63
12-27-89 JS ②

FOSSIL ENERGY

NIPER-447
(DE90000203)

USE OF SACRIFICAL AGENTS TO REDUCE CARBOXYMETHYLATED ETHOXYLATED SURFACTANT LOSS DURING CHEMICAL FLOODING

TOPICAL REPORT

By
Bonnie Gall

December 1989

Performed Under Cooperative Agreement No. FC22-83FE60149

IIT Research Institute
National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma

Bartlesville Project Office
U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma

NIPER-447
Distribution Category UC-122

USE OF SACRIFICIAL AGENTS TO REDUCE CARBOXYMETHYLATED ETHOXYLATED SURFACTANT LOSS DURING CHEMICAL FLOODING

TOPICAL REPORT

NIPER--447

DE90 000203

By
Bonnie Gall

December 1989

Work Performed Under Cooperative Agreement No. FC22-83FE60149

Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

Jerry Casteel, Project Manager
Bartlesville Project Office
P.O. Box 1398
Bartlesville, OK 74005

Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
Box 2128
Bartlesville, OK 74005

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

TABLES

TABLES -- Continued

ILLUSTRATIONS

USE OF SACRIFICIAL AGENTS TO REDUCE CARBOXYMETHYLATED ETHOXYLATED SURFACTANT LOSS DURING CHEMICAL FLOODING

By Bonnie Gall

ABSTRACT

Surfactant enhanced oil recovery can produce significant incremental oil when projects are appropriately designed for specific reservoir conditions. Excess use of expensive chemical, however, can convert a technically successful oil recovery process into one that may be economically unsuccessful. As part of the surfactant research program at NIPER, which has emphasized investigations of surfactants for high-salinity or high-temperature reservoirs, a laboratory program has been developed to measure and investigate methods to reduce surfactant losses in reservoirs.

Surfactant losses of carboxymethylated ethoxylated surfactants (CME) were measured in static and coreflood experiments. The effect of several types of sacrificial agents on CME adsorption were also measured. In static tests, lignosulfonate and sodium carbonate/bicarbonate were effective sacrificial agents at low salinity or low temperature conditions. Under these conditions, surfactant loss was mainly a result of adsorption on the rock surface. However, these agents were less effective at higher salinities and temperatures where surfactant phase separation becomes an important mechanism for surfactant loss. Similar results were observed in oil recovery experiments using Berea sandstone cores and dodecane. However, under conditions which favored low surfactant retention, the surfactant was ineffective in mobilizing oil. Under conditions which produced at least some oil from the core, surfactant losses were excessively high. The most successful oil recovery conditions were observed using a CME in solution with pH adjusted to the pK_a of the carboxylate group (pH = 4.6 for a CME surfactant with an average of 6.5 ethoxylate groups per molecule). This may help balance the surfactant affinity for both oil and brine.

Reduction of surfactant losses, therefore, requires addressing the problem of phase separation or trapping of surfactant as well as reducing surfactant adsorption. Preliminary investigations are described to determine surfactant loss from mixed anionic and nonionic surfactant solutions. Mixed surfactant systems allow more flexibility to design surfactant floods for specific reservoir conditions. One surfactant may improve the solubility of another surfactant which, in solution alone, may experience more severe phase separation at the conditions of interest. The preliminary results indicated that some improvements in surfactant performance can be achieved using mixed surfactants.

INTRODUCTION

Chemical flooding has the potential to produce significant amounts of incremental oil from a reservoir. The economics of chemical flooding are directly related to the large investment in chemicals and the amount of incremental oil recovered. Therefore, the design of chemical floods often includes preflush treatments that can reduce the amount of expensive chemicals necessary to reduce residual oil saturation or, for the same costs, increase the amount of oil recovered.

Sacrificial Agents

Adsorption, precipitation, cation exchange, partitioning, and chromatographic separation of components of a chemical treatment are factors that lead to loss of effectiveness and possible failure to recover incremental oil from the reservoir. The use of sacrificial agents in either a preflush or the chemical slug can be beneficial in several ways. They can alter surfactant loss by preferential adsorption on the mineral surface or by reduction of exchangeable divalent cations which can cause surfactant precipitation or loss through phase partitioning. In some cases, these additives may improve the chemical movement through the reservoir by altering fluid mobility. A comprehensive pre-1980 literature review[1] summarizes significant laboratory work on reservoir pretreatment in chemical flooding. Mention is also made of the use of preflush treatments during field application of chemical flooding techniques. In 1980, the published results from most of these field tests were sketchy and incomplete. Reports of subsequent results from many of these field tests have been summarized in a 1989 report.[2] More detailed information on individual field test results can be found in the literature referenced in this review.

Falcone et al.[3] reviewed the use of inorganic sacrificial agents in chemical flooding applications. Certain anions such as silicates, orthosilicates, phosphates and tripolyphosphates, selenites, and fluorides are adsorbed at the mineral oxide/solution interface.[4] These anions make the surface more negative and are relatively difficult to remove using solutions containing chloride ions. This should reduce adsorption of anionic surfactant molecules by reducing the electrostatic forces attracting these negatively charged molecules to the mineral surface. In addition, anions such as phosphates, polysilicates, and carbonates can sequester or precipitate metal ions in solution. Reduction of Ca^{++} and Mg^{++} ion concentrations should reduce the detrimental effects that these ions have on surfactant precipitation and phase behavior.

In 1981, a systematic laboratory study evaluated pretreatment methods for surfactant EOR using radial Berea sandstone cores.[5] Conclusions from this study indicated that most inorganic preflushes were beneficial for increasing oil production compared to tests conducted without a preflush. Improvement in oil recovery was seen even with the use of a soft saline preflush since this treatment removed divalent ions from the connate water and provided some opportunity for cation exchange with the divalent ions on the Berea sandstone clays. Additional benefit was observed when preflush chemicals were added which precipitated or sequestered Ca^{++} and Mg^{++}.

Organic chemicals, particularly waste products or modified waste products from the paper industry, have also been used as sacrificial agents to reduce surfactant adsorption or precipitation. The study using radial cores[5] showed that organic preflushes using lignosulfonate or other waste byproducts from the paper industry were effective as sacrificial agents. Compere et al.[6] evaluated competitive adsorbates for petroleum sulfonates and determined that the most effective were lignosulfonate and bleach plant effluent (BPE) from the washing of wood pulp by alkaline solutions after exposure to bleaching agents. Johnson[7] showed that BFE reduced adsorption of a petroleum sulfonate on montmorillonite and crushed Berea sandstone by a factor of 3 when it precontacted the solid surface. If mixed with the surfactant solution, however, the reduction in adsorption was not as significant.

Novosad[8] conducted an extensive experimental program to evaluate the effect of lignosulfonate on oil production during surfactant flooding. Experiments were conducted in Berea sandstone cores using an amine salt of alkyl orthoxylene sulfonate. When all lignosulfonate that was injected as a preflush was washed from the pore space before injecting the surfactant, the lignosulfonate did reduce surfactant adsorption but did not increase oil recovery. When lignosulfonate and surfactant were pumped through the core in different slugs but without a brine spacer, oil production increased. The conclusion was that lignosulfonate had beneficial effects when used with surfactant floods but not as a sacrificial agent. It was suggested that lignosulfonate acted as a beneficial cosurfactant.

Hong et al.[9-10] evaluated lignosulfonate as a sacrificial adsorbate in preparation for a surfactant flooding field test in a Glenn Pool reservoir. In laboratory tests, the lignosulfonate did reduce surfactant adsorption by 39%. However, the acidic nature of the lignosulfonate solution caused dissolution of minerals in Berea sandstone cores. Therefore, a brine spacer was used to remove calcium ions from the leading edge of the surfactant slug. Oil recovery was not evaluated in the laboratory. In the field test, it was concluded that lignosulfonate did reduce surfactant adsorption. However, the brine spacer was not large enough to shield the surfactant slug from divalent ions. The presence of divalent ions caused complex phase behavior for the surfactant/brine/oil system in the reservoir. Other problems in the field including inadequate reservoir description and presence of heterogeneities caused difficulties in evaluating the effectiveness of the use of lignosulfonate as a preflush.

Based on information reported in these studies, sacrificial agents have been useful in reducing surfactant adsorption. The most effective chemicals have been silicates, carbonates, and calcium sequestering agents. Their effectiveness is based on one of two mechanisms: by preferentially occupying surface adsorption sites and by removing divalent ions which can cause surfactant precipitation. Lignosulfonate has also been effective, but the exact method of effectiveness is subject to further investigation.

The relationship of surfactant adsorption to improvement in oil production is complex. Reduced surfactant adsorption may or may not increase oil production in small-scale studies such as those done in the laboratory. Reduced surfactant adsorption, however, can improve oil production on a larger scale by allowing the surfactant slug to maintain optimal conditions for oil recovery concentration further into the reservoir. Lignosulfonates are cheaper products than surfactants used for oil recovery. Preferential adsorption of the lignosulfonates, therefore, can improve the economics of surfactant flooding since lesser total amounts of the more expensive surfactant may be used during the life of a surfactant flood project.

The literature studies sited above have studied the effect of sacrificial agents mainly on the adsorption of petroleum or ethoxylated sulfonates. Over the past several years, interest has been generated in surfactants for EOR that show a broader tolerance to changes in salinity or temperature than are observed for petroleum sulfonates. One surfactant type that has been investigated at NIPER[11] and elsewhere[12-14] is carboxymethylated ethoxylates (CME). In using CME surfactants, more flexibility can be gained adjusting the hypophillic end of the surfactant to meet a variety of reservoir conditions. This may allow the design of surfactant EOR floods without the use of a cosurfactant, for example, and reduce the possibility of chromatographic separation of chemicals in the surfactant flood. Adsorption studies on crushed and consolidated Berea sandstone have been reported for various salinity and temperature conditions.[15] Oil recovery studies,[12] however, have indicated that surfactant losses can be high for the CME surfactants. Therefore, comparative studies were performed to determine the effect of the use of sacrificial agents on CME surfactant loss in both static tests and oil recovery experiments in Berea sandstone core.

Mixed Surfactant Systems

Interest in mixed surfactant systems has gained importance in recent years with the realization that mixed systems may allow greater freedom to tailor surfactant solution properties to specific reservoir conditions. In combination with a nonionic surfactant, for example, an anionic surfactant may show greater tolerance to changes in salinity. Similarly, increased temperature tolerance of a nonionic surfactant may be the result of combination with an anionic surfactant. As a result of alterations in surfactant solution properties, surfactant loss during an EOR chemical flood may be reduced.

Commercial surfactants generally consist of mixtures of components of different molecular weight and perhaps different ionic character. Most commercial CME surfactants are mixtures of anionic and nonionic surfactant because the ethoxylated surfactant (nonionic) precursor is seldom 100% converted to the carboxylated surfactant (ionic) during production. For example, the Hüls CES 5.5 and 6.5 consist of approximately 20% ethoxylate and 80% carboxymethylated ethoxylate. Balzar[12] has shown that one CME surfactant (B42 in his report) with 25% nonionic surfactant exhibited much higher surfactant loss in oil recovery experiments than a second surfactant (B103) containing 0% nonionic surfactant. The respective surfactant losses measured on unconsolidated reservoir sandstone was 3.2 and 1.7 mg/g. Similar behavior has also been observed observed for ethoxylated sulfonates.[17]

Further variations in ionic and nonionic behavior can be observed with CME surfactants because they can exist either in the acid form (–COOH) or the ionic form (–COO$^-$) depending on solution pH. Solution properties and adsorption losses may differ with pH as well as with salinity and temperature. Because many variations are possible in examining surfactant losses in mixed surfactant systems, an experimental program has been initiated to observe changes in surfactant phase separation (cloud point) of solutions of mixed CME surfactants and correlate, if possible, with surfactant losses for different salinities and temperatures.

EXPERIMENTAL PROCEDURES

Materials

Carboxymethylated ethoxylated surfactants were obtained from Sandoz Chemicals and Chemische Werke Hüls, AG. Table 1 provides information on the CME surfactants used in this study.

TABLE 1. - Commercial carboxymethylated ethoxylated surfactants

$R\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_2COO^- \ Na^+$ or H^+

Trade Name	Abbreviation	Hydrophobe, R	Average EO, n	Av. equivalent weight
Sandopan®				
JA-6	JA-6	C_{13}	3	390
MA-18	MA-18	n-nonylphenol	9	696
RS-16	RS-16	C_{16}-C_{18}	8	688
Hüls				
BW 9135AS	CES 5.5	i-nonylphenol	5.5	542
BW 9135AT	CES 6.5	i-nonylphenol	6.5	586

Surfactant solutions were prepared in brines made from reagent grade NaCl. Brine concentrations varied from 0.5 to 17% w/v for adsorption studies. Batch surfactant adsorption experiments were conducted using 180 to 212 mesh crushed Berea sandstone. The surface area of this material was 0.64 m^2/g as measured using the BET method. Reagent grade sodium metasilicate, bicarbonate, and carbonate were reagent grade from Baker Chemical Company. Sodium tripolyphosphate from Pfaltz and Bauer was 90% pure. The lignosulfonate Petrolig ERA-2, used in this study was from Reed Lignin, Inc. All solution concentrations are reported as % active weight of material per volume of solution.

Adsorption Procedures

Batch adsorption tests were used to determine the effect of sacrificial agents on the adsorption of CME surfactants on crushed Berea sandstone. Adsorption was determined for salinities ranging from 5 to 15% NaCl and for temperatures of 24°, 50°, and 90° C. Adsorption was also measured without sacrificial agents to compare adsorption values with those determined under dynamic conditions as reported previously.[15] Surfactant concentrations were determined using high pressure liquid chromatography (HPLC) techniques. In general, surfactant concentrations were measured after at least 24 hours contact with the crushed sandstone. Longer equilibration time indicated no differences in measured adsorption from that measured after the first 24 hours contact. Shorter equilibration times may also have been adequate for these experiments because the results of the static tests compared with those obtained in the dynamic tests. The dynamic tests, in general, were conducted in less than 3 hours.

Surfactant Analysis

Waters HPLC equipment was used to determine the presence and amount of surfactant for sacrificial agent adsorption and coreflood studies. The equipment consists of two Waters high-pressure chromatographic pumps, a solvent programmer, an automatic injector, a C_8 reverse-phase column, and an UV detector. A Spectro-Physics SP 4270 integrator was used to record, display, store, and recalculate surfactant chromatograms as required. CES 5.5 and 6.5 and M-18 surfactants were detected using their UV adsorption at 282 nm. JA-6, however, contains no UV active components, and detection using the HPLC was not possible. In addition, JA-6 could not be analyzed using the two-phase titration method which is often used to determine concentrations of anionic surfactants such as petroleum sulfonates. JA-6 under the acidic conditions of the two-phase titration test is not in the anionic form of a carboxylate ion but in the nonionic form of a carboxylic acid. Efforts are continuing to develop an analytical procedure to measure concentrations of nonaromatic CME surfactants.

A typical chromatogram of CES 5.5 is shown in figure 1. The surfactant was eluted using a mobile phase solvent gradient of 50/50 water/acetonitrile to 100% acetonitrile. Two surfactant peaks are eluted

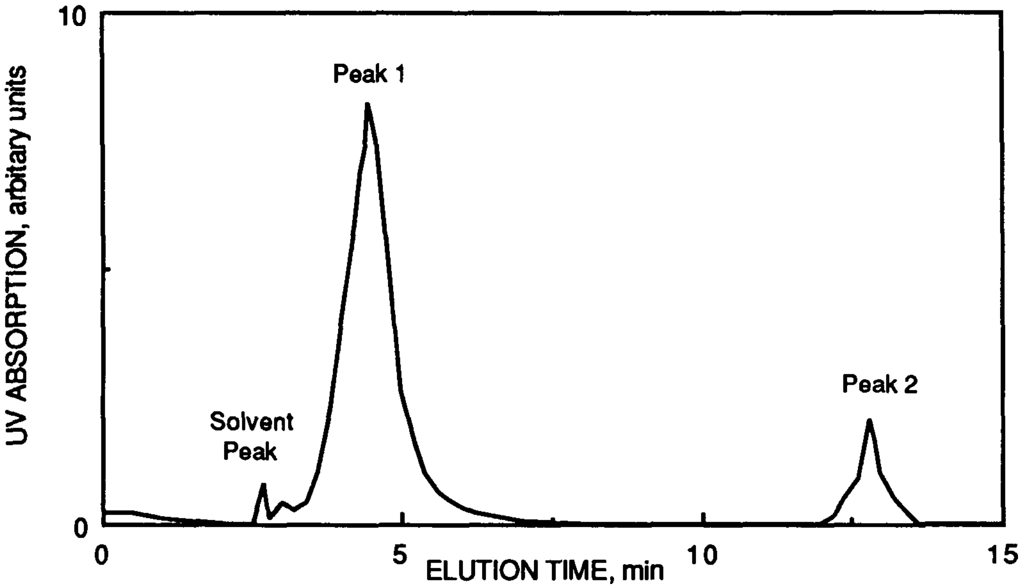

FIGURE 1. - HPLC chromatogram of Hüls CES 5.5 using a reverse phase C_8 column and water/acetonitrile solvent gradient.

under these conditions. The more hydrophilic fraction elutes first while a more lypophilic fraction elutes with the 100% acetonitrile. The second peak may represent the noncarboxylated portion of the surfactant. The manufacturer reports that approximately 20% of the ethoxylated surfactant is not converted to the carboxylated material during production. A HPLC chromatogram of M-18 is shown in figure 2. Two peaks are also observed eluting for the same solvent program as used for CES 5.5. In this case, however, a much greater percentage of the material is eluted in the second peak. For neutral pH conditions, a much greater fraction of the M-18 is in the acid form than is in the ionic form. For CES 5.5, the opposite is true. Most of the surfactant is in the ionic form at the pH of the mobile phase solvent. Therefore, for the M-18 surfactant, the second peak may consist of both noncarboxymethylated surfactant and carboxymethylated surfactant in the acid form.

Samples containing lignosulfonate and CME surfactants can be analyzed by using acetonitrile and water mixtures. Lignosulfonate elutes very close to the solvent peak. The amount of separation in the peaks can be adjusted by varying the amount of water in the mobile phase mixture. A solvent gradient to 100% acetonitrile then elutes the remainder of the more lypophilic surfactant from the column. Figure 3 shows a chromatogram of a solution containing both lignosulfonate and CES 5.5.

After baseline correction to eliminate UV absorbance changes caused by the solvent gradient, calibration curves of amount of surfactant injected verses peak area were constructed. An example is shown in figure 4. Reproducibility of results was generally within 3%. Recalibration and use of standard

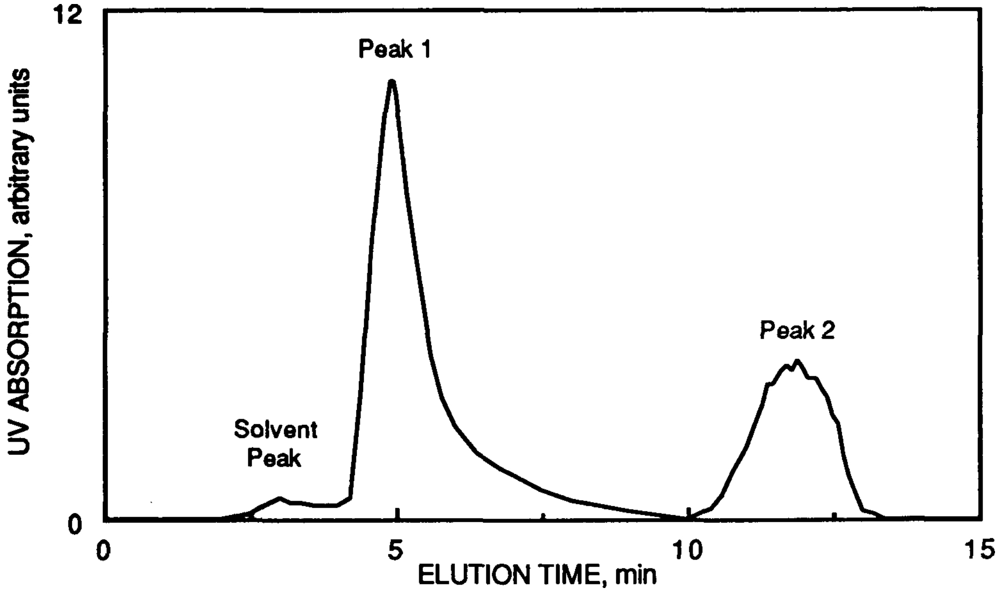

FIGURE 2. - HPLC chromatogram of Sandopan® M-18 using a reverse phase C_8 column and a water/acetonitrile solvent gradient.

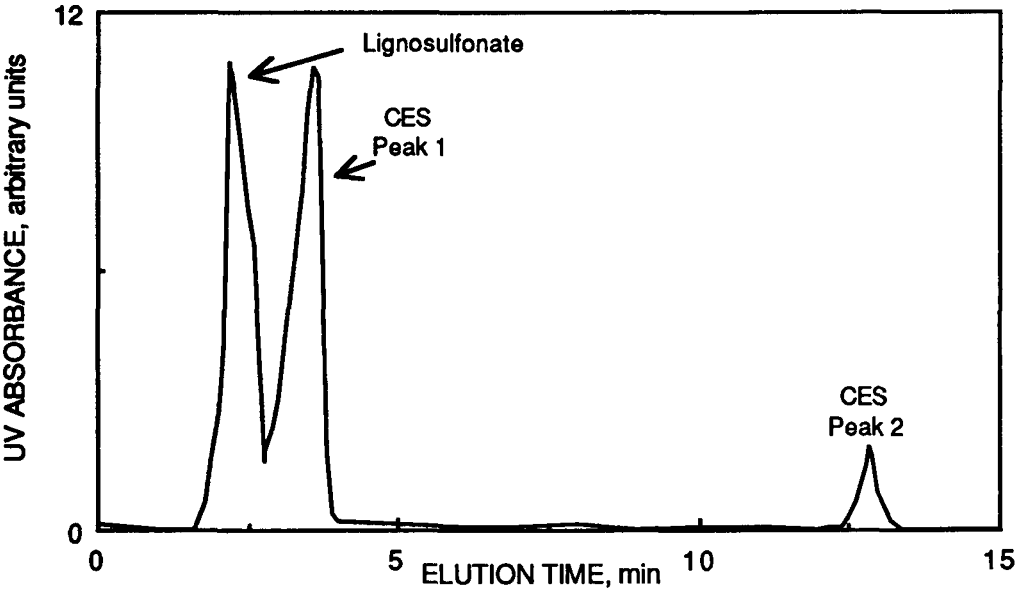

FIGURE 3. - HPLC chromatogram of Hüls CES 5.5 and Petrolig ERA-2 lignosulfonate separation using a reverse phase C_8 column and mobile phase solvent gradient of 50 to 100% acetonitrile in water.

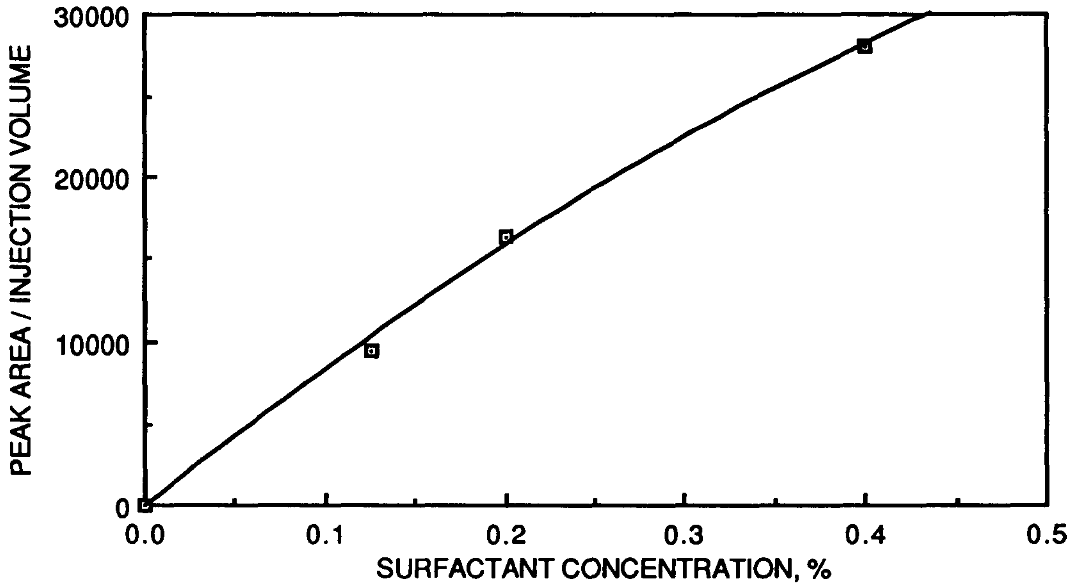

FIGURE 4. - Example of a calibration curve of peak area per injection volume as a function of surfactant concentration for baseline corrected HPLC chromatograms of CME. Detection is at 282 nm for CES 5.5.

solution concentrations with each set of measurements, however, was standard procedure to monitor for differences caused by mobile phase or column changes.

Coreflood Procedures

Corefloods were conducted to evaluate oil recovery for several sets of conditions as determined from adsorption and phase behavior experiments using carboxymethylated ethoxylated surfactants. Figure 5 shows a general schematic of the equipment used for these corefloods. Table 2 lists the experimental conditions or ranges of conditions used for the corefloods.

The following general procedures were used for all of the corefloods. Berea sandstone core plugs 3.8 cm in diameter by approximately 25 cm in length were dried, weighed, and saturated with the brine. Porosity was determined from the weight of brine in the saturated core. The saturated core was placed in the Hassler sleeve coreholder. Permeability to brine was determined before proceeding with oil recovery tests. Since phase behavior studies were conducted using dodecane, this oil was used to flood the core to residual brine saturation. Brine was then used to flood the core to residual oil saturation.

Tracer tests were conducted before and after oil was introduced into the core. Typically, 0.1 to 0.2 pore volumes (PV) of fluorescein tracer solution was pumped through the core to determine dispersion and possible chemical loss in the core for a nonadsorbing compound. Core effluent was collected using a

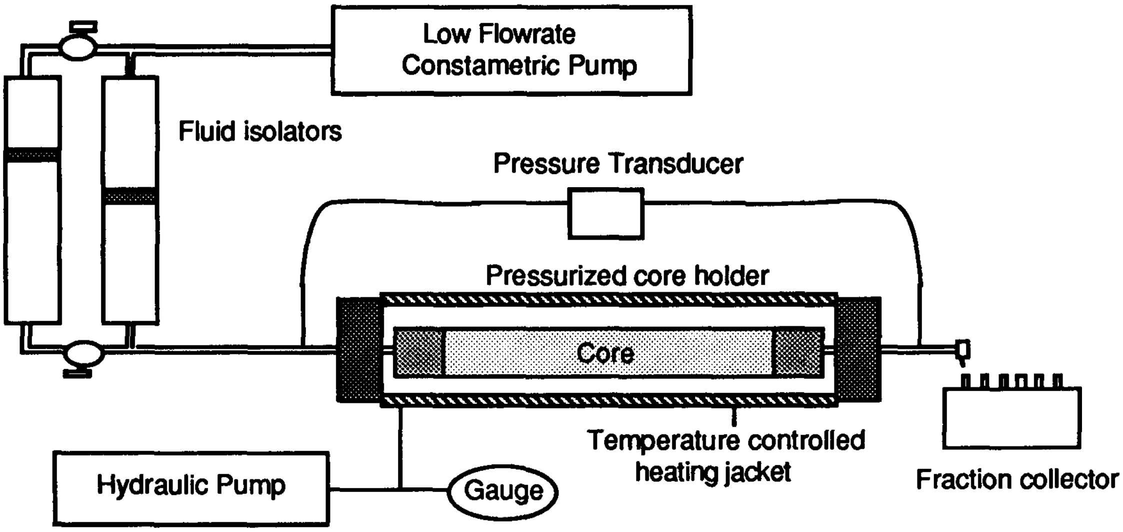

FIGURE 5. - Schematic of coreflood apparatus.

TABLE 2. - CME and sacrificial agent coreflood parameters

Temperature, ° C	50
Confining stress, psi	150 to 200
Core	Berea sandstone
Permeability to brine, md	80 to 198
Porosity, %	18.2 to 19.4
Fluids:	
Brine - NaCl, %	5 to 21
Surfactant - CME surfactants, % (active weight)	2
Sacrificial agent - lignosulfonate, %	0.5 to 0.6
Tracer - fluorescein, ppm	10.6
Polymer - Xanthan, ppm	250 to 500
Oil - dodecane	

fraction collector, and the solutions analyzed for tracer using a Perkin Elmer UV-Visible Spectrophotometer. Fluorescein adsorption at 490 nm was used to determine the amount of tracer in each fraction collector sample. Figure 6 shows a calibration curve of fluorescein absorption as a function

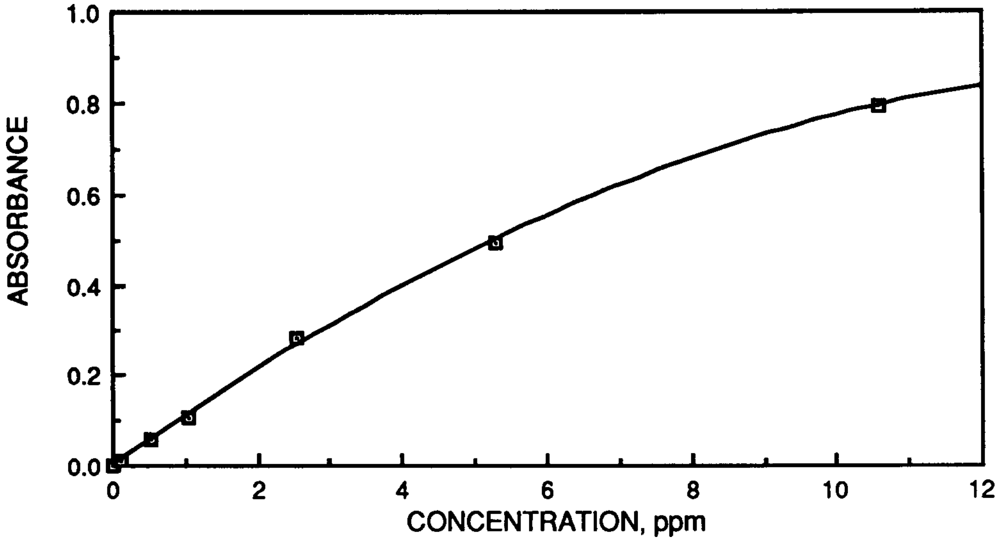

FIGURE 6. - Calibration curve for fluorescein adsorption at 490 nm as a function of concentration.

of concentration. Since fluorescein absorption decreases for pH values less than 9, all solution pH's were adjusted to values greater than 9 before analysis. The cores were then flooded with solutions containing sacrificial agent, surfactant, or sacrificial agent and surfactant as required. In most tests, 0.5 PV of preflush and/or surfactant solution were pumped through the core. All solutions were prepared in the same brine used to initially saturate the core. Brine concentrations were selected to either minimize adsorption based on results of batch adsorption tests or to minimize interfacial tension (IFT) between oil and surfactant and brine solution. Effluent was collected using the fraction collector. Samples were analyzed for incremental oil production and surfactant concentration as described in the section on surfactant analysis.

RESULTS AND DISCUSSION

Effect of Use of Sacrificial Agents on Adsorption of CME Surfactants

Inorganic Sacrificial Agents

Examination of the information published previously, as reviewed in the introduction, indicated that several types of compounds showed some effectiveness in reducing adsorption of anionic surfactants such as petroleum sulfonates. In general, compounds such as carbonate/bicarbonate mixtures, silicates, phosphates, and lignosulfonates were considered most effective in reducing surfactant adsorption. Therefore, these compounds were chosen to initiate an experimental program to determine the effect sacrificial agents may have on adsorption or other types of surfactant loss for CME surfactants.

Table 3 shows a comparison of CME surfactant loss in static adsorption tests at 24° C for solutions with and without the addition of carbonate/bicarbonate sacrificial agent. The sacrificial agent raised solution pH to 9.3. Therefore, the pH of the test solution without sacrificial agent was adjusted to the same level by the addition of NaOH. Comparing the tests with and without sacrificial agent, the average surfactant loss declined by 28%, from 1.8 to 1.29 mg/g of sand. The adsorption measured in the static test in the absence of sacrificial agent agreed well with the value of 1.9 mg/g obtained in the column adsorption tests as reported previously.[15] The dynamic adsorption tests were performed using the same crushed Berea sand (surface area = 0.64 m^2/g) as was used for the static adsorption tests. For the column tests, solution pH was adjusted to 6.5 to 7.0 to be above the pK_a of 4.6 for this CME surfactant. Surfactant loss of CES 5.5, therefore, did not vary significantly with pH changes from 6.5 to 9.2. Static adsorption tests, therefore, appear to be an adequate technique to evaluate adsorption losses of CME surfactants on crushed sandstone.

Adsorption measurements with and without carbonate/bicarbonate were also conducted at a salinity of 15% NaCl and at 50° C. Surfactant loss under these conditions had been measured previously[15] and was considerably higher than the losses measured at 10% NaCl and 24° C. This loss, 6.2 mg/g of sand, was attributed to solution properties which favored phase separation or precipitation of the surfactant in addition to adsorption of the surfactant on the rock surface as temperature and salinity increased. The effect of a sacrificial agent under these conditions is summarized in table 4.

Since previous experiments[15] had shown that surfactant loss for these conditions was partially reversible, desorption was measured using a brine of lower salinity (5% NaCl). The average amount of surfactant remaining on the rock after desorption was 1.7 mg/g for solutions containing no carbonates and 1.2 mg/g for the solutions containing carbonates. These values compare with those reported in table 3. The magnitude of desorption also compares well with results obtained in previous tests.[15]

TABLE 3. - Adsorption loss of CES 5.5 at 24° C with and without sacrificial agent

Solution additives	pH	[CES] initial, %	[CES] final, %	Δ weight, g	Weight of sand, g	Surfactant loss, mg/g
10% NaCl	9.2	0.197	0.158	0.00862	5.18	1.66
		0.198	0.155	0.00943	4.87	1.93
					ave.=	1.80 ±0.19
10% NaCl	9.3	0.207	0.176	0.00700	5.40	1.32
1.1% Na_2CO_3		0.204	0.173	0.00700	5.78	1.26
0.85% $NaHCO_3$					ave. =	1.29 ±0.04

TABLE 4. - Adsorption loss of CES 5.5 at 50° C with and without sacrificial agent

Solution additives	pH	[CES] initial, %	[CES] final, %	Δ weight, g	Weight of sand, g	Surfactant loss, mg/g
15% NaCl	8.7	0.230	0.078	0.0338	4.93	6.86
		0.226	0.079	0.0332	5.14	6.46
					ave.=	6.66 ±0.28
15% NaCl	9.2	0.234	0.095	0.0297	5.12	5.79
1.1% Na_2CO_3		0.231	0.103	0.0277	5.10	5.42
0.85% $NaHCO_3$					ave.=	5.61 ±0.26

The carbonate sacrificial agent had no effect on surfactant loss attributed to solution incompatibilities which favored surfactant phase separation. In addition, their presence in solution may be slightly detrimental to this type of surfactant loss since the total ionic strength of the surfactant/brine solution increased. In the reservoir, the conditions which lead to excessive surfactant separation can cause partition of the surfactant into the oil phase. The sacrificial agent was only effective in reducing the irreducible surfactant loss which can probably be attributed to adsorption on positive ionic sites on the rock surface.

Two other inorganic compounds, sodium metasilicate and sodium tripolyphosphate, were evaluated as sacrificial agents for CES 5.5 in solutions containing 10% NaCl at 24° C. Solution pH was approximately 9 for these tests. Results are shown in table 5. Neither compound performed well as a sacrificial agent with a CME surfactant. Measured surfactant loss was actually 25% higher than that reported for solutions containing no sacrificial agent and 80% higher than the values measured for solutions containing carbonate/bicarbonate sacrificial agent.

TABLE 5. - Effect of inorganic sacrificial agents on adsorption of CES 5.5 at 24° C

Solution additives	[CES] initial, %	[CES] final, %	Δ weight, g	Weight of sand, g	Surfactant loss, mg/g
10% NaCl 1.2% silicate	0.230	0.184	0.00477	2.05	2.33
10% NaCl 2% tripoly-phosphate	0.225	0.183	0.00448	1.91	2.35

Lignosulfonate

The effect of an organic sacrificial agent, lignosulfonate, was also evaluated for use with CME surfactants in static adsorption tests. As described in the introduction, researchers have previously shown that lignosulfonate reduced surfactant adsorption and, in some cases, demonstrated beneficial behavior in oil recovery experiments. Conflicting interpretations were reported as to the most effective method to use lignosulfonate in a surfactant enhanced oil recovery project. Therefore, surfactant adsorption was measured for three combinations of surfactant and lignosulfonate.

First, lignosulfonate was used as a preflush. Excess lignosulfonate was removed from contact with the surface of the crushed sandstone using a brine rinse. Adsorption of CES 5.5 on crushed Berea sandstone was then measured. Salinity and temperature conditions of 5% NaCl and 24° C were chosen to avoid complications arising from phase separation or precipitation of the surfactant. Second, lignosulfonate was incorporated in the surfactant solution but was not used in a preflush. Third, lignosulfonate was used in both the preflush and the surfactant solution. Table 6 summarizes the results of adsorption loss of CES 5.5 for these conditions. Each reported value represents an average of at least two separate measurements. All three methods successfully reduced CES 5.5 adsorption from that measured without the use of lignosulfonate (1.8 mg/g) as reported previously.[15] In this case, surfactant loss was reduced by 68%.

TABLE 6. - Effect of lignosulfonate on adsorption of CES 5.5 at 5% NaCl and 24° C

Test	Application method	[CES] initial, %	[CES] final, %	Δ weight, g	Weight of sand, g	Surfactant loss, mg/g
1	a. lignosulfonate preflush					
	b. brine rinse					
	c. surfactant	0.230	0.206	0.00540	5.15	1.1 ±0.1
2	a. lignosulfonate and CES 5.5	0.310	0.280	0.00604	5.07	1.2 ±0.1
3	a. lignosulfonate preflush					
	b. lignosulfonate and CES 5.5	0.284	0.272	0.00292	5.06	0.57 ±0.07

Lignosulfonate may reduce surfactant loss by several mechanisms. Researchers have previously shown that it may act as a competitive adsorbent; it may shield the surfactant from calcium ions present as calcium carbonate from crushed core material or as exchange ions on clays by complexing or precipitating with the calcium ions; or it may change surfactant solution properties and change the equilibrium balance between the solution and the rock surface. For these static tests, all of these mechanisms may have some effect on surfactant loss. Therefore, precontacting the surface and incorporating the lignosulfonate into the solution may both contribute to the effectiveness of the use of this sacrificial agent.

Summary

In conclusion, lignosulfonate and carbonate/ bicarbonate sacrificial agents significantly reduced CME surfactant loss on crushed Berea sandstone for some conditions of salinity and temperature where phase separation of the surfactant from the brine solution was not a problem. At higher temperatures and salinities where phase separation becomes more important, carbonate/bicarbonate in solution did not reduce (and may even slightly increase) this type of surfactant loss. In static adsorption tests, lignosulfonate was most effective when used in both a preflush and incorporated in the surfactant solution.

Two other sacrificial agents that were tested, sodium metasilicate and sodium tripolyphosphate, showed no positive reduction of CME surfactant adsorption. Surfactant loss actually increased slightly in these static adsorption tests.

Coreflood Evaluation of CME Surfactant Loss

Corefloods using CES 5.5

The evaluation of the effect of sacrificial agents on CME surfactant loss was extended to corefloods in Berea sandstone in the presence of oil. The objectives of these experiments were to determine the effects of sacrificial agents on CME adsorption for dynamic flow conditions through consolidated core and to determine incremental oil production for these same conditions. Experimental conditions were chosen based on the results obtained in static adsorption tests and on phase behavior and IFT measurements as reported elsewhere.[16] Six corefloods were conducted at 50° C using dodecane as the saturating oil. Core properties and fluid treatments for the six tests are summarized in table 7.

Test 1 was performed at low salinity (5% NaCl) where increased surfactant loss caused by surfactant phase separation was not a problem in the static adsorption measurements. This test would determine the effect of lignosulfonate on surfactant loss in the presence of oil. A preflush of lignosulfonate of approximately 0.5 PV was injected followed by a slug of approximately equal size

TABLE 7. - Summary of core parameters and solution properties for sacrificial agent and oil recovery evaluations using carboxymethylated ethoxylated surfactants

Parameter	Core test 1	Core test 2	Core test 3	Core test 4	Core test 5	Core test 6
Berea core	5	1	2	4	3	6
Core diameter and length,cm	3.8 x 24.75	3.8 x 24.85	3.9 x 24.9	3.8 x 24.85	3.8 x 24.7	3.79 x 24.75
Porosity, %	19.4	18.7	18.2	19.4	19.2	18.6
Saturating NaCl concentration, %	5	15	15	17	17	21
Brine permeability, md	164	148	80	198	168	133
Residual oil saturation, %	32.0	36.4	31.7	36.4	40.9	30.9
Chemical flood treatment						
Preflush	0.5% lignosulfonate	none	0.5% lignosulfonate	none	0.5% lignosulfonate	5% acetic acid 250-500 ppm xanthan
Surfactant	2% CES 5.5 0.6% ligno	2% CES 5.5	2% CES 5.5 0.6% ligno	2% JA-6	2% JA-6 0.5% ligno	2% CES 6.5 5% acetic acid
Polymer	none	none	none	500 ppm xanthan	500 ppm xanthan	250 ppm xanthan
pH adjustment	6.5	6.5	6.2	6.2	6.3	4.6-4.8

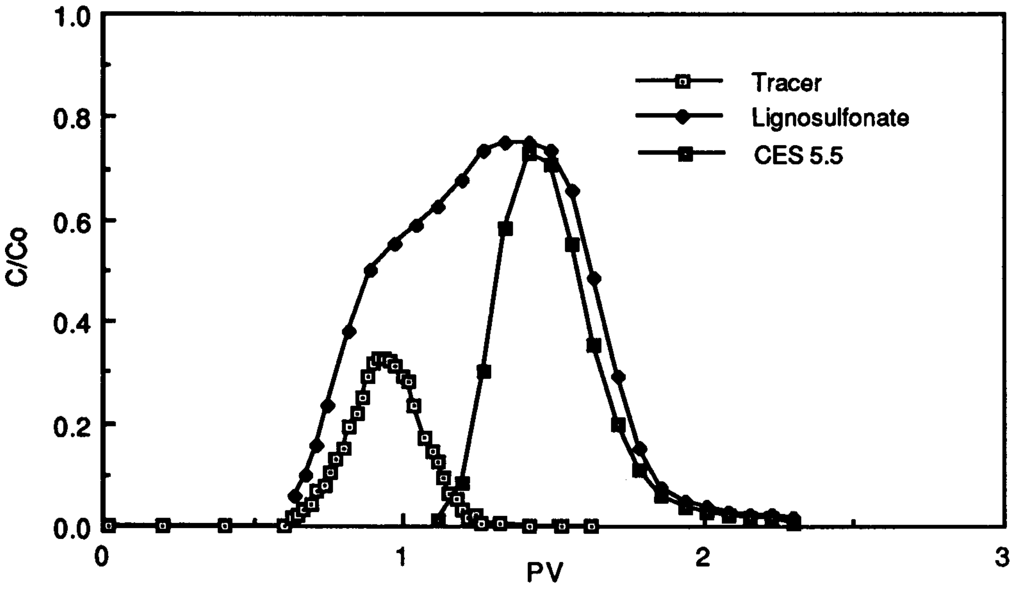

FIGURE 7. - Relative concentration profiles of CES 5.5, lignosulfonate, and tracer for coreflood test 1 conducted at low salinity (5% NaCl).

containing surfactant and lignosulfonate of slightly higher concentration than in the preflush. Core effluent fractions were collected and analyzed for lignosulfonate and surfactant concentration. Figure 7 shows concentration profiles of lignosulfonate and surfactant and fluorescein tracer as a function of pore volumes of solution through the core. Concentrations are plotted as the fraction of injected concentration to enable better comparisons of curve shapes for the different chemicals. The lignosulfonate appeared to breakthrough a little ahead of the tracer. This may indicate some fingering of the preflush solution through the core. The trailing edge of the lignosulfonate and surfactant slugs appear to exit the core at approximately the same time.

Figure 8 shows an approximate resolution of the lignosulfonate concentration profile into peaks for lignosulfonate in the preflush and with the surfactant. Each peak represents approximately 78% of the original lignosulfonate injected. No detectable difference in lignosulfonate loss was observed between the preflush solution and the surfactant solution.

Of the 0.5 pore volume of 2% CES 5.5 surfactant solution injected during the test, approximately 34% was retained in the core. This corresponds to a surfactant loss of 0.25 mg/g of rock. Previously, it had been reported that, without the use of lignosulfonate, CES 5.5 surfactant loss in consolidated Berea cores was 0.8 mg/g of rock.[15] Surfactant loss was reduced by 69% with the use of lignosulfonate as a preflush and incorporated in the surfactant slug. This magnitude of reduction compares with that observed in the static adsorption tests.

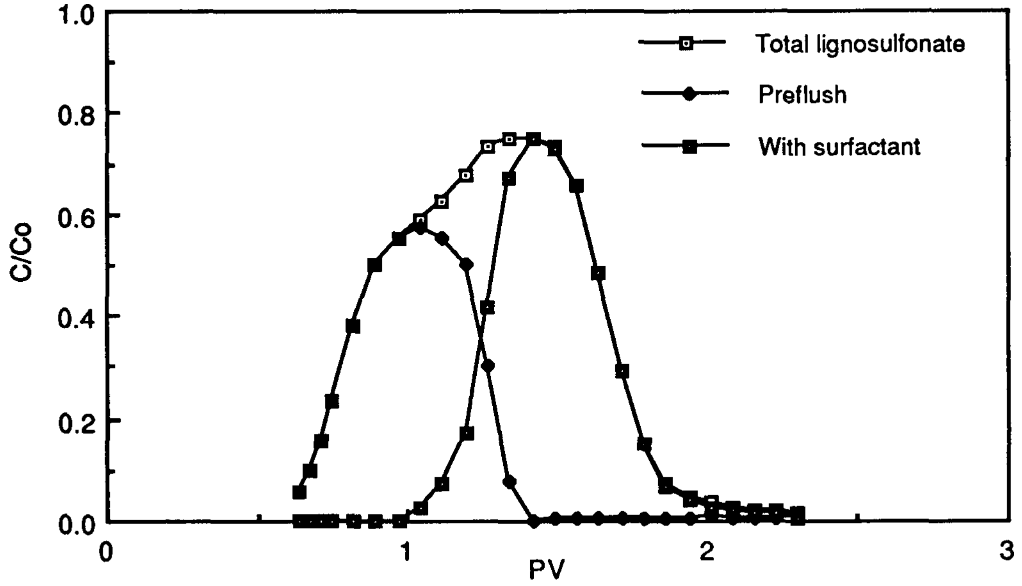

FIGURE 8. - Resolution of lignosulfonate concentration profiles from coreflood test 1 into separate peaks for the preflush and the surfactant slugs.

Although oil was present in the core during this test, no incremental oil was produced. From phase behavior studies,[16] the optimal salinity for oil solubilization and three-phase behavior was observed at a much higher salinity (15-20%). Therefore, the coreflood demonstrated that the lignosulfonate sacrificial agent successfully reduced surfactant loss but failed to augment oil production when other important considerations such as low IFT's were not met.

Tests 2 and 3 compare surfactant loss and oil production with and without the use of lignosulfonate at higher salinity (15% NaCl). Although IFT and phase behavior results are more favorable for oil production, static adsorption tests indicated that high surfactant losses and possible phase trapping may be a problem at this temperature and salinity. In test 2, no surfactant was found in the core effluent for at least 3 pore volumes after surfactant injection. In test 3, lignosulfonate from the preflush exited the core without much delay compared with nonadsorbing tracer, as shown in figure 9. However, no surfactant and probably no lignosulfonate included in the surfactant slug was found in the core effluent. In addition, no oil was produced in either test. Lignosulfonate recovery was only 17% of the total amount injected during the test.

These results indicated that the conditions of the test favored phase trapping of the surfactant. The lignosulfonate as a preflush or as a surfactant solution component was ineffective in alleviating this problem. CME surfactants have been used successfully to produce oil under high salinity conditions only

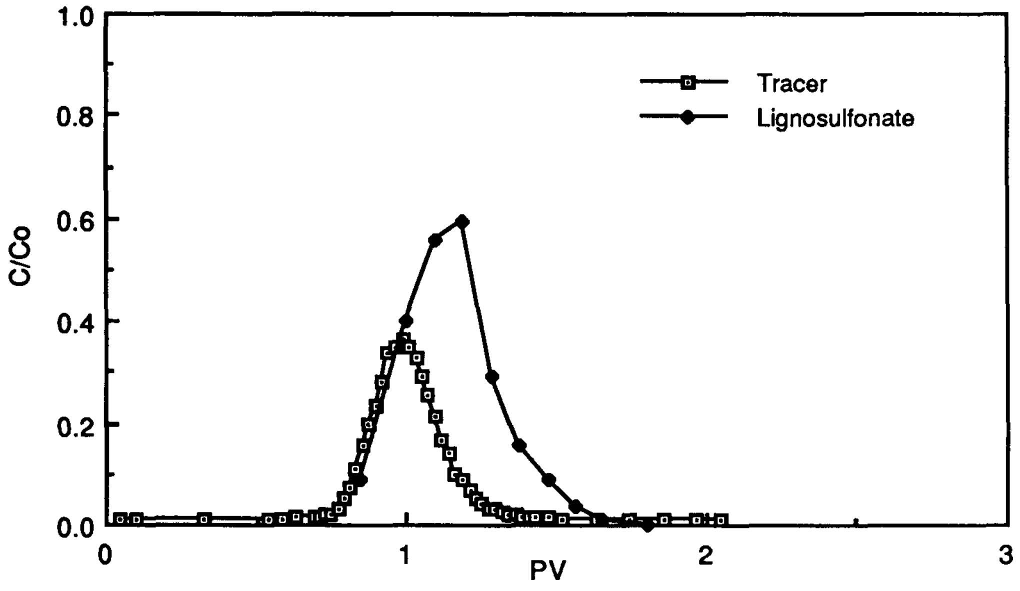

FIGURE 9. - Concentration profiles of lignosulfonate and tracer for coreflood test 3 conducted using CES 5.5 surfactant at high salinity (15% NaCl).

when used with an alcohol cosurfactant.[12] Incorporation of a cosurfactant alters CME solution properties and reduces phase trapping within the core.

In summary, the CME surfactant, CES 5.5, without cosurfactant was not a very useful surfactant in terms of oil recovery in these core tests. Lignosulfonate was only successful in reducing surfactant adsorption for tests run at low salinity. Results in these coreflood experiments paralleled those observed in the static adsorption experiments.

Corefloods using JA-6 and CES 6.5

For subsequent corefloods, other CME surfactants were chosen for testing based on IFT measurements to improve the possibility of reducing residual oil saturation in the core. Table 8 summarizes some of the IFT measurements for CME surfactants, JA-6 and CES 6.5. Tests 4 and 5 measured oil production using 2% JA-6 in 17% NaCl at 50° C with and without the use of lignosulfonate. Surfactant adsorption during each test was not evaluated because a quantitative analytical method for JA-6 analysis was not available.

Some oil was produced during each test (9% of the ROIP for test 4 and 16% of the ROIP for test 5). As expected from the IFT measurements, the JA-6 surfactant was more successful producing oil at the high salinity conditions than the CES 5.5 surfactant. Oil production was slightly greater for the test with

TABLE 8. - IFT values for CME surfactants[16]

Surfactant	Salinity, % NaCl	IFT, dynes/cm	pH
2% JA-6	16	0.105	6.22
	17	0.062	
	18	0.101	
1% CES 6.5	20	0.084	4.7
	22	0.042	
	24	0.044	

added lignosulfonate. However, the difference was probably not significant. Figure 10 shows the lignosulfonate breakthrough curve for test 5 relative to a nonadsorbing tracer breakthrough curve. No significant delay was observed for the lignosulfonate curve. Furthermore, lignosulfonate was produced significantly longer than in the case of test 3. Figure 11 shows a comparison of lignosulfonate concentration profiles for tests 2 and 3. This suggests that the JA-6 surfactant solution was not trapped in the core to the extent that the CES 5.5 surfactant was trapped. Tailing of the lignosulfonate solution also suggests that some adsorption/desorption mechanism was in operation for the lignosulfonate solution. Lignosulfonate recovery was 79% of the total amount injected. This recovery efficiency was greater than those observed for either test 1 or test 3 of the lignosulfonate CES 5.5 corefloods.

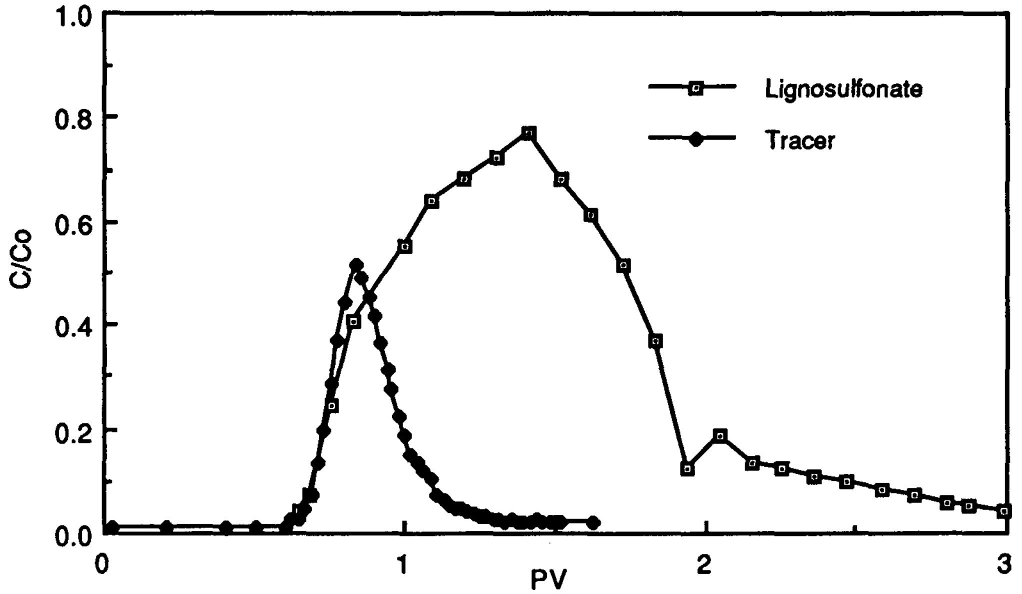

FIGURE 10. - Concentration profiles of lignosulfonate and tracer from coreflood test 5 using JA-6 surfactant in 17% NaCl brine.

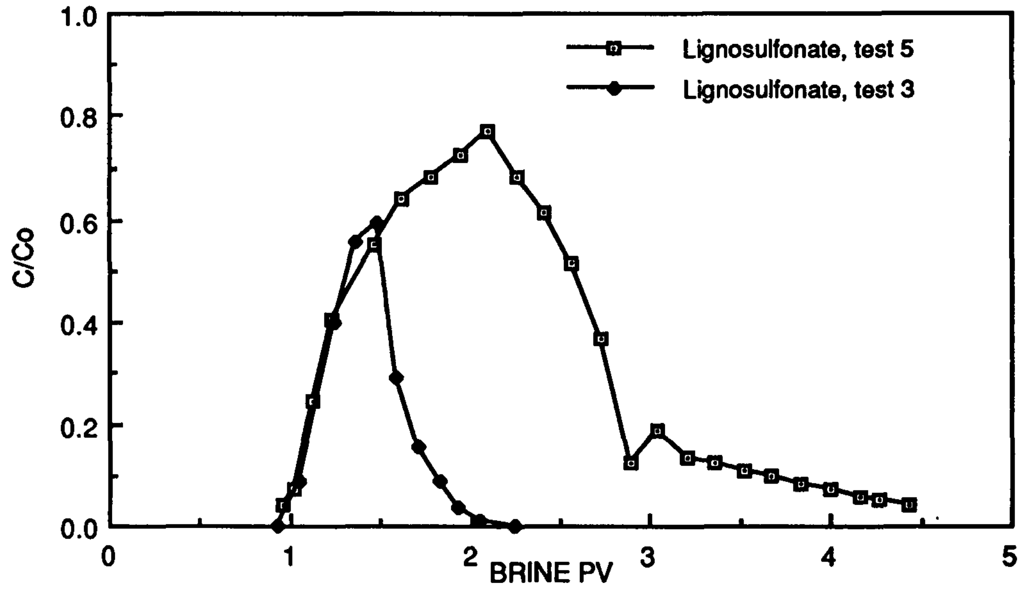

FIGURE 11. - Comparison of lignosulfonate concentration profiles for coreflood tests using different surfactants, CES 5.5 and JA-6, in high salinity brines. Surfactant PV injected was the same for both tests.

The poor oil recovery showed that a CME surfactant flood had not yet been designed to optimize oil production for these experimental conditions. However, some improvements had been observed relative to the initial coreflood experiments using CES 5.5.

Test 6 was conducted using CES 6.5 in solution adjusted to pH of 4.6 as suggested by the IFT measurements reported in table 8. This pH is the measured pKa of CES 6.5 where equal amounts of the surfactant exist in the acid form (–COOH) and in the ionic form (–COO$^-$). Lowest IFT's were measured for solutions with salinity greater than 20% NaCl at 50° C. In addition, phase inversion temperature (PIT) measurements[16] indicated that pH adjustment was required before a phase inversion temperature was observed for CES 6.5. In 21% NaCl brine, the PIT for CES 6.5 was approximately 50° C at pH 4.7.

For test 6, pH was adjusted to 4.6 using acetic acid as a buffer. A preflush of low pH brine with xanthan gum polymer for mobility control[12] was used to condition the core before injection of the surfactant. Some oil was produced by the polymer preflush. Additional incremental oil production was produced by the pH adjusted surfactant solution. Total oil recovery efficiency was 51% ROIP, the highest of all the corefloods reported for these temperature and salinity conditions.

Figure 12 shows breakthrough curves for CES 6.5 and nonadsorbing tracer. Surfactant breakthrough was delayed relative to that of the tracer indicating significant surfactant loss in the core before breakthrough of the surfactant. In addition, surfactant concentration dropped rapidly at the trailing

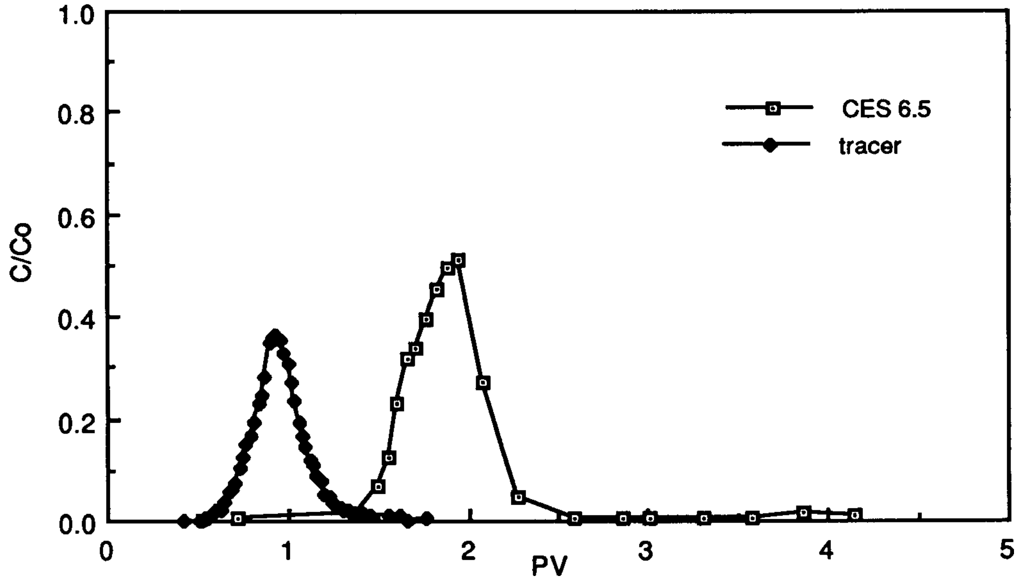

FIGURE 12. - Concentration profiles of CES 6.5 and tracer for coreflood test 6 conducted at pH of 4.6 and salinity of 21% NaCl.

edge of the concentration curve. Inadequate mobility control in the polymer pusher may account for this rapid decline. A very large surfactant slug was used in this test to determine if any surfactant would travel through the entire core. A least 90% of the surfactant was retained which indicated that phase trapping was a significant problem for these experimental conditions. Adjustment of pH to modify surfactant properties would require more extensive investigation before determining if this process could be improved by reducing surfactant loss as well as optimizing for oil production.

A series of corefloods using the Hüls CME surfactants has been summarized in a previous NIPER report.[11] Similar problems of poor oil recovery were observed for a variety of surfactant formulations using mixtures of CES 5.5 and CES 4.5. Although surfactant loss was not measured, excessive surfactant requirement was one of the difficulties which interfered with use of this type of surfactant for economic oil production. Only a low surfactant concentration, high viscosity flood resulted in reduction of residual oil saturation of more than 50%. Phase trapping was probably a major problem for many of these corefloods. Use of CME surfactants without cosurfactants or other solution designs which overcome poor phase behavior may preclude their use to enhance oil recovery in an economical manner.

Summary

Experiments using CME surfactants at 50° C showed that results observed in static adsorption tests could be used to predict surfactant loss behavior in coreflood experiments in the presence of oil. CME surfactant loss increased significantly as temperature and salinity increased. In corefloods, experiments under these conditions led to phase trapping of the surfactant for tests conducted at salinities where IFT measurements and phase behavior studies suggested that oil recovery would be most favorable. Table 9 summarizes oil recovery efficiency and surfactant retention values for the coreflood experiments.

The lowest surfactant loss values were observed in tests with very poor oil recovery efficiency. Optimum oil production was not achieved in any of these tests. The lignosulfonate sacrificial agent did effectively reduce surfactant adsorption in the low salinity test (test 1). Poor lignosulfonate recovery in the higher salinity test (test 3) indicated severe phase trapping under these conditions. Using a different CME surfactant, JA-6, oil recovery was improved and phase trapping of the lignosulfonate was reduced significantly.

Sacrificial agents may have some benefit in reducing CME surfactant adsorption. However, they have no affect on surfactant loss mechanisms arising from poor solution properties which lead to phase separation or precipitation. Understanding surfactant solution properties under conditions that optimize oil recovery would be useful information to evaluate sacrificial agent effectiveness.

Mixed Surfactant Systems

Screening tests were performed using mixtures of CME surfactants with different hydrophobic and hydrophillic functionalities. Phase separation (cloud point) of several CME surfactants were determined in a low salinity brine (0.5% NaCl) and in a high salinity brine (15% NaCl) by observing a change in solution clarity as samples were heated slowly in a water bath. Similar experiments were then performed on

TABLE 9. - Oil recovery efficiency of dodecane and surfactant retention for coreflood experiments conducted at 50° C

Test number	Surfactant type	Surfactant retention, %	mg/g	Oil recovery efficiency, %	Lignosulfonate recovery, %
1	CES 5.5	34	0.25	0	69
2	CES 5.5	100	>0.8	0	-
3	CES 5.5	100	>0.8	0	17
4	JA-6	-	-	9.3	-
5	JA-6	-	-	16.1	78
6	CES 6.5	93	3.0	51.1	-

solutions containing equal concentrations of two different CME surfactants, also for the two salinities. The mixtures were chosen to combine at least one surfactant that had no phase separation up to 90° C with one that showed a phase separation at a lower temperature for at least one of the salinities tested. Results are shown in table 10.

The CME surfactants, CES 6.5 and RS-16, showed good solubility to reasonably high temperatures even at the higher salinity. JA-6 and M-18 were much less soluble even at the lower salinity. In the mixtures, both CES 6.5 and RS-16 raise the phase separation temperatures of JA-6 and M-18. The effects were greatest at the low salinity. For the high salinity, the solubility of the M-18 was most improved by combination with RS-16. However, combination with CES 6.5 also caused some increase in the phase separation temperature compared with that observed for the M-18 alone. Less effect was seen for mixtures with JA-6 at the higher salinity although RS-16 was also more effective than CES 6.5 in improving surfactant solubility properties.

TABLE 10. - Phase separation temperatures of CME surfactants and their mixtures for two salinities

CME Surfactant	Salinity, % NaCl	Phase separation temp., °C
CES 6.5	0.5	>90
	15	74
MA-18	0.5	49
	15	<24
JA-6	0.5	<24
	15	<24
RS-16	0.5	>90
	15	76
JA-6/RS-16	0.5	>90
	15	30
JA-6/CES 6.5	0.5	>90
	15	<24
M-18/RS-16	0.5	>90
	15	58
M-18/CES 6.5	0.5	>90
	15	45

Screening of phase separation temperatures was continued using mixtures of M-18 and CES 6.5 because both surfactants could be analyzed using the HPLC with UV detector. Table 11 shows phase separation temperatures of these combined surfactants at several additional salinities between the high and low salinities reported above.

This information was then used to design a series of adsorption experiments to determine the effect of solution solubility or proximity to the phase separation temperature on surfactant loss from mixed surfactant systems. Some problems with analytical determination of surfactant concentrations have caused a delay in the completion of the entire series of measurements. However, preliminary measurements at 15% NaCl concentration and ambient temperature indicated that surfactant loss on crushed Berea sandstone of mixed M-18/CES 6.5 (2.3 mg/g) was lower than that of M-18 alone (3.5 mg/g) but was not as low as that of CES 6.5 alone (1.8 mg/g). These results indicate that more extensive investigation of surfactant loss from mixed surfactant systems could help elucidate methods to propagate surfactant deeper into the reservoir during a surfactant flood.

CONCLUSIONS

- Adsorption losses of carboxymethylated ethoxylated surfactants (CME) can be reduced significantly for low salinity and/or low temperature conditions through the use of sacrificial agents such as lignosulfonate and sodium carbonate/bicarbonate. Several other inorganic sacrificial agents did not reduce surfactant adsorption. Under these conditions, surfactant losses due to phase separation are probably not as important as losses caused by adsorption to the rock surface.
- Surfactant losses at high salinity and/or temperature are not significantly improved by the use of any sacrificial agent tested in this study. Under these conditions surfactant phase separation became an important mechanism for surfactant loss.

TABLE 11. - Phase separation temperatures of M-18 and CES 6.5 and their mixtures for four salinities

Salinity, % NaCl	Phase separation temp., ° C M-18	 M-18 and CES 6.5	 CES 6.5
0.5	49	>90	>90
5	38	76	>90
10	29	49	>90
15	<24	45	74

- These results were observed in both static adsorption tests and coreflood experiments in the presence of oil. Reduction of adsorption in coreflood experiments did not affect (or improve) oil production using CME surfactants. Conditions which favored low adsorption losses were unfavorable in terms of low IFT and oil solubilization, resulting in 0% incremental oil recovery for these coreflood experiments. Surfactant losses were excessively high for corefloods with observable oil production.

- CME surfactant solution properties can be affected by solution pH. A coreflood conducted a pH corresponding to the pK_a of the surfactant (pH = 4.6 for Hüls CES 6.5) recovered approximately 50% of the residual oil saturation. Surfactant retention was over 90% for the experiment, however.

- The use of mixed surfactant systems may be one method to reduce or adjust for unfavorable phase separation of anionic ethoxylated surfactants. This may reduce phase trapping and allow penetration into the reservoir of a surfactant system which demonstrates useful phase behavior.

REFERENCES

1. Surkalo, H. and G. Pouska. Analysis of Reservoir Pretreatment in Chemical Flooding: A Literature Review. Dept. of Energy Report No. DOE/BC/10027-11, July 1980.

2. Lorenz, Philip B. Correlation of Laboratory Design Procedures with Field Performance in Surfactant-Polymer Flooding. Dept. of Energy Report No. NIPER-408, February 1989.

3. Falcone, J. S., Jr., P. H. Krumine, and G. C. Schweiker. The Use of Inorganic Sacrificial Agents in Combination with Surfactants in Enhanced Oil Recovery. JAOCS, v. 59. No. 10, October 1982.

4. Sigg, L., and W. Strumm. The Interaction of Anions and Weak Acids with the Hydrous Goethite (-FeOOH) Surface. Colloids and Surfaces. v. 2, 1981, page 101.

5. Surkalo, H. and G. Pouska. Experimental Evaluation of Reservoir Pretreatment in Chemical Flooding. Dept. of Energy Report No. DOE/BC/10027-12. February 1981.

6. Compere, A. L., et al. Dept. of Energy Report No. DOC/BETC/OR-18. November 1981.

7. Johnson, J. S., Jr., and R. M. Jones. Sacrificial Agents for Micellar-Flooding Enhanced Oil Recovery. For Proceedings *Tensioattivi, Colloiai ed Interfasi: Proprieta'ed Applicazioni Nell'Industria.* Progetto Finalizzato Del CNR Chimica Fine E Secondaria. Belgirate, Italy, June 9-13, 1986.

8. Novosad, J. Laboratory Evaluation of Lignosulfonates as Sacrificial Adsorbates in Surfactant Flooding. J. Can. Res. Eng., v. 23, No. 3, 1984.

9. Hong, S. A., J. H. Bae, and G. R. Lewis. An Evaluation of Lignosulfonate as a Sacrificial Adsorbate in Surfactant Flooding. SPE Reservoir Engineering, February 1987, pp. 17-25.

10. Hong, S. A. and J. H. Bae. Field Experiment of Lignosulfonate Preflushing for Surfactant Adsorption Reduction. Pres. at the 63rd SPE Annual Technical Conference and Exhibition, Houston, TX, Oct. 2-5, 1988. SPE paper 18088.

11. Olsen D. K. and C. B. Josephson. Carboxymethylated Ethoxylated Surfactants. Dept. of Energy Report No. NIPER-228, August 1987.

12. Balzar, D. Carboxymethylated Ethoxylates, Tailor-Made Surfactants for Enhanced Oil Recovery. Oil Gas-European Magazine, v. 1, No. 50, 1983.

13. Chiu, Y. C. and H. J. Hwang. The Use of Carboxymethyl Ethoxylates in Enhanced Oil Recovery. Colloids and Surfaces, v. 28, 1987, pp.53-65.

14. Lysenko, V. I., V. G. Germashev, and V. D. Gisev. Effect of Amyl Alcohol on the phase behavior of Carboxymethylated Ethoxylates of Isononylphenol in a Surfactant-Water-Hydrocarbon System. Translated from Kolloidnyi Zhurdal, v. 49, No. 5, Sept.-Oct. 1987, pp. 1012-1015.

15. Noll, L. A., B. L. Gall, M. E. Crocker, and D. K. Olsen. Surfactant Loss: Effect of Temperature, Salinity, and Wettability. Dept. of Energy Report No. NIPER-385, November 1988.

16. Strycker, A. Selection of Design of Ethoxylated Carboxylates for Chemical Flooding. Dept. of Energy Report No. NIPER-449, October, 1989.

☆U.S. GOVERNMENT PRINTING OFFICE: 1989-761-030/00058