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PHASE BEHAVIOR AND OIL RECOVERY INVESTIGATIONS USING MIXED AND ALKALINE-ENHANCED SURFACTANT SYSTEMS

By
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March 1992

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Topical Report

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PHASE BEHAVIOR AND OIL RECOVERY INVESTIGATIONS USING MIXED AND ALKALINE-ENHANCED SURFACTANT SYSTEMS

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ABSTRACT

The results of an evaluation of different mixed surfactant and alkaline-enhanced surfactant systems for enhanced oil recovery are described. Several mixed surfactant systems have been studied to evaluate their oil recovery potential as well as improved adaptability to different ranges of salinity, divalent ion concentrations, and temperature. Several combinations of screening methods were used to help identify potential chemical formulations and determine conditions where particular chemical systems can be applied. The effects of different parameters on the behavior of the overall surfactant system were also studied. Several commercially available surfactants were tested as primary components in the mixtures used in the study. These surfactants were formulated with different secondary as well as tertiary components, including ethoxylated and non-ethoxylated sulfonates and sulfates. Improved salinity and hardness tolerance was achieved for some of these chemical systems. The salinity tolerance of these systems were found to be dependent on the molecular weight, surfactant type, and concentration of the surfactant components.

Oil displacement experiments in Berea sandstone cores showed considerable improvement in oil recovery potential of these mixed and alkaline-enhanced surfactant systems. Research results have shown the existence of favorable conditions for oil recovery using these two methods. Some of these displacement experiments were conducted with the aid of imaging tools such as NIPER's computer-aided tomography (CT) scanner to determine the progression of the flood. The effectiveness of the surfactant formulation and the mobility control system were monitored using this technique.

Several reservoirs were selected as the focus of the research for the application of these improved chemical flooding methods. These reservoirs included North Burbank (OK) Unit, Hepler (KS) Field, and the Government Wells (TX) field. The Burbank reservoir was selected from several Class 1 reservoirs. A database evaluation for this reservoir class was conducted. The Burbank reservoir properties were identified as grouped within the mid-range values for this class. North Burbank retains a significant reserve of unproduced oil and has been identified as a prime candidate for the application of advanced chemical EOR methods.

INTRODUCTION

Chemical flooding has the capability of being a flexible enhanced oil recovery (EOR) method. It has the potential of recovering more residual crude oil than other available methods. The capability to adjust an injected chemical formulation for a wide range of reservoir conditions and crude oil types remains a strong point for development and application of this technology. It has been identified by the Department of Energy (DOE) as an important production technique targeted for Class 1 reservoirs.[1]

For many U.S. domestic oil reservoirs, chemical flooding may be the only viable EOR method. The application of other EOR technologies may be significantly limited because of factors and parameters inherent to the reservoirs. However, from an application point of view, chemical flooding EOR still requires a broad base research and development effort for efficient and economic application, at current and projected oil prices. Concerns that have to be addressed include process design criteria, economics, cost minimization and optimization, effective mobility control and optimal injection strategies. Other key research areas to be considered include chromatographic separation of components from the chemical formulation, surfactant adsorption, precipitation, phase trapping, and variability of reservoir conditions.[2]

The National Energy Strategy-Advanced Oil Recovery Program (NES-AORP) was developed as a means of improving domestic oil production and extending the "life" of the Nation's reserves. The focus of this program is the advancement of the best currently defined EOR technologies and utilization of these methods to improve recovery from targeted reservoirs. In accordance with DOE's strategy, the goal of this NIPER research program is to develop chemical flooding systems that are both cost-effective and have improved adaptability to variations in salinity, hardness, temperature, and dilution for recovery of light crude oils from selected Class 1 reservoirs. Research under this program has been focused primarily on mixed surfactant systems that have been shown to have potential advantages over conventional chemical flooding systems. These surfactant systems can be designed to achieve improved tolerance to adverse conditions as well as variability in reservoir conditions encountered by injected fluids. These systems can be formulated with surfactant components that jointly have high oil recovery potential (i.e., high oil solubilization and ultra low interfacial tension) and improved adaptability to different ranges of salinity, divalent ion concentrations, and temperature. The existence of a synergistic effect with mixed compositions can be evaluated to develop a surfactant system or systems that will retain relatively low interfacial tension (IFT) values over a range of target reservoir conditions, while maintaining overall chemical effectiveness at an acceptable level. Factors influencing the economic potential of the chemical system(s) have to be considered as well. A balance between cost and oil recovery effectiveness has to be achieved in order to find the best surfactant systems for field application.

Most of the work conducted on chemical flooding EOR has been focused on sulfonate-type surfactants. Petroleum sulfonates have been widely investigated based on defined criteria of material cost, reservoir compatibility, and supporting results from laboratory experiments. Petroleum sulfonate-based chemical floods have also been implemented in the field with limited success, both technically and economically.[3] There are other potentially applicable surfactants. Other sulfonate-type surfactants may be more expensive to manufacture, but their improved performance potential under adverse reservoir conditions oftentimes offsets their higher costs. Several reviews of the state of the art have appeared in recent years. These reviews provide an overview of the direction of the technology.[2,4-7]

Ethoxylated sulfonates[8-10] and carboxylates[11-17] have received much attention recently because of their improved performance or tolerance under higher salinity conditions. In FY89, NIPER conducted studies on several carboxymethylated ethoxylated surfactants (CME). These studies have shown that CME surfactants have significantly better tolerance under high salinities.[18] Relatively low IFT values were measured for salinities up to 20% NaCl. The CME surfactants by themselves may be applicable in high salinity environments, but they have also exhibited excessive surfactant losses under such conditions, making them unattractive for use in EOR projects.[19]

Mixtures of surfactants have been shown to exhibit inherent properties that are far superior to those of the individual surfactants. The goal of understanding and quantifying resulting synergistic properties and identifying mixtures of surfactants that show synergism has been of primary importance to research in this area. But most of the work conducted on mixed surfactant systems has been focused on industrial applications of pure individual surfactants in aqueous surfactant systems. Empirical models have been developed for these pure surfactants and some ideal surfactant mixtures to account for adsorption, molecular interaction and synergism in interfacial tension reduction efficiency.[20-22] Commercial surfactants are typically mixtures. Extension of the models for the ideal pure surfactant mixed systems to commercial surfactants is a desirable goal. But a wide gap in terms of research effort in these two areas still exists. In particular, for EOR purposes, the surfactant systems commonly used have very diverse molecular combinations. From the point of view of economics, isomerically pure surfactant systems are often too expensive and would not be desirable for any oilfield application.

The emphasis of the work conducted in FY90 was on mixed surfactant systems containing different types of surfactants, like the CME or other similar ethoxylated surfactants with less expensive surfactants which have good oil recovery characteristics but tolerate only low salinity conditions. Similar research on improving overall surfactant system performance has been attempted. As an example, the addition of ethoxylated sulfonates to a petroleum sulfonate increased the overall optimal salinity range of the surfactant system.[23] The combination of different surfactant types can yield an overall system with improved salinity tolerance and resistance to chromatographic separation. Several surfactant combinations have been studied under this work. These include alkyl and alkyl-aryl sulfonates as primary surfactants and carboxymethylated ethoxylated surfactants and ethoxylated sulfonates as secondary surfactants. The experiments conducted included IFT measurements, phase behavior measurements, and adsorption and chromatographic separation as well as crude oil displacement experiments. In conventional chemical systems containing low-molecular-weight alcohols, chromatographic separation of these alcohols from the surfactant system can be significant and detrimental to the effectiveness of the system. On the other hand, the combination of ethoxylated surfactants and non-ethoxylated surfactants appear to have less tendency to separate. Of interest in these studies were the effects of parameters such as temperature, surfactant concentration, salinity, presence of divalent ions, hydrocarbon type, and component proportions in the mixed surfactant combinations on the performance of the targeted surfactant/hydrocarbon systems.[24]

In FY91, research on the mixed surfactant systems has targeted a specific range of reservoir conditions. The work conducted in FY89[25] and guidelines from the Federal Oil Program Implementation Plan[1] have helped to identify reservoir conditions that can be targeted for EOR application of mixed surfactant systems. Statistical and experimental design methods were used to identify the variables that have significant effects on the performance of these chemical systems, which include temperature, salinity, and hardness. One of the reservoir conditions selected for this research was that of the North Burbank Unit (NBU), Osage County, Oklahoma, which is classified as a Fluvial dominated deltaic (Class 1) reservoir with salinity and temperature parameters that lie in the mid range value for reservoirs in the same class.[26] This reservoir has a significant quantity of unproduced oil and has been identified as a prime candidate for the application of advanced chemical EOR methods.

Several commercially available surfactants were tested as primary components in the mixtures used in the study. These surfactants were formulated with different secondary as well as tertiary components, including other ethoxylated and non-ethoxylated sulfonates and sulfates. Improved salinity and hardness tolerance was achieved for some of these chemical systems. Oil displacement experiments in Berea sandstone cores showed considerable improvement in oil recovery potential of these systems compared to the CME-containing systems studied in prior work.[24] Some of these displacement experiments were conducted with the aid of advanced imaging techniques such as NIPER's computer-aided tomography (CT) scanner to determine the progression of the flood.[27] Both the effectiveness of the surfactant formulation and the mobility control system can be monitored using this technique. Studies were also conducted using two cosurfactant systems added to a primary surfactant component. The studies conducted were based on the concept of balancing the effect of the secondary and tertiary surfactant component in maintaining the oil and water affinity of the overall chemical system, similar to an hydrophillic-lipophillic balance (HLB) gradient approach.[28] Results from these studies showed favorable IFT values as well as phase behavior at the conditions tested.

NIPER's efforts in developing other cost-effective chemical flooding technologies has also been focused on the use of alkaline-enhanced surfactant flooding technology for the recovery of light, midcontinent crude oils. The positive effect of alkaline additives on the effectiveness of surfactant formulations is now fairly well-known and accepted.[29] Research on the use of alkaline agents as additives to surfactant formulations has evolved over the past few years. This research was first performed using acidic oils, and it was believed that the primary effect of the alkali was neutralization of carboxylic acids present in acidic crude oils.[30-34] However, it has been shown recently, that a synergism exists between surfactants and alkaline additives, even when the oils have very low acid numbers.[35-38] This opens up the possibility of the application of this technology to a larger number of reservoirs, including many midcontinent reservoirs that contain slightly acidic, light crude oils. In the presence of alkaline additives, very dilute (<0.4%) concentrations of synthetic surfactants have the potential to mobilize significant amounts of residual oil. Since synthetic surfactants are expensive components of the chemical formulation, low concentration requirements can improve the economics of field projects. The results from current research efforts, however, appear to show that each crude oil behaves differently, even when using similar chemical additive formulations. This has been shown by comparative testing of crude oils from different reservoirs.[39] The applicability of these chemical systems must then be determined for each target oil, brine, and reservoir type.

In FY90, research using the alkaline-enhanced surfactant method was conducted using two midcontinent crude oils: one from Teapot Dome (WY) field and the other from Delaware-Childers (OK) field. Research results have shown the existence of favorable conditions for oil recovery using alkaline-enhanced surfactant flooding method. The economics of oil recovery using this technology appears to be very favorable, such that in FY91, the development of the technology was also concurrently pursued for specific target field near-term application in a multi-year research project under the Supplemental Government Program (SGP).[40] Also for FY91, under the base program, these studies were extended to include several reservoirs that meet the selection criteria set forth in the NES-AORP Plan.

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DESCRIPTION OF SELECTED RESERVOIRS

Fluvial Dominated Deltaic Reservoirs

One of the means of classifying reservoirs is based on the dominant type depositional environment. Deltaic reservoirs represent a significant part of the clastic depositional system.[41] The fluvial-dominated deltaic (FDD) reservoirs have been identified by the U.S. Department of Energy as a major target for oil recovery efforts through the development of advanced EOR methods.[1] The fluvial-dominated deltaic class consists of plays with reservoirs resulting from the deposition of river-borne sediments. A play is a geologic group of reservoirs with common deposition lying in a contiguous geographic area.[1] Nine plays have been identified to make up this geologic class. One play of particular interest is the Northeast Oklahoma Desmonian Sandstone play. This play is considered the largest in the FDD geologic class. Within this play, two reservoirs of potential importance to the NES-AORP program are Burbank reservoirs of the Burbank field and the Earlsboro reservoir of Earlsboro field. Burbank is of particular interest because of prior efforts to apply chemical flooding in this field.

Burbank Reservoir, Osage County, Oklahoma

The Burbank reservoir was the site of an earlier surfactant/polymer EOR pilot operated by Phillips Petroleum Company with the cooperation of the DOE.[42] Prior efforts to stimulate production from this reservoir included gas injection for reservoir repressurization, waterflooding, steamflooding and polymer flooding,[43] circa 1935, 1950, 1965 and 1970, respectively. A pilot test using surfactant-polymer flooding on a 90-acre test site was initiated in 1975. This EOR pilot was deemed unsuccessful.

Several factors have been determined to have had an adverse effect on the performance of the surfactant and polymer slugs during the EOR pilot test conducted by Phillips Petroleum Company.[44] Heterogeneity, crossflow, ion exchange, and component partitioning were contributing factors in the failure of the pilot. The reservoir is considered oil-wet, primarily from the presence of chamosite clay, and has natural east-west fractures. Postflood evaluation of the pilot showed that surfactant retention exceeded that expected from laboratory adsorption measurements and simulation studies.[45] Surfactant and alcohol partitioning into the oil and aqueous phases, respectively, degraded the effectiveness of the surfactant slug. Variability of the salinity and hardness in the reservoir impacted the integrity of the chemical slug. The original chemical system used in this test was formulated with 0.9% sodium chloride (NaCl) brine. This formulation salinity was too low compared to the original formation brine and did not account of the hardness of the brine. A saline preflush was used before the chemical slug, but postflood evaluation showed that this preflush was not sufficient to condition the reservoir and protect the surfactant and polymer slug from the inherently harsh reservoir conditions. Table 1 lists some of the reservoir properties for the Burbank reservoir as well as the other fields studied.

The current production capacity of the Burbank reservoir is about 350,000 barrels of oil per year. Based on estimates using the Tertiary Oil Recovery Information System (TORIS), about 100 million barrels of unrecovered mobile oil could be recovered from this reservoir, with an additional 85 million barrels of oil through the application of advanced chemical EOR methods.[1]

Other Fields Selected

Two other fields were selected for the study. In particular, these fields were targeted for the alkaline-enhanced surfactant flooding tests. One is Hepler (KS) field and the other is Government Wells (TX) field. Under normal alkaline flooding conditions where the candidate oil has high acidity, the alkaline additives react with the oil to produce chemical agents (i.e. surfactants) that can induce lower interfacial tension between the oil and the brine. But the two above mentioned oils are not very acidic. The acid number for Hepler oil, for example, is less than 0.01 mg of KOH/g of oil, while the acid number for the Government Wells oil is 0.7 mg of KOH/g of oil. Oils that are considered acidic have acid numbers in the 1.5 to 4 mg of KOH/g of oil range. The Burbank oil is also considered a nonacidic oil. The low acidity in the oils tested in this study may result in minimal reaction between the oil and the alkaline additives. However, for low acidity oils other synergistic effects have been found that result in the formation of favorable IFT values for oil mobilization, even at fairly low total chemical concentrations. These low concentration levels are very favorable for the economics of the application of this technology.

TABLE . 1 - Properties of the oils used in mixed surfactant corefloods with and without alkaline additives

Field	State	Depth, ft.	Temp., °C	Permeability md	Gravity, °API	Viscosity, cP	TDS, mg/L
Hepler	KS	575	21	80	26.1	76	11,900
N. Burbank Unit	OK	2,900	49	52	39.5	3	87,000
Gov't. Wells	TX	2,200	45	800	20.1	20	5,680

EXPERIMENTAL PROCEDURES

Materials

The surfactant and polymer systems used in the study are listed in table 2. These chemicals were used without further purification, unless otherwise specified. The solutions were prepared using reagent grade salts, and the concentrations are reported as weight chemical to weight of solution (wt/wt).

TABLE 2. - List of chemicals used in the study

Chemical Code	Trade Name	Company	Type	Activity, wt%
S - 1	B-100	Stepan	alkyl aryl sulfonate	58.7
S - 2	B-105	Stepan	mixed anionic surfactant	51.4
S - 3	B-110	Stepan	alkyl aryl sulfonate	48.3
S - 4	B-120	Stepan	alkyl aryl sulfonate	40.2
S - 5	LXS-810	Shell	alkyl aryl sulfonate	100.0
S - 6	LXS-1112	Shell	alkyl aryl sulfonate	100.0
S - 7	LXS-1314	Shell	alkyl aryl sulfonate	100.0
S - 8	RS-16	Sandoz	ethoxylated carboxylate	90.0
S - 9	NP-4	Emery	ethoxylated nonylphenol	99.0
S - 10	NP-6	Emery	ethoxylated nonylphenol	99.0
S - 11	NP-9	Emery	ethoxylated nonylphenol	99.0
S - 12	NP-11	Emery	ethoxylated nonylphenol	99.0
S - 13	BSA-74	PPG	ethoxylated sulfonate	26.0
S - 14	CA-207	Stepan	ether sulfate	58.9
S - 15	CS-460	Stepan	ether sulfate	60.0
S - 16	SE-463	GAF	ethoxylated sulfonate	28.0
S - 17	TRS 10-410	Witco	petroleum sulfonate	62.0
S - 18	XP-100	Chevron	ethoxylated sulfonate	15.0
P - 1	4800 CX	Pfizer	biopolymer	- - -

For the S-3*/S-14* system, the (∗) designation indicates a reformulated chemical system with a reduced alcohol concentration.

Interfacial Tension (IFT) Measurements

The interfacial tension (IFT) of the different chemical systems tested was measured using a Model 300 Spinning Drop Interfacial Tensiometer, manufactured at University of Texas at Austin. These measurements were conducted using different equilibrated and non-equilibrated systems and different target crude oils at selected reservoir conditions. These measurements were usually taken after sufficient temperature equilibration time had been allowed. Multiple measurements were taken until stable and reproducible IFT values were obtained. The chemical solution properties such as densities and refractive indices were measured using a Mettler/Paar DMA 45 Calculating Digital Density Meter and a Bausch & Lomb Refractometer. These measurements are needed for the calculation of the interfacial tension. Specific details regarding this procedure have been published in previous reports.[24]

Phase Behavior Measurements

Phase behavior measurements were conducted on selected chemical systems to evaluate the effects of several experimental factors such as: total surfactant concentration, salinity, proportion of divalent ions, crude oil type, and proportion of different surfactant types on the phase behavior of the overall chemical/hydrocarbon systems. These tests were typically conducted using solutions that were made up at a fixed water-to-oil ratio (volume water : volume oil = 1), unless otherwise specified. These solutions were prepared in 10-mL glass pipets that were sealed and equilibrated in ovens at the desired temperature condition. The relative volumes of the different phases were read and recorded at set time intervals until constant readings were obtained. These constant phase volume readings were then used to calculate the solubilization parameters of the oil ($\sigma_o = V_o/V_s$) and the brine ($\sigma_w = V_w/V_s$) in the microemulsion phase. Unusual phase behavior such as the formation of gels, liquid crystalline phases, and precipitation was also recorded. The specifics of these calculations are discussed in a previous report.[46]

The preliminary chemical system screening was conducted using bottle tests. Typically, the chemical solutions and the crude oil samples tested were mixed at a fixed water-to-oil volumetric ratio of 1. These bottles were then equilibrated in an oven, and observed solution behavior was recorded after a fixed time interval. The overall chemical system's tolerance to the salinity ranges tested was observed, and a qualitative description of the solution behavior for the different chemical systems was obtained. This type of screening was used in evaluating the potential for substituting a different surfactant type for an original component in the chemical system, i.e.

substitution of ethoxylated and non-ethoxylated sulfonates and sulfates for the isobutyl alcohol (IBA) in the system 5 wt% S-17 and 3 wt% IBA.

Phase Inversion Temperature Measurements

The phase inversion temperatures (PIT) of the chemical systems studied were measured using an apparatus designed and constructed at NIPER.[47] The PIT is the temperature condition at which a water-in-oil emulsion changes into an oil-in-water emulsion and vice versa. This phase transition can be detected by measuring the electrical conductivity of a well-stirred mixture as a function of the temperature. The PIT experiment is routinely associated with measurement of the above phase transition for nonionic surfactants, and the technique has been used extensively by Shinoda to investigate surfactant-oil interaction.[48-49] PIT measurements, salinity scans, and IFT measurements are useful tools in determining the potential applicability of selected surfactant systems.

The PIT apparatus was also used for a different type of chemical screening. The apparatus was originally designed to measure the solution's transition temperature. Under conditions of fixed temperature, dependent on the selected reservoir, the salinity then becomes the parameter of interest. The apparatus was modified for certain chemical systems to measure the dynamic electrical conductivity as a function of a salinity gradient at a fixed temperature. This approach was used to determine if this type of a screening method was applicable in identifying phase boundaries (i.e. phase transitions from type II(-) to type III to type II (+))[50] in well-defined chemical systems. The combination of the modified PIT method with dilution calorimetry[51-53] was used as a means of determining solution phase behavior. Details of the procedure for the dilution calorimetry are discussed in a previous report.[24]

Coreflood Displacement Experiments

Coreflood displacement experiments were conducted in Berea sandstone core plugs measuring 3.8 cm in diameter and approximately 25 cm in length. The core plugs were evacuated followed by saturation with brine. Brine composition varied depending on the type of oil used in the test. For most of the corefloods, core plugs were then placed in a Hassler-type coreholder. A schematic of the apparatus is shown in figure 1. The cores used for the CT imaging studies were encased in epoxy resin to allow x-ray penetration of the cores to determine fluid saturation profiles.

After measuring permeability to brine, the core plugs were flooded with crude oil to residual brine saturation and then waterflooded to residual oil saturation. Chemical injection varied depending of the objectives of the specific coreflooding experiment. For the experimental studies using the alkaline-surfactant-polymer method (ASP), the sequence of chemical injections included an alkaline preflush, injection of the surfactant slug, followed by injection of the mobility-control polymer slug. Other mixed surfactant chemical floods were performed without using a preflush. For several experiments, different combinations of surfactant and polymer chemical slugs were compared. Table 3 shows typical coreflood parameters used during this study.

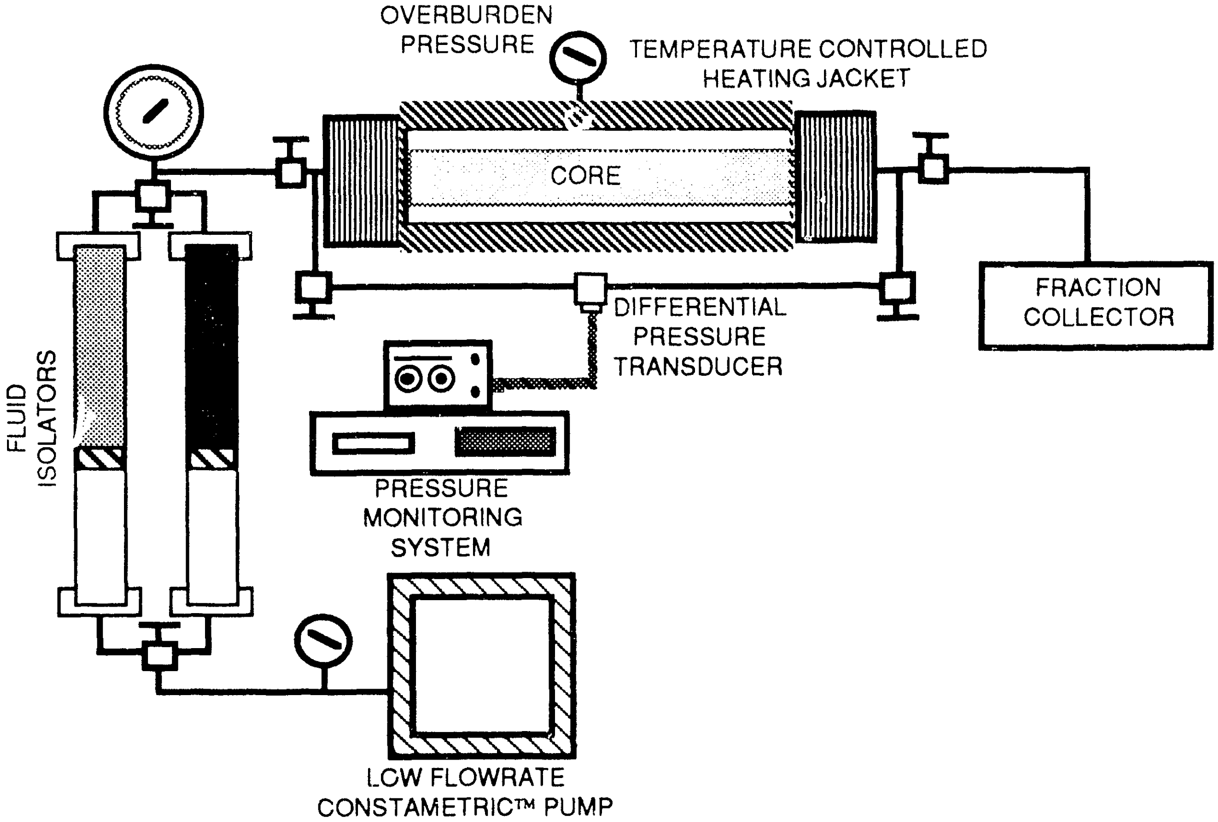


FIGURE 1. - Schematic of coreflood apparatus used for chemical flooding tests.

TABLE 3. - Coreflood parameters using mixed surfactant systems

Temperature, °C	23 to 50
Confining stress, psi	200
Core, Berea Sandstone:	
Permeability to brine, md	100-1200
Porosity, %	18-23
Brine:	
Simulated North Burbank Unit brine ($NaCl/CaCl_2/MgCl_2$), wt%	6.65/1.53/0.24
Simulated Hepler brine ($NaCl/CaCl_2/MgCl_2$), wt%	1.022/0.039/0.033
Simulated Government Wells brine	similar to Hepler
NaCl	various concentrations

TABLE 3. - Coreflood parameters using mixed surfactant systems. - continued

Oil:	
North Burbank Unit (NBU)	
Hepler Oil	
Government Wells	
Iododecane for CT experiments	
Other fluids:	
Alkaline preflush #1 ($NaHCO_3$, Na_2CO_3) + brine of interest	(0.095N, 0.095N)
Alkaline preflush #2 (STPP, $NaHCO_3$) + brine of interest	(0.5 wt%, 0.5 wt%)
pH	9.2 to 9.5
Tracer - fluorescein, ppm	10
Total surfactant, % (active weight)	0.4 to 1.0
Biopolymer, ppm	1,000 to 3,500
Alcohol: 2-butanol, wt%	2
Production:	
Fluid flow rate, ft/D	1

Effluent from the corefloods was collected in fraction collection tubes. Amounts of oil and brine were tabulated to allow determination of oil saturation changes, cumulative oil production, and recovery efficiency for each test. Additional chemical analyses of collected fluids (i.e. pH, surfactant concentration, viscosity, and tracer concentration measurements) were determined as required.

Computer-Aided Tomography Imaging Techniques

Computer-aided tomography (CT) imaging techniques use x-ray energy to determine differences in material densities within a core. Core plugs are examined to identify heterogeneities such as fractures, high permeability (low density) streaks, or mineral deposition differences which can influence the transport and distribution of fluids and chemicals within the core. Fluid distributions can be observed by tagging the brine or the oil with additives that alter or enhance their x-ray densities. Sodium iodide is usually added to brine, or iododecane is added to oil for this purpose. Because brine composition is a very important factor in the design of surfactant formulations, the tagging agent, iododecane, was added to the oil for this study Addition of iododecane to both Hepler and NBU oil reduced oil viscosity but did not appear to affect oil recovery for comparable oil recovery tests.

Description of the CT equipment used at NIPER and the general procedures for its use have been reported previously.[27] For this study, two CT monitored corefloods were conducted that were similar to two corefloods performed earlier in the year. These tests were selected because oil recovery efficiency was significantly different for floods conducted using the same chemical system. The epoxy-encased core plugs were scanned at different time intervals: (1) dry, (2) after saturation with brine, (3) after flooding with oil to irreducible brine saturation, (4) after the waterflood, (5) after the chemical flood, and (6) after the polymer flood. CT images showed that the oil saturation differences between the two floods could be observed, suggesting that this technique was a useful tool for identifying and evaluating variables that affect oil recovery efficiency of chemical floods.

RESULTS AND DISCUSSION

Surfactant Mixture Screening

The use of mixtures of surfactants for chemical flooding EOR has been the focus of several studies.[17,22,54-55] The interest in mixtures of surfactants stem from the existence of potential synergistic effects in these systems that may yield solutions that exhibit inherent properties that are far superior to those of the individual surfactants. Part of the work conducted under this program is a qualitative screening of different surfactant combinations listed in table 2. Summary of the results of this preliminary screening are presented in Table 4. Unless otherwise specified, these solutions were prepared using 100% NBU brine strength[24], and tested at 50°C.

TABLE 4. - Summary of binary and ternary surfactant mixture screening

Surfactant system	Surfactant Conc., active wt%	No. of phases	Comment
S-1	salinity too high		did not test
S-2	1.00	2	
S-3	salinity too high		did not test
S-4	salinity too high		did not test
S-5	salinity too high		did not test
S-6	salinity too high		did not test
S-7	salinity too high		did not test
S-8	1.00	2	
S-10	1.00	2	
S-11	1.00	2	
S-12	1.00	2	
S-15	1.00	2	
S-18	salinity too high		did not test
S-1 & S-13	0.10 & 0.90	2	
S-1 & S-13	0.20 & 0.80	2	
S-1 & S-13	0.30 & 0.70	2	
S-1 & S-13	0.40 & 0.60	3	low solubilization
S-1 & S-13	0.50 & 0.50	3	low solubilization
S-1 & S-13	0.55 & 0.45	3	low solubilization
S-1 & S-13	0.60 & 0.40	3	low solubilization

TABLE 4. - Summary of binary and ternary surfactant mixture screening. - cont.

Surfactant System	Surfactant Conc., active wt%	No. of Phases	Comment
S-1 & S-15	0.20 & 0.80	2	
S-1 & S-15	0.30 & 0.70	3	low solubilization
S-1 & S-15	0.40 & 0.60	3	low solubilization
S-1 & S-15	0.50 & 0.50	3	emulsion
S-1 & S-15	0.55 & 0.45	3	emulsion
S-1 & S-15	0.60 & 0.40	3	emulsion
S-3 & S-13	0.10 & 0.90	2	
S-3 & S-13	0.20 & 0.80	2	
S-3 & S-13	0.30 & 0.70	2	
S-3 & S-13	0.40 & 0.60	3	low solubilization
S-3 & S-13	0.45 & 0.55	3	low solubilization
S-3 & S-13	0.50 & 0.50	3	low solubilization
S-3 & S-14	0.10 & 0.90	2	
S-3 & S-14	0.20 & 0.80	2	
S-3 & S-14	0.30 & 0.70	2	
S-3 & S-14	0.40 & 0.60	2	
S-3 & S-14	0.50 & 0.50	2	
S-3 & S-14	0.52 & 0.48	2	
S-3 & S-14	0.55 & 0.45	2	
S-3 & S-14	0.60 & 0.40	2	
S-3 & S-15	0.10 & 0.90	2	
S-3 & S-15	0.20 & 0.80	2	
S-3 & S-15	0.30 & 0.70	2	
S-3 & S-15	0.40 & 0.60	3	low solubilization
S-3 & S-15	0.45 & 0.55	3	low solubilization
S-3 & S-15	0.50 & 0.50	3	emulsion
S-4 & S-11	0.50 & 0.50	3	low solubilization
S-4 & S-12	0.50 & 0.50	3	low solubilization
S-4 & S-13	0.10 & 0.90	2	
S-4 & S-13	0.20 & 0.80	2	
S-4 & S-13	0.30 & 0.70	2	
S-4 & S-13	0.40 & 0.60	2	
S-4 & S-13	0.50 & 0.50	2	
S-4 & S-13	0.60 & 0.40	2	
S-4 & S-15	0.10 & 0.90	2	
S-4 & S-15	0.20 & 0.80	2	
S-4 & S-15	0.30 & 0.70	2	
S-4 & S-15	0.40 & 0.60	2	
S-4 & S-15	0.50 & 0.50	3	low solubilization
S-4 & S-15	0.60 & 0.40	2	
S-7 & S-10	0.50 & 0.50	2	
S-7 & S-11	0.50 & 0.50	2	
S-7 & S-12	0.50 & 0.50	2	
S-7 & S-15	0.50 & 0.50	2	

TABLE 4. - Summary of binary and ternary surfactant mixture screening - cont.

Surfactant system	Surfactant Conc., wt%	No. of phases	Comment
S-15 & S-9	0.50 & 0.50	2	
S-15 & S-10	0.50 & 0.50	2	
S-15 & S-11	0.50 & 0.50	2	
S-15 & S-12	0.50 & 0.50	2	
S-3 & S-15 & S-10	0.33 & 0.33 & 0.33	3	gel formation
S-3 & S-15 & S-11	0.33 & 0.33 & 0.33	3	gel formation
S-3 & S-15 & S-12	0.33 & 0.33 & 0.33	3	good solubilization
S-4 & S-15 & S-9	0.33 & 0.33 & 0.33	2	
S-4 & S-15 & S-10	0.33 & 0.33 & 0.33	3	low solubilization
S-4 & S-15 & S-11	0.33 & 0.33 & 0.33	2	
S-4 & S-15 & S-12	0.33 & 0.33 & 0.33	2	

From these preliminary screening tests, several surfactants and mixtures were further tested in graduated phase tubes to determine the extent of solubilization and the effect of experimental parameters such as (a) component substitution, (b) salinity, (c) ratio of components, (d) total surfactant concentration, and (e) surfactant type combinations on the behavior of the overall surfactant system.

Secondary Surfactant Component Substitution

This type of screening was used in evaluating the potential of substituting a different surfactant type for an original component in the chemical system, in this case, the substitution of ethoxylated and non-ethoxylated sulfonates and sulfates for the isobutyl alcohol (IBA) in the system 5 wt% S-17 and 3 wt% IBA at 50 °C. This original surfactant mixture was a fairly well-studied system. This was the original chemical system formulated for use on the North Burbank Pilot Test.[56-57]

Results of the surfactant component substitution screening are presented in figure 2. The surfactants used in the study are S-13, S-14, S-15 and S-16. In each of these screening tests, the upper limit in the amount of surfactant substituted for IBA was 3 wt%. At this concentration, the chemical system did not contain any added alcohol, except the amount present in each of the stock surfactants.

The results indicated a qualitative increase in salinity tolerance of the overall chemical system, based on the amount of additive surfactant in the system. As the total concentration of secondary surfactant component added increased, the overall solution salinity tolerance improved. Compared to the original 5 wt% S-17 and 3 wt% IBA system, its upper limit was about 2 wt% NaCl. Most

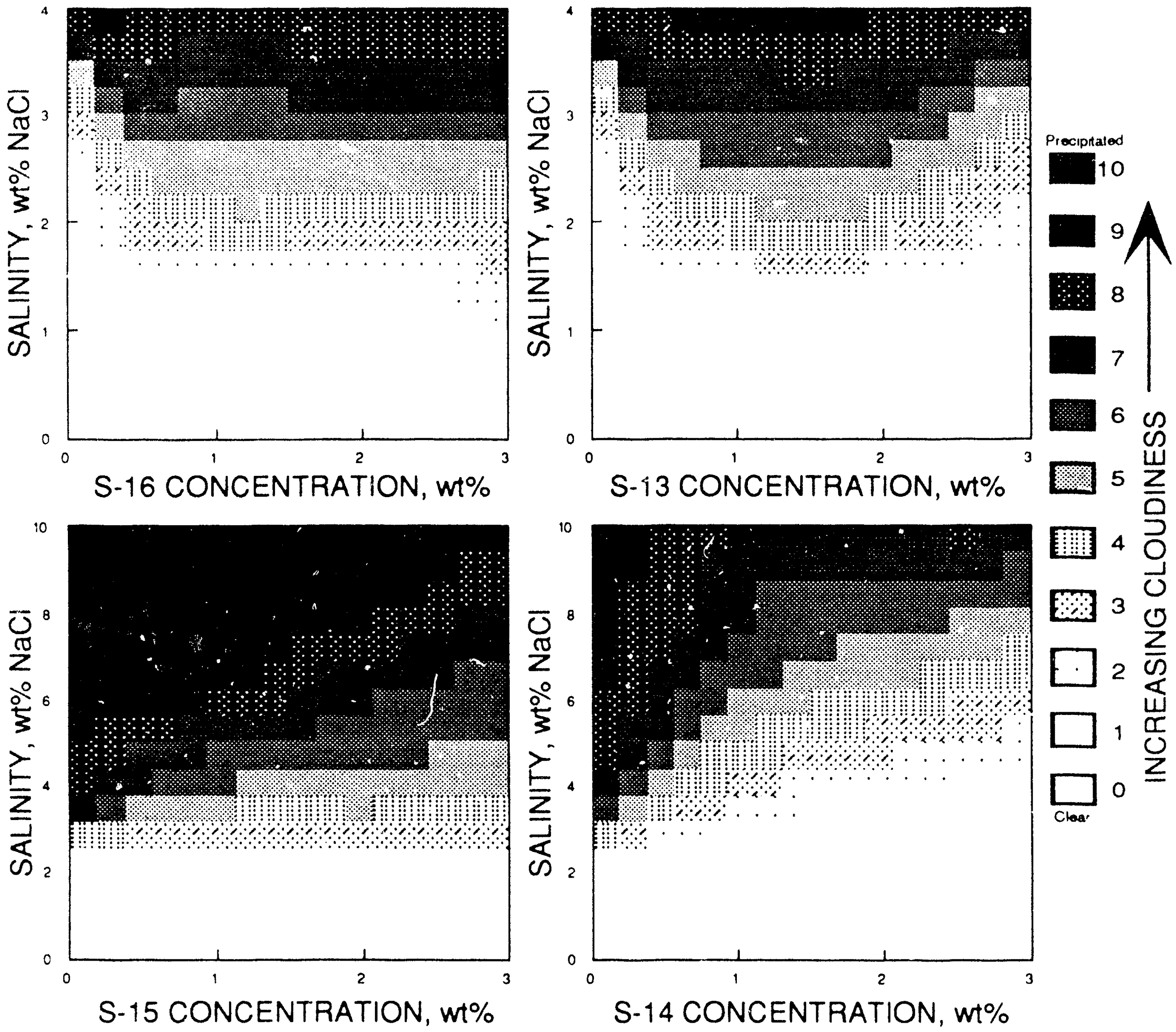


FIGURE 2. - Effect of type of secondary surfactant component substitution on the salinity tolerance of the overall surfactant system with 5 wt% S-17.

of the cases tested showed that the substitution of the secondary surfactant into the system improved the salinity tolerance beyond the 2 wt% NaCl level. The order of increasing improvement in salinity is reflected as such:

$$S\text{-}16 < S\text{-}13 \ll S\text{-}15 \ll S\text{-}14$$

The color scale on the density plot qualitatively illustrated the relative solution behavior. The darker the region on the density plot (increasing scale from 5 to 10), the more cloudy was the solution observed. The black regions indicated the presence of precipitates, considered as an upper bound in the salinity scan. The trend in increasing salinity tolerance can also be identified based on the difference in secondary surfactant type added. As listed in table 2, the S-13 and S-16 are ethoxylated sulfonates while the S-14 and S-15 are of the ethoxylated sulfate type. These results in general are consistent with previous studies that showed that sulfates have better salinity tolerance than sulfonates, ethoxylated and non-ethoxylated. The difference in the behavior of the systems containing the same surfactant type can be attributed to the difference in structures and molecular weights (MW) of these chemicals. Qualitatively, the MW of these chemicals are in the following order:

Ethoxylated Sulfonates:

$$MW_{S\text{-}16} > MW_{S\text{-}13}$$

These two surfactants are both similar in structure. The degree of ethoxylation is about 3 for both, with the S-13 surfactant being a more highly-branched shorter carbon-chain molecule compared to the S-16. The slight difference in salinity tolerance enhancement of the two systems can be attributed to the MW and branching-structure of the two surfactants. Shorter chain length and branching favored improved solubility and salinity tolerance.

Ethoxylated Sulfates:

$$MW_{S\text{-}15} > MW_{S\text{-}14}$$

These two systems are also similar in structure. The degree of ethoxylation is also about 3 units for both surfactants. The S-14 surfactant is a shorter carbon-chain molecule compared to the S-15, MW values are about 368 and 411, respectively. The MW also played an important role in the difference in behavior of these two systems. For both the sulfates and sulfonates, the shorter chain length favored an enhancement in solubility and salinity tolerance. The order of increasing salinity tolerance is shown as:

ethoxylated sulfates >> ethoxylated sulfonates

Effect of Salinity and Surfactant Concentration

The salinity level within a target reservoir or field application is a major determining factor for the types of chemical systems that can be applied. Recent successful field experience has shown that optimizing the chemical formulations with respect to the dominant brine salinity can have a significant impact of the flooding performance.[58-60] The use of surfactant mixtures has the primary advantage in this case, from the point of view of the capability to formulate the chemical system based on the proportion of the different types of surfactants that can be applied. These systems can be formulated with surfactant components that have high oil recovery potential (i.e., high solubilization and ultra low IFT values) and improved adaptability to different ranges of salinity, divalent ion concentrations, and temperature.

One potential chemical system that was studied was the S-2 surfactant. The S-2 surfactant itself was a blend of a sulfonate and an ethoxylated sulfate. At a fixed proportion of the two components, the salinity became an important factor in the range of application for this surfactant system. The results of the S-2 surfactant system screening are presented in figure 3. This figure shows a plot of the calculated solubilization parameters and IFT for this surfactant system.

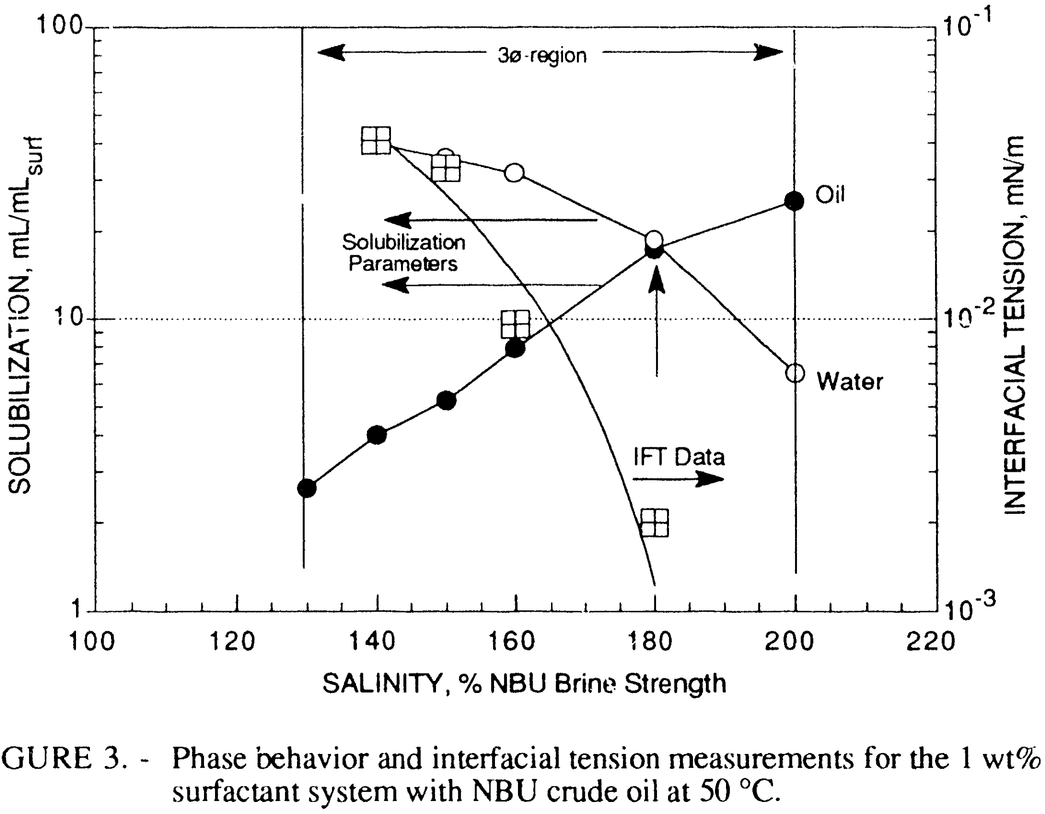


FIGURE 3. - Phase behavior and interfacial tension measurements for the 1 wt% S-2 surfactant system with NBU crude oil at 50 °C.

These studies were conducted at 50 °C using NBU crude oil, at a total surfactant concentration of 1 wt%. The results from these phase behavior screening showed that the S-2 surfactant had a fairly high salinity tolerance (up to 200% NBU brine strength tested). The system exhibited three-phase behavior between 130 to 200% NBU strength, with about 180% NBU brine strength being close to optimal. The interfacial tension (IFT) of the system with NBU crude oil (equilibrated) was measured as a function of the % NBU brine strength salinity. The IFT values for this system were fairly low, about 10^{-3} to 10^{-2} mN/m, even at these high salinity levels. The solubilization parameters for this system, calculated from the phase volume measurements, were fairly high. The approximate intersection of the solubilization parameters for the oil and water (about 15 mL/mL$_{surf}$) coincided with the lowest IFT value measured.

Figure 4 shows a plot of the calculated solubilization parameters as a function of salinity with the total surfactant concentration varied from 1 to 2 wt%. This plot indicated a shift of the salinity range as a function of the total surfactant concentration. Prior literature studies on the effect of concentration on IFT measurements showed that an optimum surfactant concentration was necessary to achieve a fairly low IFT value, at a fixed salinity.[61] Too low or too high a concentration yielded higher IFT's, indicating a shift in the optimal salinity range as a function of concentration. Limited screening at 0.5 and 4 wt% supported this trend. A coreflood displacement experiment was conducted using 0.5 wt% S-2 surfactant at about 140% NBU brine strength. This

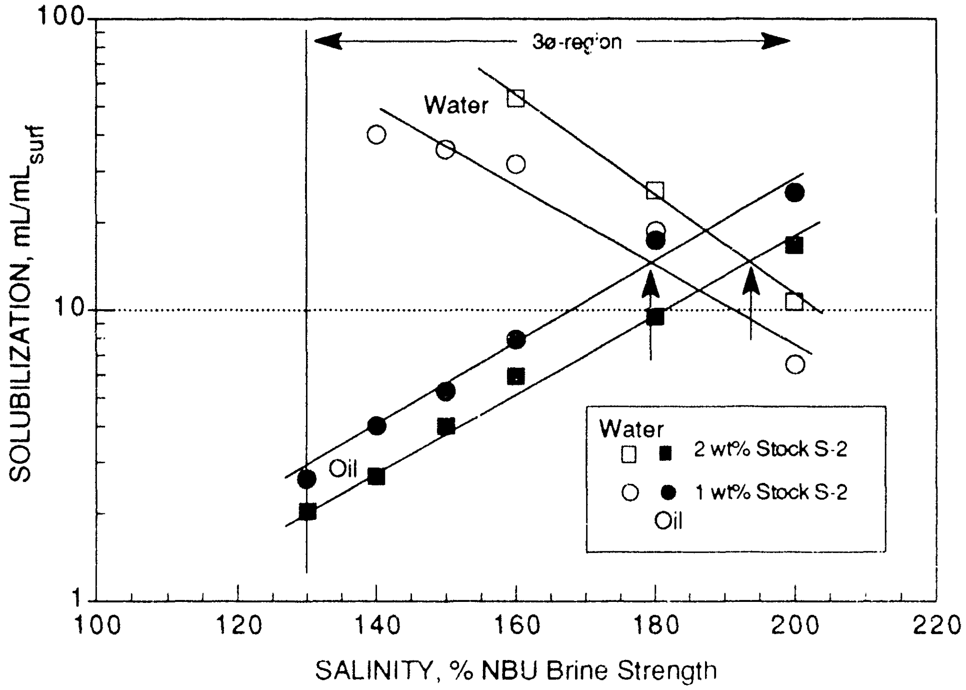


FIGURE 4. - Effect of total surfactant concentration on the phase behavior of the S-2 surfactant with NBU crude oil at 50 °C.

experiment was conducted at the lower salinity range to account for the lower total surfactant concentration. Details of this experiment are presented in a later section.

Effect of Proportion of Different Surfactant Types

The results from the previous section indicate that the S-2 surfactant has a fairly good salinity tolerance. This is particularly true when the favorable salinity range occurred around 140 to 180% of NBU brine strength. Several ways of shifting this salinity range were investigated. Several surfactant combinations with S-2 were tested to determine the effect of different surfactant proportion (sulfonate to sulfate ratio) on the phase behavior and interfacial tension properties of the overall system. The combinations using the S-2 and the other surfactants were tested in order to facilitate a shift the three-phase window closer to 100% NBU brine strength at 50 °C. The addition of the other surfactants to S-2 altered the proportion of the sulfonate and sulfate in the overall formulation, resulting in favorable salinity tolerance closer to Burbank conditions.

The first combination tested was the stock S-2 surfactant with the addition of the stock S-3 surfactant. The S-3 surfactant is a high-molecular-weight (≈ 500) alkyl aryl sulfonate surfactant. Results of the study are presented in figures 5 and 6. Figure 5 shows a plot of the calculated solubilization parameters and the interfacial tension as a function of the sulfate component in the

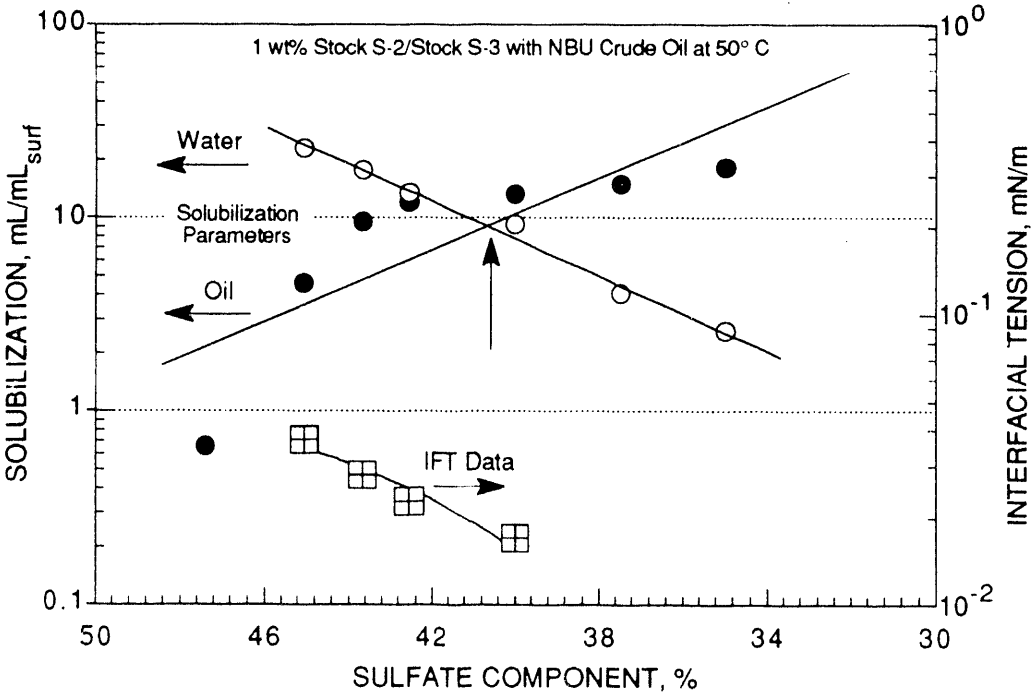


FIGURE 5. - Effect of proportion of secondary surfactant component on the phase behavior and IFT of the S-2/S-3 surfactant system with NBU crude oil at 50 °C

mixture. The results of the study showed the formation of a three-phase region at a fixed proportion of the two surfactants (38 to 46% sulfate component) at 100% NBU strength. The IFT values measured were fairly low ($<10^{-2}$ mN/m for non-equilibrated systems) but higher compared to the S-2 surfactant alone at the higher salinity range. The slight drop in solubilization parameter (about 8 mL/mL_{surf} at optimal conditions) supported the increase in IFT values between the aqueous phase and the oil. The alcohol concentration of the stock S-3 (> 6 wt%) may have suppressed the reduction in IFT values for this mixture. A number of oil recovery experiments using this surfactant mixture are described in later sections of this report.

Figure 6 shows a plot of the relationship of the formation of the multiphase region boundary as a function of sulfate component, salinity and total surfactant concentration. The results indicated a shift to lower salinity range tolerance with a decrease in total surfactant concentration. The results also showed that at a fixed salinity (i.e. 100% NBU brine strength) the sulfonate/sulfate proportion range that yielded multiphase behavior decreased as a function of total surfactant concentration. The interdependence of surfactant type proportion and total concentration is very important because in terms of application design, the "candidate system" needs to be formulated in such a way that the component proportions do not drastically change (as insensitive to total surfactant concentration as possible) during the progression of the flood. Component partitioning should be kept to a minimum in order to maintain the integrity of the chemical slug.

Another chemical system tested was the combination of the stock S-2 surfactant with the stock S-4 surfactant. The S-4 surfactant is a low molecular weight (≈ 360) alkyl aryl sulfonate

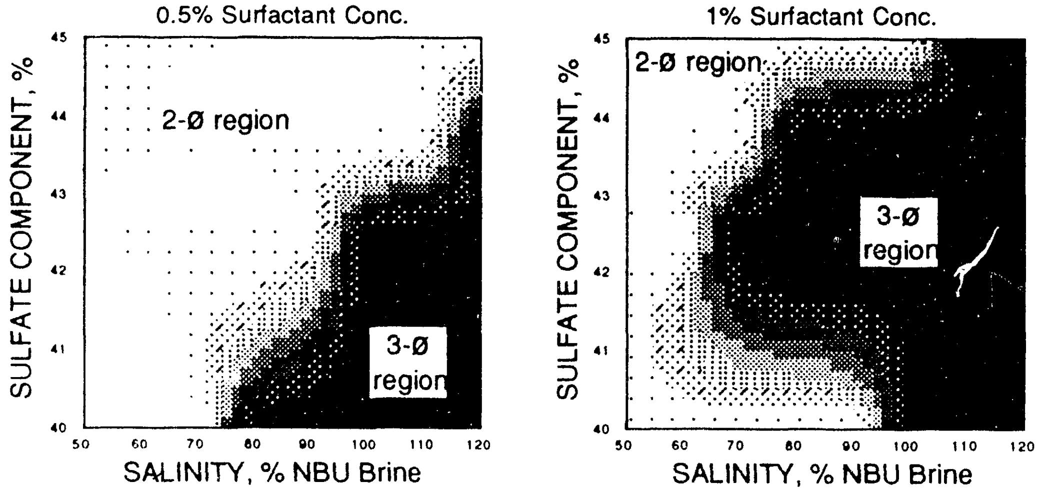


FIGURE 6. - Effect of total surfactant concentration on the dependence of phase behavior on component proportion and salinity for the S-2/S-3 surfactant system with NBU crude oil at 50 °C.

surfactant. Results of the study are presented in figures 7 thru 10. Figure 7 shows a plot of the calculated solubilization parameters and the interfacial tension as a function of the sulfate component in the mixture at 50 °C and 100% NBU brine strength. The results showed the formation of a three-phase region at various proportions of the two surfactants (15 to 40% sulfate component) at 100% NBU strength. The IFT values measured for the equilibrated solutions were fairly low ($<10^{-2}$ mN/m) but still slightly higher compared to the S-2 surfactant alone at the higher salinity range. The solubilization parameter (about 5 mL/mL$_{surf}$ at optimal conditions) was also considerably lower than that using the S-2 system alone. In both the S-3 and S-4 cases, the higher alcohol concentration of these stock surfactants may have suppressed the reduction in IFT values. Several oil recovery experiments were performed using different amounts of S-4 in the surfactant formulation. Oil recovery, however, declined with added S-4, as described in later sections of this report.

Figure 8 shows a plot of the effect of total surfactant concentration on calculated solubilization parameter as a function of the sulfate component in the mixture. The results indicated a slight shift in the sulfate component needed in order to maintain the phase behavior under optimal conditions. More of the sulfate component was needed to maintain favorable

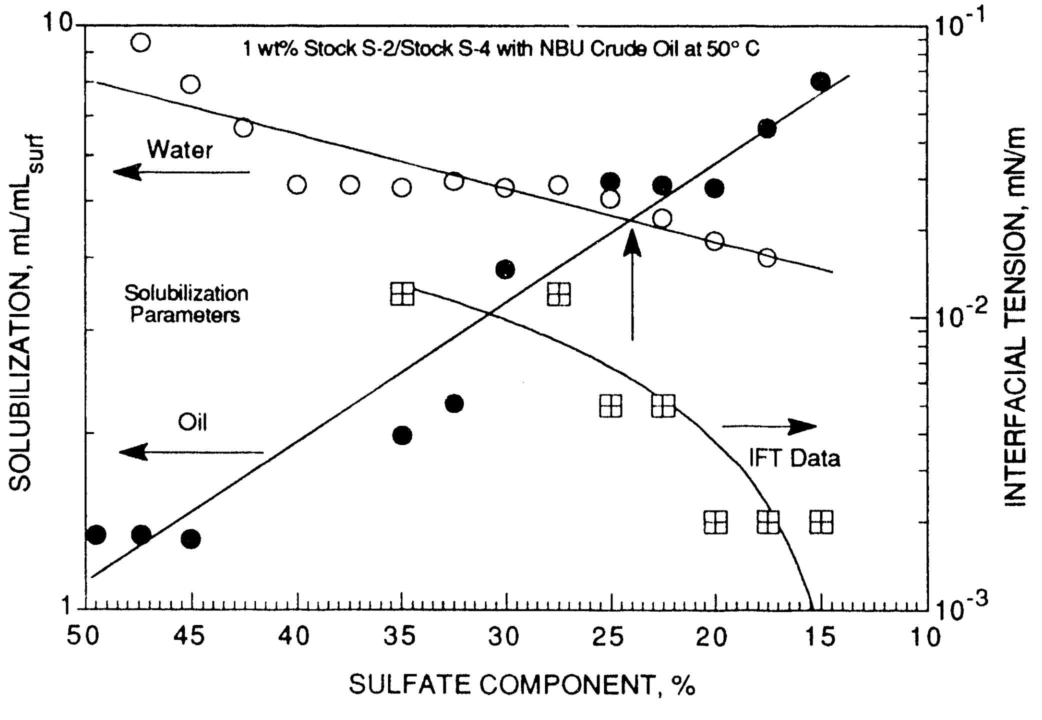


FIGURE 7. - Effect of proportion of secondary surfactant component on the phase behavior and IFT for the S-2/S-4 surfactant system with NBU crude oil at 50 °C.

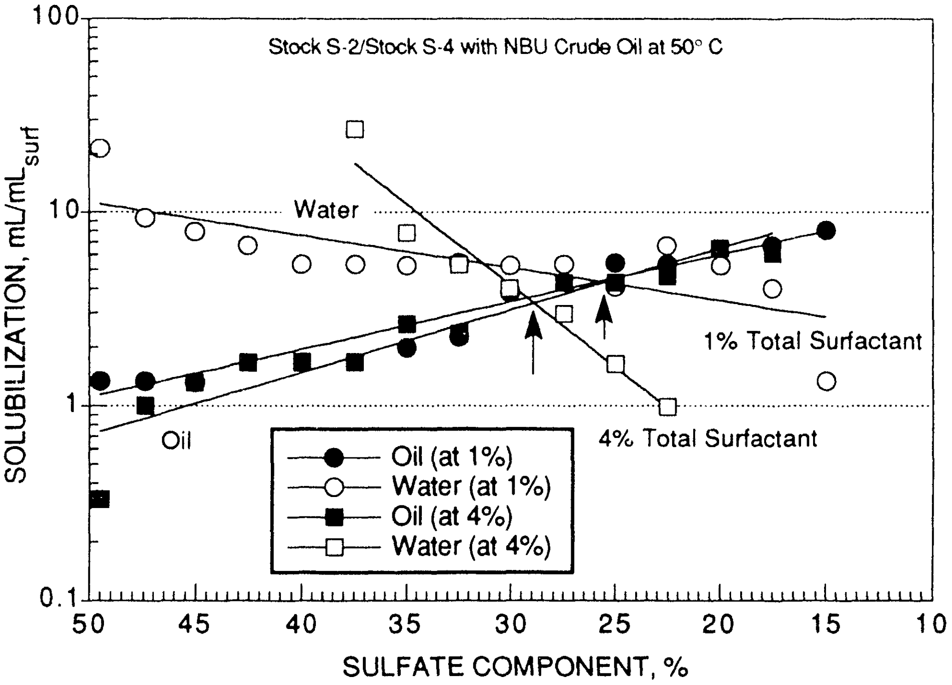


FIGURE 8. - Effect of total concentration and proportion of secondary surfactant component on the phase behavior of the S-2/S-4 surfactant system with NBU crude oil at 50 °C.

conditions as the total surfactant concentration increased. This trend agreed with previous results that indicated a shift in salinity range as a function of increase in surfactant concentration. A slight decrease in solubilization parameter was also indicated. Comparing the results using the S-3 and S-4 surfactants in figure 9, the molecular weight of the surfactant had a significant effect on the phase behavior of the overall system. This is in line with previous observations that higher molecular weights favor a reduction in IFT and an improvement in solubilization parameter, up to a certain limit.

Figure 10 shows a plot of the multiphase region as a function of sulfate component proportion and total surfactant concentration. These results indicated a "shrinking" of the multiphase boundary with an increase in total surfactant concentration. At a fixed surfactant proportion, the three phase boundary decreased as a function of increasing total surfactant concentration. In terms of application design parameters, a range of surfactant concentrations that yield fairly wide multiphase windows will be necessary to maintain favorable conditions. The selected surfactant concentration injected must be appropriate to yield a fairly broad multiphase region over the range of component proportions. Component partitioning should also be kept to a minimum in order to maintain favorable phase behavior conditions.

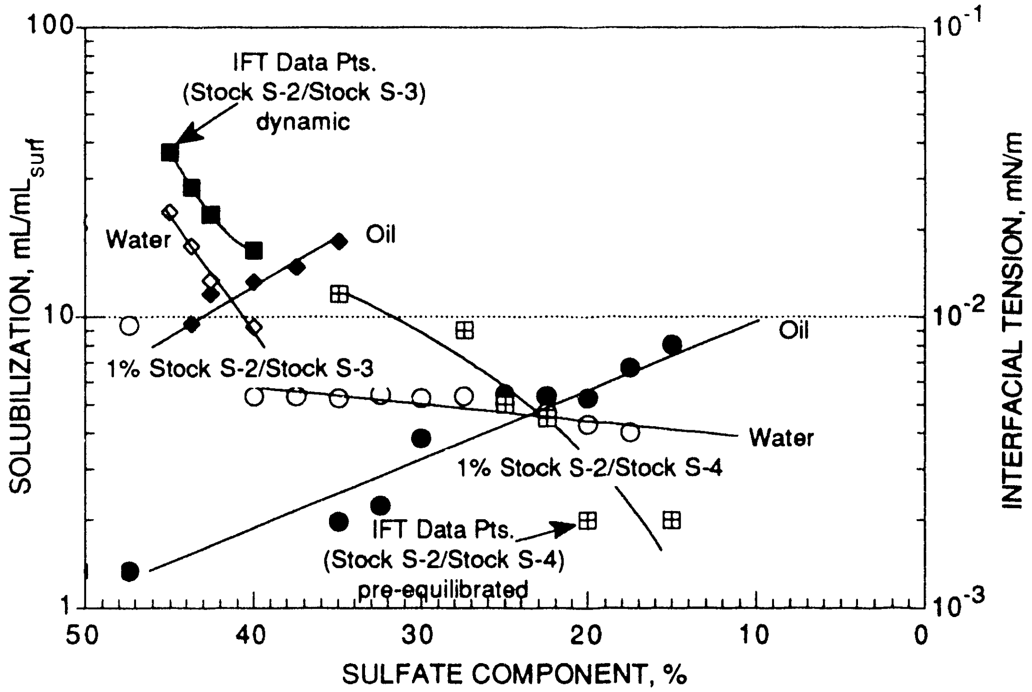


FIGURE 9. - Comparison of behavior of S-2/S-3 system with S-2/S-4 system.

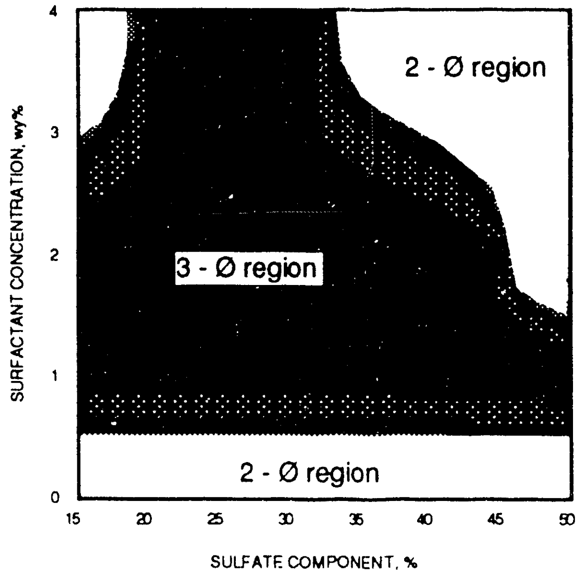


FIGURE 10. - Effect of total surfactant concentration and component proportion on phase behavior of S-2/S-4 surfactant system.

Similar phase behavior combination studies were conducted using the S-2 surfactant with the stock S-1 surfactant, with limited success. The S-1 surfactant in this case is a mid-molecular weight (≈ 415) alkyl aryl sulfonate surfactant. Severe phase behavior conditions, characterized by surfactant precipitation, were encountered and only a limited range of component proportions tested yielded any acceptable phase behavior. The cosolvent present in the S-1 surfactant may have been the reason for this difference in behavior observed. This behavior did not conform with the trends observed for the S-2/S-3 and S-2/S-4 systems.

In summary, the results from the study indicated that the salinity range and total surfactant concentration affected the behavior of the overall system. The shift in phase behavior due to salinity has been fairly well known, i.e. transition from different Winsor-type phase behaviors.[50] The dependence of the optimal salinity range of the chemical system with surfactant concentration was observed. Higher surfactant concentration resulted in the shift of optimal salinity to a higher range. The proportions and type of surfactants in the chemical formulation was also observed to have a significant impact on the behavior of these systems. At fixed salinities, a decrease in the molecular weight of the primary component resulted in a decrease in the solubilization parameters of the formulation with a corresponding increase in IFT values. The range of proportions of (alkyl aryl) sulfonate/(ethoxylated) sulfate components that yielded multiphase behavior also decreased as a function of the surfactant concentration. Less amount of the ethoxylated sulfate component was needed at low total surfactant concentrations, depending on the target salinity range.

Effect of Alcohol Concentration

The presence of alcohol in surfactant systems has been fairly well accepted as favorable for enhancing solution solubility but detrimental on the IFT and solubilization capacity of the overall system. Conventional chemical systems containing low molecular weight alcohols tend to degrade in effectiveness primarily because of the chromatographic separation of these alcohols from the surfactant system. The concern for the presence of alcohol is also true when comparing the stock S-2 with the direct combination of S-3/S-14 surfactant. The comparison between the two surfactant system was made based on information from the manufacturer that the stock S-2 surfactant was a preformulated mixture of the S-3 and S-14 surfactants. The phase behavior of the S-3/S-14 is somewhat dissimilar with what the S-2 surfactant exhibited, under the conditions tested. The IFT values ranged from as high as 1 mN/m down to 10^{-2} mN/m at 100% North Burbank Unit salinity, depending on the proportions of the two components. The results from these studies as shown in figure 11 were somewhat different compared to the results of the S-2 surfactant presented in figure 3. The behavior difference may be attributed to the difference in alcohol concentrations in the stock samples. The amount of alcohol (> 6 wt%) in the stock S-3 and

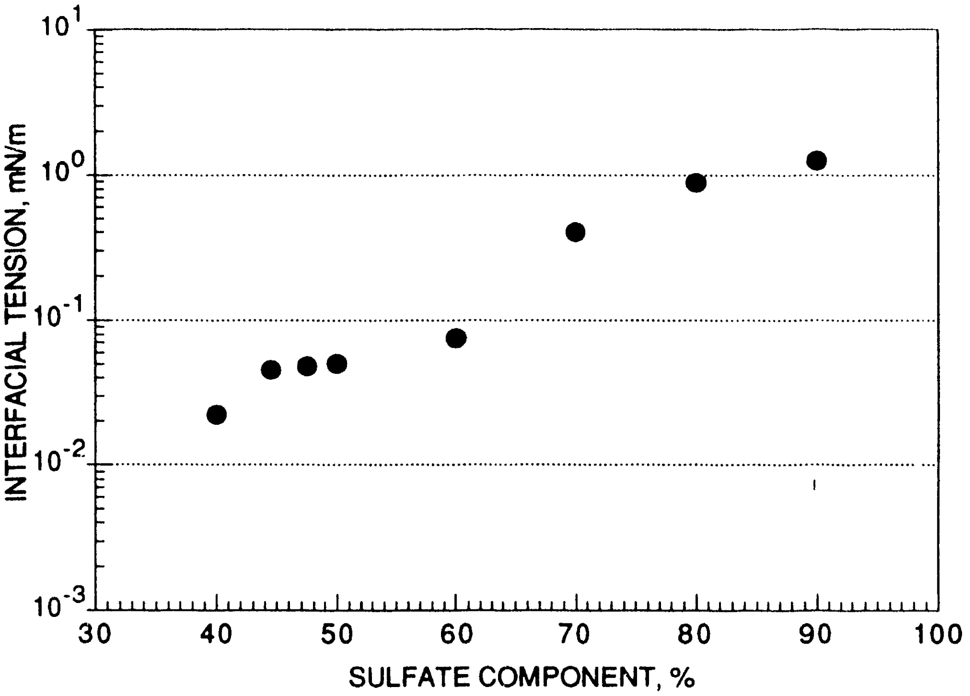


FIGURE 11. - Change in IFT as a function of ethoxylated sulfate component in the S-3/S-14 surfactant system with NBU crude oil at 50 °C.

in stock S-14 surfactant may have shifted the phase behavior of the overall system. This amount of alcohol yielded about 0.12 wt% alcohol in a 1 wt% S-3/S-14 system, while the 1 wt% S-2 system contained about 0.04 wt% alcohol.

A batch of the S-3/S-14 system was also prepared, such that the total alcohol concentration was comparable to the stock S-2 sample. The results are presented in figure 12. This figure shows a plot of the comparison of the IFT values measured using the stock S-2 system and the S-3*/S-14* system. The IFT and phase behavior measurements using this "reformulated" system

(S-3*/S-14*) were comparable to the results using the S-2 stock sample. The IFT values using the S-3*/S-14* and the S-2 samples ranged from 10^{-3} to 10^{-2} mN/m at the salinity ranged tested.

Effect of Other Surfactant Additives

The combination of other surfactant types was also tested. One particular system tested was the S-2/S-7 system. The S-7 surfactant is a straight chain alkyl aryl sulfonate (C_{13-14}), with a MW of about 500. These results can be directly compared with the results using the stock S-3 surfactant (a branched long chain alkyl aryl sulfonate of similar MW) added to the S-2 system. The results of this study are presented in figure 13. Direct comparison of the S-2/S-7 system with

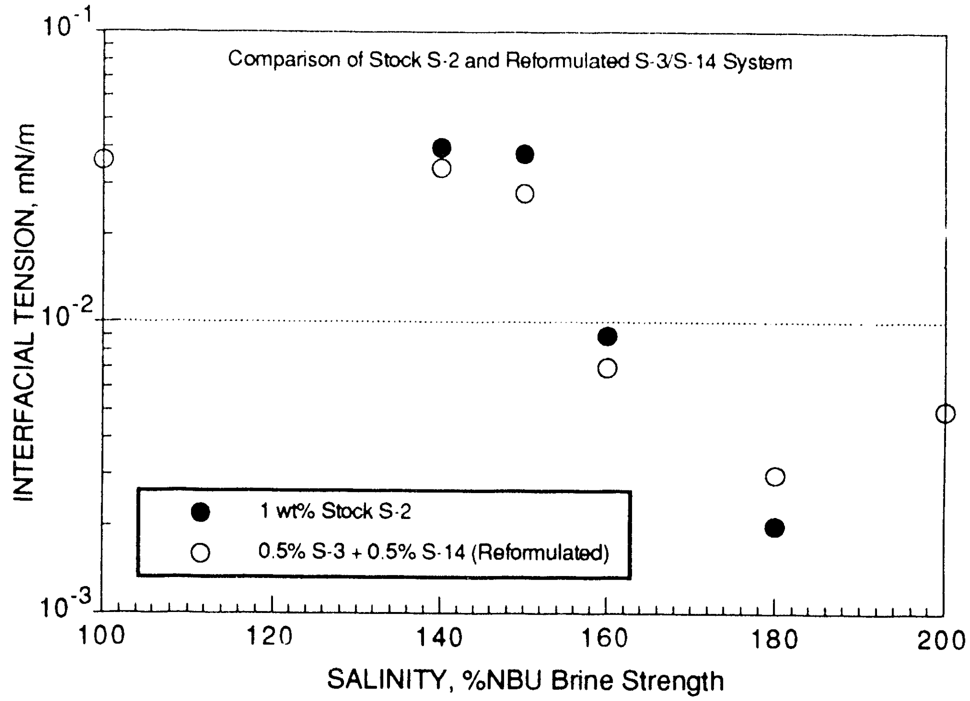


FIGURE 12. - Comparison of the IFT measurements for the S-2 with the S-3*/S-14* surfactant system with NBU crude oil at 50 °C.

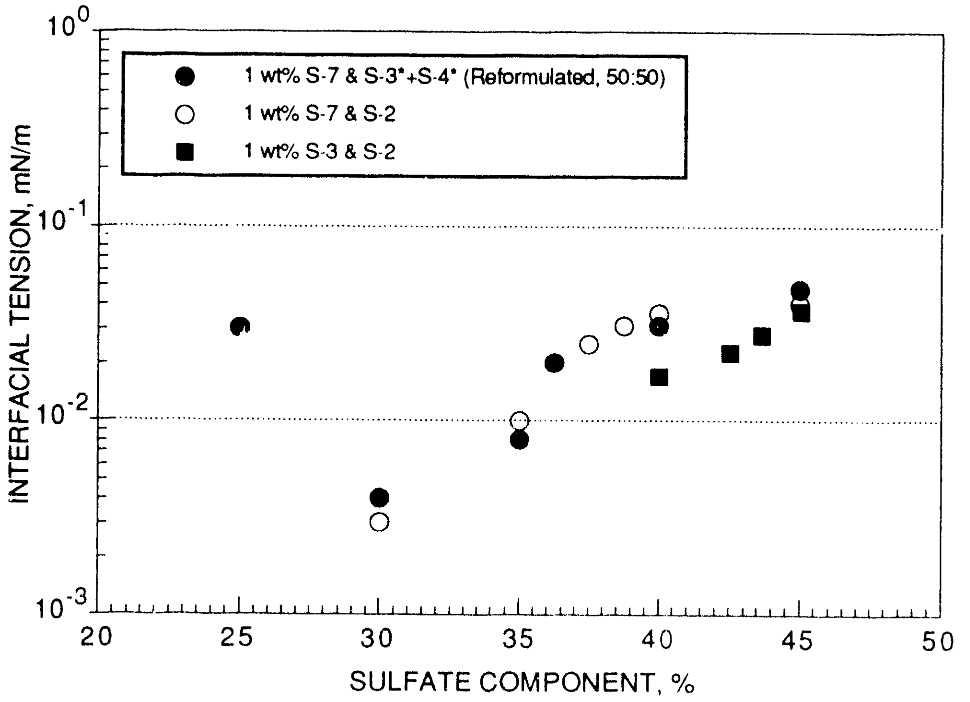


FIGURE 13. - Effect of surfactant chain length structure on the measured IFTs of different surfactant systems with NBU crude oil at 50 °C.

the S-2/S-3 system can only be made based on the amount of the sulfate component needed to maintain favorable conditions. The approximate IFT minima for the S-2/S-3 system occurred at 40% sulfate component while a similar minima occurred at about 30% sulfate component for the S-2/S-7 system. This difference in sulfate component requirement can be attributed to the longer chain length in the S-3 surfactant compared to the S-7 surfactant. The longer chain in the S-3 surfactant resulted in a qualitatively reduction in the overall solubility and salinity tolerance of the system. A higher sulfate component proportion was then required in order to shift the overall system back to favorable conditions. In the case of the S-3 surfactant, the hydrocarbon chain branching was not effective in counterbalancing the effect of the longer length to maintain a similar degree of solubility or salinity tolerance.

The IFT values for these two systems cannot be directly compared because the S-2/S-3 and S-2/S-7 measurements were conducted on equilibrated and non-equilibrated solutions, respectively. This disparity resulted in IFT values for the S-2/S-7 system that were lower than the values measured for the S-2/S-3 system. Compared to the S-2/S-4 system, these IFT values were similar in range.

Figure 14 shows a comparison of measured IFT values for the S-2/S-7 system with other surfactant systems. The results show that the range of IFT values measured for the S-2/S-7

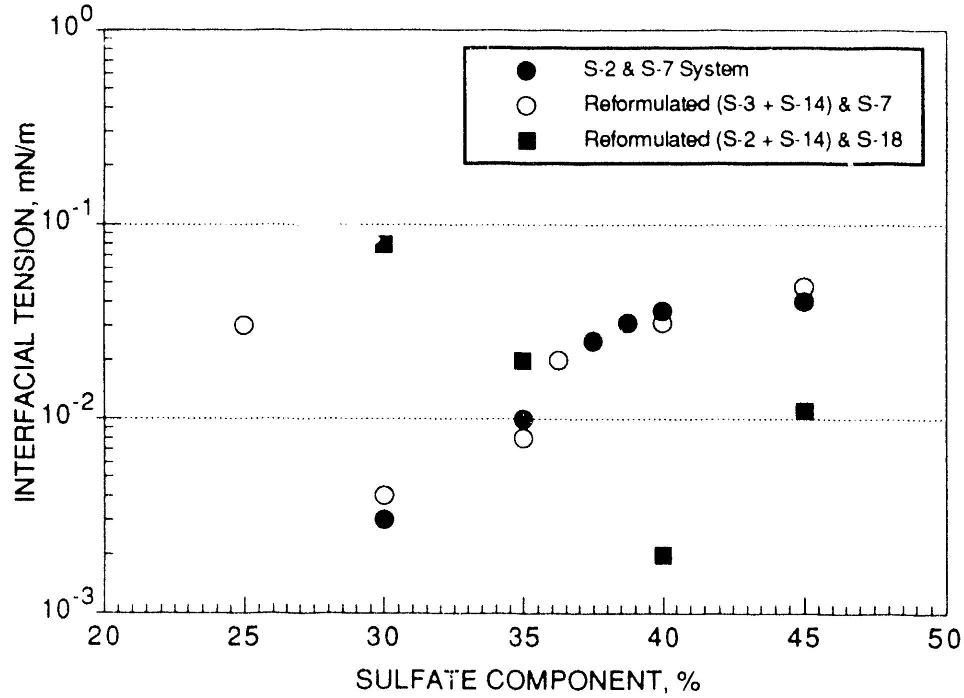


FIGURE 14 - Comparison of the IFTs of different surfactant combinations with NBU crude oil at 50 °C and NBU salinity.

system were comparable with the IFT values using the S-3*/S-14*/S-7 system, as a function of sulfate component in the system. The S-3*/S-14* behaved similarly to that of the stock S-2 system, as shown in figures 12 and 14. Comparison of the S-3*/S-14*/S-7 and S-3*/S-14*/S-18 systems showed a marked difference in the range of sulfate component where relatively low IFT values were measured. The S-18 is a branched ethoxylated sulfonate (M.W. ≈ 434), compared to the straight-chain alkyl aryl sulfonate S-7 surfactant. The location of the approximate IFT minima for the S-3*/S-14*/S-18 system indicated a higher sulfate requirement need to maintain fairly low IFT values, at a fixed salinity of 100% NBU brine strength. In this case, 40% sulfate component compared to about 30% for the S-3*/S-14*/S-18 and S-3*/S-14*/S-7 (same with S-2/S-7 system) systems, respectively. This meant that less amount of the S-18 surfactant would have to be added to the S-2 or the S-3*/S-14* system. The ethoxylation in the S-18 system did help limit the need to add this component to shift the favorable range of conditions closer to the targeted Burbank conditions. The lower molecular weight may have had some effect on the range of IFT values measured.

Development of Surfactant Screening Methods

Several screening methods were tested in order to facilitate ease of identifying candidate surfactant systems. These methods included the use of phase behavior (including salinity scans and PIT measurements), IFT measurements, titration calorimetry, and HLB gradient approach.

Correlation of Experimental Parameters

Time-consuming phase behavior studies and IFT measurements have become the standard means of identifying candidate surfactant systems for further testing. Other experimental means of screening can be developed to help identify other potential chemical formulations. An example of this method is the phase inversion temperature measurement. Conventionally, this method has been primarily applied for non-ionic surfactants.[48,49] But fast screening methods such as this can also be used to correlate some information obtained using the conventional IFT and phase behavior (salinity scan) studies.

An example screening study would be the S-5/S-8 surfactant system. The S-5 is a straight-chain alkyl aryl sulfonate (C_{8-10}), while the S-8 is an ethoxylated carboxylate surfactant (C_{13}). This system was fairly well studied in previous work.[24] Although this system is not a candidate for the targeted Burbank conditions, several correlations may be developed from the results of the screening studies that were conducted. Figures 15 through 18 show the results of the different experimental screenings conducted with this system. Figure 15 shows a plot of the electrical

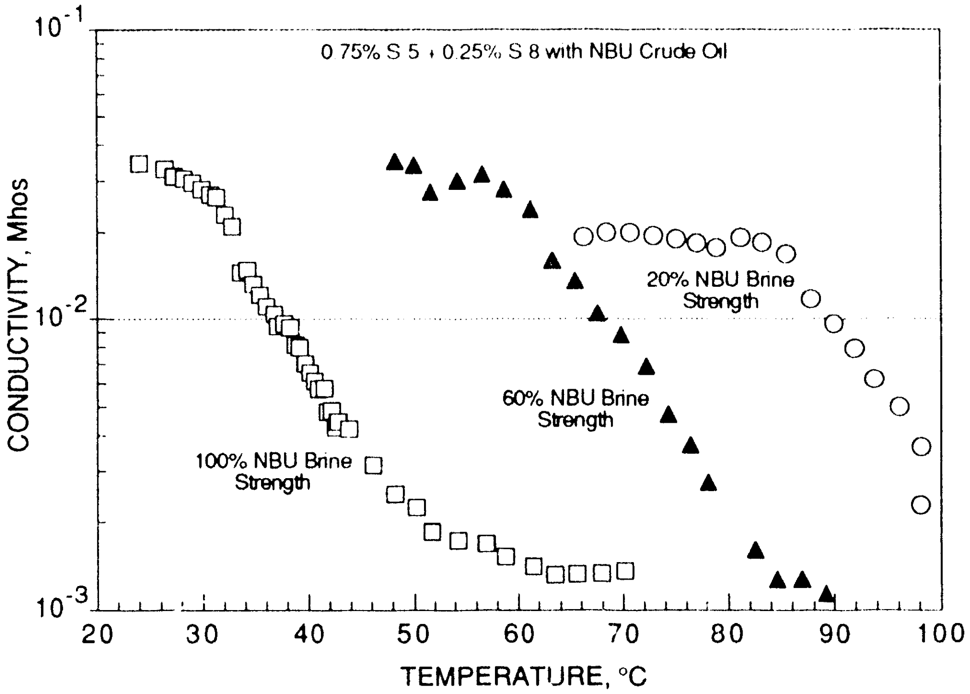


FIGURE 15. - Effect of salinity on solution electrical conductivity as a function of the temperature for the S-5/S-8 surfactant system

conductivity of the different solutions tested (as a function of % NBU brine strength) as a function of temperature, at a fixed S-5/S-8 proportion. Bottle test of this mixture shows a fairly clear solution up to 100% NBU brine strength. The target being that of the NBU brine salinity, the electrical conductivity trend appeared to drop significantly at about 25-30 °C. The other solution PITs were estimated to be between 45-60 °C and 80-90 °C, for the 60% and 20% NBU brine strength, respectively. At 100% NBU brine strength, the PIT results seem to indicate favorable behavior at the lower 30 °C conditions.

Figure 16 shows the trend of the IFT values measured for this system at 50 °C. The approximate IFT minima occurred close to the 40% NBU brine strength region. This seemed to correspond with the PIT behavior of the 60% brine strength salinity solution at about 50 °C. Figure 17 shows a plot of the IFT values measured for this system as a function of the solution temperature, at a fixed salinity of 100% NBU brine strength. The IFT trend clearly indicated an increasing trend with temperature. This observation corresponded with the estimated PIT for the 100% NBU brine strength solution of about 25-30 °C Figure 18 shows a 3-dimensional (3-D) map of the relationship of the IFT measured with respect to salinity and solution temperature. The trend indicated favorable conditions for the system at lower temperatures, about 25-30 °C and at the

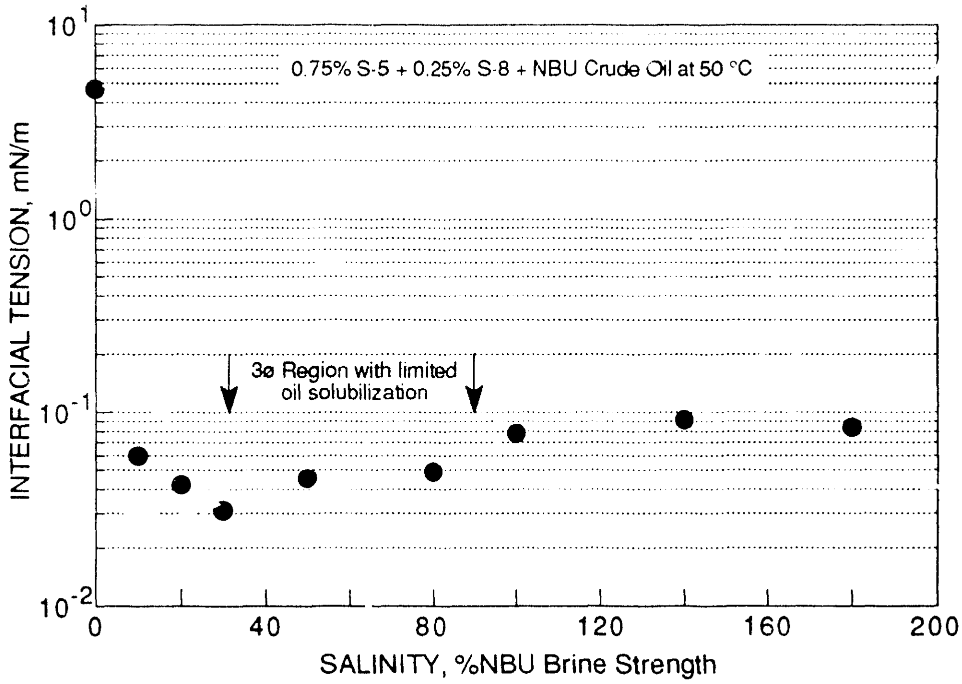


FIGURE 16. - Effect of salinity on measured IFTs for the S-5/S-8 surfactant system with NBU crude oil at 50 °C.

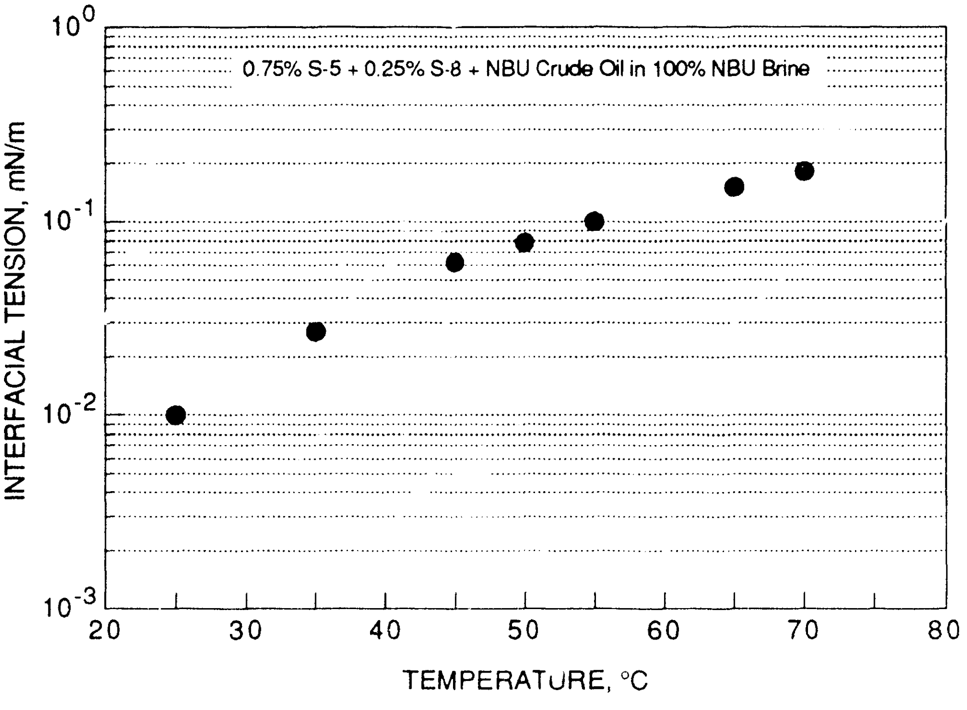


FIGURE 17. - Effect of temperature on measured IFTs for the S-5/S-8 surfactant system at 100% NBU brine strength.

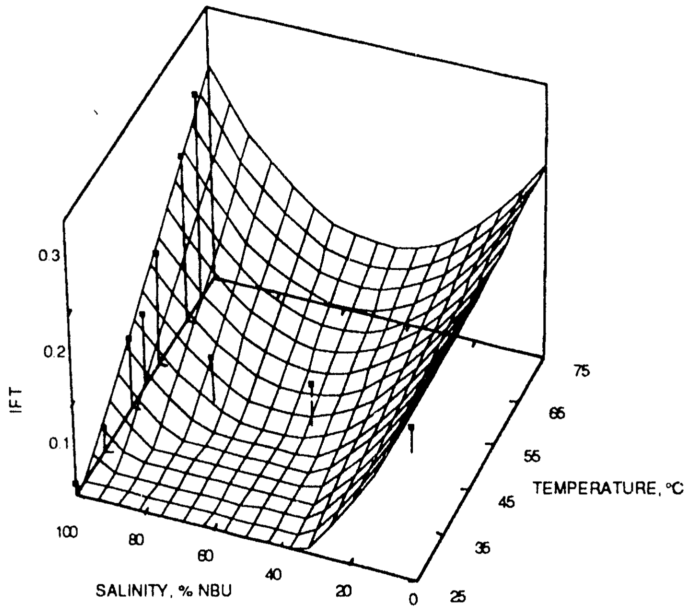


FIGURE 18. - Effect of temperature and salinity on measured IFTs for the S-5/S-8 surfactant system.

salinity ranges between 80 to 100% NBU brine strength salinity. Operating under these conditions, this surfactant system may be a candidate system for improved oil recovery.

This example illustrates the possibility of using fast screening methods such as PIT measurements to determine favorable regions of operating conditions for different surfactant systems. This screening method can be used prior to conducting the conventional time-consuming screening using IFT and phase behavior measurements. Although this method may be relatively faster, precaution still needs to be taken because there are anionic systems that exhibit complicated phase behavior manifestations that may not directly follow the patterns just described. For such complicated system, IFT measurements and phase behavior (salinity scans) still appear to be the primary screening methods.

Salinity Gradient Inversion and Titration Calorimetry

The PIT apparatus was also used for a different type of screening. The apparatus, which was originally designed to determine the solution's transition temperature, to measure the dynamic electrical conductivity of the solution as a function of a salinity gradient at a fixed temperature. This approach was used to determine if this type of screening method was applicable in identifying phase boundaries (i.e. phase transitions from type II(-) to type III to type II (+))[50] in well-defined chemical systems. The combination of the modified PIT method with titration calorimetry has been used by other researchers $^{51-53}$ as means of determining solution phase behavior.

For this study, the inversion temperature (PIT) and salinity gradient phase inversion experiments were conducted on a well-studied surfactant system, the 5 wt% S-17 + 3 wt% IBA. This was the original chemical system formulated for use on the North Burbank Pilot Test.$^{56-57}$ The purpose of these experiments was to observe the change in solution conductivity and determine any relationship that may exist with respect to the behavior that was exhibited in the phase tubes. The width of the three-phase region for this surfactant system with the two oils has been determined by previous researchers and was reconfirmed during this study. The salinity gradient tests involved monitoring the electrical conductivity of the solution as a function of salinity, at a fixed temperature of 50 °C. Results of these tests are presented in figure 19. The results from the salinity gradient tests indicated that the peak in solution conductivity appears to coincide with the estimated mid-point of the three-phase region of this surfactant system. No indications of phase boundaries were observed.

Calorimetric experiments were also conducted for the surfactant/hydrocarbon systems. Smith et al.$^{51-53}$ reported using titration calorimetry to detect phase boundaries in systems

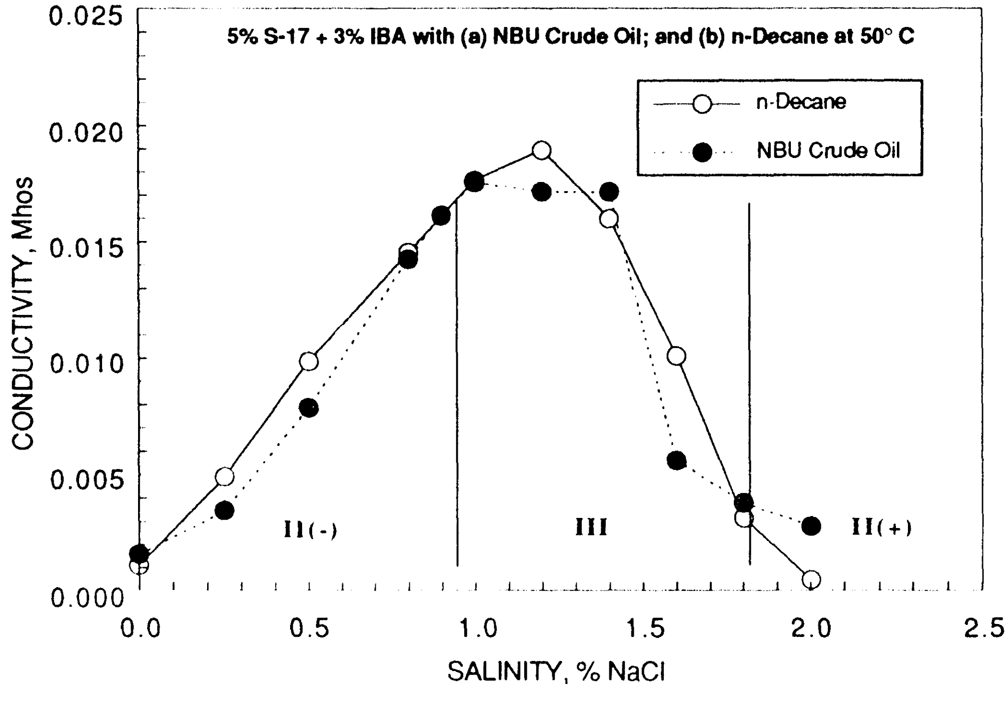


FIGURE 19. - Solution electrical conductivity as a function of salinity with different oils at 50 °C

containing nonionic surfactants. Titration calorimetry on an anionic surfactant system has been carried out to determine whether this technique can be used to detect the conditions at which multiphase regions begin to form for ionic surfactants. The heats of mixing were measured for different experiments: (1) the decane was titrated into the surfactant solution at brine salinities of 0.25, 1.25 and 2 % NaCl and (2) the surfactant solution at the different salinities was titrated into decane. The results of these titrations are shown in figures 20 and 21. The measured heats were endothermic. In figure 20, the measured heat was plotted as a function of the oil/water ratio with the amount of oil starting at zero. This oil/water ratio increased during the course of the titration as more decane was titrated into the vessel. In figure 21, the heat was plotted as a function of water/oil ratio with the amount of water startup at zero. A change in shape was observed for each of the curves this slope change occurred at the highest oil/water ratio for the solution closest to optimal salinity of the system. If the heat released during the formation of a (i.e. solubilization) type III region is different than mixing excess surfactant and oil (including dilution of the micellar region) a change in slope should be observed. Increased solubilization should move the position of the slope change to higher oil/water ratio values. This change appeared to be small in magnitude and further investigations would be required to determine if quantitative information can be obtained from these investigations. Little experimental differences were observed titrating surfactant solution into oil as shown in figure 21. If solubilization occurred, the heat affects were hidden by the dilution of the aqueous phase. Changes in slope were also observed in measuring

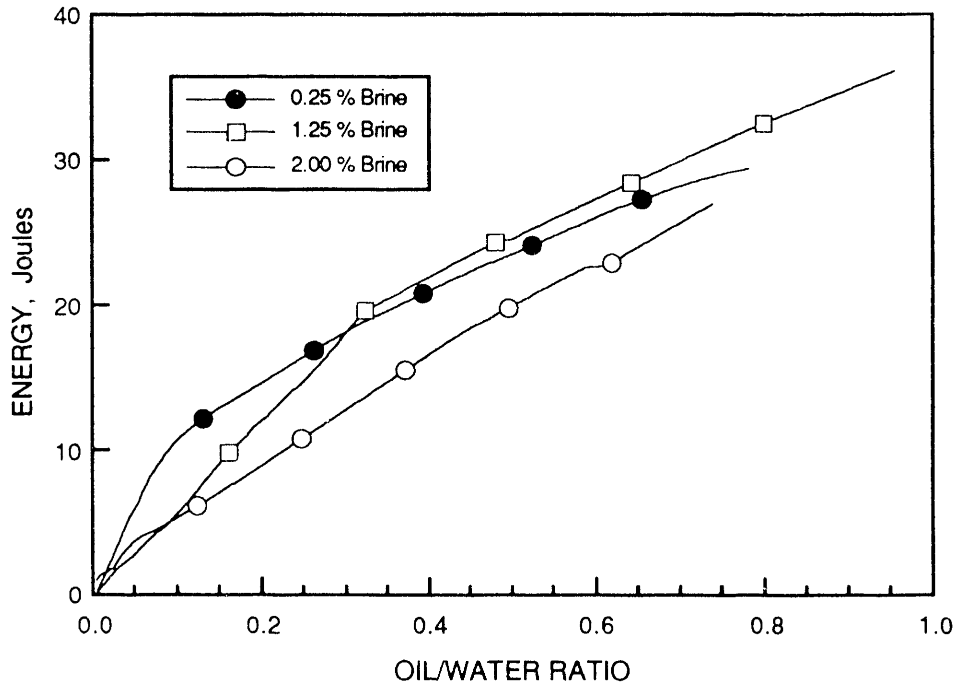


FIGURE 20. - Heat of mixing measured in titration of decane into 5 wt% TRS 10-410 + 3 wt% IBA surfactant solution at 50 °C.

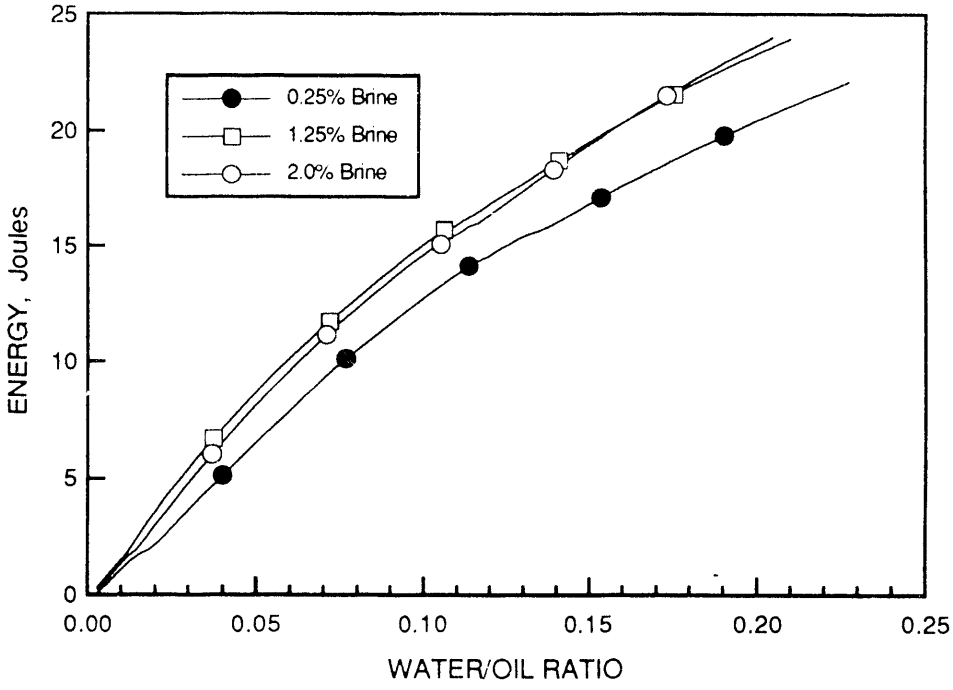


FIGURE 21. - Heat of mixing measured in titration of 5 wt% TRS 10-410 + 3 wt% IBA surfactant solution into decane at 50 °C.

heat released during a salinity scan (figure 22). The injection at 1.75% NaCl occurred slightly above the optimal salinity region.

The final solutions from these (and all) calorimetric runs were placed in tightly stoppered bottles and allowed to equilibrate. After equilibration, the formulations with 0.25% brine was type II(-) (two phase with surfactant in the lower aqueous phase), the formulations at 1.25% brine formed three phase systems, and formulations at 2.0% brine was type II(+).[50] The observed phase behavior agreed with that of previous observations.[56-57]

These titration experiments required considerable skill and sophisticated equipment to obtain significant information. The subtle heat effects that were observed suggest that use of this technique as a screening tool may be impractical. At best, further evaluation is required to interpret observed heat effects in these mixed phase systems.

A 1:1 mixture of distilled water/decane (as a control) and a 1:1 mixture of surfactant system (formulated with no salt) and decane were titrated with 25% NaCl brine. This experiment was designed to mimic a salinity scan. The results of this experiment are shown in figure 22. The dashed line in this figure denotes the blank experiment, which was essentially a dilution experiment of brine into decane without any surfactant added. The solid line shows the trend of the heat of mixing when the brine was added to the surfactant/decane mixture. The difference between these two experiments was striking. There was a bend in the heat of mixing curve that occurred at about 1.6% salinity. This salinity appeared to tie-in with the 1.5% salinity value where a maxima in the solution's electrical conductivity was measured using the modified PIT apparatus. The occurrence of both the inflection in the heat of mixing curve and the maxima in the electrical conductivity at around 1.5 to 1.6% NaCl seemed to correspond with the approximate optimal salinity of the surfactant solution. It was not clear what phenomenon was responsible for these experimental results. Similar results were also obtained using a series of brines of different salinities which were titrated with the surfactant solution. These results are not shown here.

In comparing these results with the results of Smith et al.[51-53], it was noted that the heat effects for the ionic surfactants were smaller than those previously reported for nonionic surfactants. Part of the heat generated or adsorbed in this study was accounted for by the dilution of the electrolyte. Some further manipulations of the data from these experiments were carried out, but the results appeared to be essentially negative. For the set of conditions and solutions tested, titration calorimetry was not helpful in defining the phase behavior of the systems of interest.

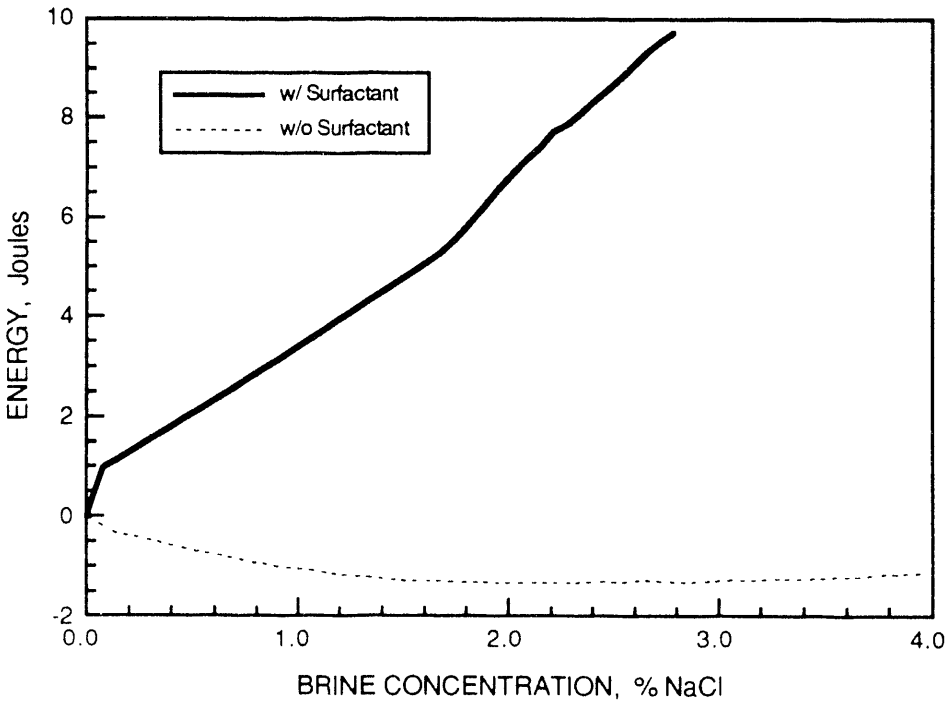


FIGURE 22. - Heat of mixing measured in simulated salinity scan at 50 °C for the 5 wt% TRS 10-410 + 3 wt% IBA surfactant system.

Chemical Gradient Approach

Another screening method used was the selective combination of primary, secondary, and tertiary surfactant mixtures. For this screening, two cosurfactants were added to a primary surfactant component. The primary surfactant selected had high oil solubilization and low IFT potential. The two other surfactants were selected based on the concept of balancing the effect of the secondary and tertiary surfactant component in maintaining the oil and water affinity of the overall chemical system, similar to an hydrophillic-lipophillic balance (HLB) gradient approach.[28]

For this approach, several surfactant mixtures were evaluated, including systems containing S-1 to S-7 surfactants as primary components. The secondary or tertiary components in the mixture included several ethoxylated sulfonates, ether sulfates, ethoxylated phenols, and ethoxylated nonyl phenols. Results of some of the observations from the preliminary screening of different binary and ternary combinations are presented in table 4. Results from these studies showed favorable phase behavior in bottle samples at the conditions tested. Additional tests, such as IFT and phase behavior measurements, were conducted on potential chemical systems. Some of these mixtures showed good solubilization and fairly low IFT values.

One candidate system contained the S-3 surfactant, an alkyl aryl sulfonate, and S-15, an ethoxylated sulfate, and one nonionic surfactant, S-12, an ethoxylated alcohol. IFT values of 10^{-3} mN/m were measured at 1 wt% total surfactant concentration with equal component weight mixtures of the three surfactants (1:1:1). This surfactant system was formulated with 100% NBU brine. This system was also used in a coreflood experiment for displacement efficiency comparison with previous selected systems because it exhibited favorable solubilization and low IFT values. A discussion of the results of this coreflood is presented in a later section. The overall conclusion regarding the coreflooding experiment was that it was disappointing. Only limited oil recovery was achieved using this system. A possible reason for the failure of this system to recover more oil was the relative proximity of the solubility limit of the S-3 component in the system. Additional solubility and phase scans showed that higher proportion of the S-3 component in the formulation resulted in significant phase separation. The results of these measurements are presented in figure 23. The figure shows that the (1:1:1) mixture that yielded the low IFT values was at the borderline of this solubility limit. Additional scans were conducted at lower component proportions to further map the phase boundaries of this system. Only a few component combinations have been found, and no significant solubilization was achieved using these combinations. This surfactant system appeared to have limited application under the conditions being tested. Oil recovery with this mixture was less effective than the S-2/S-3 surfactant system. These results are described in the oil recovery section of this report.

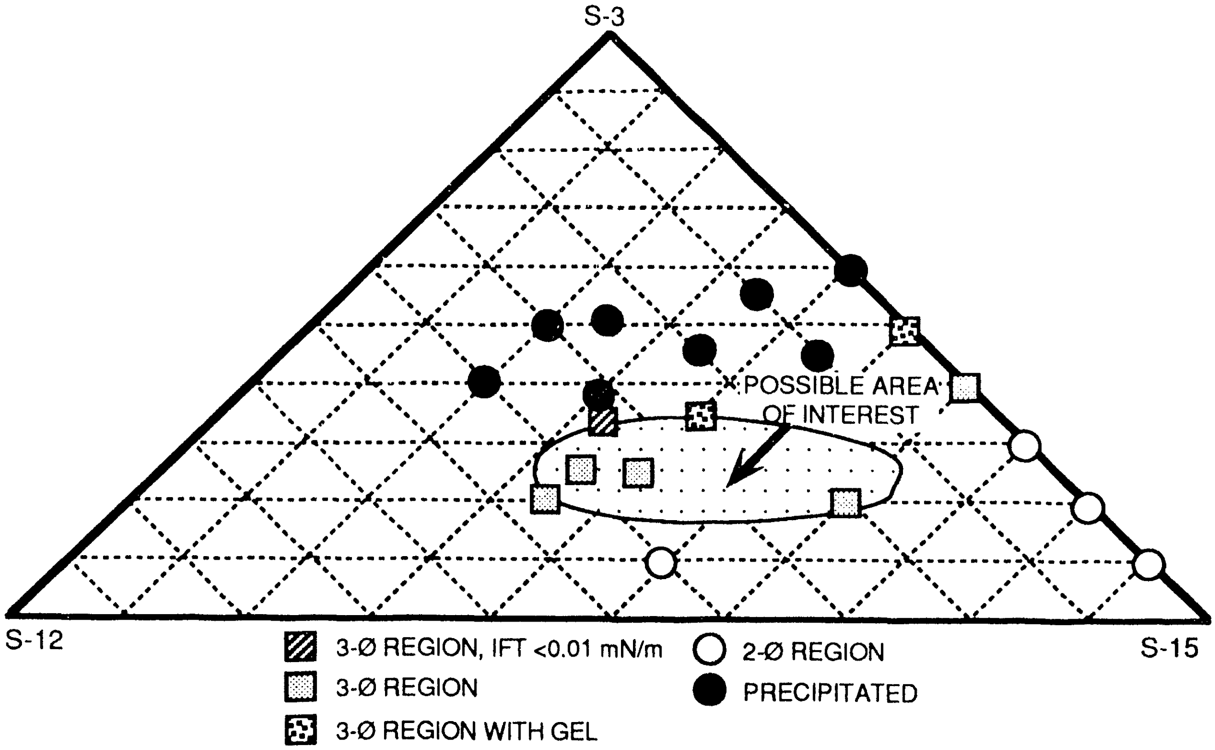


FIGURE 23. - Ternary diagram for the S-3/S-12/S-15 surfactant system with NBU crude oil at 50 °C.

Although the general results from this screening method were not favorable, the methodology still presented possibilities of different surfactant combinations that may prove to be applicable. The concept of identifying two surfactants that can synergistically balance the oil and water affinity of the primary surfactant and the overall chemical system is promising. Additional studies will be conducted in this area.

Summary of Mixed Surfactant Studies

Several mixed surfactant systems have been studied to evaluate their advantages over conventional chemical flooding systems. These systems were screened for possible combinations of surfactant components that jointly yield high oil recovery potential as well as improved adaptability to different ranges of salinity, divalent ion concentrations, and temperature. The effects of parameters such as (a) component substitution, (b) salinity, (c) ratio of components, (d) total surfactant concentration, and (e) surfactant type on the behavior of the overall surfactant system were studied. Combinations of different surfactants and types have been shown to exhibit different phase behavior patterns. Some of these patterns can be identified as a function of the structure, molecular weight (MW), and proportion of the different surfactant components.

The results showed that a trend can be observed, in terms of a qualitative dependence of the salinity tolerance on the molecular weight, surfactant type, and concentration of the surfactant components in the system. The ethoxylated sulfates were better than the ethoxylated sulfonates in improving the tolerance of the overall chemical system, with the primary component being a sulfonate-type surfactant. The results showed that for both cases when ethoxylated sulfonates and ethoxylated sulfates were added to a primary sulfonate surfactant system such as TRS 10-410, the MW and the branching-structure of these ethoxylated components affected the overall salinity tolerance of the surfactant mixture. Shorter hydrocarbon chain length and branching in the secondary ethoxylated surfactants favored improved solubility and salinity tolerance of the overall chemical system.

The total surfactant concentration was also a parameter that can significantly affect the performance of these mixed system. A shift in the range of salinity tolerance was observed as a function of the total surfactant concentration. As the total concentration increased, the favorable salinity region appeared to have slightly increased. This shift seemed to be in line with the results from prior studies of the dependence of IFTs measured on surfactant concentration, at a fixed salinity. The proportion of the different types of surfactants can also effectively adjust the region favorable salinity for a given surfactant system. Several studies on adjusting salinity tolerance showed that the proportion of the salinity-tolerant surfactant (i.e. ethoxylated sulfates) was critical to whether or not the overall system exhibited good phase behavior.

The MW and branching of the primary surfactant, in this case the non-ethoxylated or alkylaryl sulfonate component, also affected the phase behavior of the system. These results are comparable to previous studies that have shown that longer hydrocarbon chains in the surfactant molecule favors a reduction in interfacial tension. For the mixed surfactant systems, the longer chain lengths also favored good solubilization and low IFT values. The branching-structure of the primary surfactant also affected the behavior of these systems. The combined effect of the chain length and branching structure differences can alter the requirement of the overall system for salinity tolerant surfactants. The ethoxylation in the primary component was also found to be helpful in reducing the salinity-tolerant surfactant requirement and shifted the salinity range of the chemical system. The alcohol content of the surfactant solutions may have also affected the behavior of these mixed systems. The presence of the alcohol may have enhanced in the solubility of the mixture to some degree but may have had some negative effect on the IFT and oil solubilization potential. A reduction in the total alcohol concentration in the system may be necessary to maintain favorable phase behavior without significantly impacting the IFT capacity of the system.

Several screening methods were evaluated to help identify methods that can be used to screen other potential chemical formulations. One of these methods was the phase inversion temperature measurement. This method has been primarily applied for non-ionic surfactants.[48-49] But fast screening methods such as this can be used to help identify regions of operating conditions that may be of interest (i.e. temperature, salinity, oil type, surfactant type) as well as tie-in some information obtained using the conventional IFT and phase behavior (salinity scan) studies. Combinations of these screening methods can be used to determine conditions where particular chemical systems can be applied with a significant probability of success. One example was shown that illustrated the advantage of correlating the results of these combined methods.

Another combination of screening methods used was the salinity gradient phase inversion measurement and the titration calorimetry. The purpose of these experiments was to observe the changes in solution properties and determine any relationship that may exist with respect to the behavior that was exhibited in the phase tubes. A well-studied chemical system was used in these evaluations. The salinity gradient tests involved monitoring the electrical conductivity of the solution as a function of salinity, at a fixed temperature. The results from the salinity gradient tests indicated that the peak in solution conductivity appeared to coincide with the estimated mid-point of the three-phase region of this surfactant system. The phase boundary transitions (type II(-) to type III to type II(+)) were not directly observed using this method.

The titration calorimetry method involved the measurement of the heats of mixing for different experiments: (1) the oil was titrated into the surfactant solution at brine salinities, (2) the surfactant solution at the different salinities were titrated into oil and (3) an equal volume mixture (water-to-oil ratio equal to 1) of surfactant solution and oil was titrated with a highly saline brine, mimicking a salinity gradient mixing. Although no phase boundary transitions were observed using this method, one interesting observation was made that can be compared to the results from the salinity gradient phase inversion experiment. The salinity gradient titration experiment indicated a bend in the heat of mixing curve that occurred at about 1.6% salinity. This titration salinity seemed to correlate with the optimal salinity value (1.5% NaCl) identified using the previous gradient method and from phase tube studies. The time and effort involved in performing these experiments suggest that its use as a chemical screening tool for purposes of this work was limited. The observed heat effects were relatively small and the further evaluation was needed to interpret the results from a number of simultaneously occurring phenomena including solubilization, mixing, and dilution.

Coreflooding Experiments

Summary of Coreflooding Conditions

The results of coreflood experiments conducted using mixed surfactant systems with and without alkaline additives will be discussed in this section of the report. Table 5 lists the chemicals used during the various stages of the mixed surfactant corefloods (MS-CF), the alkaline/surfactant/polymer corefloods (ASP-CF), and the CT-monitored ASP floods (CT-CF). Surfactants and brines are identified in the chemical listing in table 2.

Table 6 summarizes initial core permeabilities, oil saturations after waterflood and chemical flood, and oil recovery efficiency as percent of oil remaining after the waterflood. Recovery efficiencies for these tests appear to be affected by a number of variables including surfactant slug composition, polymer concentration, and core permeability.

Surfactant Floods with Alkaline Additives

Effect of Core Permeability

Several coreflood experiments were conducted using a mixed surfactant system prepared with alkaline additives to recover Hepler crude oil. The surfactant mixture had previously been designed to provide low IFT values between the oil and Hepler brine containing alkaline chemicals.[62] Figure 24 shows dynamic IFT values for several different surfactant ratios and added alcohol. The formulation that was chosen for testing included 2% alcohol (2-butanol) to reduce solution turbidity. The alcohol did cause a slight increase in IFT value for this system. Hepler oil recovery efficiencies and residual oil saturations after chemical flooding are summarized in table 6.

The same surfactant system was used to test the recovery of NBU and Government Wells oil at low salinity conditions. The IFT values between the three oils and the surfactant system are listed in table 7. With Hepler and NBU oils, the IFT values declined with time; with Government Wells oil, the IFT values increased with time. Oil recovery efficiencies and final residual oil saturations can also be found in table 6.

TABLE 5. - Description of surfactant/polymer chemical floods

Coreflood name	Oil	Surfactant	ratio, % of total conc	total surf. conc, wt %	brine for preflush or surfactant	preflush	biopolymer conc., ppm
Polymer	NBU	none			Hepler	no	3,500
Mixed surfactant corefloods (cores initially saturated with NBU brine)							
MS-CF 1	NBU	S-2/S-3	87.5/12.5	0.5	NBU	no	3,500
MS-CF 2	NBU	S-2/S-3/S-4	60/12/28	0.5	NBU	no	3,480 in 70%NBU
MS-CF 3	NBU	S-2	100	0.5	150% NBU	no	3,480 in 70%NBU
MS-CF 4	NBU	S-2/S-4	40/60	0.5	NBU	no	3,480 in 70%NBU
MS-CF 5	NBU	S-2/S-3	87.5/12.5	0.5	NBU	no	3,500
MS-CF 6	NBU	S-3/S-15/S-12	33/33/33	1.0	NBU	no	3,500
MS-CF 7	NBU	S-2/S-7	72.5/27.5	1.0	NBU	no	3,500
MS-CF 8	NBU	S-2/S-7	80/20	1.0	NBU	no	3,500
MS-CF 9	NBU	S-2/S-3	87.5/12.5	1.5	NBU	no	3,500
MS-CF 10	NBU	S-2/S-3	87.5/12.5	0.5	NBU	no	3,500
MS-CF 11	NBU	S-2/S-3	87.5/12.5	1.5 and 0.5	NBU	no	3,500
Mixed surfactant corefloods with alkaline additives (cores initially saturated with Hepler brine)							
ASP-CF 1	HEPLER	S-4	100	0.4	2.12% NaCl + alka #1	yes	3,500
ASP-CF 2	HEPLER	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	3,500
ASP-CF 3	HEPLER	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	3,500
ASP-CF 4	HEPLER	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	3,500
ASP-CF 5	HEPLER	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	3,500
ASP-CF 6	NBU	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	1,000
ASP-CF 7	NBU	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	3,500
ASP-CF 8	GOV'T WELLS	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	3,000
ASP-CF 9	GOV'T WELLS	S-18	100	0.5	0.25% NaCl + alka #2	yes	3,000
CT-CF 1	HEPLER	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	3,500
CT-CF 2	NBU	S-2/S-3	37.5/62.5	0.4	1.0% NaCl + alka #1	yes	1,200

TABLE 6. - Oil recovery results for chemical corefloods

Coreflood name	Core brine permeability, md	Temp. °C	Surfactant volume injected, PV	S_{orwf}, %	S_{orcf}, %	Recovery efficiency, % S_{orwf}
Polymer	206	23	0	41.6	40.5	2.8
Mixed surfactant corefloods						
MS-CF 1	625	50	0.60	40.0	20.9	47.6
MS-CF 2	200	50	0.60	39.5	27.0	27.0
MS-CF 3	452	50	0.59	40.8	28.3	30.7
MS-CF 4	650	50	0.62	39.8	29.0	26.9
MS-CF 5	604	50	0.63	37.3	18.0	51.7
MS-CF 6	207	50	0.34	39.0	29.5	24.4
MS-CF 7	237	50	0.36	36.1	26.7	27.7
MS-CF 8	163	50	0.30	37.3	21.5	42.4
MS-CF 9	208	50	0.20	40.2	25.2	37.4
MS-CF 10	250	50	0.60	37.4	21.6	42.3
MS-CF 11	240	50	0.05 and 0.47	40.0	24.2	39.5
Mixed surfactant corefloods with alkaline additives						
ASP-CF 1	800	23	0.75	35.1	28.7	18.2
ASP-CF 2	855	23	0.75	35.1	4.96	85.6
ASP-CF 3	1,240	23	0.75	45.1	7.2	84
ASP-CF 4	41	23	0.75	42.5	25.6	39.7
ASP-CF 5	331	23	0.75	43.4	14.6	66.4
ASP-CF 6	220	23	0.75	45.5	29.2	35.8
ASP-CF 7	260	23	0.75	38.3	19.4	49.5
ASP-CF 8	705	23	0.74	42.4	13.8	67.6
ASP-CF 9	497	23	0.75	42.0	16.2	61.5
CT-CF 1	561	23	0.79	35.6	6.7	81.2
CT-CF 2	110	23	0.87	43.2	26.7	39.3

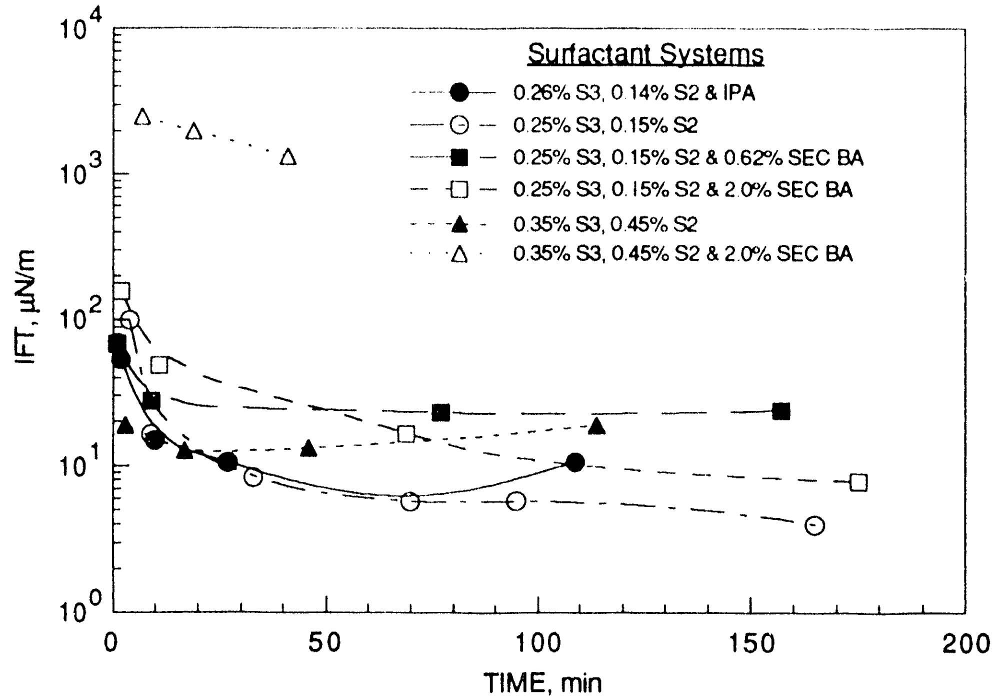


FIGURE 24. - Dynamic IFT's the S-2/S-3 surfactant system with Hepler oil. (SEC BA = secondary butyl alcohol)

Comparison of the IFT values suggested that recovery of Government Wells oil might be more favorable than Hepler, which in turn might be more favorable than NBU. Actually, after completing several coreflood tests, it was noted that oil recovery using this surfactant system and the same polymer mobility control solution of 3,500 ppm biopolymer for all the oils used appeared to decline as initial permeability of the Berea sandstone plugs declined. The dependence on core permeability appeared to be significantly larger than the differences caused by surfactant-oil interactions. Similar behavior was observed by other researchers conducting corefloods with ethoxylated and propoxylated surfactant systems.[58] In those studies, oil recovery correlated with initial brine permeability for corefloods conducted in Berea sandstone core plugs and with oil

TABLE 7. - IFT values for the S-2/S-3 system with 2% 2-butanol with different oils

Oil	Temperature, °C	Initial IFT, mN/m	IFT after 150 min., mN/m
Hepler	22	0.016	0.008
NBU	22	0.026	0.014
Government Wells	25	0.002	0.006
Government Wells	47	0.002	0.009

permeability at residual water saturation for corefloods conducted in reservoir rock.

Figure 25 shows the increase in final oil saturation after the chemical flood as initial core permeabilities declined. The surfactant system appeared to be more efficient in recovering Hepler oil than for either NBU or Government Wells oil, although the same trend was observed for each oil type.

The decline in oil recovery suggested that core properties and pore structure could affect the movement of chemicals and liquid phases through the core. It was noted that the polymer appeared to filter out more on the core face as permeability decreased. It can also be expected that surfactant loss by adsorption, phase trapping, or fluid bypass can occur to a greater extent in lower permeability core. These cores, however, did not show obvious or extensive heterogeneities. In order to understand the transport of fluids through the cores during chemical flooding, CT scanning of the cores was initiated. Two corefloods were conducted that repeated two earlier corefloods with different oil recovery results. These corefloods will be described in a later section of this report.

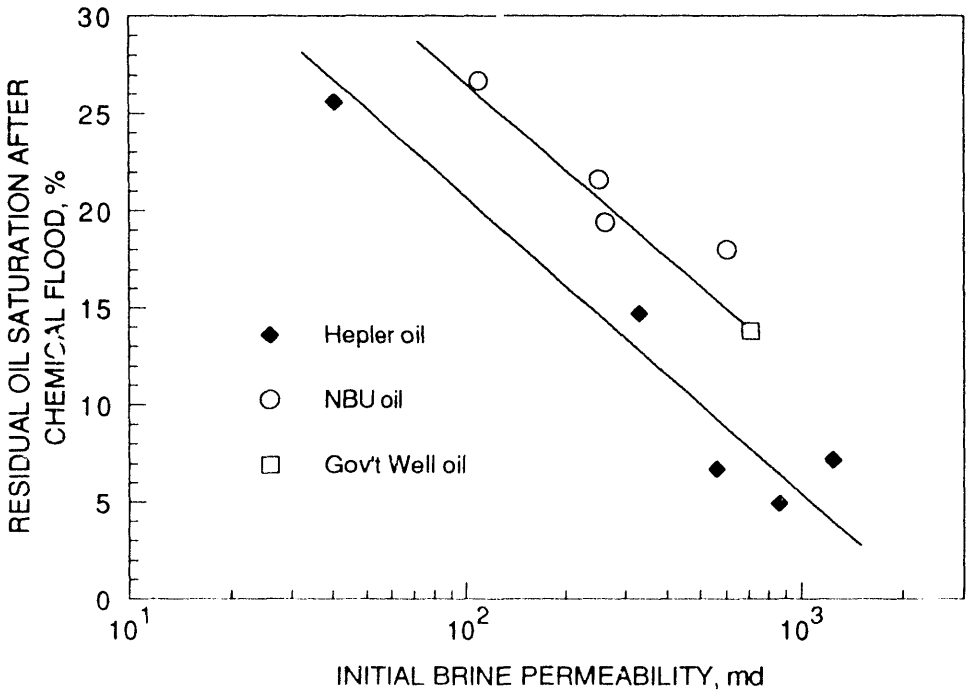


FIGURE 25. - Relationship between oil saturation after the chemical flood and core permeability for the S-2/S-3 surfactant system.

Effect of Polymer Concentration

Most of the corefloods conducted using alkaline preflushes described in this report used a fairly high concentration biopolymer solution (approximately 3,500 ppm) for mobility control. This polymer used without surfactant produced very little additional oil after the waterflood as shown in the oil production curve, figure A1 in appendix A.

The 3,500 ppm polymer concentration was first selected because Hepler oil had a very high viscosity at reservoir temperature, 76 cP. Figure 26 shows polymer viscosity as a function of shear rate for several concentration and temperatures of interest. The shear rate in sec^{-1}, $\dot{\gamma}$, experienced during the coreflood was calculated from the following relationship:

$$\dot{\gamma} = 268\ V(\phi/k)^{0.5}$$

where V, ϕ, and k are frontal advance rate in ft/day, porosity, and permeability in md, respectively.[63] This relationship was derived from a capillary model[64] using the value 5 for tortuosity.[65] For the Berea core plugs used in this study, the polymer should experience shear rates in the range of 4 to 9 sec^{-1}.

Initial tests using high permeability cores, ASP-CF 2 and ASP-CF 3, indicated that the

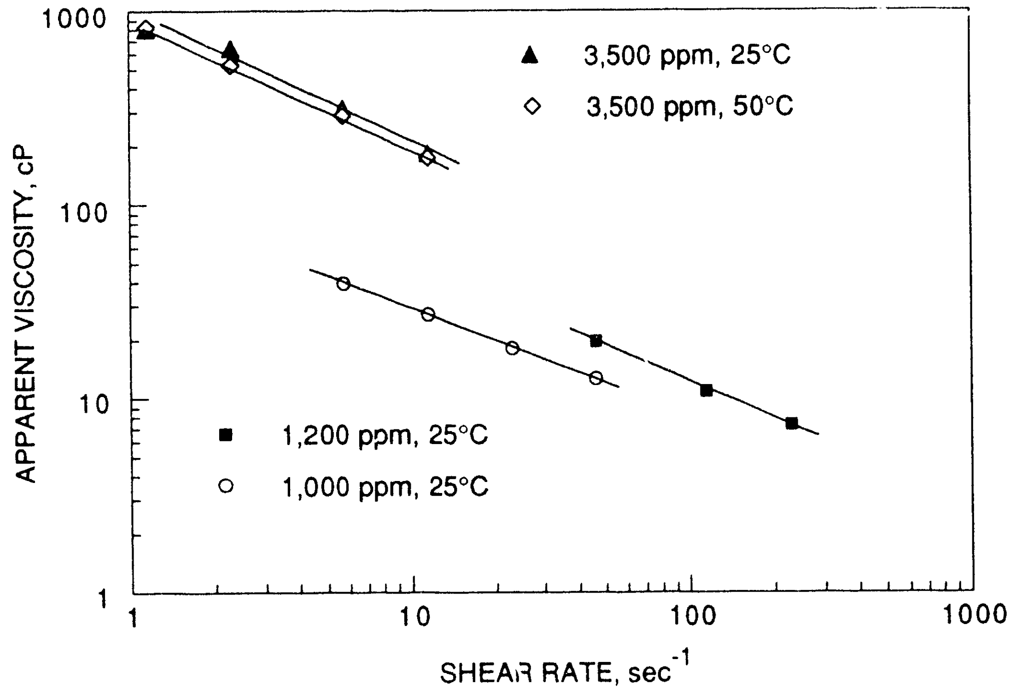


FIGURE 26. - Apparent viscosity of 4800 CX biopolymer used for mobility control for the mixed surfactant coreflood experiments.

S-2/S-3 surfactant system followed by the 3,500 ppm polymer mobility slug was an efficient system for recovery of Hepler oil. Residual oil saturation after the chemical flood, S_{orcf}, was reduced to 5 to 7%. Polymer that passed through the core for ASP-CF 2 and several other corefloods was detected by monitoring the viscosity of the effluent samples. For ASP-CF 2 after injection of 1 PV of polymer, the maximum viscosity of the effluent only reached 20% of the viscosity of the initial value. If the initial polymer viscosity was approximately 200 to 300 cP for the shear rate range of interest (see figure 26), the maximum viscosity of the effluent was 40 to 60 cP. This is a significant drop in viscosity within one foot of the injection point. However, this viscosity range is still close to the viscosity of the oil at this temperature (76 cP).

Viscosity was also monitored for several other corefloods. Maximum viscosities of the effluents samples ranged from 20 to 32% of the initial polymer viscosities. Examples are listed in table 8. Reasons for the viscosity decrease including dilution, filtration, degradation, and loss in the core were not extensively studied. It was noted, however, that as permeability of the core plugs declined, polymer filtration on the core face increased. Filtration was especially severe for cores with permeabilities less than 100 md but was also observed for the 200 and 300 md cores even though the polymer was prefiltered before use through 0.8 µm filters. However, since viscosity also declined significantly for 800 md core where filtration at the face was not observed, other mechanisms of viscosity degradation must also be important.

The viscosity of NBU oil is much lower than that of Hepler oil, 8 cP at ambient temperature and 3 cP at reservoir temperature. It was anticipated that a lower polymer concentration would be required to maintain mobility control during oil recovery experiments using NBU oil. A 1,000 ppm biopolymer concentration was therefore used for the first coreflood conducted with NBU oil.

For the same salinity, surfactant composition, and temperature, the oil recovery of this test, ASP-CF 6, (35.8% of S_{orwf}) was significantly lower than the oil recovery of ASP-CF 5 conducted

TABLE 8. - Maximum viscosity of effluent for mixed surfactant oil recovery experiments

Coreflood	k, md	PV of polymer injected	Maximum viscosity of effluent, % initial polymer viscosity
ASP-CF 2	855	1.0	20
ASP-CF 5	331	0.9	23
Polymer flood	206	1.1	24
MS-CF 2	200	1.1	20
MS-CF 9	208	0.8	32

using Hepler oil (66.4% of S_{orwf}). Figure 27 shows the oil production history of the two tests. Early production (production before injection of polymer mobility control solution) was comparable for both tests. The major difference that resulted in higher oil production for ASP-CF 5 was a significant amount of oil production that peaked at approximately 0.4 PV after the start of the polymer flood. ASP-CF 6 shows almost no oil production in this area. The second oil production peak accounted for the difference in oil recovery efficiency for the two tests.

The next experiment, ASP-CF 7, was conducted to determine the effect of higher concentration polymer (3,500 ppm) on oil recovery of NBU oil under the same conditions used for tests ASP-CF 5 and 6. Figure 28 shows a comparison of oil production for tests ASP-CF 5 and 7 which both used 3500 ppm biopolymer mobility control solutions. Both tests showed significant oil production of comparable amount which peaked at 0.4 PV after the start of the polymer injection.

These results suggested that a polymer concentration of 1,000 ppm or less was insufficient to maintain oil production initiated by surfactant injection. A higher concentration polymer (3,500 ppm) in conjunction with surfactant injection was required to efficiently sweep these cores.

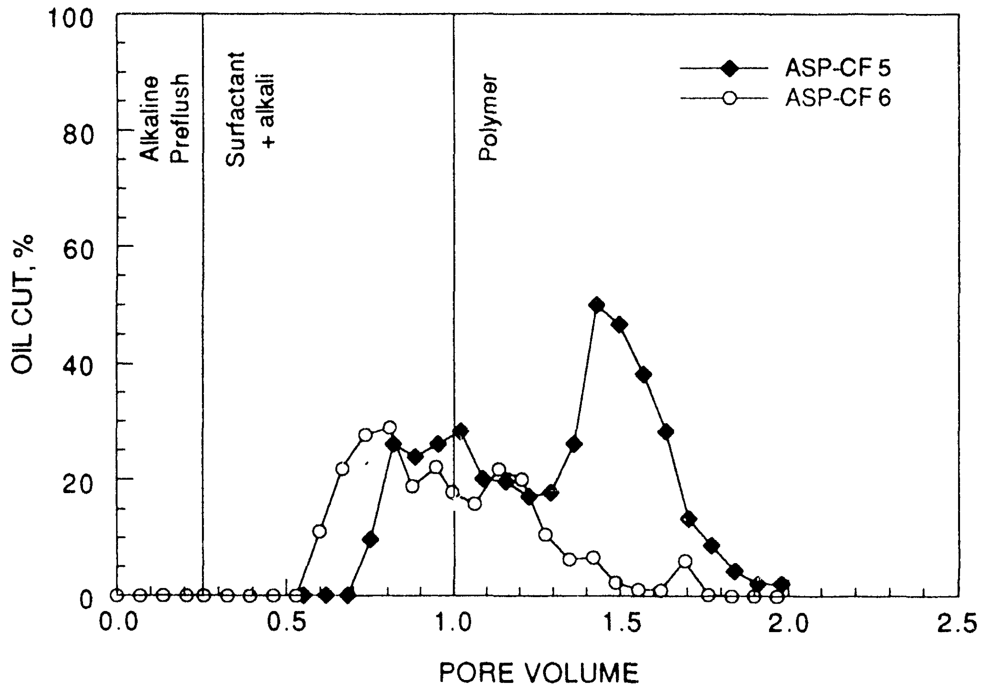


FIGURE 27. - Comparison of two tests showing the effect of different polymer concentrations on oil production. (ASP-CF 5: Hepler oil with 3,500 ppm polymer; ASP-CF 6: NBU oil with 1,000 ppm polymer)

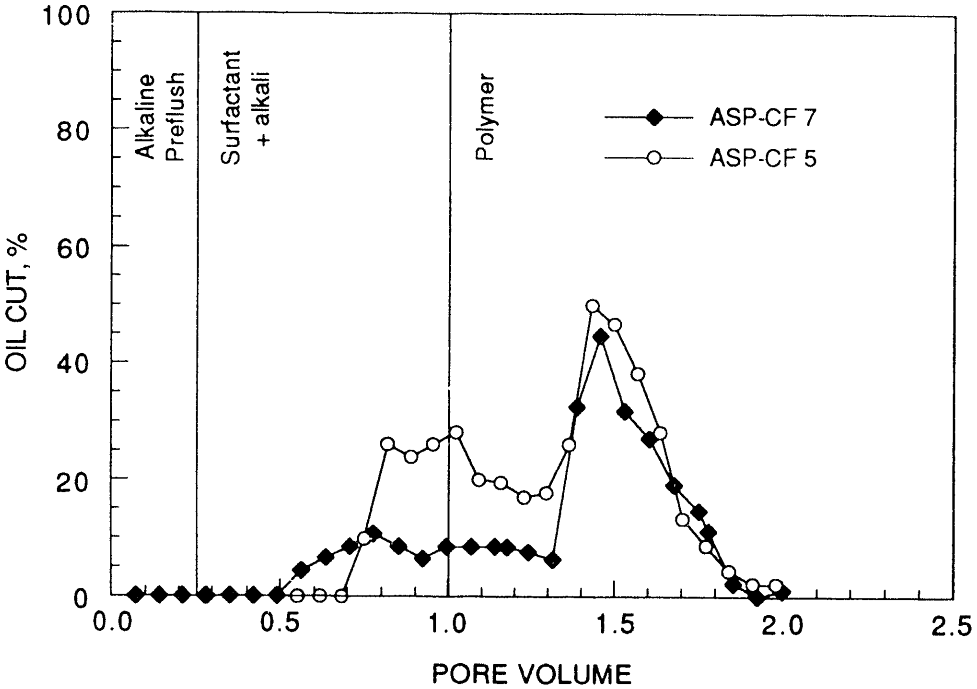


FIGURE 28. - Hepler and NBU oil production for the same chemical systems at the same temperature and salinity conditions. (ASP-CF 5: Hepler oil with 3,500 ppm polymer; ASP-CF 7: NBU oil with 3,500 ppm polymer)

At this time, no systematic study has been made to investigate the polymer concentration range between these two values to determine the minimum polymer concentration required to maintain oil mobility. However, because of polymer cost, the requirement to use this level of mobility control would be detrimental to economical oil recovery using this chemical flooding system.

No other polymer mobility control agent was investigated for this study. However, for similar studies conducted at NIPER to evaluate oil recovery of Hepler oil when other mobility control polymers (e.g., 1,000 ppm polyacrylamide) were used, oil recovery was less than the comparable tests conducted with higher concentration polymer solutions.[62]

In summary, oil recovery of both Hepler and NBU oil using the S-2/S-3 mixed surfactant system with alkaline additives was affected by amount of polymer in the mobility control solution injected following the surfactant injection. Viscosity of the mobility agent was reduced 70 to 80% within less than 1 ft of the injection area. This reduction occurred for both high (855 md) and moderate (200 md) permeability cores. Lower permeability cores definitely showed some polymer filtration at the core face which would contribute to a decrease in polymer effectiveness. Dilution, adsorption, precipitation, or filtration inside the core may also contribute to polymer loss. Oil recovery in high permeability cores was sufficiently high (80-86%) to suggest that the observed loss of viscosity occurred at a time or place within the core in a manner that was not detrimental to oil recovery. The CT experiments that will be described in a later section were designed to help identify reasons for the differences in oil recovery results described above.

Bimodal Oil Production Curves

Using the injection strategy that separated the surfactant slug and the polymer mobility slug, most of the oil production history curves show some type of bimodal distribution in the oil recovery history. Figure 29 shows the oil production for tests ASP-CF 2 and 3, which were duplicate oil recovery experiments using the same preflush, surfactant system, polymer, and high permeability core. Both show large production peaks after injection of the polymer, indicating the formation of an oil bank and good sweep of oil from the core plugs. ASP-CF 3, however, also produced a significant amount of oil ahead of the oil bank. ASP-CF 2, on the other hand, showed much less oil production before the large oil peak.

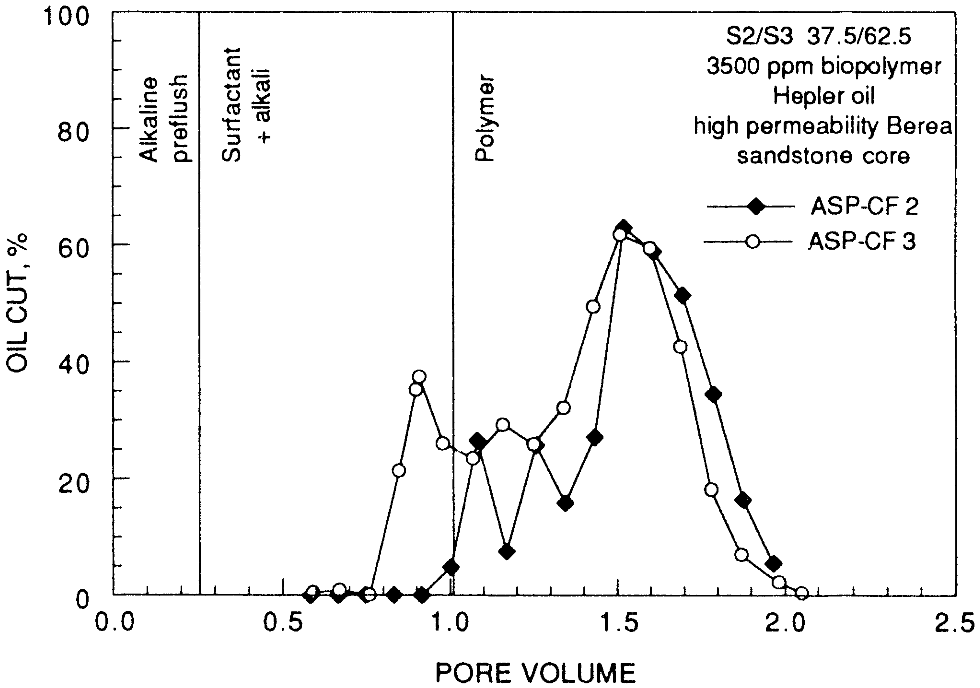


FIGURE 29. - Comparison of Hepler oil production from high permeability core with different oil saturations at the end of the waterflood.

The difference in these two tests was the residual oil saturation at the end of the waterflood. The oil saturation for ASP-CF 3 was 10% higher than it was for ASP-CF 2. Such wide variation in oil saturation at the end of the waterflood may be an indication of heterogeneities in the core that resulted in by passed oil during the waterflood or in capillary effects that caused differences in oil retention for the two tests. Both waterfloods were conducted with an injection rate of 1 ft/day. A higher injection rate may have resulted in more uniform oil saturations at the end of the waterflood.

Injection of the surfactant solution appeared to produce oil in this area in an amount relative to the amount of oil saturation present in the core that was greater than 30% of the core pore volume. Adequate or efficient mobility control polymer was then required to reduce oil saturation to lower values. For example, figure 30 shows a comparison of oil production for tests ASP-CF 3 and ASP-CF 6. Both floods started with similar S_{orwf} (45.1 and 45.5%) and core pore volume (64.8 and 65.8 mL). The chemical recovery system was the same for each test, but different oils were used (Hepler and NBU). After injection of 1.3 PV of chemical solutions, the same amount of oil had been produced for each test (9.6 and 9.4 mL).

Examination of other corefloods using this surfactant formulation suggested that a correlation existed between residual oil saturation at the end of the waterflood and the amount of oil produced ahead of the oil bank (i.e., the large production peak that occurred approximately 0.3 to 0.5 PV's after the start of polymer injection, as discussed in the previous section). Figure 31 shows this correlation for a number of corefloods that used the S-2/S-3 surfactant formulation. These tests included corefloods with alkaline additives as well as tests conducted at higher salinity and temperature conditions that will be described in the next section. Core permeabilities ranged from 110 to 1,250 md. Tests using all three oils were also included. However, to use the S-2/S-3 surfactant mixture at different salinities or temperatures, the ratio of one surfactant to the other was adjusted to obtain minimum IFT values or phase behavior as described in previous sections.

This correlation does not predict the overall effectiveness of the surfactant/polymer system which depends on polymer mobility and core properties for production of the oil bank. However, it does indicate that the surfactant mixture has the capability of mobilizing oil. The tests must be conducted in a manner that allows a method to separate the effectiveness of the surfactant from the polymer slug. Comparison of oil recovery using other surfactant mixtures and similar test methods with the results shown above may provide a method of ranking surfactant mixtures for their effectiveness in mobilizing oil. In the next section on the use of mixed surfactants without alkaline

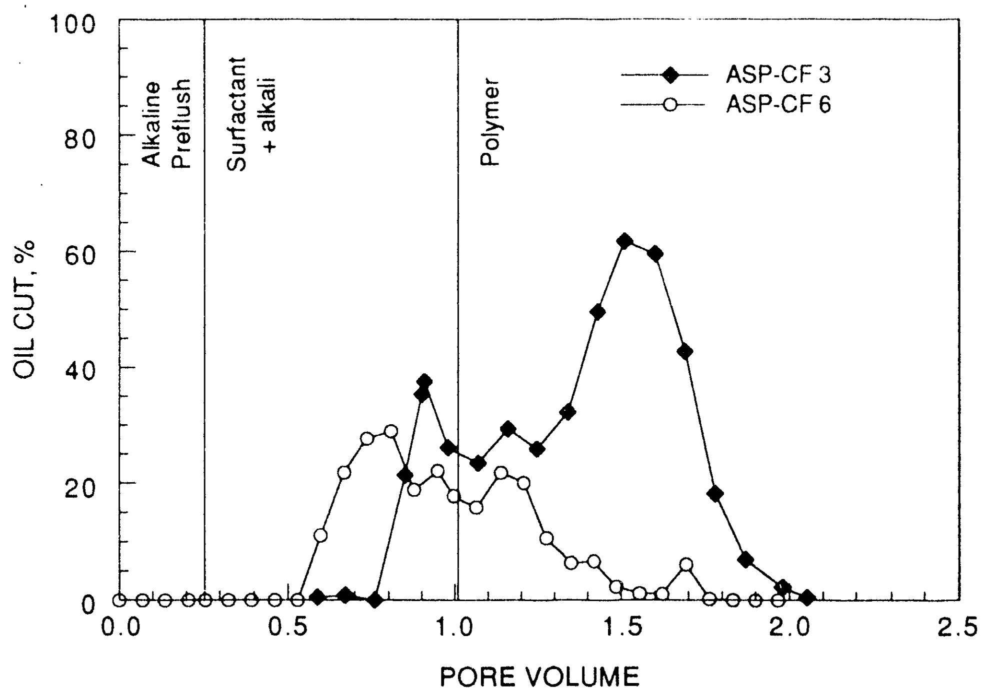


FIGURE 30. - Comparison of two corefloods with the same S_{orwf} but different polymer mobility control.

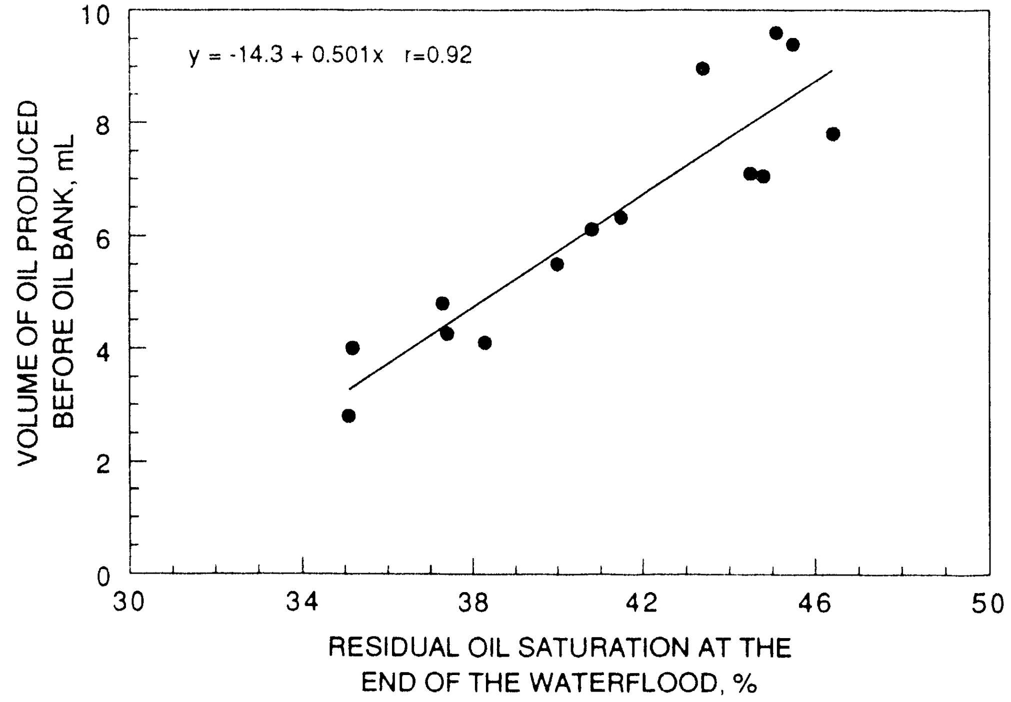


FIGURE 31. - Correlation of amount of oil produced before oil bank with S_{orwf} for oils produced using the S-2/S-3 surfactant system.

additives, several other surfactant mixtures were evaluated for recovery of NBU oil. They tended to show lower recovery relative to S_{orwf} (points fell below the line for the correlation in figure 31) as well as lower overall effectiveness in the corefloods experiments.

CT-Aided Displacement Experiments

Two corefloods were conducted using Berea sandstone core plugs encased in epoxy to allow the use of the CT scanner to monitor oil saturations at various times during the progress of the coreflood. The experimental conditions for these tests were selected to duplicate conditions of highest oil recovery and conditions when the oil bank did not appear to propagate through the core. For the first test, CT-CF 1, the mixed surfactant system, S-2/S-3, with alkaline additives followed by a 3,500 ppm mobility control polymer slug was used to produce Hepler oil. Core permeability was relatively high, 561 md. Oil recovery results should compare with the tests, ASP-CF 2, 3, and 5. The second test, CT-CF 2, used the same surfactant system with a lower concentration polymer slug, 1200 ppm, to recover NBU oil in a low permeability core, 110 md. The oil recovery results of this test should compare with those for ASP-CF 6.

The oil were tagged with iododecane to provide increased contrast in the CT images between oil and brine solutions. Addition of iododecane reduced the viscosity of the Hepler oil to 39 cP and did not change the viscosity of NBU oil for ambient temperature conditions.

The CT images after the oil flood indicated that oil distributions were relatively uniform throughout the core plugs. After waterflooding, oil saturations appeared to be slightly greater at the core outlets than at the inlets. Figures 32 and 33 show images of the core saturation distributions reconstructed from individual CT images taken every 8 mm along the core lengths for the two tests. Lightest gray-scale color indicates the most dense parts of the core and, for these images, the highest oil saturations.

The next two figures (figures 34 and 35) show oil distributions after injection of the surfactant solutions. For CT-CF 1, formation of an oil bank could easily be observed. Uneven distribution in the oil saturation behind the oil bank could also be observed, indicating some nonhomogeneous movement of surfactant through the core plug. No oil bank was formed in the CT-CF 2 test. An additional test in higher permeability core with NBU oil would be required to determine if the lack of oil bank formation was a function of the lower permeability of the core plug or because of the surfactant/oil phase behavior.

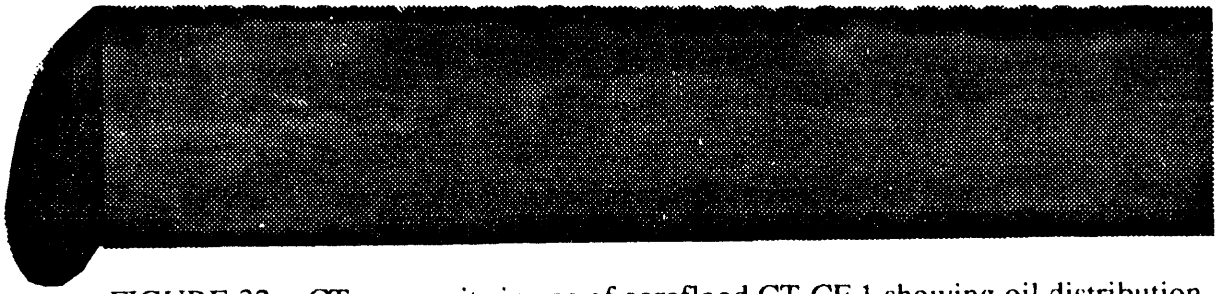


FIGURE 32. - CT composite image of coreflood CT-CF 1 showing oil distribution after the waterflood. Oil appears to be slightly more concentrated at the core outlet.

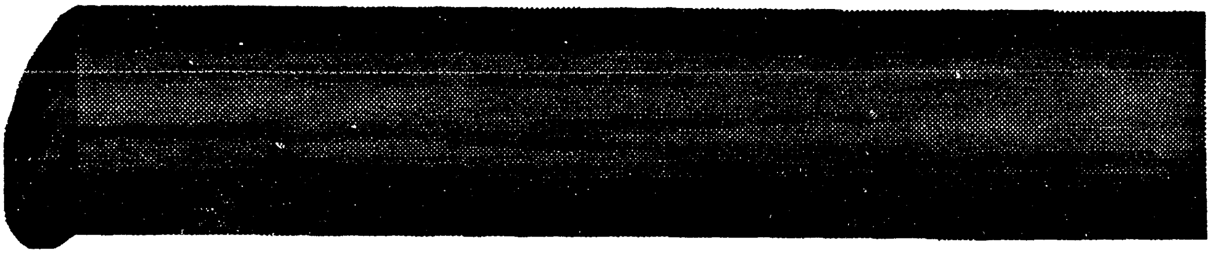
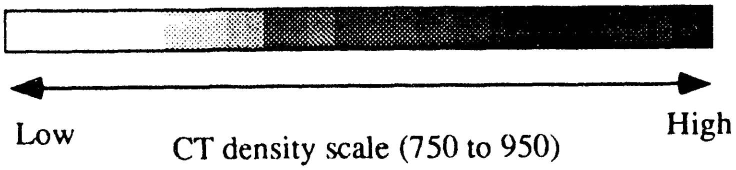


FIGURE 33. - CT composite image of coreflood CT-CF 2 showing oil distribution after the waterflood. Oil appears to be more heterogeneously distributed for the lower permeability Berea sandstone core than for the higher permeability core used for coreflood CT-CF 1.



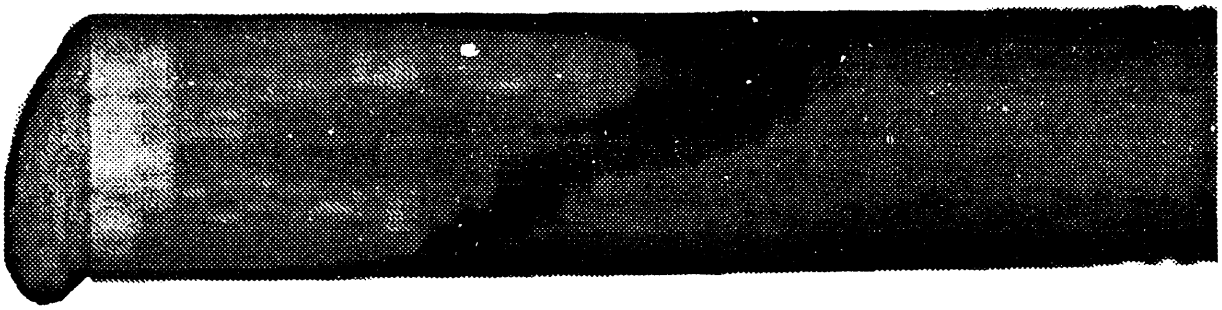


FIGURE 34. - CT composite image of coreflood CT-CF-1 showing oil distribution after surfactant injection. An oil bank was observed ahead of the surfactant.

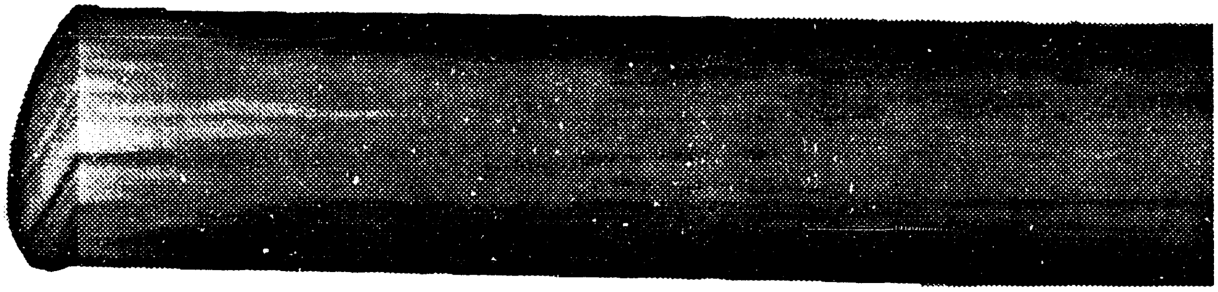
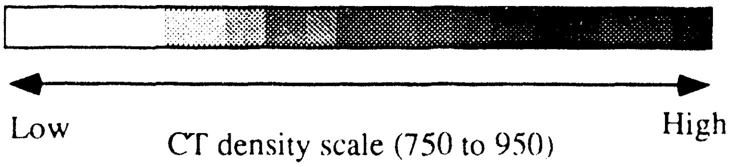


FIGURE 35. - CT composite image of coreflood CT-CF-2 showing oil distribution after surfactant injection. No oil bank was observed.



The final two CT figures (figures 36 and 37) show oil distribution after completion of the polymer flood. CT-CF 1 appeared to be well swept. Most oil remaining in the core plug can be seen near the outer edges of the core and near the core outlet. For CT-CF 2, however, much larger amount of oil remained around the outer edges of the core and near the core outlet. The polymer solution appeared to channel down the center of the core plug. Oil recovery results compare with previously conducted corefloods as shown in table 9.

Oil production curves also were comparable for these tests. Figure 38 shows a comparison between CT-CF 1 and ASP-CF 2, and figure 39 shows oil cuts for CT-CF 2 and ASP-CF 6.

In summary, the use of CT image analysis may help identify the factors that lead to or hinder the successful application of chemical flooding techniques. Relative effectiveness of surfactant formulations and polymer mobility control agents can be evaluated. It may also be a technique that can help evaluate the influence of rock structure and/or heterogeneities. Continued study in this area is planned during the next research year.

TABLE 9. - Coreflood results for good and moderate oil recovery tests using the same chemical oil recovery system.

	k, md	Oil type	[biopolymer], ppm	S_{orcf}, %	Recovery efficiency, % S_{orwf}
CT monitored corefloods					
1	561	Hepler	3,500	6.7	81.2
2	110	NBU	1,200	26.7	39.3
Comparative corefloods					
ASP-CF 2	855	Hepler	3,500	5.0	85.6
ASP-CF 6	220	NBU	1,000	29.2	35.8

Summary of ASP Corefloods

A surfactant mixture consisting of an alkyl aryl sulfonate and an ethoxylated sulfate was used with alkaline additives to produce over 80% of a high viscosity oil remaining after waterflooding in laboratory scale corefloods. Many factors were identified, however, that reduced the recovery efficiency of the chemical system. Oil recovery was reduced as core permeability decreased. Oil recovery also declined as polymer concentration in the mobility control slug was reduced. These

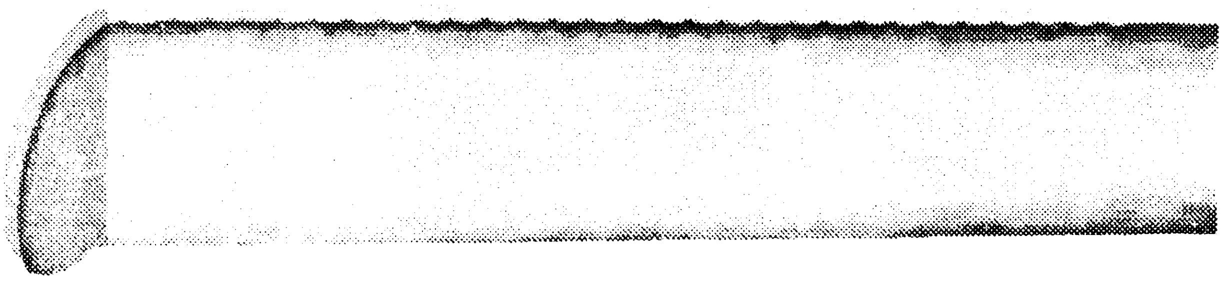


FIGURE 36. - CT composite image of coreflood CT-CF 1 showing oil distribution after the polymer flood. The core was well swept of oil in agreement with the final oil saturation from oil recovery measurements.

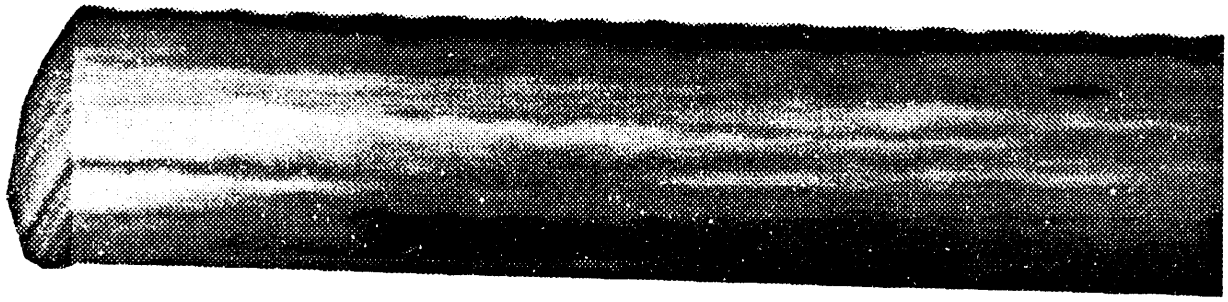
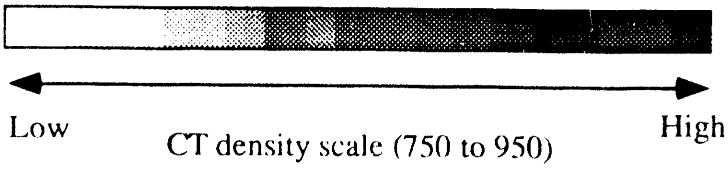


FIGURE 37. - CT composite image of coreflood CT-CF 2 showing oil distribution after the polymer flood. Fluids channelled through the center of the core leaving significant amounts of oil in the core in agreement with oil recovery measurements.



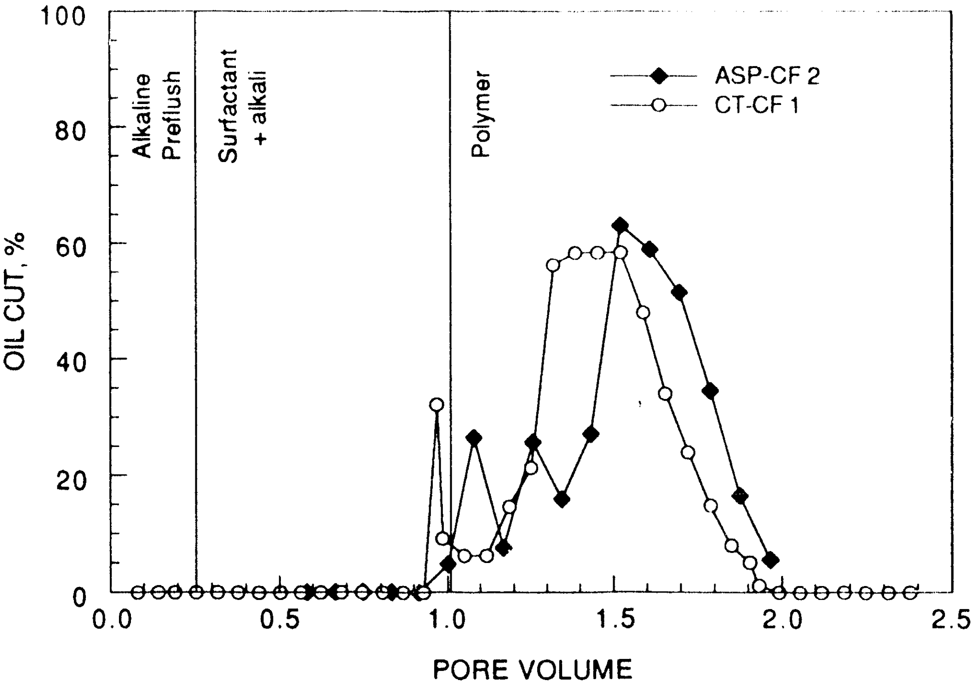


FIGURE 38. - Comparison of Hepler oil production history for high permeability cores using the same chemical system.

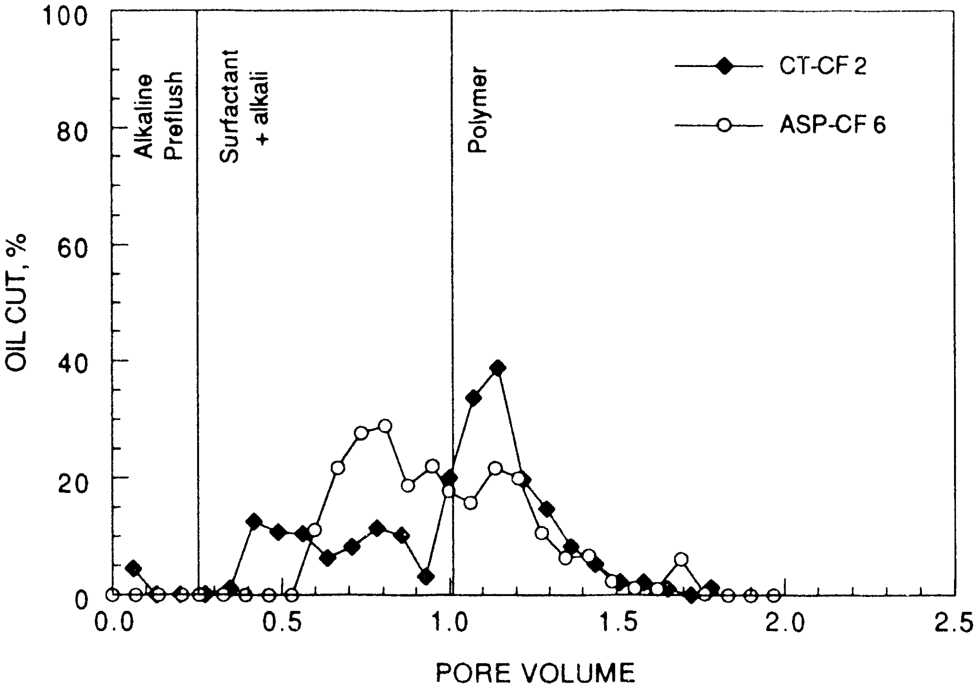


FIGURE 39. - Comparison of NBU oil production history for cores using the same chemical system.

factors may be related because polymer and/or surfactant may filter out, precipitate, or adsorb to a greater extent as core permeability declines.

The surfactant system appeared to produce an amount of oil from the core plugs independent of the formation of an oil bank or the presence of a good mobility control agent. The amount of oil was proportional to the oil saturation at the end of the waterflood. If other surfactant systems were more or less efficient in producing this oil, this may be a test method to compare the effectiveness of different surfactant systems.

CT imaging may be another method to evaluate surfactant chemical systems. Other factors affecting oil recovery may also be examined using this technique, including the effect of different core permeabilities and structures.

Mixed Surfactant Chemical EOR Without Alkaline Additives

NBU Oil Production Using the S-2/S-3 Surfactant System

High divalent ion concentration in reservoir brine is one problem that precludes the use of alkaline additives to improve surfactant flood technology.[45] Addition of bicarbonate/carbonate chemicals can cause significant precipitation of calcium and magnesium carbonates and/or hydroxides. Consumption of alkaline chemicals would be excessively high for reservoirs having divalent ion concentrations in reservoir brine. In addition, precipitation of these chemicals may block pore throats and cause injection problems. Reservoir brine from the North Burbank Unit, Osage County, Oklahoma, contains relatively large amounts of divalent ions. Addition of bicarbonate/carbonate chemicals or sodium tripolyphosphate (STPP) to surfactant solutions prepared with NBU brine resulted in the formation of white precipitates. Therefore, the oil recovery potential of mixed surfactant systems using the temperature and salinity conditions of the NBU reservoir was tested without addition of alkaline additives.

As discussed in the phase behavior section of this report, changing the relative ratio of ethoxylated surfactant to non-ethoxylated surfactant in a mixed surfactant system changed the salinity at which most favorable IFT and phase behavior occurred. For the lower salinity conditions of the Hepler and Government Wells reservoirs, the S-2/S-3 surfactant system contained surfactant in a relative proportion of 37.5 to 62.5%. For higher salinity conditions of the NBU reservoir, the proportion of ethoxylated surfactant was increased Initial studies indicated that a ratio of 87.5 to 12.5% S-2 to S-3 was a reasonable candidate for coreflooding experiments.

Several corefloods were conducted at 50 °C in Berea sandstone core saturated with NBU brine. Surfactant was injected for 0.6 PV at a total concentration of 0.5%, followed by approximately 1 PV or polymer. The oil recovery results are summarized in table 10.

MS-CF 5, a repeat of experiment MS-CF 1, was conducted because the core overheated (to approximately 70°C) for a short time while injecting surfactant for MS-CF 1. A 2.9% difference in final oil saturation was observed for the two tests suggesting that overheating did not cause large differences in oil recovery characteristics.

The difference in final saturations of tests MS-CF 5 and MS-CF 10 suggested that core permeability had some effect on oil recovery under these conditions. This difference agreed with the results obtained for NBU oil recovery as a function of core permeability at the lower salinity conditions, as shown in figure 25. Recovery of NBU oil at the lower salinity conditions resulted in a final oil saturation of 19.4% for 260 md core (ASP-CF 7). The difference in final oil saturations for ASP-CF 7 and MS-CF 10 was 2.2%. This relatively small difference suggested that the S-2/S-3 surfactant system, adjusted for salinity, was equally effective in producing NBU oil from Berea sandstone core. The oil production histories for the two tests are compared in figure 40. Although the same amount of surfactant was injected for each test, the concentration for ASP-CF 7 was lower and the PV injected was slightly larger than for test MS-CF 10. Therefore, the oil curves were compared relative to the start of the polymer injection. Both curves show a small oil peak approximately 0.4 PV after the start of the polymer slug. Production at the higher salinity conditions appeared to be less efficient than at the low salinity conditions, however, because of slow oil production for up to 0.8 PV after the oil peak. Slow oil production would be economically detrimental.

In summary, the S-2/S-3 surfactant system, with the ratio of surfactant adjusted for salinity, appeared to recover NBU oil from Berea sandstone cores with approximately the same efficiency for corefloods with and without alkaline additives. The salinity conditions were significantly different for the two cases. Using alkaline additives, the brine composition was approximately 1%

TABLE 10. - Recovery of NBU oil at 50° C using the S-2/S-3 surfactant system

Name	Initial brine permeability, md	S_{orcf}, %	Recovery efficiency, $\%S_{orw}$
MS-CF 1	625	20.9	47.6
MS-CF 5	604	18.0	51.7
MS-CF 10	250	21.6	39.5

NaCl and 0.12% divalent ions; while the composition of simulated NBU brine was 6.65% NaCl and 1.77% divalent ions. The most efficient corefloods using this surfactant system, however, only reduced oil saturation in the core to 18 to 20%, making this surfactant system much less effective in producing NBU oil than in producing Hepler oil.

Questions still remain concerning the role of the polymer and of core permeability in assessing surfactant effectiveness. Additional studies and application of methods to evaluate surfactant and polymer effectiveness such as CT imaging need to be performed.

Injection Strategy

Studies with the alkaline-enhanced surfactant corefloods, as described previously, indicated that injection of low concentration/large PV surfactant slug followed by a polymer mobility control slug was a good way to study the effectiveness of the flooding process. This method, however, resulted in production of the majority of the oil well after the injection of the chemicals. Even if the process was economical in terms of cost of chemicals, the long delay before production of the oil would cause problems with return on investment. Therefore, several injection strategies were investigated to determine differences in oil production using higher concentration/smaller PV

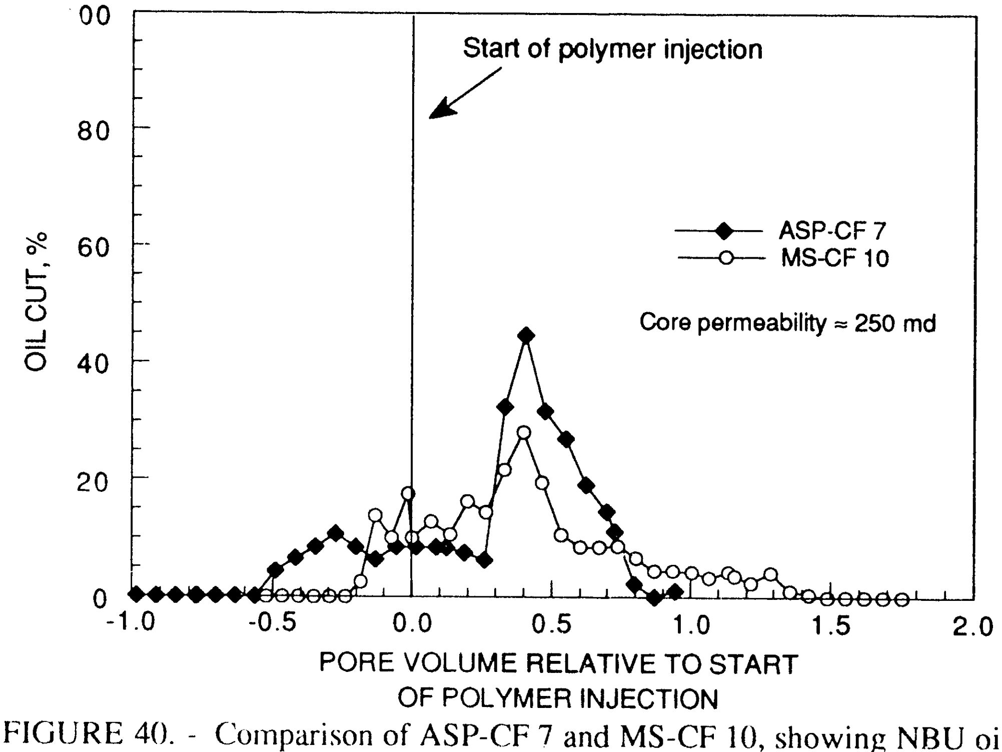


FIGURE 40. - Comparison of ASP-CF 7 and MS-CF 10, showing NBU oil production histories using the S-2/S-3 surfactant system.

surfactant slugs as well as differences in timing of polymer injection for earlier production of the oil. Figure 41 summarizes the sequence of fluid injections for the following cases: the low surfactant concentration strategy that injected 0.6 PV of 0.5% total concentration of the S-2/S-3 surfactant mixture, followed by 3,500 ppm biopolymer; the higher surfactant concentration strategy that used 0.2 PV of 1.5% total surfactant concentration, followed by polymer: and a surfactant concentration gradient technique that started surfactant at the higher concentration level and changed to lower concentration. Polymer was also incorporated with some of the surfactant injection. All the corefloods were conducted in 200 to 250 md Berea sandstone core at 50° C. The corefloods are identified as MS-CF 10, 9, and 11, respectively.

Results of oil recovery tests are summarized in table 11. The most successful injection strategy used the low concentration, larger PV surfactant slug. However, large differences in the three methods were not observed. Figure 42 shows the oil production history for the three tests. (Individual oil production curves can be found in appendix A.) The high concentration surfactant slug and the concentration gradient produced the majority of the oil within 1 PV of injected fluids, with the high concentration slug producing the most oil within 0.5 PV of the start of surfactant injection. The low concentration/large PV injection method produced most of the oil within 1.2 PV, although oil continued to be produced in low quantities for almost 1 more PV. None of these tests appeared to produce as large an oil peak after injection of the polymer (oil bank) as was formed with the alkaline-enhanced surfactant tests at lower salinity described in the previous sections.

Since only minor differences in oil recovery were observed for these three injection methods, these results suggested that high concentration/small slugs may be more favorable for field application since earlier production of oil would favor the economics of the EOR application. However, use of low concentration/large slugs may be more suitable in laboratory studies to determine the relative effectiveness of the surfactant formulation and the polymer mobility control agent. Therefore, subsequent studies evaluating other mixed surfactant systems were conducted using this injection method.

TABLE 11. - Oil production results for three surfactant injection strategies.

Coreflood	[Surfactant], wt%	Surfactant PV	S_{orcf}, %	Recovery efficiency,%
MS-CF 9	1.5	0.2	25.2	37.4
MS-CF 10	0.5	0.6	21.6	42.3
MS-CF 11	1.5 and 0.5	0.05 and 0.47	24.2	39.5

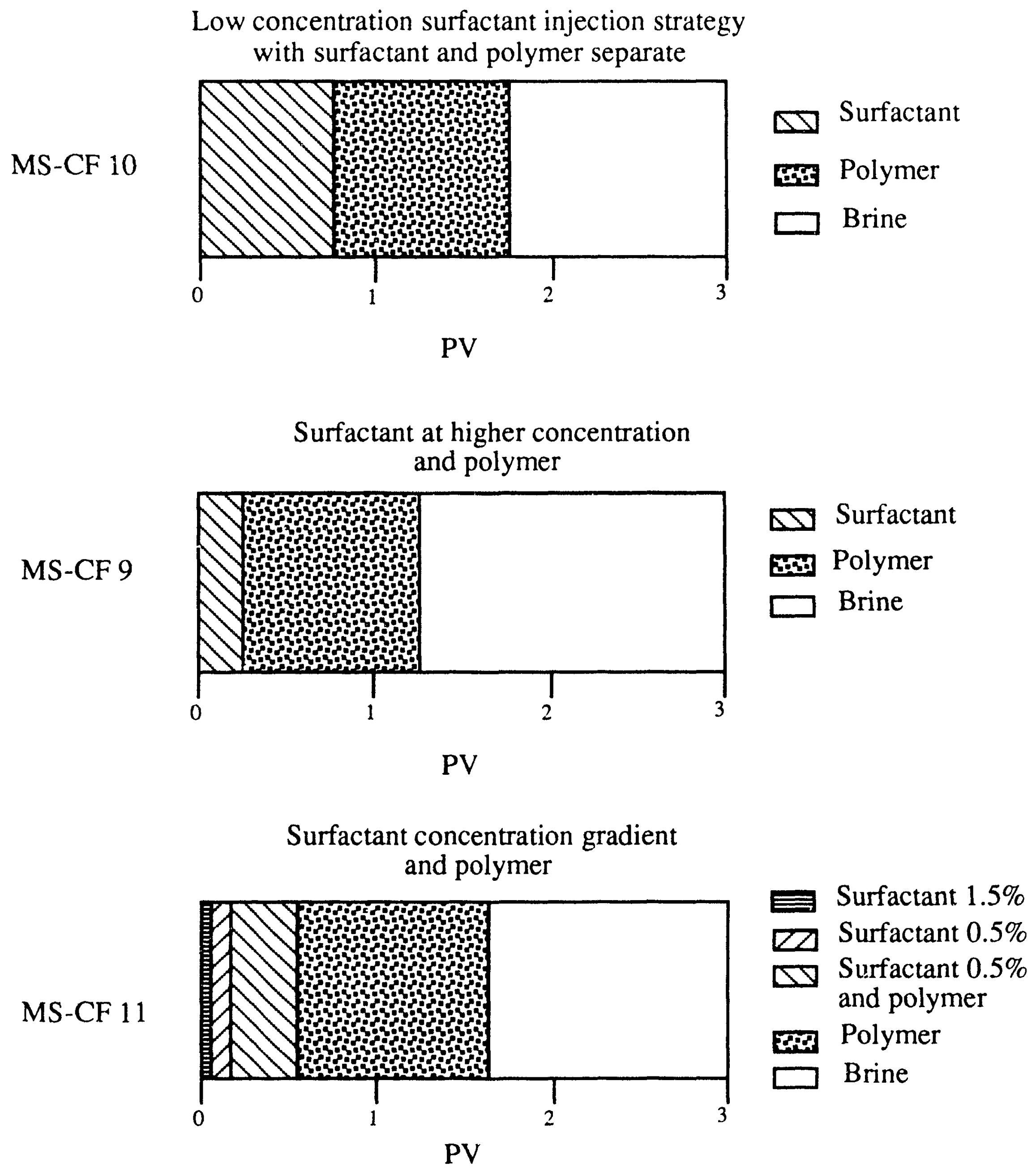


FIGURE 41. - Different injection schemes to produce NBU oil using the S-2/S-3 surfactant mixture.

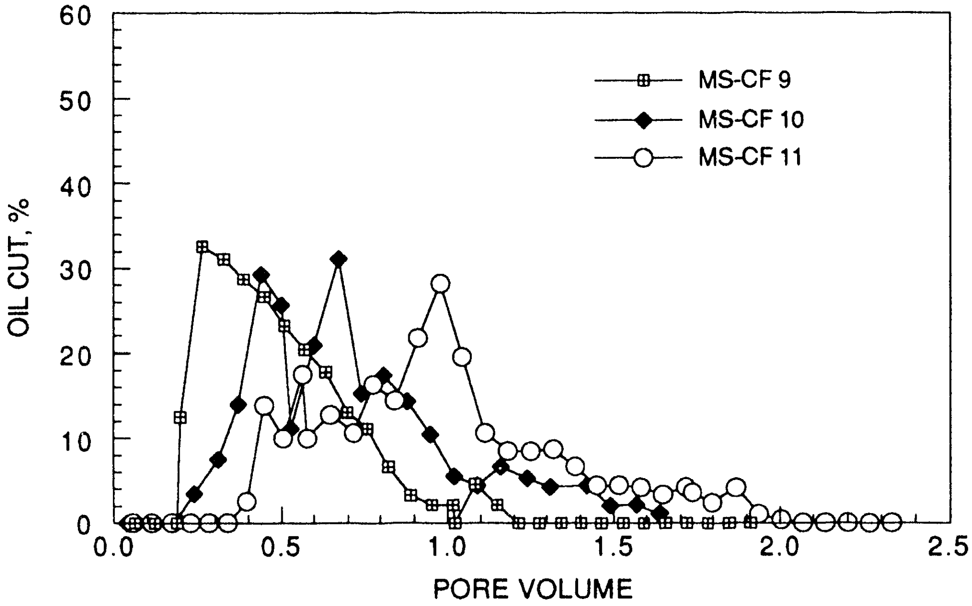


FIGURE 42. - Oil production history as a function of surfactant injection strategy.

Evaluation of Different Mixed Surfactant Systems

For some conditions, as described previously, the S-2/S-3 was an excellent surfactant system for recovery of Hepler oil, but somewhat less successful at producing NBU oil in the laboratory coreflood tests.

In addition to the S-2/S-3 surfactant system, four other surfactant mixtures were used to recover NBU oil from Berea sandstone core plugs for NBU temperature and salinity conditions. Selection of these mixtures were based on preliminary phase behavior and IFT evaluations of these mixtures with NBU oil. Surfactants of lower molecular weight than that of S-3 were chosen for testing. This selection criteria was based on the knowledge that NBU oil, on the average, contained hydrocarbons of lower molecular weight than Hepler oil. The average carbon number for NBU oil was 10, while that for Hepler oil was 14. As a result, the mixed surfactant system was changed to include alkyl sulfonates with shorter hydrophobic carbon chain lengths than were found in the S-3 surfactant. The surfactants S-4 and S-7 were two alkyl sulfonates that were used to replace some or all of the S-3 surfactant in the S-2/S-3 mixture. (The S-2 surfactant itself is a mixture of the surfactants S-3 and S-14 so that these mixed surfactant systems still contain some of the S-3 surfactant.) Another surfactant mixture that included one nonionic surfactant in addition to an ethoxylated sulfonate, S-15, and an alkyl sulfonate, S-3, was also tested.

In all but one case, NBU oil recoveries were lower than those using the S-2/S-3 surfactant system. Table 12 lists IFT values, residual oil saturations after chemical flood, and recovery efficiencies for these corefloods including one test using the S-2/S-3 surfactant system. All tests injected the same amount of surfactant. However, in some cases, total surfactant concentration was 1%, and in other cases, 0.5%. Individual oil production history curves are shown in appendix A.

TABLE 12. - NBU oil recovery results using different mixed surfactant systems. Tests were run at 50° C.

Name	Surfactant mixture	Ratio, % total	IFT, mN/m	S_{orcf}, %	Recovery, %S_{orwf}
MS-CF 2	S-2/S-3/S-4	60/12/28	<0.001	27.0	27.0
MS-CF 4	S-2/S-4	40/60		29.0	26.9
MS-CF 6	S-3/S-15/S-12	33/33/33	0.046-0.001	29.5	24.4
MS-CF 7	S-2/S-7	72.5/27.5	(1)	26.7	27.7
MS-CF 8	S-2/S-7	80/20	0.031	21.5	42.4
MS-CF 10	S-2/S-3	87.5/12.5	0.001	21.6	42.3

[1] Formed an emulsion in the IFT tube, causing difficulty in measuring an IFT value.

As the amount of S-4 was increased and S-3 decreased in the S-2/S-3/S-4 surfactant mixture, oil saturation after the chemical flood increased. Figure 43 shows this relationship. The decline in

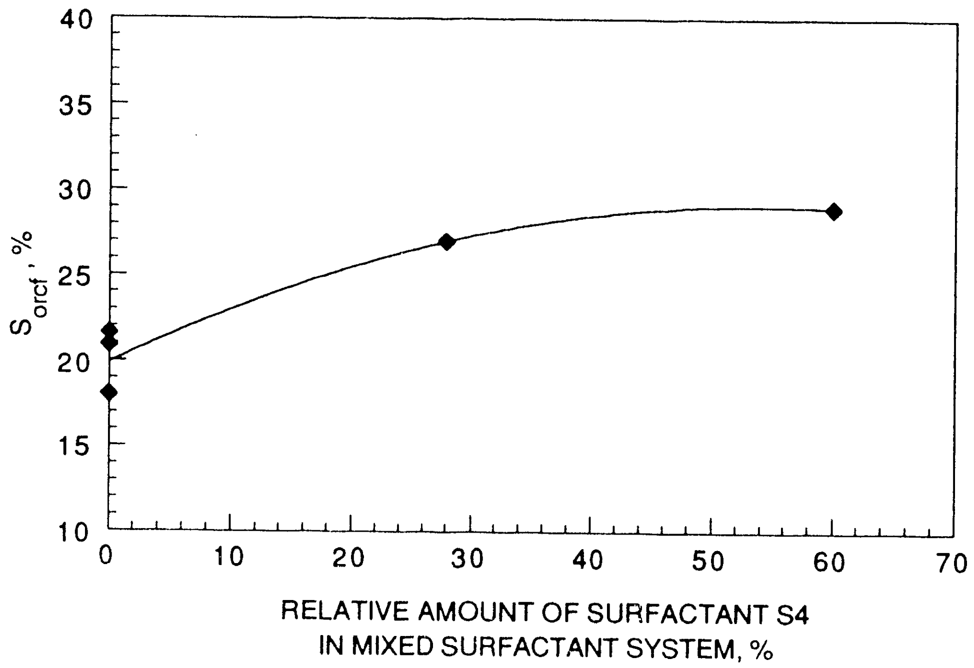


FIGURE 43. - Reduction in S_{orcf} as a function of increased amount of surfactant S-4 in a mixed surfactant system.

oil recovery occurred even though IFT measurements appeared to indicate that the surfactant mixtures were equally effective. None of the oil production histories indicated that the polymer mobility slug was very effective in contrast to the behavior in producing Hepler oil, as described previously. Either an oil bank was not produced by the surfactant mixture, or the polymer itself was ineffective. Using higher permeability core did not improve oil recovery results. For example, MS-CF 4 was conducted in core with permeability of 650 md.

MS-CF 6 was conducted using a complex surfactant mixture, S-3/S-15/S-12, including one nonionic surfactant component. The mixture was less effective than the S-2/S-3 system. Phase behavior and IFT results suggested that the ratio of surfactants would be more effective if they could be used at lower temperature. The IFT values increased from 0.001 to 0.046 mN/m as temperature increased from 23° to 50 °C. Oil solubilization was good at ambient temperature. Additional corefloods would be required to determine if oil recovery could be improved by adjusting this surfactant mixture.

Corefloods MS-CF 7 and MS-CF 8 used the S-2/S-7 mixed surfactant system to recover NBU oil. The difference in the two systems was a slight decrease in the amount of S-7 in the mixture. For the 80/20 system, oil recovery was as efficient as the S-2/S- 3 surfactant mixture. In addition, the MS-CF 8 coreflood was conducted in a 163 md core plug, one of the lowest of any of the tests run with mixed surfactants. S_{orcf} was 21.5% as compared to 21.6% for MS-CF 10. Figure 44 shows a comparison of oil production history for the two tests.

From these results, it is possible to adjust the ratio of mixed surfactant systems to improve oil recovery. It is also possible to develop systems which are equally effective. However, for NBU oil, at NBU salinity, a surfactant system has not yet been tested that reduced oil saturation in corefloods below 18% S_{orwf}.

Salinity Gradients

As mentioned previously, S-2 is a mixture of anionic sulfonate surfactants and ethoxylated sulfates. Minimum IFT values with NBU oil were obtained at salinities greater than the salinity of simulated NBU brine. Coreflood, MS-CF 3, was conducted using S-2 in 140% NBU brine. The polymer, however, was prepared with lower concentration brine, creating in essence a salinity gradient behind the surfactant slug. The oil recovery in this test was relatively poor compared to the S-2/S-3 tests. This may be because the test should actually have been run at higher salinity. IFT values for this surfactant decreased from 0.04 to 0.002 mN/m as salinity increased from 140%

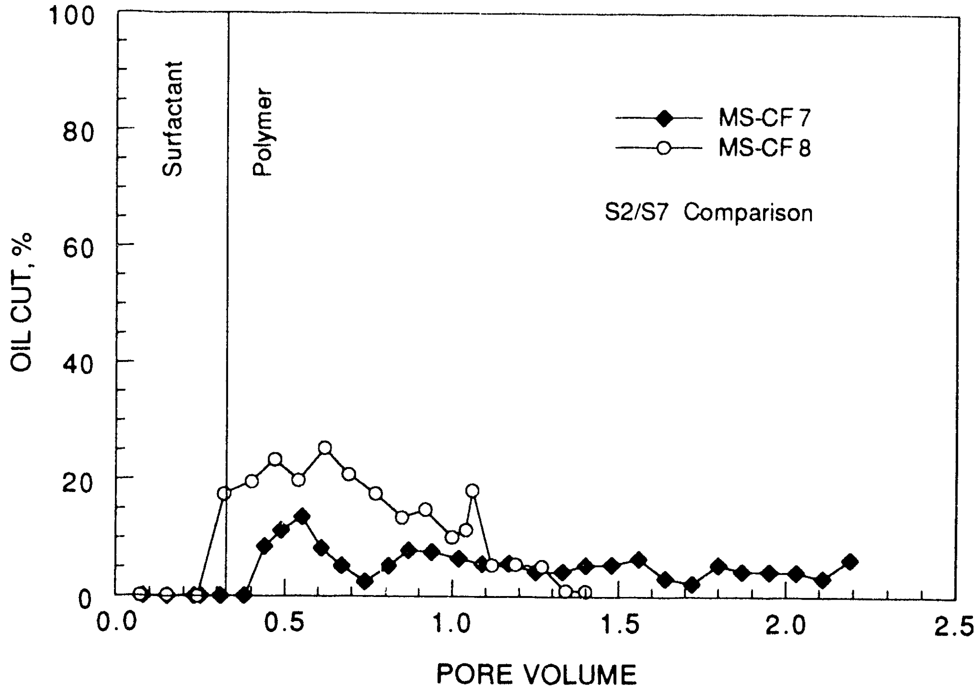


FIGURE 44. - Comparison of MS-CF 7 and 8 NBU oil recovery using the S-2/S-7 mixed surfactant system.

NBU to 180% NBU brine composition. The salinity gradient should not have improved oil recovery because the salinity of the test was already too low.

Several other tests were conducted using a slight salinity gradient by using lower salinity in the polymer solution (in 70% NBU brine). These tests included MS-CF 2 and 4. Figure 45 shows a slight increase in oil production for each test at approximately 0.9 PV after the start of the polymer injection. While neither test was as successful in an overall manner for producing oil, the use of a salinity gradient may be an additional mechanism for improving the overall recovery efficiency of mixed surfactant systems.

The alkaline corefloods described in previous sections actually contained a salinity gradient as part of the recovery mechanism. While both the surfactant and polymer solutions were prepared with the same sodium chloride and divalent ion concentrations, the surfactant solution also contained alkaline additives which raised the ionic strength and effective salinity of the solution. The highly effective surfactant formulation banked the oil such that a salinity gradient effect could not be detected relative to overall oil recovery. However, for surfactant that must travel longer distances either in corefloods in the laboratory or in the field, the effect of a salinity gradient that would keep the surfactant/oil within a favorable three-phase region may be more evident.

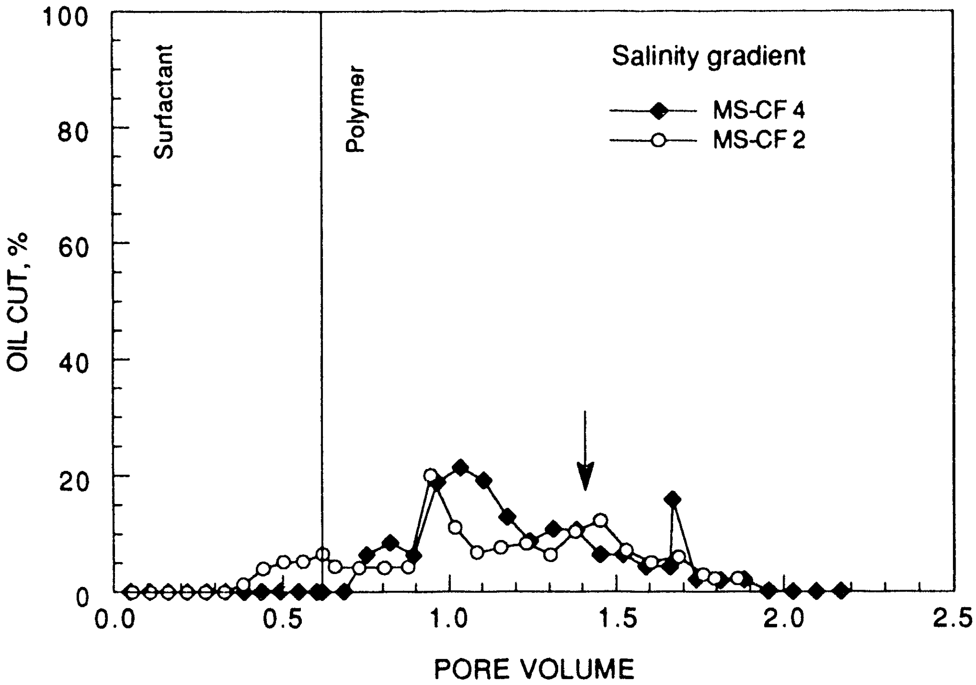


FIGURE 45. - Indications of an increase in oil production from the use of lower salinity in the polymer mobility control slug.

Coreflood Summary

Moderate success was achieved using mixed surfactant systems to produce NBU oil from sandstone cores saturated with simulated NBU brine. At least two surfactant formulations reduced NBU oil saturations to 18 to 20%. A similar system was no more effective at producing NBU oil for low salinity conditions using alkaline additives to reduce calcium ion concentrations ahead of the surfactant system.

Production of Hepler oil, which has a higher viscosity and lower API gravity than that of NBU oil, using the same surfactant system was greater than that for NBU oil for the same production conditions. Alkaline preflushes appeared to increase the production of Hepler oil. Of the tests with Government Wells oil, oil recovery results appeared to correlate more with those of NBU oil than with Hepler oil.

Oil recovery with the mixed surfactant systems appeared to depend on effective mobility control and/or core permeability. Corefloods which were monitored using CT imaging may give important clues concerning the reasons why some mixed surfactant systems or polymer mobility control agents are more effective than others.

Additional studies are planned to examine the effects of core properties, chemical formulations, and oil properties on oil recovery potential of mixed surfactant systems.

Chemical Flooding Applications in Class 1 Reservoirs

Chemical flooding EOR has been identified by the Department of Energy (DOE) as an important production technique targeted for Class 1 reservoirs.[1] One of the Class 1 reservoirs selected for the mixed surfactant research work was the North Burbank Unit (NBU), Osage County, Oklahoma. Comparatively, it has a significant quantity of unproduced oil and is a prime candidate for the application of advanced tertiary oil recovery methods. A brief description of the production history of the NBU was discussed earlier.

The purpose of this section is to identify reservoir parameters within the same class as the NBU as well as provide some conceptual strategy of how the overall chemical flooding research program may be applicable to this class. This would help provide an overview of the scope or range of different conditions for Class 1 fields and also provide some way to quantify the target oil resources. This section does not in any way exhaust all the possible areas of evaluating the potential application of EOR methods in this class. A comprehensive discussion of Deltaic reservoirs was reported in a recent publication.[41]

As mentioned in an earlier section, the current production capacity of the Burbank reservoir is estimated to be about 350,000 barrels of oil per year.[1] Another estimated 100 million barrels of unrecovered mobile oil can be recovered from this reservoir. Projections of an additional 85 million barrels of more oil can be recovered through the application of advanced chemical EOR methods.[1] This represents a fairly sizeable target oil resource. But before an EOR technology can be successfully applied in a reservoir like the Burbank, several key issues inherent within this particular reservoir need to be addressed. The relatively high degree of geological heterogeneities within this reservoir can be directly related to the deltaic depositional processes. As discussed earlier, the Burbank reservoir has been the site of an earlier unsuccessful surfactant/polymer.[42] Several factors have been determined to have had an adverse effect on the performance of the EOR pilot test.[43] In particular, heterogeneity, crossflow, ion exchange, and component partitioning, relative hardness of the brine were contributing factors in the failure of the pilot. This problem of reservoir heterogeneity has been well documented as one of the major factors in the failure of this earlier pilot test. Table 13 lists some of the reservoir properties for the Burbank reservoir, Bartlesville Sand and fluvial dominated deltas. This table allows for some comparison of the properties of the Burbank reservoir with other similar fields classified under the Bartlesville Sand. The Bartlesville or Cherokee sand in Oklahoma and Kansas is one of several plays within the

TABLE . 13 - Reservoir data of Burbank, Bartlesville Sand and all deltaic reservoirs[26]

	Burbank		Bartlesville Sand	Fluvial Deltas
	Upper Burbank	Lower Burbank	(Median Values)	(Median Values)
No. of Fields	1	1	32	229
Formation Temperature, °C	50	50	38	60
Formation Pressure, psi	885	885	600	1274
Porosity, %	17	17.5	17.5	19
Permeability, mD	300	50	43	128
API Gravity, °	39	37	38	39
Oil Viscosity, cP	3.7	2.4	3.3	1.0
Total Dissolved Solids, %	8.0	10.0	9.7	5.0
Depth, ft	2,900	2,900	2170	4954
Well Spacing, acres	20	20	20	41
Net Pay, ft	20	31	24	16
Gross Pay, ft	24	37.2	30	22
Original-Oil-in-Place, 10^6 (bbl)	494	744	83	27
Original Oil Saturation, %	70	70	66	68
Current Oil Saturation, %	31	41	47	43
Oil Saturation (Swept Zone), %	25	25	25	25

fluvial-dominated deltaic reservoirs. The Burbank reservoir properties, particularly the temperature and salinity, fall in the mid-range value for reservoirs in this class.

Figure 46 shows a scatter plot of the available oil resource in deltaic reservoirs as a function of the different reservoirs parameters such as salinity, temperature, permeability and porosity. These plots show the relationship of the Burbank reservoir with respect to the Bartlesville Sand play and the overall class of the fluvial-dominated deltas. The Burbank contains a fairly high amount of remaining oil, ranking close to the highest in barrels of remaining-oil-in-place. The salinity, in terms of total dissolved solids, is fairly mid-range with some relatively large quantities of oil present in the lower salinity category (< 10% TDS). The scatter in temperature is fairly high, but the majority of the Bartlesville Sand play fall in the less than 50 °C range. The permeability and porosity ranges for the Bartlesville Sand are fairly uniform within this play. Figure 47 shows a scatter plot of the relationship between the permeability and porosity for the deltaic reservoirs. A certain degree correlation, in terms of porosity and permeability, may be possible for these reservoirs. A monotonic trend in the permeability as a function of porosity appears to be indicated. The Burbank reservoir fall about mid-range in value, in terms of porosity.

The histograms presented in figures 48-52 show a better picture of how the Burbank reservoir compares with the Bartlesville Sand and all the other deltaic reservoirs. Figure 48 shows a histogram plot of the permeability distribution for the Bartlesville Sand and the fluvial-dominated

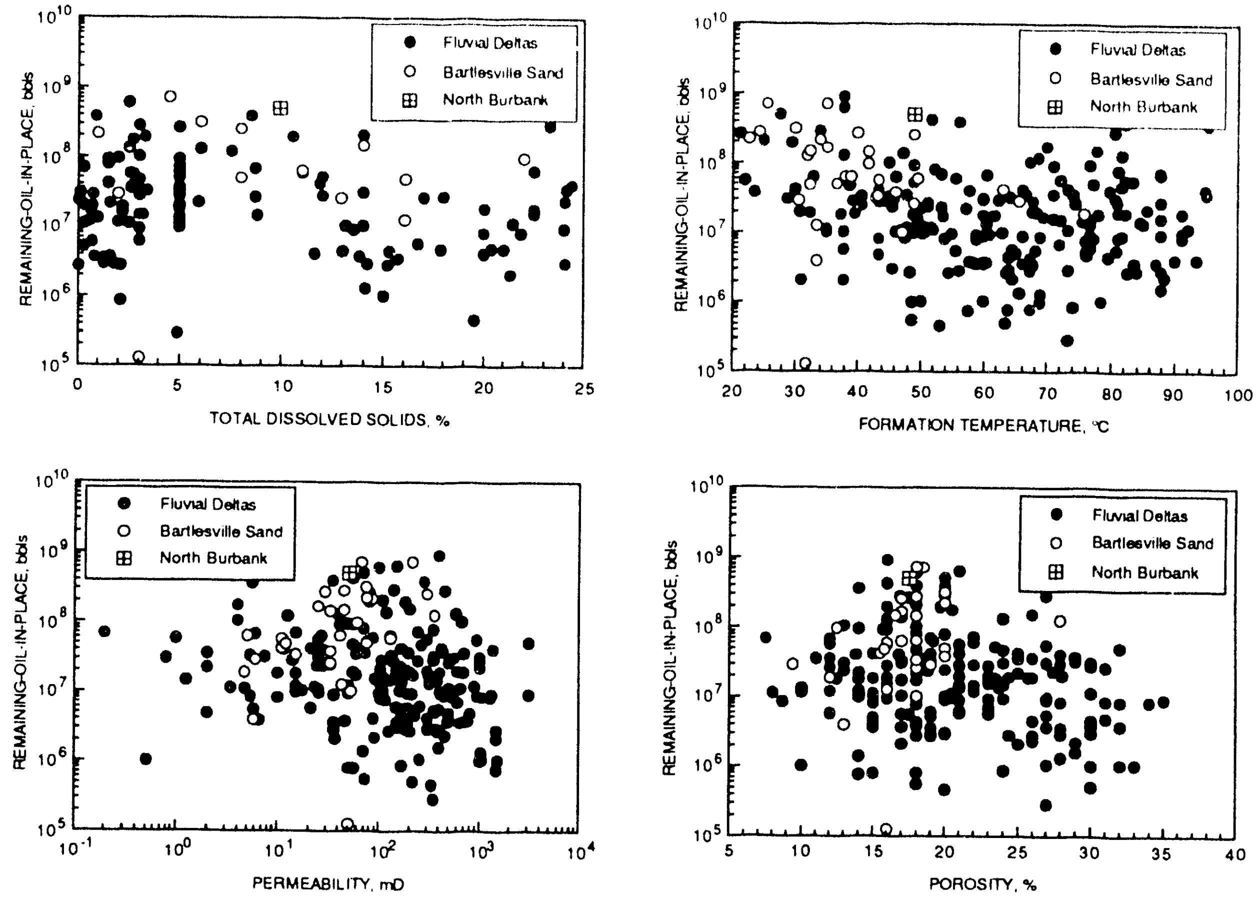


FIGURE 46. - Scatter plot of the comparison of the data on remaining-oil-in-place and different reservoir parameters for Burbank, Bartlesville Sand, and other fluvial-dominated deltaic reservoirs.

deltas. The figure shows relatively low values (<100 md) for majority of the deltaic reservoirs. The Burbank is close to the relative median within the Bartlesville Sand play. Figure 49 shows a plot of the frequency distribution for the porosity within this class. In both comparisons, the Burbank was fairly mid-range. Figures 50 and 51 show a wide distribution in temperature and salinity, respectively. The range in property distribution is relatively broad, from 0 to 24% TDS and 20 to 95 °C. On the other hand, the frequency distribution for the oil gravity appeared to be relatively normal (bell-shaped curve), with the Burbank oil gravity close to average. The data on the oil gravity is presented in figure 52.

Figure 53 and 54 show plot of the reservoir frequency distribution and the remaining-oil-in-place versus total dissolved solids and temperature. Figure 53 shows that a large number of these reservoirs fall within the less than 10% TDS category but the temperature distribution is fairly

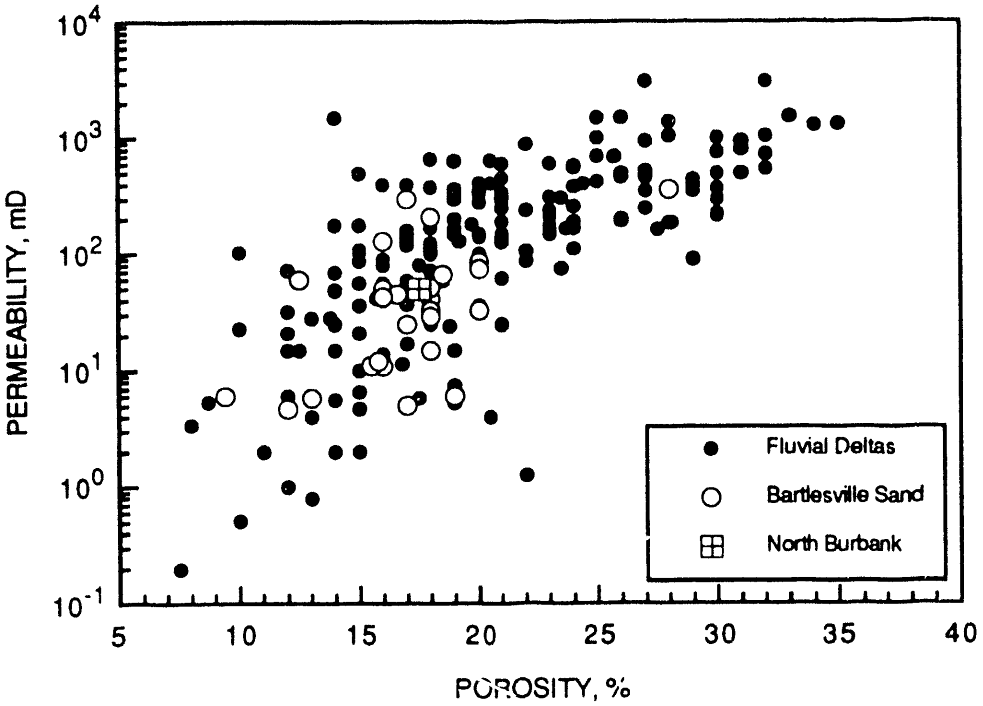


FIGURE 47. - Scatter plot of the comparison of the data on permeability and porosity for Burbank, Bartlesville Sand and other fluvial-dominated deltaic reservoirs.

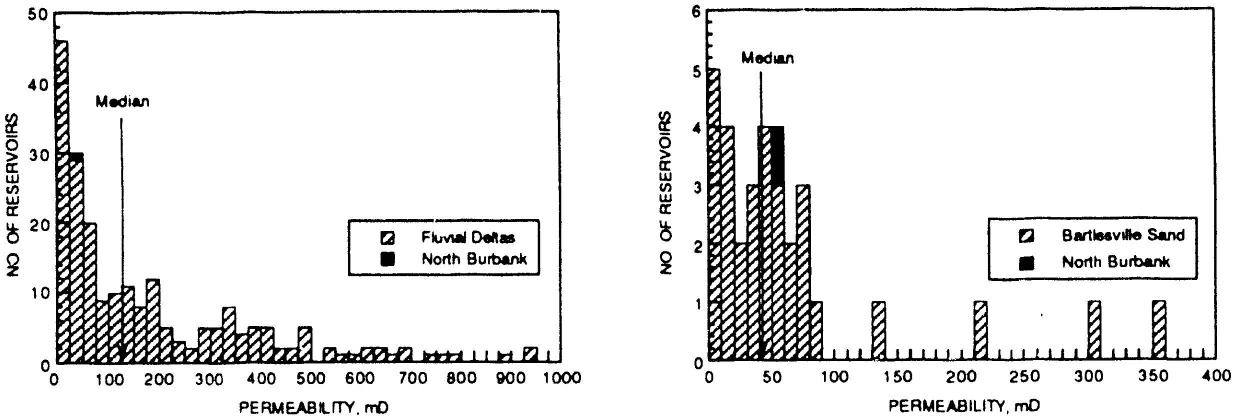


FIGURE 48. - Histogram plot of the comparison of the data on permeability for Burbank, Bartlesville Sand and other fluvial-dominated deltaic reservoirs.

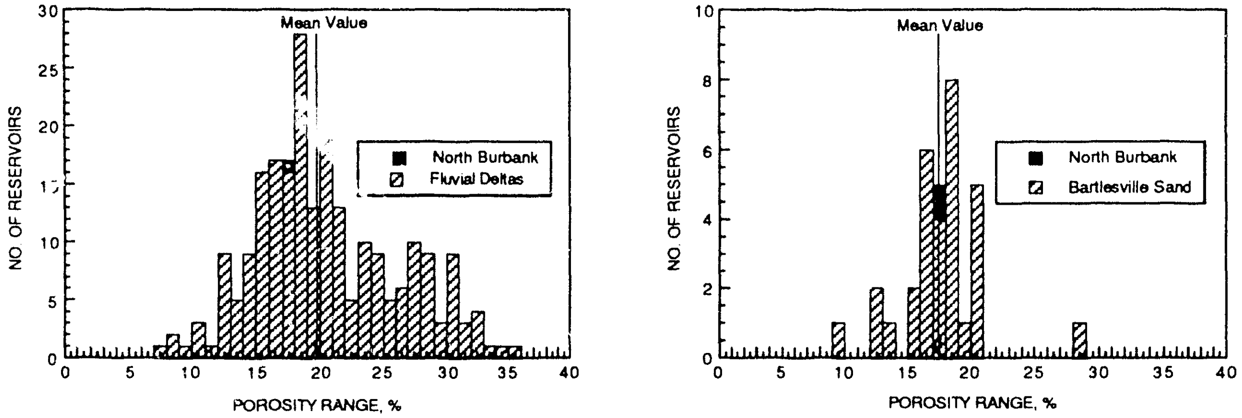


FIGURE 49. - Histogram plot of the comparison of the data on porosity for Burbank, Bartlesville Sand, and other fluvial-dominated deltaic reservoirs.

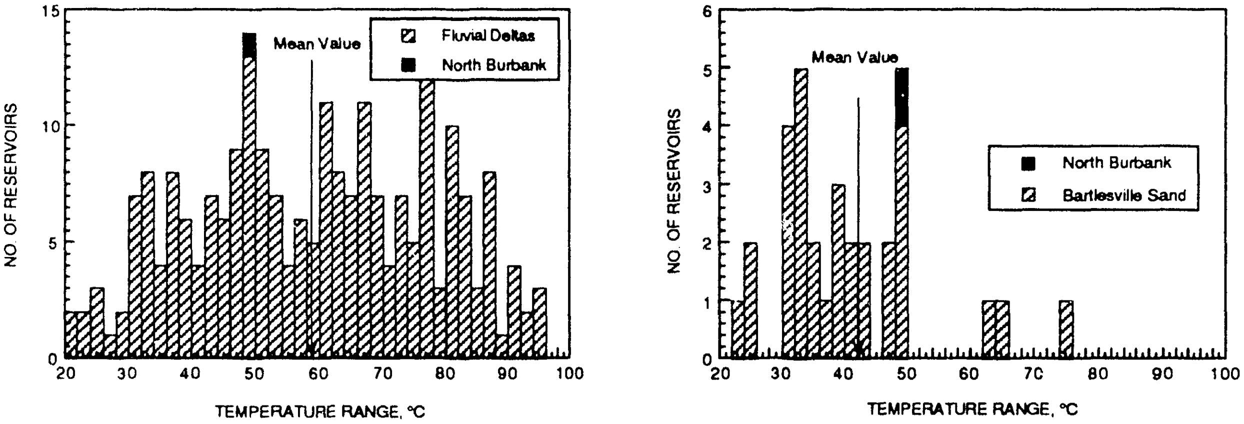


FIGURE 50. - Histogram plot of the comparison of the data on temperature for Burbank, Bartlesville Sand, and other fluvial-dominated deltaic reservoirs.

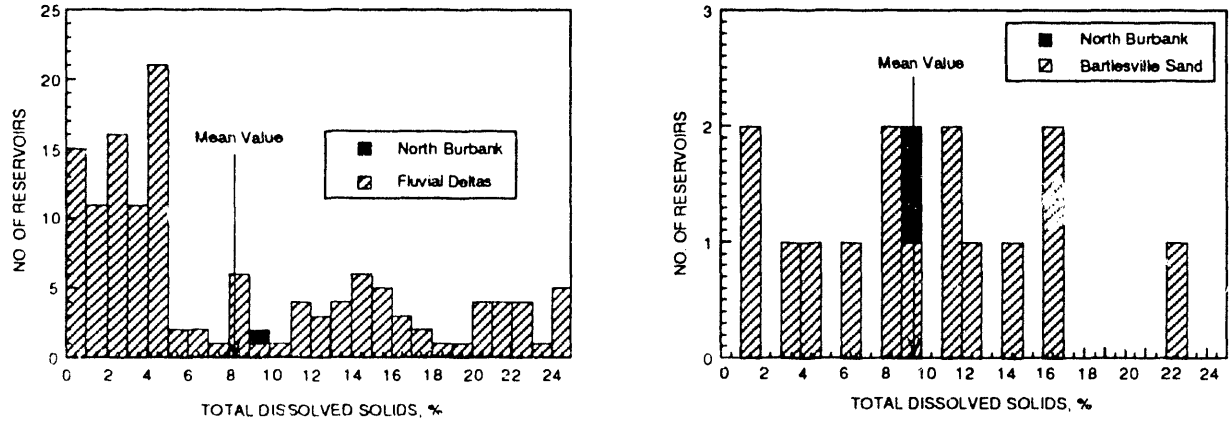


FIGURE 51. - Histogram plot of the comparison of the data on salinity for Burbank, Bartlesville Sand, and other fluvial-dominated deltaic reservoirs.

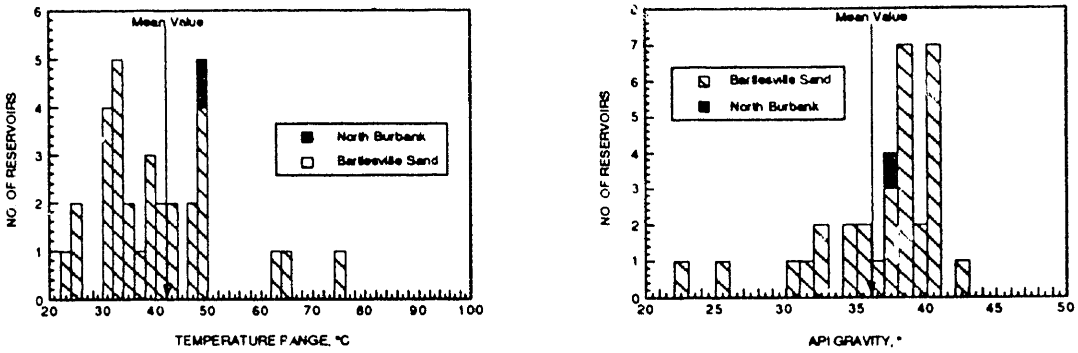


FIGURE 52. - Histogram plot of the comparison of the data on oil gravity for Burbank, Bartlesville Sand, and all deltaic reservoirs.

Figure 53 and 54 show plot of the reservoir frequency distribution and the remaining-oil-in-place versus total dissolved solids and temperature. Figure 53 shows that a large number of these reservoirs fall within the less than 10% TDS category but the temperature distribution is relatively wide, 40 to 70 °C. The Burbank falls in the mid-range in terms of temperature but relatively higher in salinity. Figure 54 is a plot of the oil resource within the Bartlesville Sand play. The data plotted may be scarce primarily because of the lack of available information for both reservoir parameters, in particular the salinity data. The Burbank reservoir represents is a fairly sizeable oil resource for this play.

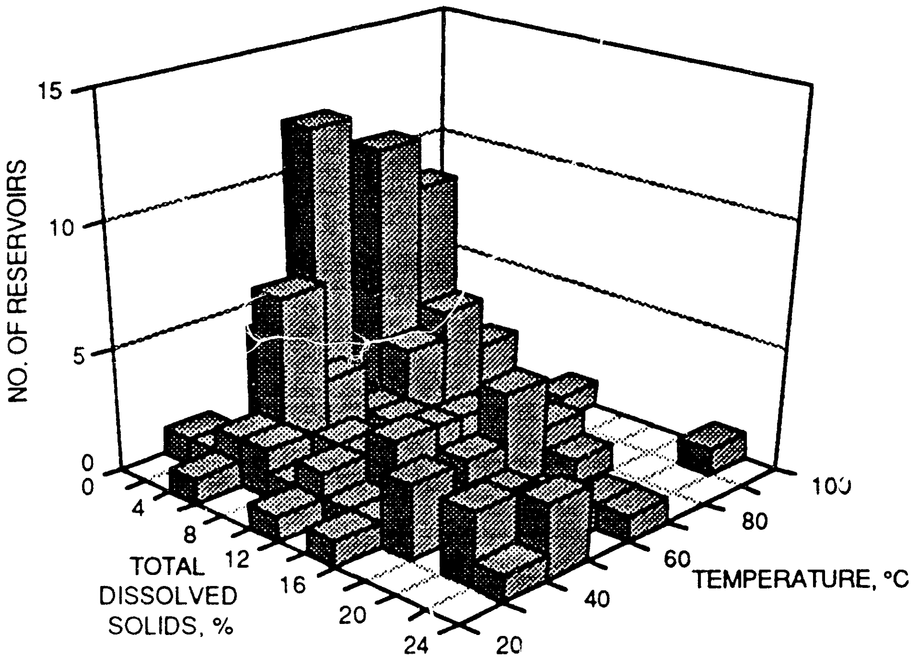


FIGURE 53. - Three-dimensional bar graph on salinity and temperature data of deltaic reservoirs.

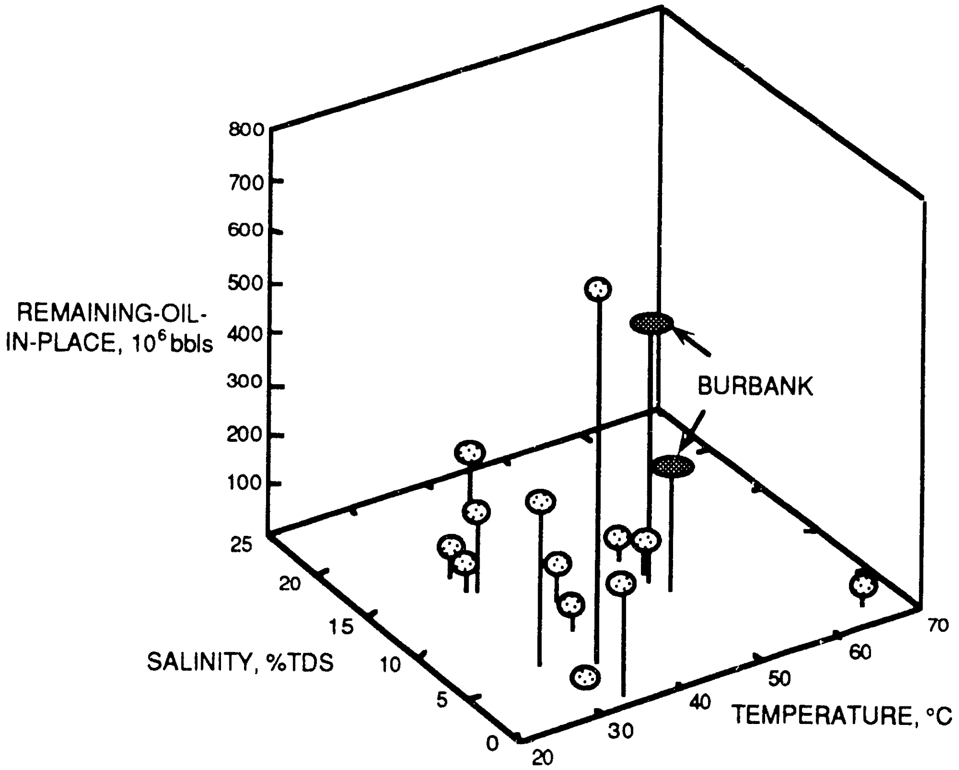


FIGURE 54. - Three-dimensional plot of remaining-oil-in-place (million barrels) vs. temperature and salinity for Bartlesville Sand and Upper and Lower Burbank reservoirs.

reservoir inherent parameters that have been identified as representative of the fluvial-dominated deltas, and for that matter within the Bartlesville or Cherokee Sand play. This in turn will help develop some conceptual strategy of how the NIPER's research work in the chemical flooding area may be applied in the Class 1 group of reservoirs.

SUMMARY AND CONCLUSIONS

- Several mixed surfactant systems have been studied to evaluate their oil recovery potential as well as improved adaptability to different ranges of salinity, divalent ion concentrations, and temperature. The effects of different parameters on the behavior of the overall surfactant system were studied. Several combinations of different surfactants and types have been shown to exhibit different phase behavior. Some of these behavior was attributed to the structure, molecular weight, and proportion of the different surfactant components.

- A qualitative dependence of the salinity tolerance on the molecular weight, surfactant type and concentration of the surfactant components in the system was observed. The ethoxylated sulfates were better than the ethoxylated sulfonates in improving the tolerance of the overall chemical system. The molecular weight and the branching-structure of both the ethoxylated sulfonates and sulfates affected the overall salinity tolerance of the mixture. Shorter chain length and branching favored improved solubility and salinity tolerance.

- The total surfactant concentration can also affect the performance of these mixed system. As the total concentration increased, the favorable salinity region appeared to have slightly increased. The proportion of the different types of surfactants effectively adjusted the region favorable salinity for a given surfactant system. The proportion of the salinity-tolerant surfactant (i.e. ethoxylated sulfates) was critical on whether or not the overall system exhibited good phase behavior.

- The degree of ethoxylation in the primary component (sulfonate-type) was found to be helpful in reducing the salinity-tolerant surfactant requirement and shifted the salinity range of the chemical system. The alcohol content in the chemical solutions also affected their behavior . The presence of the alcohol enhanced in the solubility of the mixture but had a deleterious effect on the IFT and oil solubilization potential.

- Several screening methods were used to help identify techniques that can be used to screen other potential chemical formulations. One of these methods was the phase inversion temperature measurement. This method was used to help identify regions of operating conditions that may be of interest (i.e. temperature and salinity) as well as tie-in some information obtained using the IFT and phase behavior measurement. Combinations of these screening methods was useful in determining conditions where particular chemical systems can be applied.

- The salinity gradient phase inversion measurement and the titration calorimetry were also used as screening methods. A well-studied chemical system was used in these evaluations. The results from the salinity gradient tests indicated that the peak in solution conductivity appeared to coincide with the estimated mid-point of the three-phase region of this surfactant system. One interesting observation was made when using the titration calorimetry method, a bend in the heat of mixing curve occurred that seemed to correlate with the optimal salinity value (1.5% NaCl) identified using previous gradient method and from phase tube studies. The phase boundary transitions though were not observed both methods. In spite of the failure of the combination of the salinity gradient phase inversion measurement and titration calorimetry in defining the phase boundary transitions, this type of screening may be used in determining an optimal salinity for the selected chemical system. The time and effort involved in the titration experiments however, suggests limited usefulness as a screening tool.

- For the mixed surfactant systems studied in this report, oil recovery depended on both the efficiency of the surfactant system and on the effectiveness of the polymer mobility control slug. Core permeability, polymer injectivity, or effective viscosity ratio of the polymer and surfactant/oil solutions may affect the oil recovery properties of the chemical system.

- CT imaging can be a valuable tool in evaluating the performance of chemical flooding systems. The effect of different operating parameters on oil recovery can be examined using this technique.

- Oil recovery was more efficient for mixed surfactant systems with alkaline additives than without these additivities. This may be related to the lower salinity conditions of these tests, however.

- Using the same surfactant system, little difference was observed between overall recovery efficiency of a lower concentration, larger PV injection strategy as compared to a higher concentration, smaller slug. The former method is useful for investigations and comparisons of parameters affecting oil recovery. The later method, however, would be more favorable for economic considerations.

- For coreflood experiments using a mixed surfactant system conducted using separate injection of surfactant and polymer, a correlation existed between residual oil saturation at the end of the waterflood and the amount of oil produced ahead of the oil bank (i.e., the large production peak that occurred approximately 0.3 to 0.5 PV's after the start of polymer injection). This correlation was independent of oil type, salinity, and core permeability.

- The Burbank reservoir properties was grouped in the mid-range of values for Class 1 reservoirs. A comparison was made between the reservoir properties inherent to the Burbank and the Bartlesville Sand play. These data were then in turn compared to the overall fluvial-dominated delta class. The information provided was useful in developing some conceptual map of how the NIPER's research work in the chemical flooding area may be applied in this class of reservoirs.

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APPENDIX A

The following graphs summarize the oil production history (oil cut as a function of volumetric throughput) and cummulative oil production for the corefloods discussed in this report. Composition of chemical slugs and core permeability are also indicated.

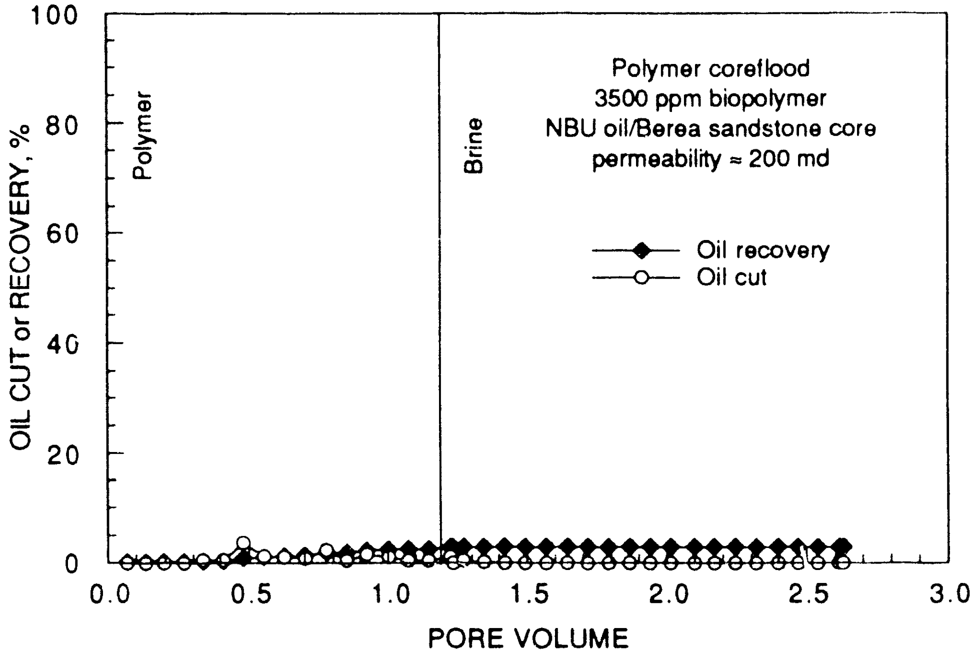

FIGURE A1.- Coreflood information for polymer flood with added surfactant.

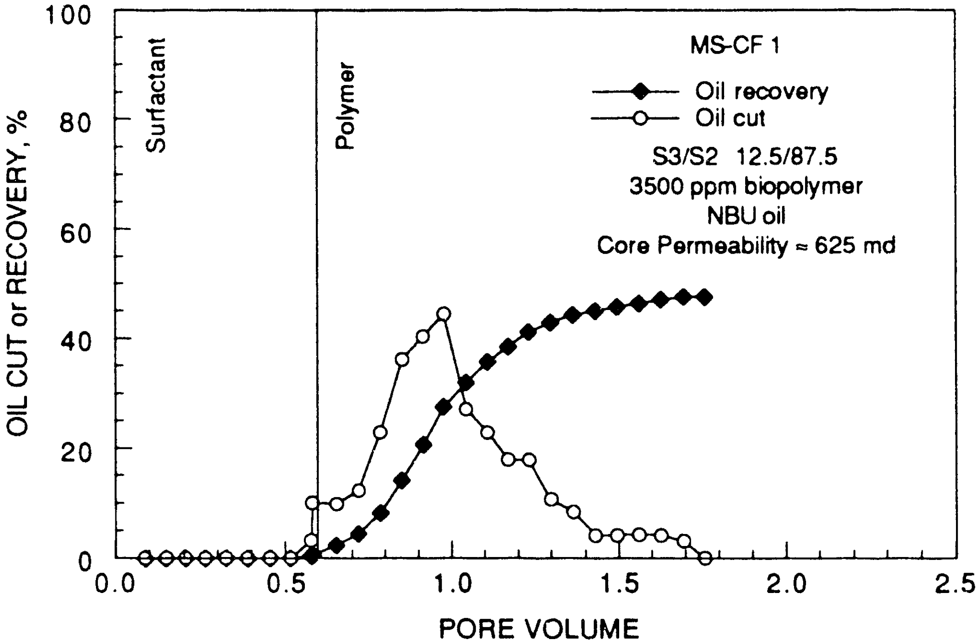

FIGURE A2.- Low salinity and temperature mixed surfactant coreflood, MS-CF 1, using high permeability core.

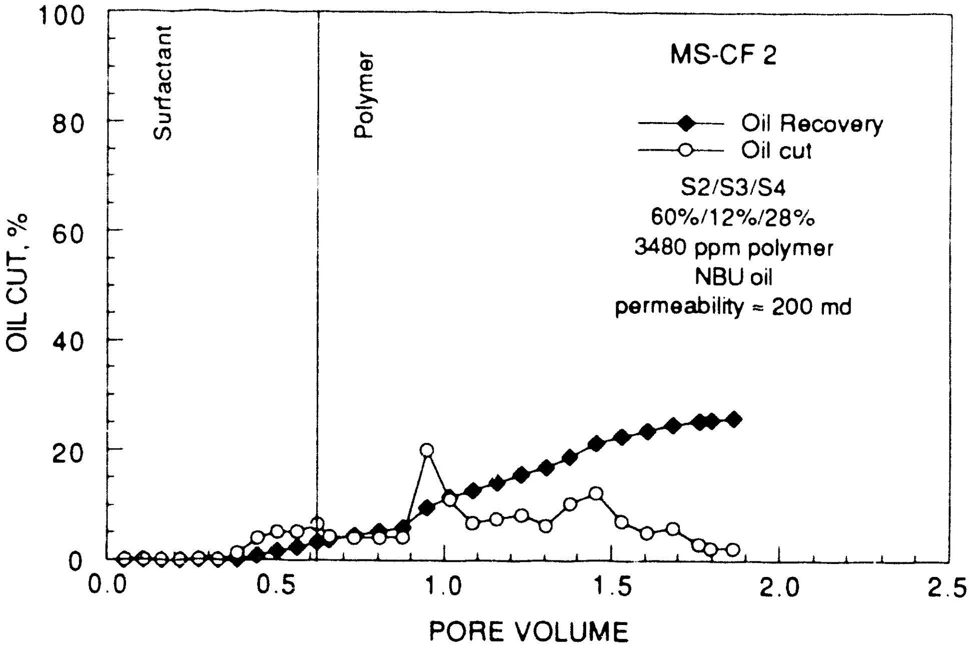

FIGURE A3.- Mixed surfactant coreflood, MS-CF 2, at NBU temperature and salinity.

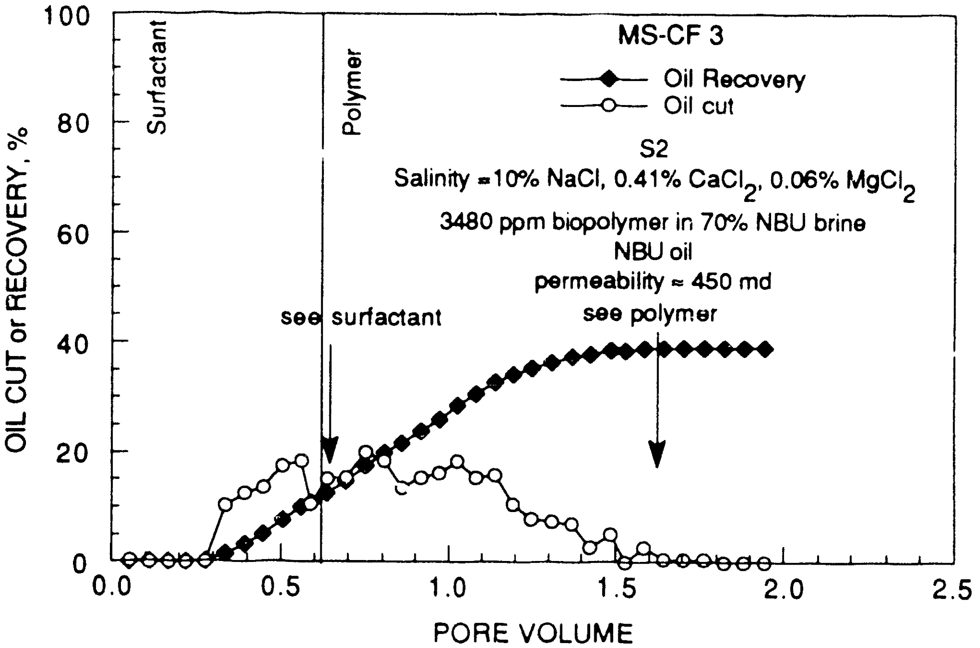

FIGURE A4 - Coreflood MS-CF 3, NBU oil recovery at using a surfactant at salinity greater than NBU salinity. Salinity gradient also used in the during polymer injection.

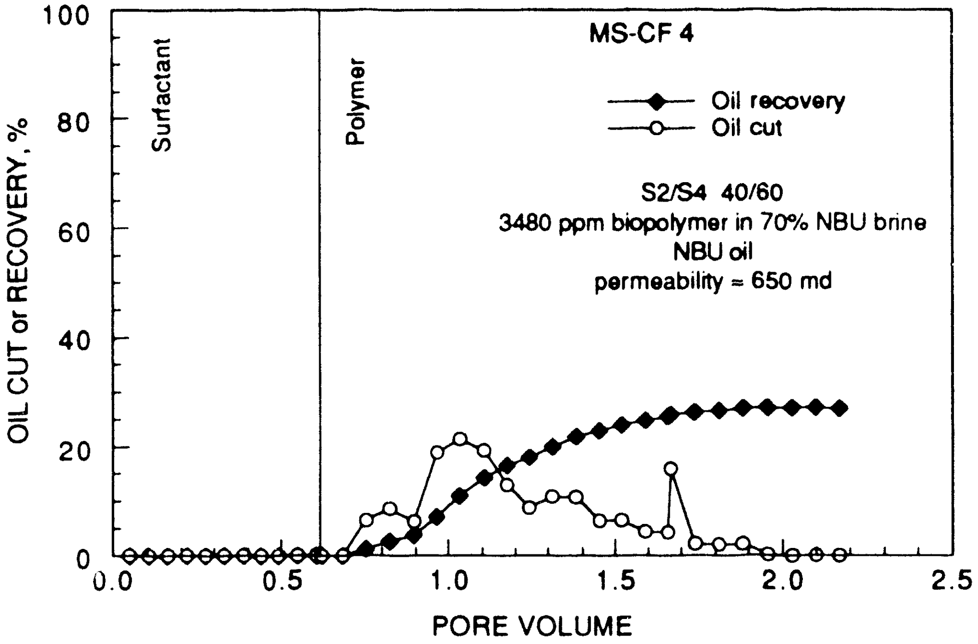

FIGURE A5.- Mixed surfactant coreflood. MS-CF 4, at NBU temperature and salinity.

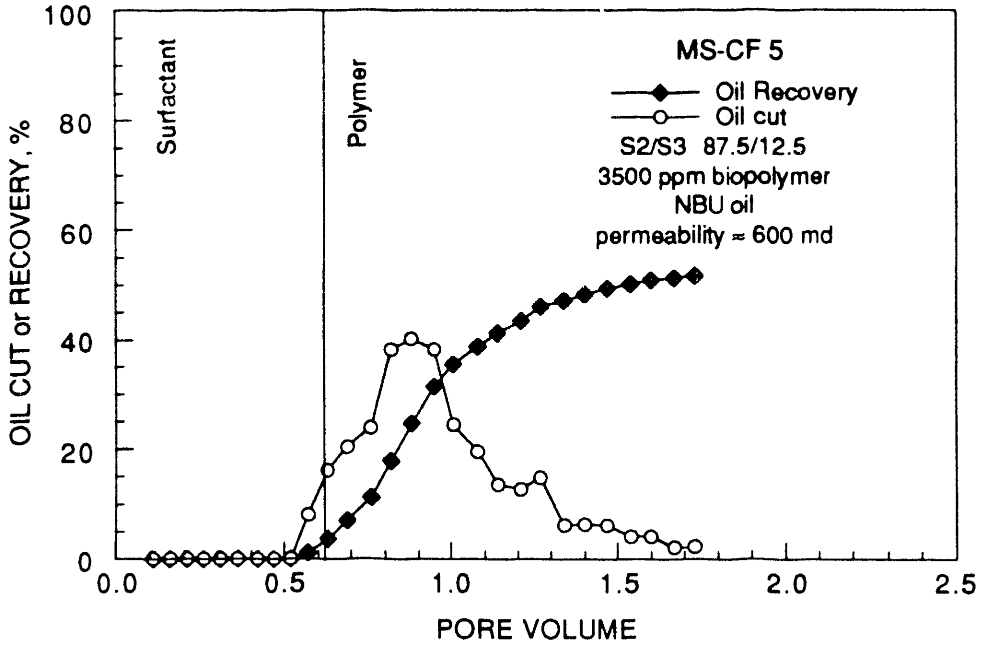

FIGURE A5.- Mixed surfactant coreflood, MS-CF 5, at NBU temperature and salinity.

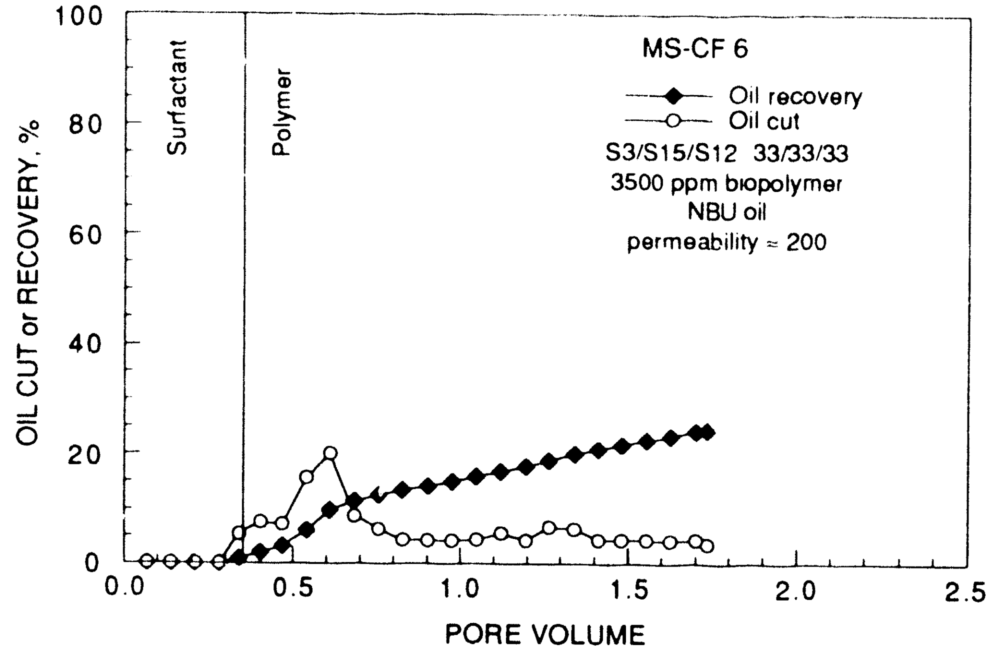

FIGURE A7.- Mixed surfactant coreflood, MS-CF 6, using both the anionic and nonionic surfactants at NBU temperature and salinity.

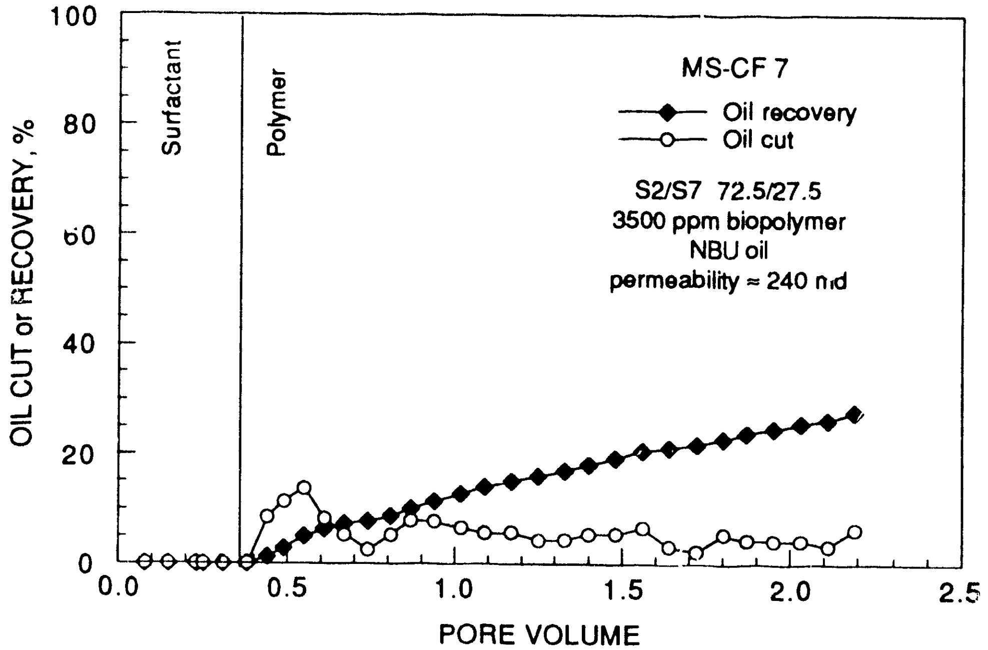

FIGURE A8.- Mixed surfactant coreflood, MS-CF 7, at NBU temperature and salinity.

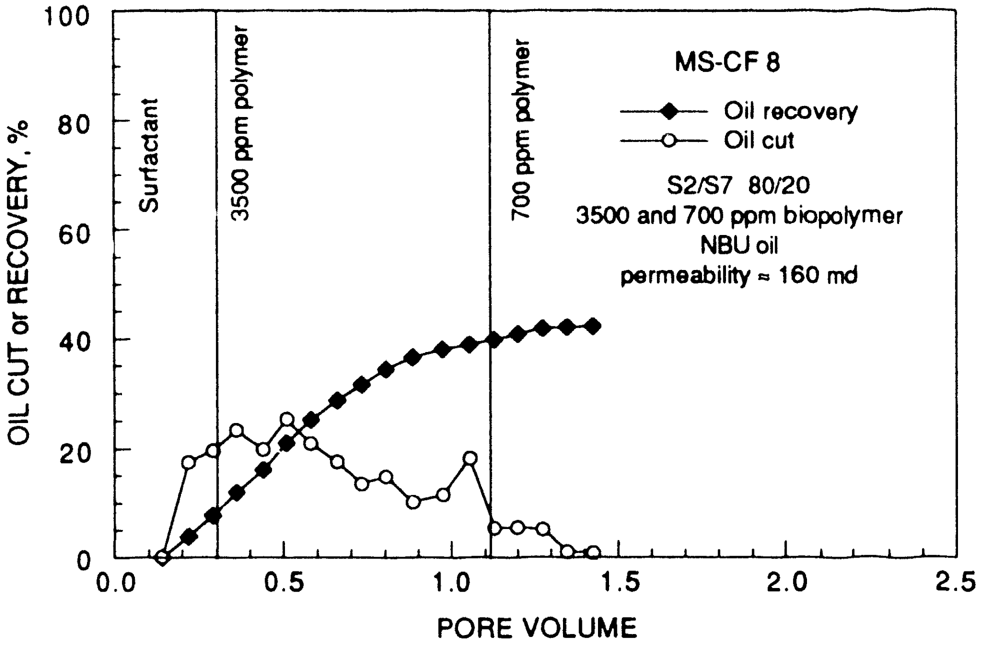

FIGURE A9.- Mixed surfactant coreflood, MS-CF 8, at NBU temperature and salinity.

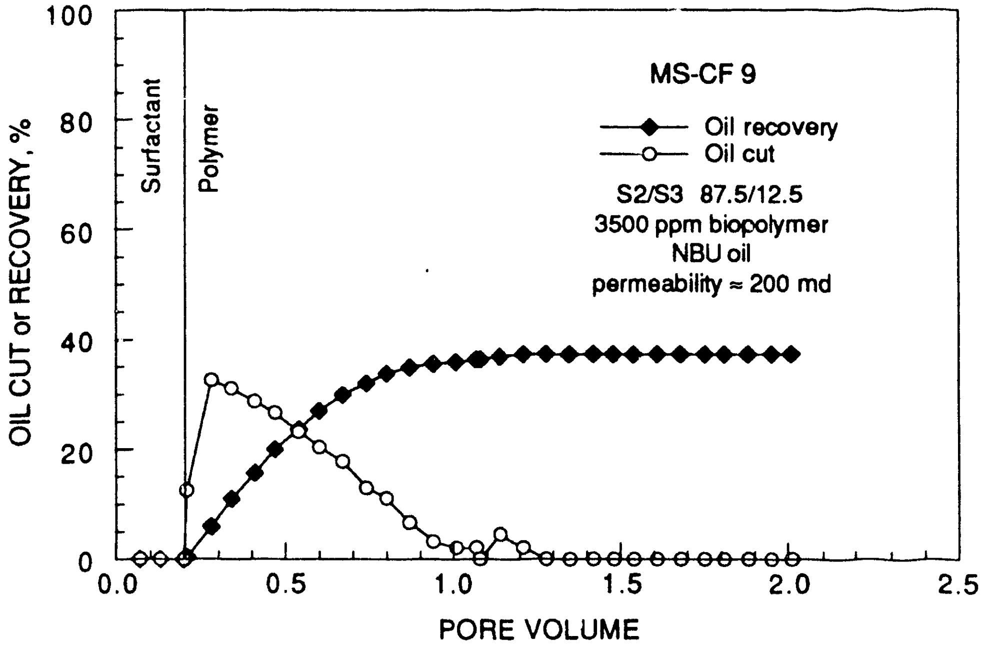

FIGURE A10.- Mixed surfactant coreflood, MS-CF 9, at NBU temperature and salinity. Higher surfactant concentration and smaller slug size than MS-CF 10.

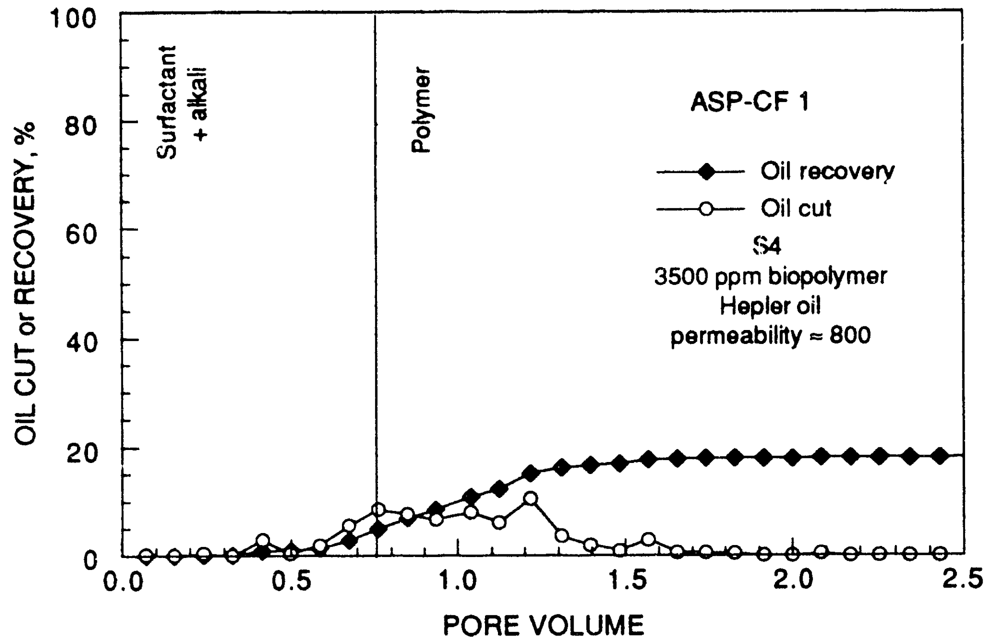

FIGURE A13.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 1, conducted at ambient temperature and low salinity.

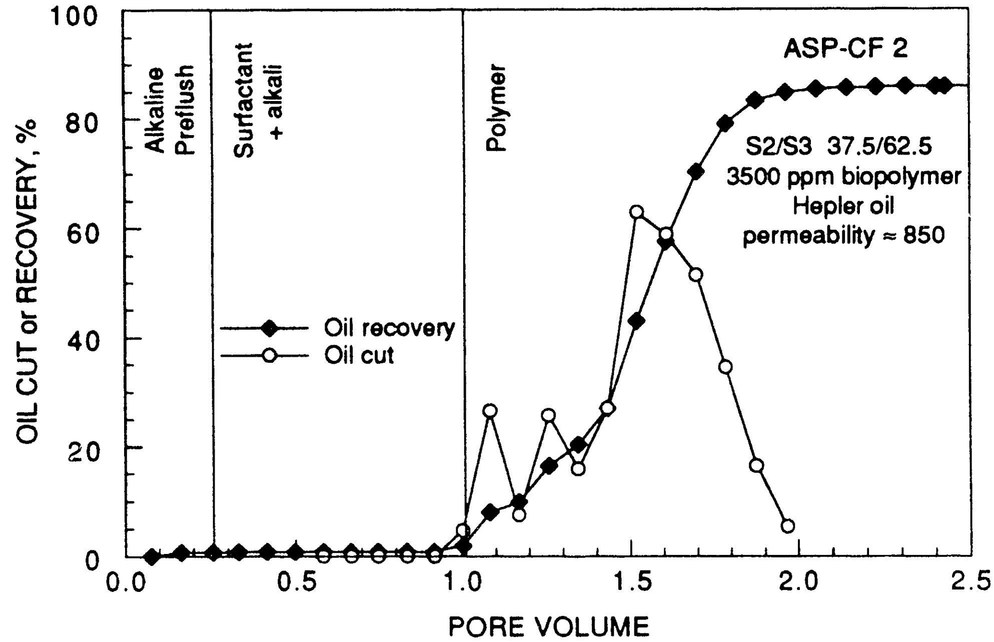

FIGURE A14.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 2, conducted at ambient temperature and low salinity.

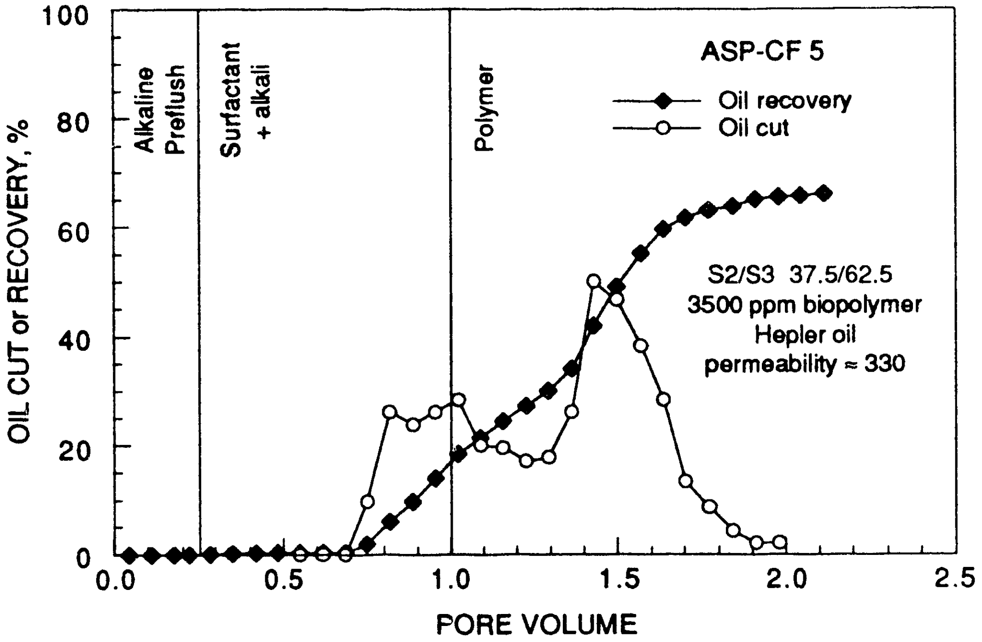

FIGURE A17.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 5, conducted at ambient temperature and low salinity.

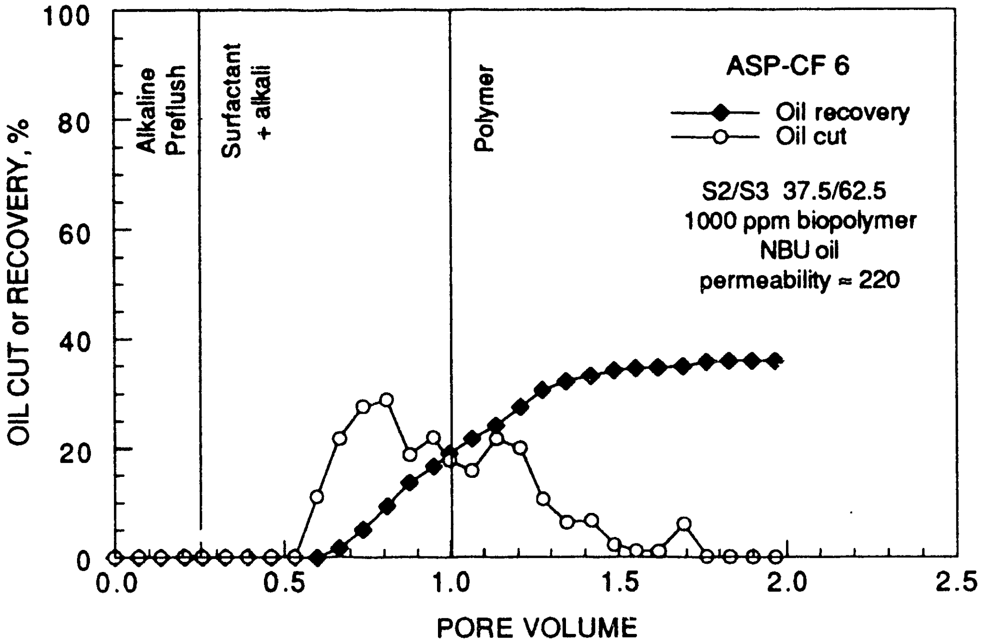

FIGURE A18.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 6, conducted at ambient temperature and low salinity using a different oil and polymer concentration.

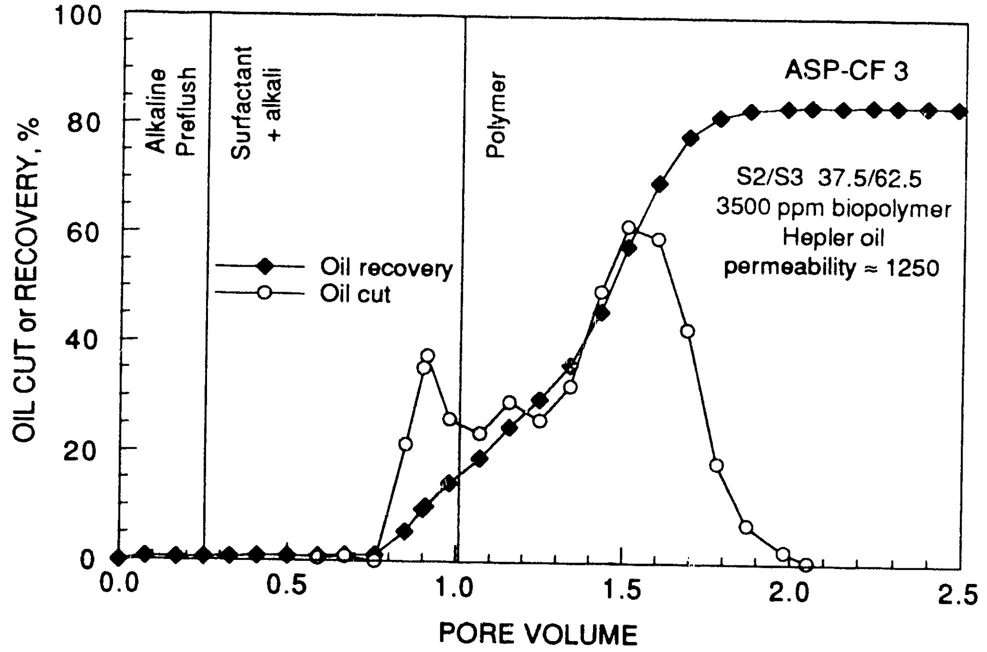

FIGURE A15.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 3, conducted at ambient temperature and low salinity.

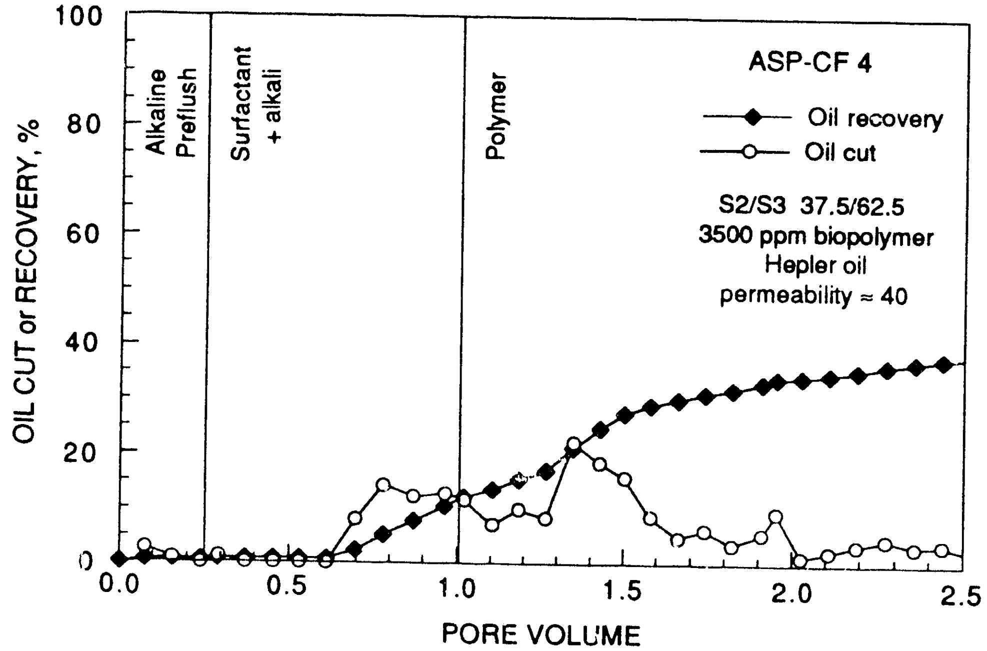

FIGURE A16.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 4, conducted at ambient temperature and low salinity in low permeability core.

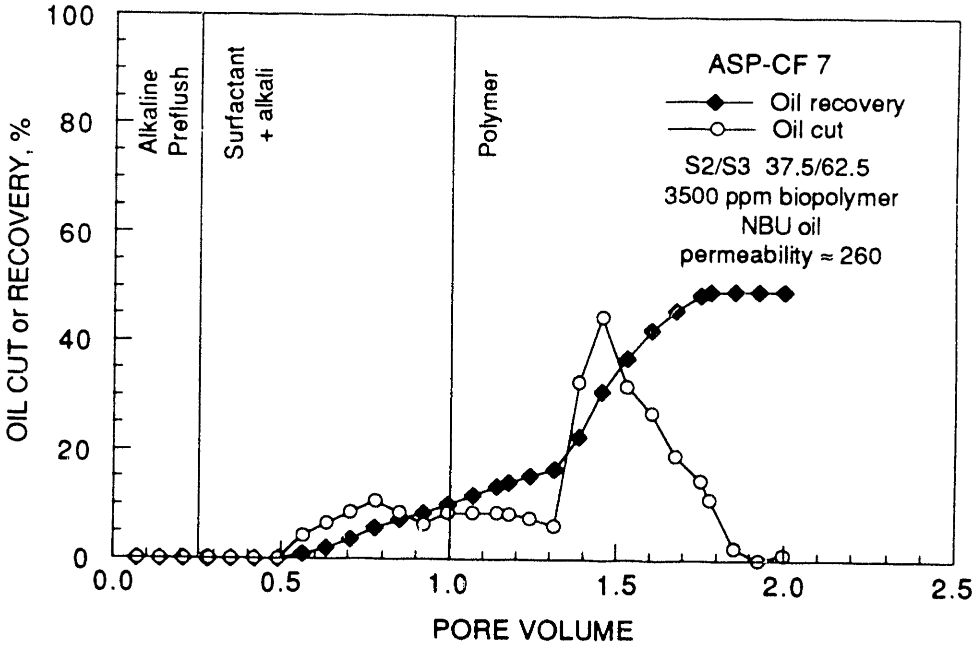

FIGURE A19.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 7, conducted at ambient temperature and low salinity.

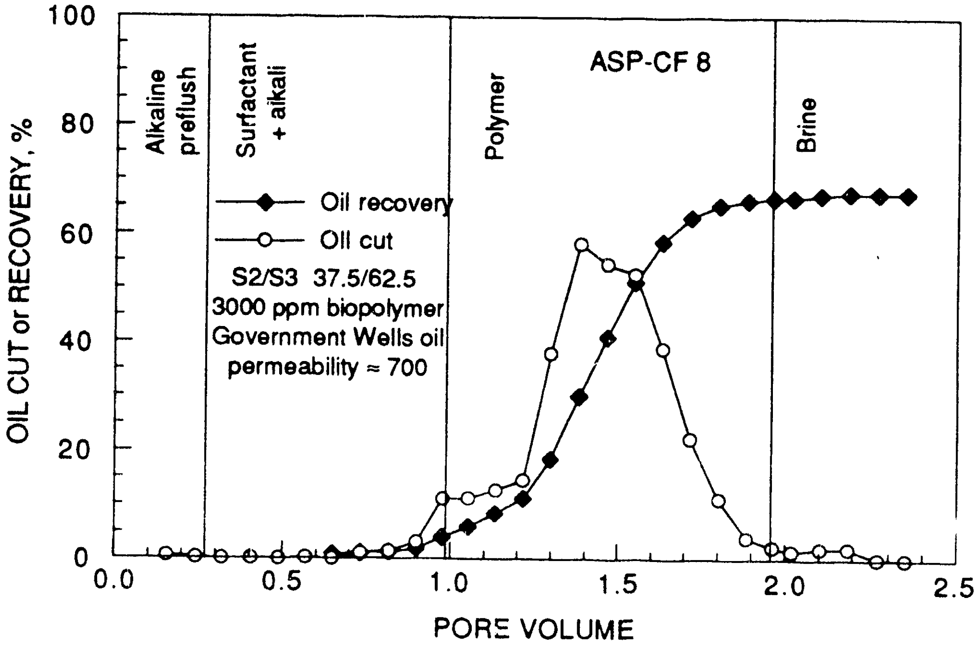

FIGURE A20.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 8, conducted at ambient temperature and low salinity with Government Wells oil.

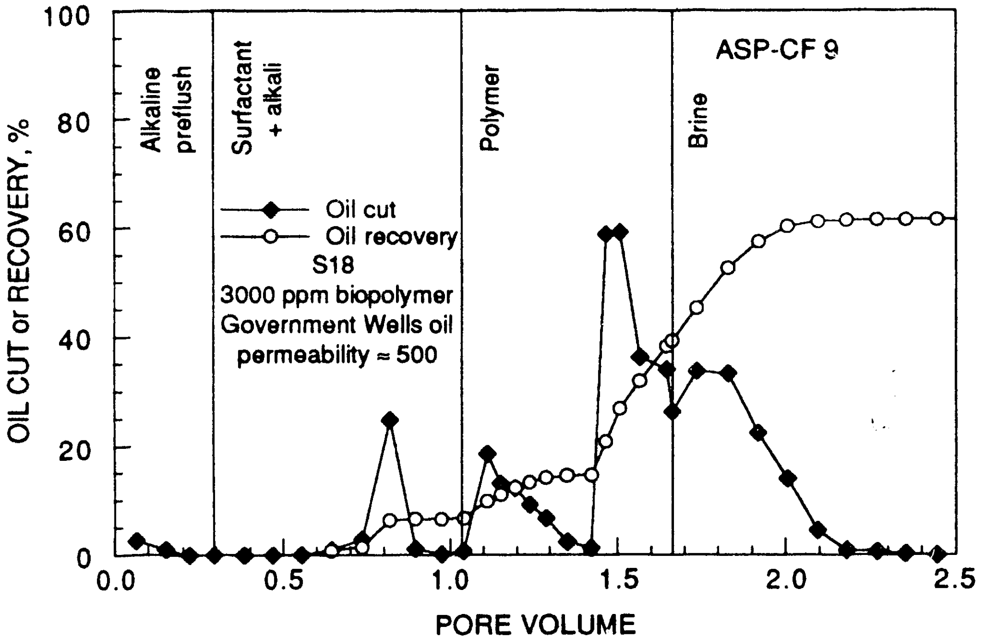

FIGURE A21.- Alkaline-enhanced mixed surfactant coreflood, ASP-CF 9, conducted at ambient temperature and low salinity with Government Wells oil and a second surfactant system.

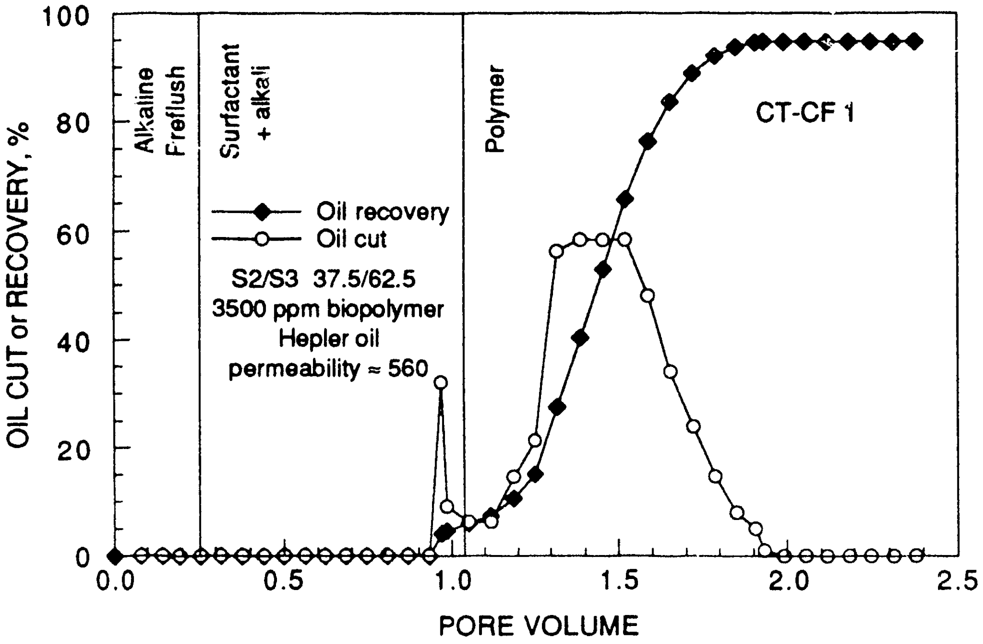

FIGURE A22.- Alkaline-enhanced mixed surfactant coreflood, CT-CF 1, that repeated coreflood conditions of tests ASP-CF 2 and 3. Coreflood progress was monitored using CT imaging techniques.

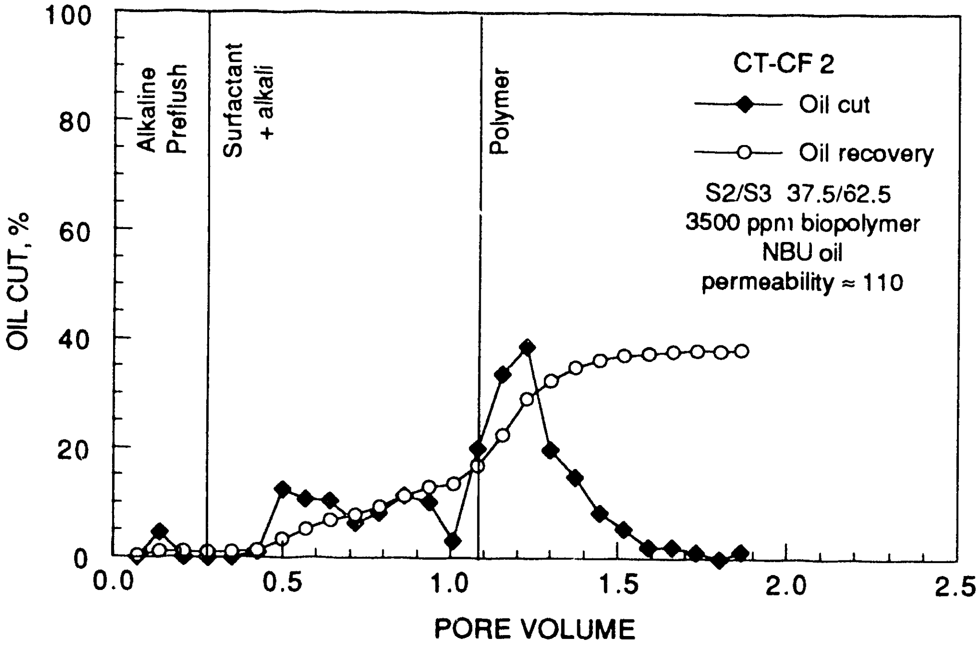

FIGURE A23.- Alkaline-enhanced mixed surfactant coreflood, CT-CF 2, that repeated coreflood conditions of test ASP-CF 5. Coreflood progress was monitored using CT imaging techniques.

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