoints and curvatures as has been suggested in the past. Camilleri shows how to calculate the relative permeability curvatures using oil

breakthrough and oil-cut data. The rate of oil displacement by the surfactant is also very important in determining breakthrough and cut. The reduction of the residual oil saturation to a particular value does not necessarily guarantee the correct breakthrough and cut; the rate at which this residual is reached has a great effect on the oil bank size and position. For example, if the chemical residual is reached instantaneously with the presence of surfactant, then a large oil bank is produced and consequently early breakthrough results. However, if chemical flood residual is reached slowly, or even in steps, then a smaller oil bank is produced, with an accompanying later breakthrough. This latter case will produce the oil over a larger time compared to the previous case. This effect is noticeable in the results presented, where the rate of oil displacement was varied through the interfacial tension parameters.

The new phase-behavior model proved to give reliable results, despite the fact that the model is approximate in that the alcohol partition coefficients are considered constants. The match of the surfactant and alcohol histories in all cases where data were available supports its validity. It should be pointed out that the Hand equations are still part of the phase behavior, which also makes the calculations only approximate. An alternative to the Hand equations is suggested through further improvements of the pseudophase theory. It is, however, believed that any phase behavior model would require some form of approximation in order to keep it simple. An advantage of the present model is that it produces satisfactory results with a negligible increase in computer time compared to the old model.

Static phase behavior experiments further support the pseudophase

theory. Comparison of the middle-phase composition as obtained experimentally and by material balance show that better representation is obtained when results are plotted on a pseudoternary as calculated from theory than on a pseudoternary where surfactant and alcohol are lumped into one pseudocomponent. The comparison is made in Figures 4.13(c), (d), (e).

Capillary pressure effects were detected during the core flood experiments. Their presence is important in interpreting the pressure histories and help identify any fingering. Experimental results confirmed that the oil displacements were done under favorable mobility conditions.

The cation exchange model of Hirasaki⁶⁰ as implemented in the 1-D simulator successfully matches calcium histories.

Sensitivity studies with all types of phase behavior and alcohol partition coefficients, show that the new phase behavior model can successfully simulate chromatographic separation.

8.3 Recommendations

As a result of experience gained from the second part of this study, i.e. the experimental work, the following are considered important in obtaining good quality data:

- (i) Use of a low permeability core so as to have larger pressure drops, thus making the pressure readings more accurate.

- (ii) Use closely spaced pressure taps to locate fluid fronts more accurately.

- (iii) When low pressures are being recorded, set the pressure recording system in a way so as to be able to measure negative pressures.

This will help in determining the cause of any pressure fluctuations.

(iv) Before injecting any slugs, check their viscosity to insure mobility control thus eliminating the risk of fingering.

(v) Use a core with a larger pore volume than used here. This will provide samples of smaller pore volume, thus helping in analyses, and also reducing the error due to volume averaging.

(vi) Seal the samples properly to avoid loss by evaporation when stored for a long time.

Viscosity is very important in describing the movement of the phases at the back of the oil bank. For the reasons discussed above, the correct movement of the phases in this region is very important since it can affect flow in other parts of the core directly or indirectly. This part of the core is also where any three-phase region may occur. Multi-phase flow is difficult to model for two reasons. The first is a lack of an experimentally tested relative permeability model. Secondly, phase viscosities are known at only a relatively few compositions and have to be calculated from an empirical correlation for other compositions. These two factors are believed to be the reason for getting only a fair match of the oil-bank tail. A better viscosity correlation is suggested for an improvement in the simulation of the oil bank tail. More viscosity data for phases of known composition, especially microemulsion phases, will help in determining the required viscosity parameters, or in developing a new correlation if the presently used one is found to be inadequate.

The pressure drop for the oil bank and polymer drive are matched satisfactorily, but the pressure drop corresponding to the microemulsion region is not. This discrepancy can be attributed to the relative

permeability model, but could also be in part due to the microemulsion viscosity model, especially its polymer dependence.

Two problems worth investigating are the polymer inaccessible pore volume and the dispersivities. Although both gave reasonable answers for simple cases, application of these models to complex problems resulted in large material balance errors. Problems of this kind are especially created when different dispersivities are used for different components and phases. The physical implication and constraints generated by use of the above parameters should be studied in an attempt to understand what causes the problems.

More complex thermodynamic models recently appeared in the literature^{67, 113}, but as the authors suggest, their complexity inhibits their application to simulators nor have they been shown to quantitatively match experimental data. Perhaps these models could later be used to provide input data (plait points and binodal curve heights) for the simpler models.

A persistent problem neglected in this study is the difficulty of matching the polymer transport. Surfactant/polymer interaction is a well-known phenomenon, but no attempt has ever been made to model this effect in the simulator. The understanding of the polymer effects on the phase behavior may be more important than studying phase behavior models which do not include polymer. Laboratory phase behavior data with polymer can be found in the literature¹⁰⁸. These should be helpful in developing models for simulation use.

It is suggested that the pseudophase theory as used in this study for the calculation of the pseudocomponent composition for use in a

pseudoternary representation, be extended to model two or more surfactant species. Ideas from the literature¹¹⁹ should be used in this respect.

9. CHEMICAL INTERACTIONS OF ALUMINUM-SOLUTIONS WITH FORMATION MINERALS

In order to test the effectiveness of complexing agents for in-depth cross-linking and mobility control in polymer and waterfloods, we investigated the transport of aluminum citrate solutions in sandstone and limestone cores. The study was prompted by experimental observations indicating that crosslinking attempts cause plugging of the inlet end of core sections unless special precautions were observed. The plugging was caused by poor transport of the aluminum citrate solutions, which, in turn, was caused by precipitation of aluminum hydroxide in limestone cores, and of both aluminum and ferric hydroxide in sandstone cores. The formation of these precipitates, and the poor transport of the aluminum citrate solution was confirmed experimentally and modeled quantitatively by a geochemical flow simulator.

We then used the flow simulator to design injected solutions that would avoid precipitation, generally by raising the injected pH and by using a larger citrate to aluminum ratio. By using these solutions the precipitation could be avoided, and the aluminum citrate could be transported in an unretarded fashion. Polymer cross-linking treatments using solutions designed to eliminate precipitation generally showed more uniform mobility reduction, and an absence of the plugging observed in the first set of flow experiments.

During the latter stages of their lives, producing wells experience a steadily increasing water-oil ratio. One cause for a premature occurrence of this phenomenon is the channeling of large volumes of water through oil-depleted high-permeability zones and fractures. Although methods have been devised to treat isolated high-permeability zones in the vicinity of the wellbore, remedial measures to plug channeling zones in-depth are few.

In recent years, several methods of injecting polymer solutions into channeled formations have been shown to be effective in reducing the water-oil ratio.^{17,18,49,77,85} One such method involves injecting polymer-thickened aqueous solutions followed by multivalent metal cation solutions. The purpose of the multivalent cation is to link the first adsorbed layer of injected polymer with subsequent injected polymer to form a network or gel which ultimately decreases permeability to water. A "retarding" anion is injected with the cation to prevent premature precipitation of the multivalent metal ion. A number of formulations involving polymers, multivalent ions, and retarding anions have been proposed and patented.^{17,18,77,87-89} This paper deals only with the use of partially hydrolyzed polyacrylamide and aluminum.

While early investigators did not report problems with this formulation,¹⁸ aluminum citrate injections into laboratory cores will, under certain circumstances, induce chemical precipitation.^{7,90} The precipitation complicates the treatment and, hence, limits the application of this permeability correction method. The principal objective of this paper is to use a geochemical

flow simulator to define which mineralogies are likely candidates for precipitation, identify the insoluble products, and establish design criteria that prevent precipitation. We show this by both experimentally and theoretically investigating the transport of aluminum citrate solutions in sandstone and limestone media. The experimental portion consists of single phase core displacements that were designed mainly to study the transport of aluminum and citrate ions. The results of the experiments are summarized here, along with a brief description of the experimental techniques. The experimental data are modeled using a geochemical compositional flow simulator⁹¹⁻⁹³ which accounts for the complex speciation of water-soluble components and the dissolution and precipitation of mineral species. The simulator is then used to predict the flow behavior of other aluminum citrate compositions and for different mineral conditions.

In our flow experiments the injected aluminum concentration did not elute from some of the cores even after twenty pore volumes of injection, and was accompanied by precipitated solids. The simulation attributes the delay in aluminum transport to aluminum hydroxide precipitation. The simulations also show that, by appropriately matching the aluminum citrate composition to the formation, it is possible to eliminate precipitation and achieve unretarded propagation of injected aluminum. To confirm simulator predictions, coreflood experiments were performed to test the design established by the model calculations. These experiments show that by using larger ratios of citrate to aluminum the precipitation could be eliminated.

9.1 Chemical Description of Species and Reactions

To chemically describe the fluid/rock system, we must account for the speciation that results when an aluminum citrate solution contacts and dissolves some of the minerals comprising the formation rock. Inasmuch as there are many different minerals composing the rock, the speciation can be quite complicated. To model the injection of aluminum citrate solutions into sandstone and limestone formations, we considered nine basic species: aluminum, citrate, carbonate, calcium, sodium, iron, chloride and hydrogen ions, and oxygen. In aqueous solutions, these can form the thirty-six secondary aqueous species shown in Table 9.1.

For our study, the most important of these are the three aluminum citrate complexes. At low pH's (below 3.1) aluminum reacts with citric acid, forming the neutral species, $\text{AlC}_6\text{H}_{11}\text{O}_{10}$, and liberating three protons. At higher pH's, this aluminum citrate complex behaves like a diacid and dissociates to form $\text{AlC}_6\text{H}_{10}\text{O}_{10}^-$ and $\text{AlC}_6\text{H}_9\text{O}_{10}^{2-}$, progressively.^{104,109} According to Das et al.,¹⁰⁶ the molecular structures of the three aluminum complexes, along with that of the free citrate anion, are those shown in Figure 9.1. Note that when a metal combines with the citrate anion, it changes the citrate structure from a branched-chained tricarboxylic acid to a double-ring structure composed of both 5- and 6-membered rings.¹⁰⁶

Other cations which are readily chelated by citrate are:^{16,18,19}

Generally, the higher valence cations form stronger complexes than lower valence cations except for hydrogen, which forms a relatively strong complex. For example, aluminum has a much greater tendency to be chelated by citrate than does sodium. For this reason, and because we are always concerned with solutions containing aluminum, we do not include sodium citrate in Table 9.1.

Ten mineral species derived from the 9 basic species are also shown on the bottom of Table 9.1. Although minerals other than those listed (i.e., quartz, clays and feldspar) exist in sandstones and limestones, and while the simulator is not limited by the number and type of species, the ones listed are the most important for this study. The intra-aqueous and mineral solubility reactions that take place between the species, and their respective equilibrium constants, are shown in Tables 9.2 and 9.3, respectively.

Because we include iron species in two different oxidation states (Fe^{2+} and Fe^{3+}), the flow is complicated by oxidation-reduction (redox) reactions which are also included in the simulator.⁹² The extent of these redox reactions can be summarized by the following oxidation reaction:

and reduction reaction:

The former reaction describes the oxidation of ferrous iron to ferric iron and the latter complementary reduction reaction represents the reduction of dissolved oxygen to form water.

9.2 Chemical Equilibria and Flow

When fresh fluids such as aluminum citrate contact minerals initially present in a formation, new water-soluble species, and a new fluid composition will result from the ensuing mineral dissolution. As reactants are fed from one reaction zone to the next, the solubility limit of a specific aqueous species may be exceeded and it will precipitate. Once formed, the precipitates, too, may redissolve. Our approach to describe dissolution, speciation, precipitation and flow is to assume local thermodynamic equilibrium. This is equivalent to assuming that the reaction rates are infinitely fast compared with the fluid flow rates. The calculations are, therefore, most likely to be realized in practice at rates which would be typical for reservoir flow rates except perhaps close to wells.

The computation of chemical equilibrium is based on the formulation of mass balance equations, equilibria relationships, charge, electron balances, and the following idealizations and assumptions:

- (1) the porous medium is one-dimensional, homogeneous and isothermal with constant porosity
- (2) there is only one fluid phase whose density and viscosity is independent of composition
- (3) fluid and solid phases are incompressible and in chemical equilibrium
- (4) there is no supersaturation of aqueous species
- (5) there is no flow or migration of solid mineral species
- (6) no adsorption or ion exchange occurs.

Owing to its length and presentation elsewhere, neither the model formulation nor the numerical methods used will be discussed here. The reader is referred to previous papers.^{91,92}

9.3 Experimental Results and Model Comparisons

Batch Tests - The geochemical model has two modes of operation: a batch mode and a flow mode. To evaluate the equilibrium model and the accuracy of its data, several aluminum citrate solutions were prepared in the laboratory and the pH measured. These measurements were compared to those predicted by the model in the batch mode. The solutions were prepared by adding various amounts of solid citric acid monohydrate ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$), aluminum chloride (AlCl_3), and, in some cases, sodium hydroxide (NaOH), to a prepared fresh brine containing 200 ppm NaCl , 50 ppm CaCl_2 and 50 ppm NaHCO_3 .

The prepared batch solutions were divided into two groups, according to whether precipitation was observed or not. The purpose of the group in which no precipitation was observed was to evaluate the intra-aqueous equilibrium data. The second group -- those involving precipitation -- were used to examine and model the observed aluminum hydroxide precipitation.

Listed in the Table 9.4 are the solution composition and both the measured and the predicted pH for the first group. Generally, the model makes use of an extended Debye-Huckel activity coefficient relation^{120,121}; however, thermodynamic data for some of the more obscure citrate complexes required in this calculation are unknown. For this reason, the calculations in Table 9.4 did not correct for

activity coefficients (ideal solutions). Despite this limitation, the model was able to approximate the correct intra-aqueous speciation.

The second group of batch experiments involved the intentional precipitation of aluminum hydroxide. The purpose of this study was to evaluate the model's ability to correctly predict precipitation of this species. Before presenting the experimental findings and the model predictions, we should state that aluminum hydroxide precipitation was observed to be a time-dependent phenomena. Specifically, some of the aluminum citrate solutions, initially free of solids, precipitated aluminum hydroxide after several weeks of storage. Furthermore, the physical appearance of the precipitate changed with time. The following different categories of aluminum hydroxide precipitation were observed: (i) an immediately cloudy precipitate which, after several weeks, settled as small particles, (ii) an immediately cloudy precipitate which, after several weeks, completely disappeared, and finally (iii) an initially clear solution which, after several weeks, became cloudy and remained cloudy. This time-dependent precipitation complicated the matter of concluding whether or not a solution was stable.

Time-dependent aluminum hydroxide precipitation and the resulting formation of metastable aluminum oxides and hydroxides is well-documented by others.^{123-126,129} At low temperatures, Ervin and Osborne¹²⁴ identified the tri-hydrated aluminum oxide, gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), as the stable form. During the precipitation process, however, a sequence of several less hydrated forms (metastable states) are typically encountered. In general, at early times the least hydrated forms ($\text{Al}(\text{OH})_3$ and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) are

present.^{123,125,126} A spontaneous change occurs and these species convert to another metastable species, bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), and then finally to gibbsite.

Not only is there a persistence of metastable states when dealing with aluminum hydroxide precipitation, but since each species has its own unique solubility, there is also a corresponding sequential change in the apparent aluminum hydroxide solubility. Because the least hydrated form, $\text{Al}(\text{OH})_3$, is the most soluble,¹²⁹ and there is a progressive decrease in solubility as the hydration increases, the apparent solubility of a solute will decrease with time. In addition, because the solubility product between the least and most soluble forms differ by several orders of magnitude, the results are observable. This explains why some solutions, initially free of precipitate, will eventually acquire a precipitate if stored for enough time.

From a standpoint of equilibrium modeling, which demands that the final state be reached instantaneously, this time-dependent process poses an uncertainty about which solubility product is correct. One of the purposes of the second group of the batch experiments was to identify the applicable solubility product. Of course, the final choice is dependent on the time allowed for equilibration. The experimental observations after two weeks, and model results are summarized in Table 9.5. In these experiments, three solutions were prepared, each containing the same concentration of aluminum and citrate, but different concentrations of sodium hydroxide. The lowest pH solution (7.9) contained no precipitation and the two higher pH solutions (9.1 and 11.0) both contained

precipitates. From these measurements, the pH at which precipitation first occurs (for these aluminum and citrate concentrations) is between 7.9 and 9.1. Each aluminum hydroxide species has a unique pH at which precipitation first occurs, a fact we use to determine which solubility product best models the experimental results. To do this, we computed the pH at which precipitation first occurs for all of aluminum hydroxide precipitates for the given aluminum and citrate concentrations. The least hydrated, most soluble species agreed with the experimental observations the best. Thus, we used the solubility data for the simple hydroxide $\text{Al}(\text{OH})_3$ for these short time data. The model predictions shown in Table 9.5 are based on the solubility of the simple hydroxide. The result that the $\text{Al}(\text{OH})_3$ form best describes the observed precipitation is not unexpected because our experiments are for relatively short times.

Even with this qualification, there is not complete agreement between the experimental and model results in Table 9.5. Specifically, the model predicts precipitation in the pH 7.9 solution and, experimentally, this solution did not precipitate. This disagreement suggests that the solubility product used in the model calculations is not large enough. However, the solubility product of $\text{Al}(\text{OH})_3$ is the largest for any aluminum oxide in the literature.¹²⁹ The disagreement must then be explained by one or more of the following reasons: (i) there exists a more soluble species than the unhydrated species, (ii) supersaturation of aluminum hydroxide occurs, or (iii) the experiments were not in equilibrium. Despite the disagreement, we used the solubility product of the simple hydroxide to describe the observed precipitation because: (1) we cannot document a greater

solubility product, and (ii) we prefer our calculations to be conservative estimates of precipitation. By this we mean that if our calculations do not predict precipitation, then precipitation will not occur. Conversely, if our calculations predict precipitation, the precipitate may or may not be formed.

9.4 Corefloods

Before initiation of any model calculations, several limestone cores from the Pettit formation had been flooded with polymer and aluminum solutions to evaluate the crosslinking process for this particular formation. These experiments were done at 82°C (180°F) using actual crude oil and simulated brines. Initial brine permeabilities of the uncleaned cores ranged from about 0.6 md. to 6.0 md. Except for the initial brine flood to establish permeability, the same fresh brine as used in the batch experiments discussed previously was used. The polymers used were TIORCO's Watercut[®] 160 and Watercut[®] 110, cationic and anionic polyacrylamides, respectively. The flooding sequence used was (1) formation brine (2) crude oil to residual brine (3) fresh brine to residual oil (4) 300 ppm Watercut 160 polymer (5) fresh brine (6) 300 ppm Watercut 110 polymer (7) Watercut[®] 676 aluminum citrate supplied by TIORCO, (8) 300 ppm Watercut 110 polymer and (9) fresh brine. Each of these fluids was injected to steady state pressure drop, which was achieved in all cases, even for the polymers in the very low permeability cores. The purpose of this flooding sequence was to evaluate both resistance factors (R.F.) (mobility of brine divided by mobility of polymer solution) and residual resistance factors (R.R.F.) (mobility of

initial brine divided by mobility of brine after polymer) before and after crosslinking with aluminum, and to ascertain if any problems with the process were apparent or any changes in the process were deemed to be desirable.

One experiment (10X-456) is now summarized which indicated a problem did exist. Three one-inch-diameter Pettit core samples were mounted end-to-end in a core holder. The core samples were 4.8, 5.1, and 4.1 cm (1.9, 2.0, and 1.6 inches) in length with a total pore volume of 15.3 qc (porosity 22%). The brine permeabilities at residual oil saturation were 0.78, 0.26, 0.19 md for these three core samples. Resistance factors (R.F.) for Watercut 160, the cationic polymer, were low but fairly consistent (2.95, 1.69, and 1.68 for the three core sections). Resistance factors for Watercut 110, the anionic polymer, were 3.75, 2.63, and 2.08. But following the aluminum citrate flood, these values for Watercut 110 changed to 49.9, 1.78, and 3.41. This indicates the crosslinking did not increase the resistance factor (i.e. decrease the permeability to brine) except for the first 4.8 cm core segment, for which there was perhaps too much increase. Those and other polymer and aluminum citrate floods reported in this paper were done at a frontal velocity of about 1 ft/D unless otherwise noted.

The next series of flow experiments used 2-inch-square-by-1-foot Berea sandstone cores with a higher permeability than the Pettit limestone cores. The experimental procedure was simplified by eliminating the crude oil and reducing the temperature to 30°C (87°F), the value for all of the remaining corefloods reported in this paper. We wanted to see how the aluminum citrate process would perform in

cores of higher permeability and of a mineralogy more typical of the cores used earlier.¹⁸ The Berea sandstone was mounted in Epoxy[®] with pressure taps inserted 7.6 cm (3 inches) from each end. For other details of the experimental procedure, see Senol.⁷

For Exp. CPL-1 the core was flooded in the following sequence: (1) fresh brine (2) 500 ppm Watercut 160 polymer (3) 500 ppm Watercut 110 polymer (4) Watercut[®] 677 aluminum citrate (5) 500 ppm Watercut 110 polymer and (6) fresh brine. The crosslinking was effective only for the first 7.6 cm (3 inches) of the core. The steady state R.F. for the anionic polymer following the aluminum (step 5) was only 4.6 for the intermediate 15.2 cm (6 inches) of core, and the R.R.F. only 2.0 for the same section. But for the inlet 7.6 cm (3 inches) the R.R.F. was 44.3.

Because we had not yet measured or calculated aluminum transport, we thought that the elimination of the cationic polymer might improve performance, and so Exp. CPL-2 was conducted without the Watercut 160 step. The R.F.'s for Watercut 110 polymer before aluminum were similar to CPL-1 and about the same for each section of core (7.9, 7.5, and 5.0 respectively). The equivalent shear rate in the core at 1 ft/D is estimated to be about 4.1 sec^{-1} . Polymer viscosity at this shear rate is about 5 cp. The injection rate was increased in 7 steps up to a maximum of 44 ft/D (179 sec^{-1} equivalent shear rate) without any significant change in R.F.'s. Injected aluminum concentration was 580 ppm by atomic absorption (AA) measurement. Aluminum was not produced until 1.05 pore volumes and had reached only 485 ppm (84%) after 6.0 pore volumes. After 17.5 pore volumes of polymer, the R.F.'s were 23.1 for the first three inches of core and

9.6 for the intermediate six inches. Again, this shows a problem with in-depth crosslinking. The R.R.F.'s were 13.2 and 2.5 for these same sections. Since aluminum transport appeared to be at least a contributing factor to this problem, a third Berea coreflood (ALCI-1) was done without polymer to evaluate its transport under the simplest conditions.

Starting with this flow experiment, we prepared our own aluminum solutions as described earlier for the batch tests. For Berea Exp. ALCI-1, the injected solution contained 0.01 M Al^{3+} (270 ppm) and 0.0045 M citrate (850 ppm) and had a pH of 2.9.

Effluent samples were collected and analyzed for soluble aluminum, calcium, iron, and pH. The elution history for these components is shown in Figs. 9.2-9.5 (aluminum is normalized by its injected concentration). All samples collected after one pore volume of injection contained either one or both of two distinct precipitates: one precipitate was white and rather gelatinous, and the other was light-yellow to light-brown. The samples (between 1 and 3 pore volumes injected) contained primarily the white precipitate. After 3 pore volumes of injection, all samples contained the yellowish-brown precipitate. The effluent history for aluminum (Fig. 2) clearly reveals that after approximately three pore volumes, the eluted aluminum reached only 45% of its injected value and remained there for the duration of the experiment. Since precipitated aluminum hydroxide is typically white,¹³⁰ we expected the observed white precipitation to be aluminum hydroxide, and attributed the retarded aluminum transport to this precipitation.

Figure 9.5 also reveals that considerable soluble iron was eluted from the core (approximately 200 ppm at 20 pore volumes). Clearly there is a dissolvable iron species in the core since we injected no iron. An X-ray analysis of the Berea sandstone identified the presence of siderite, FeCO_3 , so we attributed the iron elution to the dissolution of this mineral. Because ferric hydroxide many times appear as a light-brown precipitate,¹³⁰ we expected that the yellow-brown precipitate was ferric hydroxide.

Two samples of precipitate were analyzed by both X-ray fluorescence and diffraction. The first sample analyzed was produced at 1.5 pore volumes. This precipitate consisted of CaCO_3 plus unidentified solids containing iron, aluminum, magnesium and chloride. The weight ratio of iron to aluminum was about 1. The second sample analyzed was produced at 10.7 pore volumes. This precipitate consisted entirely of amorphous solids containing iron, aluminum and chloride. The weight ratio of iron to aluminum was 1.7. Unfortunately these analyses do not tell us which minerals the iron and aluminum formed, but did at least confirm the presence of solids containing these elements.

To model the injection of aluminum citrate in Berea sandstone, we considered a porous media composed of 0.5 wt. % siderite, 5 wt. % calcite, and 94.5 wt. % inert (siliceous) material. The "calcite" represents both calcite and dolomite. The model prediction is shown in Fig. 9.6. The results are in terms of a dimensionless time-distance diagram. On such a diagram, lines emanating from the origin represent concentration changes or waves which separate regions of constant composition.¹³¹ The time-distance diagram is a useful representation

because it contains information to construct either a concentration profile or an elution history.¹³¹ For example, an elution history, which is the concentration of a species as a function of time at a fixed position, is represented by a horizontal line on a time-distance diagram.

The time-distance diagram in Fig. 9.6 shows five distinct and separate regions:

- I. A region of initial conditions where the in-place brine is in equilibrium with the siderite, calcite, and inert material ($\text{pH} = 8.5$, $\text{Eh} = -0.35$ volts). Eh is oxidation potential.
- II. A region where the initial amounts of siderite and calcite are in equilibrium with a fully-spent aluminum citrate mixture ($\text{pH} = 5.1$, $\text{Eh} = +0.16$ volts).
- III. A region where aluminum and ferric hydroxide are jointly precipitated ($\text{pH} = 4.1$, $\text{Eh} = +0.98$ volts).
- IV. A region where only precipitated ferric hydroxide (and inert material) is present ($\text{pH} = 2.2$, $\text{Eh} = 1.10$ volts).
- V. A region at the injected conditions ($\text{pH} = 2.2$, $\text{Eh} = 1.10$ volts).

There are several very interesting features of this prediction. First, the model predicts precipitation of two different species, aluminum and ferric hydroxide. Second, the model predicts the aluminum transport to be greatly retarded. Third, the model and experimental results quantitatively agree that the aluminum should be eluted at 45% of its injected value after several pore volumes. This comparison is illustrated in Fig. 9.2.

Note that the breakthrough time of the 45% aluminum solution in the experiment lags that predicted by the model. This is the result of cation exchange of the aluminum cations with calcium and sodium on the resident clays (note the peak in calcium concentration, Fig. 9.4). However, cation exchange was not included in the model. From Fig. 9.6, the model predicts that an aluminum concentration 160% of the injected value will form, but this concentration will not break through until 115 pore volumes of solution have been injected, much too late to appear in Exp. ALCI-1. The theoretical prediction for pH agrees fairly well with the observed. The soluble iron prediction does not agree at all. We think that this is the result of colloidal iron precipitates in the solution which were captured by the experimental solution analysis.

A limestone coreflood (ALCI-4) was also done to evaluate aluminum transport in the absence of polymer. A 1-inch-diameter Pettit limestone core, with a porosity of 26% and a permeability to brine of 13 md at residual oil saturation was flooded with twelve pore volumes of the aluminum citrate mixture (pH = 2.8). Substantial amounts of a single white gelatinous precipitate were present in all collected samples after 1 pore volume of injection which we again speculate to be aluminum hydroxide. The elution histories for aluminum, pH, and calcium are shown in Figs. 9.7-9.9. The aluminum elution history (Fig. 9.7) reveals that the aluminum reached only about 40% of its injected value after eight pore volumes.

We carried out a simulation that considered a porous medium composed of 90% wt. calcite and 10% inert (siliceous) material with the same injected solution as in this carbonate experiment. The model

result, summarized as a time-distance diagram in Fig. 9.10, predicts the formation of four distinct and separate regions:

- I. An initial condition region where brine is in equilibrium with CaCO_3 (pH = 8.3)
- II. A region of fully-spent aluminum citrate in equilibrium with CaCO_3 (pH = 5.3).
- III. A region of precipitated $\text{Al}(\text{OH})_3$ (pH = 4.2).
- IV. A region of injected conditions (pH = 2.2).

Again, the model and experiment are in qualitative agreement on the essential features. First, both agree that aluminum hydroxide precipitation occurs. Second, both agree that the aluminum concentration will be eluted at a level no higher than 45% of its injected value, Fig. 9.7. Although the agreement at 2-7 pore volumes of throughput is not good, the model does roughly agree with the later pore volume data. Mechanisms such as surface adsorption (not included in the model) of aluminum ions can cause a delay in its elution. The pH elution history prediction (Fig. 9.8) does not agree at all. This could be due to silicate minerals not accounted for in the model.

Based on chromatographic theory,¹³¹ Figs. 9.6 and 9.10 yield several notable conclusions about the effect of formation mineralogy on the observed precipitation. First, the concentration of aluminum hydroxide precipitation is directly related to the initial concentrations of calcite and dolomite. This means that the larger the combined amount of calcite and dolomite initially present, the larger the amount of precipitation. Conversely, if no calcite or dolomite were present, the model would predict no precipitation. Second, the concentration of ferric hydroxide precipitated is directly

proportional to the concentration of siderite initially present. For mineralogies that contain no iron-bearing minerals, as is the case for the Pettit limestone, no ferric hydroxide will be precipitated.

Of course, as chromatographic theory predicts, the aluminum and ferric hydroxide precipitation is not only dependent on the formation mineralogy but also on the composition of the injected mixture. If the precipitation-inducing minerals such as calcite, dolomite and siderite, are not present, then the composition of the injected mixture should not induce precipitation, provided the injected solution itself is stable at the pH of the formation rock, which was true over the time period of these two experiments. However, if the precipitation-inducing minerals are present, the possibility of precipitation exists and the injected fluid composition must be designed to avoid precipitation. We now address the issue of how to do this.

9.5 Avoiding Precipitation

To transport soluble aluminum efficiently, the aluminum hydroxide precipitation must be eliminated. To do this either the aluminum concentration must be reduced or the citrate concentration must be increased. Either measure promotes the chelation of aluminum by citrate, and, hence, reduces the effective aluminum available for precipitation. The ratio of citrate to aluminum must be increased to where aluminum hydroxide will not precipitate at the formation pH. A pH of 8 should be sufficient for most operations. One of the purposes of this section is to determine, using our geochemical simulator, the ratio of citrate to aluminum necessary to avoid precipitation.

Figure 9.11 is a plot of calculated aluminum-hydroxide-precipitating pH as a function of citrate concentration for two different aluminum concentrations from the batch equilibrium model. The aluminum-hydroxide-precipitating pH is defined as the pH at which precipitation first occurs for given aluminum and citrate concentrations. The shape of the curves in this figure indicates that the pH of precipitation is a very strong function of the citrate concentration at intermediate concentrations; however, for low or high concentrations it is virtually independent of the citrate concentration. In general, a molar ratio of citrate to aluminum of about 1.5 or greater should be used to avoid precipitation below pH 8. An injected molar ratio of citrate to aluminum of 0.45 was used in Exp. ALCI-1 and ALCI-4 and from Fig. 9.11 this ratio would be predicted to precipitate aluminum hydroxide, as was observed.

If we change the solubility product of aluminum hydroxide from $10^{20.6}$ to $10^{26.6}$ (this better represents the precipitation results of Table 9.5), and compute the precipitating pH, we find that the aluminum hydroxide solubility is now so large that precipitation is not possible for high citrate concentrations. This unique condition, where aluminum hydroxide precipitation cannot be induced even at high pH, is due to the amphoteric nature of aluminum solutions and the formation of the $\text{Al}(\text{OH})_4^-$ species. For the aluminum and citrate concentrations used in the Exp. ALCI-1 and ALCI-4 (0.01 M aluminum and 0.0045 M citrate), aluminum hydroxide precipitation is not possible for the larger solubility product. Because precipitation was indeed observed, the arbitrary raising of the solubility product to correct the disparity noted in Table 9.5 cannot be the proper explanation.

Therefore, the lack of complete agreement in Table 9.5 is due to either supersaturation or insufficient equilibration time.

When flooding a medium that contains siderite, one way to minimize or avoid ferric hydroxide precipitation is to minimize the siderite dissolution. This can be accomplished by flooding with a neutral pH solution. Of course, this does not necessarily eliminate precipitation, but should minimize it. For porous media containing only small amounts of siderite this is probably more than sufficient. However, for porous media containing unusually large amounts of siderite it may prove inadequate. For these cases, suppressing the oxidation reaction whereby ferrous iron is converted to ferric is an additional remedial measure. Because the solubility of ferrous hydroxide is much greater than ferric hydroxide, this approach serves to reduce the likelihood of iron hydroxide precipitation. To suppress the oxidation reaction one needs to add an oxygen scavenger to the injected solution to remove the dissolved oxygen. Rather than do this, we chose to increase the injected pH as described below.

9.6 Testing the Model Design Guidelines

To test the proposed model design guidelines, we did two aluminum citrate floods to see if precipitation could be avoided. One was in a Berea sandstone core (Exp. ALCI-5) and the other was in a Pettit limestone core (ALCI-6). A solution composed of 0.01 M aluminum (270 ppm) and 0.02 M citrate (3780 ppm) in the same fresh brine as before and adjusted to a pH of 7 by drop-wise addition of 1.0 M NaOH, was injected into a 2-inch-square-by-1-foot Berea core with an initial brine permeability of 270 md. The molar ratio of injected citrate to

aluminum was 2, above the minimum predicted value of 1.5 necessary to prevent aluminum hydroxide precipitation (Fig. 9.11).

The Berea elution histories for aluminum, calcium, magnesium and iron are shown in Figs. 9.12-9.15. No precipitates were observed. The aluminum elution indicates that the injected aluminum is transported in a much more satisfactory fashion than before. Clearly, the appearance of no precipitates and relatively unretarded transport of aluminum are strong evidence supporting the design criteria given in the previous section.

The computed time-distance diagram for this displacement is shown in Fig. 9.16. The calculation assumes an initial core composition of 5 wt. % calcite, 0.5 wt. % siderite and 94.5 wt. % inert material. The injected concentrations of aluminum and citrate and the pH are the same as those used in the experiment. The model agrees with the experiment and predicts no aluminum hydroxide precipitation. The comparison of model and experimental elution histories for aluminum, pH and iron are shown on Figs. 9.12, 9.13, and 9.15. The model agrees well with the experimental aluminum elution results except at early time. Note also the very small concentrations of produced iron, indicating only slight siderite dissolution. Once again, there is evidence of cation exchange taking place (the intermediate plateau of 75% injected aluminum between 1 and 2.5 pore volumes produced). This exchange is directly confirmed by the calcium and magnesium effluent histories (Fig. 9.14) where a large peak in both is present at the same time. The model agrees fairly well with the experimental pH (Fig. 9.13). Both model and experimental results show that the eluted pH remains between pH 7.5 and 8.0 after one pore volume. This pH level is in great

contrast to the pH 5.4 that was experienced when an injected pH of 2.9 was used. Both experimental and model results show that eluted soluble iron is about 5-20 ppm although there are some unexplained changes. This level of eluted iron is in great contrast to the 200 ppm iron eluted when an injected pH of 2.9 was used, Fig. 9.5.

Although no precipitation was observed in this experiment, the model does predict ferric hydroxide precipitation to take place behind a very slow moving front. Actually, the front is moving so slow (Fig. 9.16) that, in the 12 pore volumes injected, virtually no precipitation would be realized.

The Pettit limestone core used in Exp. ALCI-6 was 1.25 inches in diameter and 2.5 inches long. This core was cleaned to remove all crude oil and then flooded with formation brine followed by fresh brine. The permeability to the latter was 43 md. Samples were collected and analyzed for soluble aluminum, pH, calcium, and magnesium. The elution histories are shown in Figs. 9.17-9.19. As for the Berea core, no precipitates were observed, and so efficient aluminum transport was achieved. The computed time-distance diagram for this displacement is shown in Fig. 9.20. The model results agree fairly well with the experimental results for both eluted aluminum and pH. This comparison is shown in Figs. 9.17 and 9.18, respectively.

Because we were greatly encouraged by the aluminum transport during these last two experiments, polymer tests were done following the aluminum results just discussed. The entire flooding sequence in both cases was: (1) fresh brine, (2) aluminum citrate, (3) fresh brine, (4) 500 ppm Watercut 110 polymer in fresh brine, (5) fresh brine, (6) aluminum citrate (7) fresh brine, (8) 500 ppm Watercut 110

polymer in fresh brine and (9) fresh brine. Step 3 was to flush out the aluminum initially injected so we could establish a base line for polymer performance.

For Exp. ACLI-5 the aluminum had decreased to less than 10 ppm after 3.5 pore volumes (Step 3). The steady state R.F.'s for the polymer at 1 ft/D were 6.9, 6.2, and 7.1 across the first three inches, intermediate six inches, and outlet three inches, respectively. Then a solution of 0.01 M aluminum and 0.02 M citrate in fresh brine was injected (Step 6) for 2.2 pore volumes, enough to reach almost 100% injected aluminum concentration. A small slug or buffer of 0.16 pore volumes of fresh brine was then injected (Step 7) to prevent direct contact of aluminum and polymer before entering the core. Watercut 110 polymer was injected to steady state again (Step 8) and the R.F.'s were now 9.6, 7.3, and 4.8 for each core section and 8.2 for the entire core. These values are not too different from the R.F.'s before crosslinking with aluminum and, although not uniform, they are far closer than ever achieved by us before. The R.R.F.'s to the final fresh brine were 2.4, 2.0, and 2.4 across the same core sections, more uniform than the R.F.'s. Note that the approximate uniformity has been achieved at the cost of only slightly higher R.F.'s, however.

Intermediate pressure taps did not exist for the limestone core (Exp. ALCI-6), but based on the R.F.'s before and after the second aluminum flood, the behavior was similar to the Berea core just described. These values of R.F. were 18.6 and 19.4 before and after aluminum citrate.

9.7 Summary and Conclusions

Experiments in both sandstone and limestone cores were conducted to evaluate in-situ crosslinking of polyacrylamide polymer with aluminum. Although this process is intended to cause an in-depth reduction of permeability to brine, we found that under the conditions initially tested, only the inflow section of each core was affected by the crosslinking. Since this appeared to be at least in part an aluminum hydroxide precipitation problem, we did other experiments and calculations with a geochemical flow simulator to study and remedy this problem. The simulator was first compared with batch precipitation experiments as a function of pH, aluminum, and citrate concentrations to validate the appropriate equilibrium constants. Predictions were then made to estimate the ratio of citrate to aluminum required to prevent precipitation at the pH of our cores.

Additional coreflood experiments confirmed that the precipitation under these circumstances was in fact eliminated. However, even with this change, there are still some unresolved concerns about precipitation over longer time periods appropriate to reservoir floods. Also, subsequent polymer flood tests showed that, although the permeability reduction was more uniform, the effectiveness of the polymer was no longer significantly increased after aluminum citrate flooding compared to the initial polymer flood. Much more research will be required to evaluate the complex chemical interactions of the rock, electrolytes, and polymer, so that we can optimize this process and tailor it to specific reservoir conditions. However, the use of a geochemical simulator to model the transport of the crosslinking agent as a function of the complex and highly variable mineralogy of

different reservoir rocks represents a significant step toward understanding and successfully designing this or other similar polymer treatment processes. Since the slug sizes of both polymer and crosslinking agents actually used under economic reservoir conditions are much smaller than those used in this process study, certain effects such as cation exchange need to be added to the simulation to better evaluate the process.

TABLE 9.1

CHEMICAL SPECIES CONSIDERED BY MODEL

Aqueous Species

H^+	Al^{3+}	$C_6H_5O_7^{3-}$
OH^-	$Al(OH)^{2+}$	$C_6H_6O_7^{2-}$
Ca^{2+}	$Al(OH)_2^+$	$C_6H_7O_7^-$
$CaOH^+$	$Al(OH)_4^-$	$C_6H_8O_7$
$Ca(OH)_2$	$AlC_6H_{11}O_{10}$	Fe^{3+}
$CaHCO_3^+$	$AlC_6H_{10}O_{10}^-$	$FeOOH^-$
CO_3^{2-}	$AlC_6H_9O_{10}^{2-}$	$Fe(OH)^+$
HCO_3^-	$CaC_6H_5O_7^-$	$Fe(OH)_2$
H_2CO_3	Fe^{2+}	$Fe(OH)^{2+}$
Na^+	$FeC_6H_5O_7$	$Fe(OH)_2^+$
$FeC_6H_4O_7$	$Fe_2(C_6H_4O_7)_2^{2-}$	$Fe(OH)_3^-$
Cl^-	$FeC_6H_6O_7$	$Fe(OH)_4^-$

Solid species

$Ca(OH)_2$	$Al(OH)_3$	$H_3C_6H_5O_7H_2O$ (citric acid) monohydrate
$CaCO_3$ (calcite)	FeO	Fe_2O_3 (hematite)
$FeOOH$ (goethite)	$Fe(OH)_3$	Fe_3O_4 (magnetite)
$FeCO_3$ (siderite)		

TABLE 9.2

INTRA-AQUEOUS CHEMICAL REACTIONS AND THEIR
EQUILIBRIUM CONSTANTS AT 25°C

CHEMICAL REACTION	LOG OF EQUILIBRIUM CONSTANT
$\text{OH}^- \rightleftharpoons \text{H}_2\text{O} - \text{H}^+$	14.00
$\text{CaOH}^+ \rightleftharpoons \text{H}_2\text{O} - \text{H}^+ + \text{Ca}^{2+}$	12.60
$\text{CaHCO}_3^+ \rightleftharpoons \text{Ca}^{2+} + \text{H}^+ + \text{CO}_3^{2-}$	-11.55
$\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{H}_2\text{O} - 2\text{H}^+$	28.09
$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	- 3.20
$\text{AlC}_6\text{H}_{11}\text{O}_{10} \rightleftharpoons \text{Al}^{3+} + \text{C}_6\text{H}_5\text{O}_7^{3-} + 3\text{H}_2\text{O}$	= 8.40
$\text{AlC}_6\text{H}_{10}\text{O}_{10}^- \rightleftharpoons \text{Al}^{3+} + \text{C}_6\text{H}_5\text{O}_7^{3-} - \text{H}^+ + 3\text{H}_2\text{O}$	- 4.91
$\text{AlC}_6\text{H}_9\text{O}_{10}^{2-} \rightleftharpoons \text{Al}^{3+} + \text{C}_6\text{H}_5\text{O}_7^{3-} - 2\text{H}^+ + 3\text{H}_2\text{O}$	1.88
$\text{C}_6\text{H}_6\text{O}_7^{2-} \rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-}$	- 5.70
$\text{C}_6\text{H}_7\text{O}_7^- \rightleftharpoons 2\text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-}$	-10.00
$\text{C}_6\text{H}_8\text{O}_7 \rightleftharpoons 3\text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-}$	-13.10
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	-10.33
$\text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$	-16.60
$\text{Al}(\text{OH})^{2+} \rightleftharpoons \text{Al}^{3+} + \text{H}_2\text{O} - \text{H}^+$	5.01
$\text{Al}(\text{OH})_2^+ \rightleftharpoons \text{Al}^{3+} + 2\text{H}_2\text{O} - 2\text{H}^+$	9.60
$\text{Al}(\text{OH})_4^- \rightleftharpoons \text{Al}^{3+} + 4\text{H}_2\text{O} - 4\text{H}^+$	22.06
$\text{CaC}_6\text{H}_5\text{O}_7^- \rightleftharpoons \text{Ca}^{2+} + \text{C}_6\text{H}_5\text{O}_7^{3-}$	- 3.22
$\text{FeOH}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{O} - \text{H}^+$	8.30
$\text{FeOOH}^- \rightleftharpoons \text{Fe}^{2+} + 2\text{H}_2\text{O} - 3\text{H}^+$	30.70
$\text{Fe}(\text{OH})_2^+ \rightleftharpoons \text{Fe}^{2+} + 1\frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 - \text{H}^+$	0.14
$\text{Fe}(\text{OH})_2 \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{O} - 2\text{H}^+$	17.60

CHEMICAL REACTION	LOG OF EQUILIBRIUM CONSTANT
$\text{Fe}(\text{OH})^{2+} \rightleftharpoons \text{Fe}^{2+} + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 \uparrow$	- 5.59
$\text{Fe}(\text{OH})_3^- \rightleftharpoons \text{Fe}^{2+} + 3\text{H}_2\text{O} - 3\text{H}^+$	31.98
$\text{Fe}(\text{OH})_4^- \rightleftharpoons \text{Fe}^{2+} + 3\frac{1}{2}\text{H}_2\text{O} - 3\text{H}^+ + \frac{1}{4}\text{O}_2 \uparrow$	14.24
$\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+} + \text{H}^+ - \frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 \uparrow$	- 7.76
$\text{O}_2\text{dissolved} \rightleftharpoons \text{O}_2 \uparrow$	2.86
$\text{H}_2\text{dissolved} \rightleftharpoons \text{H}_2\text{O} - \frac{1}{2}\text{O}_2 \uparrow$	44.64
$\text{FeC}_6\text{H}_5\text{O}_7 \rightleftharpoons \text{Fe}^{2+} - \frac{1}{2}\text{H}_2\text{O} + \text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-} + \frac{1}{4}\text{O}_2 \uparrow$	-19.17
$\text{Fe}_2(\text{C}_6\text{H}_4\text{O}_7)_2^{2-} \rightleftharpoons 2\text{Fe}^{2+} + 2\text{C}_6\text{H}_5\text{O}_7^{3-} - \text{H}_2\text{O} + \frac{1}{4}\text{O}_2 \uparrow$	-36.71
$\text{FeC}_6\text{H}_6\text{O}_7 \rightleftharpoons \text{Fe}^{2+} + \text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-}$	- 2.65
$\text{FeC}_6\text{H}_5\text{O}_7^- \rightleftharpoons \text{Fe}^{2+} + \text{C}_6\text{H}_5\text{O}_7^{3-}$	- 4.40

TABLE 9.3

SOLUBILITY REACTIONS AND THEIR EQUILIBRIUM
CONSTANTS AT 25°C

CHEMICAL REACTION	LOG OF EQUILIBRIUM CONSTANT
$\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{H}_2\text{O} - 2\text{H}^+$	22.89
$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	- 8.26
$\text{Al}_2(\text{OH})_6 \rightleftharpoons 2\text{Al}^{3+} + 6\text{H}_2\text{O} - 6\text{H}^+$	20.60
$\text{H}_3\text{C}_6\text{H}_5\text{O}_7\text{H}_2\text{O} \rightleftharpoons 3\text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-} + \text{H}_2\text{O}$	28.75
$\text{FeO} \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{O} - 2\text{H}^+$	12.36
$\text{Fe}_2\text{O}_3 \rightleftharpoons 2\text{Fe}^{2+} + 2\text{H}_2\text{O} - 4\text{H}^+ + \frac{1}{2}\text{O}_2\uparrow$	-17.46
$\text{Fe}_3\text{O}_4 \rightleftharpoons 3\text{Fe}^{2+} + 3\text{H}_2\text{O} + \frac{1}{2}\text{O}_2\uparrow - 6\text{H}^+$	-11.79
$\text{Fe(OH)}_3 \rightleftharpoons \text{Fe}^{2+} + 2\frac{1}{2}\text{H}_2\text{O} - 2\text{H}^+ + \frac{1}{4}\text{O}_2\uparrow$	- 2.96
$\text{FeOOH} \rightleftharpoons \text{Fe}^{2+} + 1\frac{1}{2}\text{H}_2\text{O} - 2\text{H}^+ + \frac{1}{4}\text{O}_2\uparrow$	- 8.83
$\text{FeCO}_3 \rightleftharpoons \text{Fe}^{2+} + \text{CO}_3^{-2}$	-12.73

TABLE 9.4

COMPARISON OF BATCH EQUILIBRIUM MODEL PREDICTIONS
WITH EXPERIMENTAL OBSERVATIONS - NO PRECIPITATION INDUCED

DESCRIPTION OF PREPARED SOLUTION	LABORATORY MEASURED pH	MODEL PREDICTED pH
0.0185 M AlCl_3 , 0.0360 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	2.2	1.9
0.0100 M AlCl_3 , 0.0045 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	2.4	2.2
0.0185 M AlCl_3 , 0.0191 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	2.5	2.0
0.0185 M AlCl_3 , 0.800 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$, 2.240 M NaOH	5.6	6.2
0.0185 M AlCl_3 , 0.0360 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$, 0.155 M NaOH	9.4	9.1

TABLE 9.5

COMPARISON OF MODEL PREDICTED ALUMINUM HYDROXIDE PRECIPITATION
WITH EXPERIMENTAL OBSERVATIONS

SOLUTION DESCRIPTION	EXPERIMENTAL OBSERVATION	MODEL PREDICTION
0.010 M AlCl_3 , 0.0045 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ 0.198 M NaOH	Sample cloudy immediately, after two weeks precipitation has settled as fine particles at pH 11.0	$\text{Al}(\text{OH})_3$ ppt.
0.010 M AlCl_3 , 0.0045 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ 0.0455 M NaOH	Sample initially clear, after three weeks cloudiness appears and settles as a dense cloud at pH 9.1	$\text{Al}(\text{OH})_3$ ppt.
0.010 M AlCl_3 , 0.0045 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ 0.03575 M NaOH	Sample initially clear and remains clear at pH 7.9	$\text{Al}(\text{OH})_3$ ppt.

CITRATE ANION, $C_6H_5O_7^{3-}$

ALUMINUM CITRATE COMPLEX, $[AlC_6H_5O_7 \cdot 3H_2O]$

ALUMINUM CITRATE COMPLEX, $[AlC_6H_4O_7 \cdot 3H_2O]^-$

ALUMINUM CITRATE COMPLEX, $[AlC_6H_5O_8 \cdot 2H_2O]^{2-}$

FIGURE 9.1 Molecular Formulas of Selected Citrate Compounds

FIGURE 9.2 Experimental and Theoretical Aluminum Concentration Elution Histories for ALCI-1

FIGURE 9.3 Experimental and Theoretical pH Elution Histories for ALCI-1

FIGURE 9.4 Experimental Calcium Concentration Elution History for ALCI-1

FIGURE 9.5 Experimental and Theoretical Iron Concentration Elution History for ALCI-1

	REGION I	REGION II	REGION III	REGION IV	REGION V
CALCITE, (CaCO_3)	5.0M (5% wt)	5.0 M	_____	_____	_____
SIDERITE, (FeCO_3)	0.43M (0.5% wt)	0.43M	_____	_____	_____
pH	8.5	5.1	4.1	2.2	2.2
Eh, (Oxidation potential)	-0.35 volts	0.16 volts	0.98 volts	1.10 volts	1.10 volts
TOTAL DISSOLVED Al^{3+}	_____	0.0045M	0.016 M	0.01M	0.01M
$\text{Al}(\text{OH})_3$ ppt.	_____	_____	1.5M	_____	_____
$\text{Fe}(\text{OH})_3$ ppt.	_____	_____	0.43M	0.43M	_____
TOTAL DISSOLVED Fe	_____	2 ppm	< 1 ppm	< 1 ppm	_____

FIGURE 9.6 Theoretical Time-Distance Diagram for ALCI-1

FIGURE 9.7 Experimental and Theoretical Aluminum Concentration Elution Histories for ALCI-4

FIGURE 9.8 Experimental and Theoretical pH Elution Histories for ALCI-4

FIGURE 9.9 Experimental Calcium Concentration Elution History for ALCI-4

	REGION I	REGION II	REGION III	REGION IV
CALCITE, (CaCO_3)	90 M (90 % wt)	9 C	_____	_____
pH	8.5	5.3	1.2	2.2
TOTAL DISSOLVED Al^{3+}	_____	0.0045 M	0.018 M	0.01 M
$\text{Al}(\text{OH})_3$ ppt	_____	_____	30.6 M	_____

FIGURE 9.10 Theoretical Time-Distance Diagram for ALCI-4

FIGURE 9.11 pH at Onset of Precipitation for Various Aluminum and Citrate Concentrations

FIGURE 9.12 Experimental and Theoretical Aluminum Concentration Elution Histories for ALCI-5

FIGURE 9.13 Experimental and Theoretical pH Elution Histories for ALCI-5

FIGURE 9.14 Experimental Calcium and Magnesium Elution History for ALCI-5

FIGURE 9.15 Experimental and Theoretical Iron Concentration Elution Histories for ALCI-5

	REGION I	REGION II	REGION III	REGION IV	REGION V
CALCITE, (CaCO_3)	5.0M (5% wt)	5.0 M	5.0 M	_____	_____
SIDERITE, (FeCO_3)	0.43M (0.5% wt)	0.43 M	_____	_____	_____
pH	8.5	7.8	7.0	7.5	7.0
E_h , (Oxidation potential)	-0.35 volts	0.15 volts	0.75 volts	0.77 volts	0.80 volts
TOTAL DISSOLVED Al^{3+}	_____	0.01M	0.01M	0.01M	0.01M
TOTAL DISSOLVED IRON	_____	6 ppm	1 ppm	70 ppm	_____
$\text{Fe}(\text{OH})_3$ ppt	_____	_____	0.43M	0.43M	_____

FIGURE 9.16 Theoretical Time-Distance Diagram for ALCI-5

FIGURE 9.17 Experimental and Theoretical Aluminum Elution Histories for ALCI-6

FIGURE 9.13 Experimental and Theoretical pH Histories for ALCI-6

FIGURE 9.19 Experimental Calcium and Magnesium Elution Histories for ALCI-6

	REGION I	REGION II	REGION III
CALCITE	90 M (90% wt.)	90 M	_____
pH	8.5	7.8	7.0
TOTAL DISSOLVED Al	_____	0.01 M	0.01 M

FIGURE 9.20 Theoretical Time-Distance Diagram for ALCI-6

N O M E N C L A T U R E

a_i, a_{i1}, a_{i2}	Surfactant and polymer adsorption parameters
A	Cross-sectional area or Hand Parameter
A_0, A_1, A_2	Variables used in the calculation of Hand parameter A
A_{p1}, A_{p2}, A_{p3}	Polymer viscosity parameters
b_i	Surfactant and polymer adsorption parameter
b_p	Permeability reduction parameter
B	Hand parameter
C_i	Overall concentration of species i in mobile phase
$\tilde{C}_i$	Overall concentration of species i in mobile and rock phases
$\bar{C}_i$	Concentration of adsorbed species i
C_{ij}	Concentration of species i in phase j
C_{pip}	Concentration of pseudocomponent i at the plait point
C_{piM}	Concentration of pseudocomponent i at the invariant point
C_{p2PL}	Concentration of the oil pseudocomponent at the left plait point
C_{p2PL}^*	Concentration of the oil pseudocomponent at the left plait point for Type II(+) phase behavior
C_{p2PR}	Concentration of the oil pseudocomponent at the right plait point

C_{p2PR}^*	Concentration of the oil pseudocomponent at the right plait point for Type II(-) phase behavior
C_{SE}	Effective salinity (phase behavior)
C_{SEOP}	Optimal effective salinity
C_{SEP}	Effective Salinity (ion strength) for polymer properties
C_{51}	Anion concentration on an aqueous basis
C_{51}^*	Anion concentration in the absence of calcium and alcohol
$C_{51 \text{ opt}}$	Anion concentration at optimum phase behavior
$C_{51 \text{ opt}}^*$	Anion concentration at optimum phase behavior in the absence of calcium and alcohol
C_{SEL}	Lowest effective salinity for Type III phase behavior
C_{SEU}	Highest effective salinity for Type III phase behavior
C_{p3MAX0}	Maximum C_{p3} along binodal curve (height of two phase region) at $C_{SE} = 0$
C_{p3MAX1}	Maximum C_{p3} along binodal curve at $C_{SE} = C_{SEOP}$
C_{p3MAX2}	Maximum C_{p3} along binodal curve at $C_{SE} = 2C_{SEOP}$
C_{RMS}	Root mean square concentration norm
C_{6j}^o, C_{9j}^o	Free calcium and sodium concentrations in phase j
$\bar{C}_6, \bar{C}_9$	Calcium and sodium concentrations on clay
C_{6j}^S, C_{9j}^S	Calcium and sodium concentrations associated with surfactant (counterion on micelles) in phase j

$\bar{c}_6^S, \bar{c}_9^S$	Calcium and sodium concentrations associated with the adsorbed surfactant
c_7^1	Ratio of alcohol to water in brine pseudophase
c_7^2	Ratio of alcohol to oil in oil pseudophase
c_7^3	Ratio of alcohol to surfactant in surf. pseudophase
D_{ij}	Effective binary diffusion coefficient of component i in phase j
$e, \exp$	exponent, (mathematical constant = 2.7183)
e_j	Relative permeability exponent for phase j
e_{jw}	Relative permeability exponent for low capillary number conditions (constant)
e_{jc}	Relative permeability exponent for high capillary number condition (constant)
E	Hand parameter
f_j	Fractional flow of phase j
f_6^S	Fraction of calcium ions of the total surfactant associated counterions
f_7^S	Fraction of alcohol in surfactant pseudocomponent
$F(Y)$	Capillary desaturation function
F	Hand Parameter
F_Y	Interfacial tension factor
FG_i	Convection term of the continuity equation
FU_i	Diffusion term of the continuity equation
$g(Y)$	Capillary desaturation function
G_{ij}	Interfacial tension parameters
$G(S_1, S_2)$	Lake's interpolating function

h	Variable used in phase behavior calculations
k	Absolute permeability
k_r	Relative permeability of flowing phase
k_{rj}	Relative permeability of phase j
k_{rj}^0	End point relative permeability of phase j
k_{rjw}^0	End point relative permeability of phase j for low capillary numbers
k_{rjc}^0	End point relative permeability of phase j for high capillary numbers
K_{ij}	Dispersion coefficient of component i in phase j
K_a^O	$\left. \begin{array}{l} C_7^2 / C_7^1 \\ C_7^3 / C_7^1 \end{array} \right\} \text{alcohol partition coefficients}$
K_a^S	
L	Absolute length
M	Number of phases
n	Shear rate viscosity index
N	Number of components
N_c	Capillary number
N_i	Flux of species i
P_j	Phase pressure
P_α	Shear rate dependence parameter for polymer
q	Flow rate
q_j	Flow rate of phase j
Q_v	Cation exchange capacity, meq/ml P.V.

R_k	Permeability reduction
R_{ij}	Variables used in phase behavior calculations
$R_{k, \max}$	Maximum value of R_k
R_{rf}	Residual resistance factor
R_{96}^C, R_{96}^S	Variables used in cation exchange calculations
S_p	Salinity dependence parameter for polymer solution viscosity
S_j	Saturation (volume fraction) of phase j
S_{jr}	Residual saturation of phase j
S_{jrw}	Residual saturation at low capillary numbers (constant)
S_{nj}	Normalized saturation of phase j
t	Time
t_D	Normalized time (dimensionless)
Δt_D	Discretized time (time step)
T_{ij}	Capillary desaturation parameters
u, u_T	Darcy velocity (flux)
u_j	Darcy velocity of phase j
v_j	Phase velocity
V	Volume or velocity
V_j	phase volume
V_p	Pore volume
V_r	Rock (solid phase) volume
W_i	Overall mass concentration of component i [=] $\frac{M}{L^3(V_p)}$

x	Position
x_D	Dimensionless Distance
Δx_D	Discretized distance (block size)
α	Angle or variable used in phase behavior calculations
$\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5$	Phase viscosity parameters
α_{lij}	Longitudinal dispersivity of species i when in phase j
α_{Dij}	Dimensionless dispersion coefficient
α_{Dij}^1	α_{Dij} when $S_j = 1$
α_{NUM}	Numerical dispersion
$\alpha_{physical}$	Dispersion produced by dispersive term of continuity equation
α_{TOT}	Sum of α_{NUM} and $\alpha_{physical}$
β	Variable used in phase behavior calculations
$\beta_1, \beta_2, \beta_3$	Dilution effect parameters (old model)
β_6, β_7	Parameters used in new effective salinity equation
β_p	Parameter used in calculating C_{SEP}
β^C	Cation exchange coefficient for clays (meq/ml) ⁻¹
β^S	Cation exchange coefficient for surfactants (meq/ml) ⁻¹
γ	Interfacial Tension
$\dot{\gamma}$	Shear rate
$\dot{\gamma}_{1/2}$	Shear rate at which viscosity is half its value at zero shear rate

$\dot{\gamma}_j$	Shear rate of phase j
δ_{ij}	Rate of saturation dependence of dispersivity
ϵ	Scalar tolerance used as convergence criteria in the cation exchange calculations
θ	Variable used in phase behavior calculations
λ_{rj}	Relative mobility of phase j
λ, λ_{rt}	Total relative mobility
μ_j	Viscosity of phase j
μ_p	Polymer viscosity at a shear rate $\dot{\gamma}$
μ_p^*	Effective polymer viscosity
μ_0	Polymer viscosity at zero shear rate
μ^∞	Polymer viscosity at an infinite shear rate
ρ_j	Phase density
ρ_0	Pure component density
ρ_i	
τ	Tortuosity factor
ϕ	Porosity
ϕ_4	Apparent porosity for polymer
$\phi_4, \text{ eff}$	Effective polymer porosity
ω_{ij}	Phase concentration [=] $\frac{M(i)}{L^3(Vj)}$
ω_{is}	Concentration in solid phase [=] $\frac{M(i)}{L^3(Vr)}$

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