**The Effect of Polymer-Surfactant Interaction on the Rheological
Properties of Surfactant Enhanced Alkaline Flooding Formulations**

Topical Report

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NIPER--635
DE93 000118

February 1993

Work Performed Under Cooperative Agreement No. DE-FC22-83FE60149

**Prepared for
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THE EFFECT OF POLYMER-SURFACTANT INTERACTION ON THE RHEOLOGICAL PROPERTIES OF SURFACTANT-ENHANCED ALKALINE FLOODING FORMULATIONS

by

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ABSTRACT

Surfactant-enhanced, lower pH (weak) alkaline chemicals are effective for mobilizing residual oil. Polymer is used for mobility control because if mobility control is lost, then oil recovery is reduced. The ability to maintain mobility control during surfactant-alkaline flooding can be adversely affected by chemical interaction. In this work, interaction between polymers and surfactants was shown to be affected by pH, ionic strength, crude oil, and the properties of the polymers and surfactants. Polymer-surfactant interaction (phase separation, precipitation, and viscosity loss) occurred between most of the polymers and surfactants that were tested. Polymer-surfactant interaction is difficult to eliminate, and no method was found for completely eliminating interaction.

Polymer-surfactant interaction occurred at optimal salinity and below optimal salinity. Polymer-surfactant interaction had an adverse effect on polymer rheology; however, the adverse effect of interaction on polymer rheology was lessened when oil was present. Increasing the pH of chemical systems further reduced the adverse effects of interaction on polymer rheology.

This work was performed for the Department of Energy and represents milestone 5, project BE4B in the FY92 Annual Research Plan.

BACKGROUND

Production from many of the onshore oil reservoirs in the United States has declined to such low levels that much secondary production is no longer economic. Even though large amounts of crude oil remain in place, many of these reservoirs have been waterflooded to high water-to-oil ratios and will soon be abandoned unless cost-effective enhanced oil recovery (EOR) methods are developed. Surfactant-enhanced alkaline flooding, a technology developed in the past 10 years, is a potentially cost-effective method for recovery of a significant quantity of the remaining oil.¹

Surfactant-enhanced alkaline flooding formulations with weak alkaline agents have great potential for some reservoirs. These alkaline formulations react less with reservoir minerals than

other chemicals and facilitate the use of low concentrations of surfactants because surfactant adsorption is reduced in the presence of alkaline agents. Moderately basic alkaline chemicals, such as sodium carbonate and sodium bicarbonate, are also effective for mobilizing residual oil when relatively low concentrations of surfactant are added to the formulation.²

Strong alkalis such as sodium hydroxide and sodium orthosilicate are very effective for mobilizing residual oil in laboratory corefloods, but fundamental research on the reaction kinetics of alkaline formulations with reservoir minerals has indicated that it is nearly impossible to prevent the deleterious reactions that occur when strongly alkaline chemical formulations are injected into reservoir formations.³⁻⁴ This is the primary reason why many field projects conducted by major oil companies have failed. In some cases, oil production has actually declined as a result of alkaline flooding with strong alkalis.⁵

This work led to investigations of milder alkaline agents that are less reactive with reservoir rocks. Initial studies on formulations using sodium carbonate and sodium bicarbonate indicated that the displacement efficiency in corefloods was much less with certain crude oils than that obtainable with highly alkaline chemicals such as sodium hydroxide and sodium orthosilicate. Fundamental research on coalescence phenomena and dynamic interfacial tension behavior indicated that addition of small amounts of synthetic surfactants to moderately alkaline formulations significantly improved the properties of these chemical systems. The efficacy of these surfactant-enhanced alkaline flooding formulations was subsequently verified in oil displacement tests in cores.¹

In recent years, there has also been some field testing of surfactant-enhanced alkaline flooding. Most of the field activity has been in Wyoming, Louisiana, and Texas.⁶⁻⁷ Initial results from field tests have been promising, but surfactant-enhanced alkaline is not yet a commercial-scale reality, and the objective of Project BE4B is to help develop cost-effective and efficient surfactant-enhanced alkaline chemical flooding formulations and share this information with the petroleum industry.

Initial investment costs for purchasing chemicals for injected formulations have been a significant economic constraint that has hindered commercial applications of many chemical flooding technologies. Surfactant-enhanced alkaline flooding formulations are potentially more cost-effective than some other flooding methods because the cost of alkaline chemicals is comparatively low. The key to obtaining favorable economics is a synergism between alkali, surfactant, and oil that results in mobilization of some crude oils at greatly reduced surfactant

concentrations. Another favorable property of surfactant-enhanced alkaline systems is reduced loss of surfactant onto reservoir rock by precipitation and adsorption.

INTRODUCTION

The objective of Project BE4B is to develop cost-effective and efficient chemical flooding formulations using surfactant-enhanced, lower pH (weak) alkaline chemical systems. It has been shown previously that these chemical systems can be effective in mobilizing residual oil when relatively low concentrations of surfactant are used in the formulation. Several strategies have been suggested for applying surfactant-enhanced alkaline flooding.⁸⁻¹¹ Some examples are (1) a combination of alkali, surfactant, and polymer into a single slug followed by more polymer, (2) a combination of alkali and surfactant into a single slug, followed by polymer, (3) pre-injection of alkali to condition the reservoir, (4) surfactant followed by alkaline polymer, (5) injection of oil soluble acids followed by alkali, and (6) various injection strategies that utilize surfactant gradients.

Some results obtained from oil recovery tests conducted at NIPER are as follows:

1. Oil recovery was highest when alkaline surfactant was followed by polymer.
2. Oil recovery was only slightly decreased when the alkali, surfactant, and polymer were simultaneously injected (mixed in single slug), and oil production occurred faster.
3. Oil recovery was significantly reduced when surfactant was followed with alkaline polymer.
4. Oil recovery was lowest when surfactant was followed by polymer and there was no alkali in any of the injected solutions.

In all four cases, polymer was used for mobility control. If mobility control is lost, then oil recovery is further reduced. The ability to maintain mobility control during surfactant-alkaline flooding is more strongly affected by chemical interactions than is commonly believed.¹²⁻¹⁶ Although considerable research has been conducted on this subject, the results of that research do not now appear to be common knowledge among many operators who are unaware of the potential chemical interactions that might affect an EOR project. Many types of chemical interactions are possible, and when chemical flooding systems are designed, the effects of chemical interactions may be overlooked. Some interactions may have negligible effect in laboratory corefloods; however, all chemical interactions have the potential to affect the outcome of field projects.

For economic reasons, it may be advantageous to inject surfactant, polymer, and alkali as a single slug. Chemical interactions can occur between any of the chemicals contained in the single slug. In a short coreflood, interactions that occur between the polymer and other chemicals can be minimized by injecting the polymer as a separate slug, rather than mixing the polymer in the same slug that contains surfactant and alkali. In this procedure, an operator can decrease the total amount of polymer used, which is economically favorable, because the ionic strength of the polymer slug can be less than the ionic strength of the alkaline slug. However, segregation of polymer in a separate slug will not eliminate interaction with chemicals in a preceding chemical slug. In the absence of adsorption, polymer molecules will propagate through reservoir rock at a faster rate than small molecules such as water. This is attributed to a phenomenon called inaccessible pore volume (IPV) which can be significant -- 35% PV is not uncommon.^{15,17} Because of IPV, polymer will invade and dilute the chemical slug ahead. This will affect the mobility and stability of the chemical slug and the required volume of mobility buffer bank. It also means that if there are incompatibilities between the polymer and constituents in the lead slug, then chemical interactions will not be eliminated by injecting polymer as a separate slug.

The interactions that can occur during surfactant-enhanced alkaline flooding are complex. Some of the parameters are pH level, ionic strength, polymer properties, cosurfactant (alcohols) properties, and surfactant properties. The presence of crude oil may also affect interaction, as can other chemicals.¹² At least six types of surfactant-polymer complexes have been described,¹²⁻¹⁶ and the interactions that occur between polymers and surfactants could be the most significant of the possible interactions that can occur during surfactant-enhanced alkaline flooding. Polymer-surfactant interaction was the focus of this work. Rheological properties of polymer solutions were monitored over a long period of time in the presence of surfactants, at different pH levels, and in the presence of crude oil.

CHEMICALS AND PROCEDURES

Reagents and Chemicals

Hepler (KS) Tucker Sand (class I reservoir) crude oil

Surfactants:

Chevron Chaser XP-100, an anionic surfactant, mol wt = 434

Chevron Chaser CF-100, an experimental anionic surfactant

Stepan Petrostep B-110, an anionic surfactant, mol wt = 500

Stepan Petrostep B-105 an anionic surfactant mixture, mol wt about 424

Shell Neodol 25-9, ethoxylated alcohol, mol wt = 610

Polymers:

Pfizer Flopaam 3230E, a low-molecular-weight partially hydrolyzed emulsion polyacrylamide, mol wt = 7.8×10^6

Pfizer Flopaam 3230S, a low-molecular-weight partially hydrolyzed solid polyacrylamide, mol wt = 7.8×10^6

Pfizer Flocon 4800CX, a biopolymer

Allied Colloids Alcoflood 1135, a medium-molecular-weight partially hydrolyzed solid polyacrylamide polymer

Alkalis:

Sodium carbonate, analytical reagent

Sodium bicarbonate, certified ACS

Sodium hydroxide, certified ACS

Sodium tripolyphosphate (STPP), technical

Make-up water:

Deionized water (DIW)

Hepler supply well water:

Sodium and potassium	830	mg/L
Chlorides	908	mg/L
Calcium and Magnesium	21	mg/L
Bicarbonate	720	mg/L
TDS	2,483	mg/L
pH	7.9	

Procedures

Rheology and pH of mixtures were periodically monitored for 191 days. All compositions are given as weight per volume, and each solution contained 300 ppm formaldehyde as a preservative. A Contraves low-shear viscometer was used for initial measurements of viscosity. Because of mechanical problems with the Contraves, the later measurements were made with a Brookfield Model LVT-C/P 1.565° cone and plate viscometer. Samples were aged at room temperature and viscosity was measured at 23° C. Rheological measurements were displayed graphically in 3-dimensions using a computer program that was specifically designed for 3-dimensional plots. An Orion Model 601 digital pH meter was used for pH measurements. Samples were monitored visually for phase separation, cloudiness, and precipitation.

Interfacial properties of selected systems were measured with a University of Texas spinning drop interfacial tensiometer. Transient (dynamic) IFT behavior was monitored over a time interval of several hours.

DISCUSSION

Interactions that occur between alkaline chemicals, polymers, surfactants, and co-surfactants are complex. Interactions have been shown to be affected by pH level, ionic strength, crude oil, and the properties of polymers, surfactants and co-surfactants. Additionally, reservoir rock may play a significant role. The interactions that occur between polymers and surfactants under alkaline conditions are very significant, and are the focus of this discussion. Table 1 presents the results of visual observations from a series of interaction tests. Many of these systems were mixed in water from a water supply well in Hepler (KS) oil field where a field test is planned. Many of the experiments were performed after it was observed that interactions occurred between polymers and surfactants in chemical systems that produced good oil recovery in laboratory corefloods.¹⁸

Polymers used for the tests shown in Table 1 were Pfizer Flocon 4800 CX biopolymer, Pfizer Flopaam 3230E (emulsion polyacrylamide), Pfizer Flopaam 3230S (solid polyacrylamide), and Allied Colloids Alcoflood 1135, which is a solid polyacrylamide. Alkalis were sodium bicarbonate, sodium carbonate, and mixtures of sodium bicarbonate and sodium carbonate.

The surfactants were Shell Neodol 25-9 nonionic surfactant, a mixture of Stepan Petrostep B series anionic surfactants, and Chevron anionic surfactants Chaser XP-100 and CF-100. The anionic surfactants supplied by Chevron Chemical Company are of special interest because they are expected to be used in the field test mentioned above.

The results in Table 1 show that some phase separation occurs when the emulsion polyacrylamides are dispersed in brine. Biopolymers dispersed into brines as hazy, stable solutions, and the solid polyacrylamides, 3230S and 1135 dispersed as clear, stable solutions.

Neodol 25-9, a nonionic ethoxylated alcohol, dispersed into brine as a clear solution. Anionic surfactants, Stepan B series, XP-100, and CF-100, dispersed as stable, cloudy suspensions, except at high ionic strengths where they became insoluble.

When surfactants and polymers were dispersed into solutions together, phase separation and precipitation usually occurred. The exception was Neodol 25-9 (nonionic), which gave

stable, hazy solutions with biopolymer and only a trace of precipitate with polyacrylamide polymer. Combinations of anionic surfactants with polyacrylamides always resulted in phase separation and/or precipitation. Precipitation of anionic surfactants occurred more slowly with biopolymer, but the amount of precipitate was about the same as that for polyacrylamides.

When surfactants and polymers were dispersed into aqueous solutions and then contacted with Hepler crude oil, the interaction between surfactant and polymer still existed, but was much different from the interaction that was observed when crude oil was absent. With XP-100 surfactant and 3230S polymer, the emulsion that was formed showed less phase separation when oil was present. This was most apparent at low XP-100 concentrations.

Interactions between polymers and surfactants are of special interest when the conditions of salinity (ionic strength) are such that optimum IFT behavior occurs between the surfactant mixture and a particular crude oil. For this reason, the surfactant-enhanced alkaline mixtures presented in Table 1 are for chemical systems that were optimized to give low IFT values with specific crude oils. The Neodol 25-9 chemical system was optimized with crude oil from Wilmington (CA) oil field.¹⁹ The XP-100, CF-100, and Petrostep surfactants were optimized with Hepler produced oil.

One chemical system was selected for further study of the effects of polymer-surfactant interaction on rheology. The system selected contained 0.5% XP-100 surfactant and sodium chloride. The dynamic IFT between this chemical system and Hepler oil is shown in Fig. 1. Optimum salinity (lowest IFT) occurred with 1.2% NaCl. With 1.2% NaCl, XP-100 solutions were stable, hazy dispersions.

The mixtures shown in Table 2 contain 0.4, 0.6, or 1.2% NaCl. NaCl concentrations of 0.4 and 0.6% are below optimum and 1.2% is equal to optimum salinity. Adjustment of pH was accomplished with sodium hydroxide, a strong alkali. Weak, buffered alkalis have properties that are advantageous for field use.² For these studies, however, the strong alkali is more useful because pH can be adjusted with the addition of small amounts of the strong alkali; therefore, the ionic strength is changed only very little during pH adjustment. The polymer used for the tests was Alcoflood 1135, a medium-molecular-weight anionic polymer which is furnished in solid form. Alcoflood 1135 is a partially hydrolyzed polyacrylamide.

The pH, viscosity, and appearance of the mixtures shown in Table 2 were monitored periodically for 191 days. The detrimental effects of salt solutions on the rheological properties of polyacrylamide polymers is well known. The effects of salinity and shear rate on apparent viscosity are shown in Fig. 2 (pH less than 7) and Fig. 3 (pH greater than 10). The pH level had

negligible effect on the rate of viscosity reduction as salinity was increased. Some downward drift in viscosity with time occurred at both pH levels.

The rates of change in apparent polymer viscosity with time are shown in Figs. 4, 5, 6, and 7. Figures 4 and 5 show the results of periodic measurements of polymer solutions at pH 5.74 and pH 10.43, respectively, in 0.4% NaCl. At pH 5.74, there was a slight increase in viscosity at early time, followed by decreased viscosity that became nearly stable after 50 days. Overall, viscosity decreased from 46 to 38 cP over 191 days at low shear rate. At pH 10.43, there was also an initial increase in viscosity that was followed by a relatively stable value of viscosity. Overall, viscosity decreased from 51 to 44 cP.

For comparison, Figs. 6 and 7 show the results of periodic measurements of polymer solutions at pH 5.60 and pH 10.50, respectively, in 1.2% NaCl. At pH 5.60, there was a slight increase in viscosity at early time followed by a decrease in viscosity until about 60 days, after which viscosity was relatively stable. Overall, viscosity decreased from 21 to 18 cP at low shear rate. For pH 10.50, behavior was very similar, with an overall viscosity decrease from 23 to 19 cP.

The pH levels of polymer solutions with pH values of 5.74 and 5.60 were unaltered, i.e. these pH levels were the pH values that resulted from mixing the polymer without addition of any chemicals to alter the naturally occurring pH. The pH levels of the polymer solutions with pH values of 10.43 and 10.50 were adjusted by addition of sodium hydroxide. Adjusting the pH of these polymer solutions by addition of sodium hydroxide resulted in a 10% increase in apparent viscosity at low shear rate. Otherwise, the rate of change of viscosity over 191 days was not much different for the four polymer mixtures.

The pH changes in these solutions are shown in Figs. 8 and 9. The pH values of the two polymer mixtures that were below pH 7 were virtually unchanged over the entire time of periodic measurement, whereas the pH values of the alkaline polymer mixtures declined over the entire period of measurement. It is possible that some loss of viscosity was due to hydrolysis occurring in these polymer mixtures.²⁰ All of the polymer mixtures exhibited a very slow degradation of viscosity.

The rates of change in apparent viscosity for mixtures that contain polymer and surfactant are shown in Figs. 10, 11, 12, and 13. Figures 10 and 11 show the results of periodic measurements of polymer - surfactant mixtures at pH 7.04 and 10.70, respectively, in 0.4% NaCl. At pH 7.04, viscosity decreased sharply for 50 days and continued to decline over the entire time interval. Overall, viscosity decreased from 60 to 19 cP at low shear rate, a decrease

of 68%. For pH 10.70, behavior was very similar. After a slight initial increase in viscosity at early time, viscosity decreased sharply during the first 40 days of measurements. Overall, viscosity decreased from 58 to 27 cP at low shear rate, a decrease of 54%. A slight increase in viscosity at early time was measured for all of the mixtures that contained polymer and surfactant. A typical example of this is shown more clearly in Fig. 14.

For comparison, Figs. 12 and 13 show the results of periodic measurements of polymer-surfactant mixtures at pH 6.88 and 10.77, respectively, in 1.2% NaCl. At pH 6.88, a sharp decrease in viscosity occurred over the first 40 days. Viscosity then increased slightly, followed by a gradual decline over the remainder of the time interval. Overall, viscosity decreased from 25 to 8 cP, a decrease of 68%. For pH 10.77, behavior was very similar with an overall decrease in viscosity from 24 to 9 cP, a decrease of 60%. Viscosity decrease was much greater for these polymer-surfactant mixtures than for the polymer solutions discussed above.

Viscosity changes for the four polymer-surfactant mixtures were quite similar, except for the second occurrence of viscosity increase in both of the graphs for 1.2% NaCl. In 0.4 and 1.2% NaCl, the viscosity of the alkaline mixtures was about the same as for the non-alkaline mixtures. The changes that occurred in pH, shown in Figs. 8 and 9, are about the same as was observed for polymer solutions that did not contain surfactant, except that the pH of the solutions without pH adjustment are nearer to pH 7, because XP-100 surfactant is slightly alkaline.

The rates of change in apparent polymer viscosity for polymer-surfactant-oil mixtures are shown in Figs. 15 through 18. Figures 15 and 16 show the results of periodic measurements of polymer-surfactant-oil mixtures at pH 7.07 and pH 10.73, respectively, in 0.4% NaCl. At both pH values, initial viscosity was lower and the rate of viscosity decrease was less steep than for the previously discussed mixtures of polymer-surfactant mixtures. Polymer-surfactant-oil mixtures were more homogeneous in appearance and there was less scatter in measurements. At pH 7.07, viscosity decreased from 50 to 19 cP over the time interval, an overall decrease of 62%. At pH 10.73, viscosity decreased from 52 to 40 cP, an overall decrease of only 23%.

In 1.2% NaCl (Figs. 17 and 18), similar results were obtained for polymer-surfactant-oil mixtures. At pH 6.87, overall viscosity decrease at low shear rate was from 20 to 8 cP, or 60%. At pH 10.79, viscosity decrease was from 25 to 15 cP, or 40%.

OBSERVATIONS AND CONCLUSIONS

1. Polymer-surfactant interaction can be expected to have an adverse effect on oil recovery, especially when permeability is low.

2. Polymer-surfactant interaction (phase separation, precipitation, and viscosity loss) occurred between most of the polymers and surfactants that were tested.
3. Polymer-surfactant interaction is difficult to eliminate, and no method was found for completely eliminating interaction.
4. Polymer-surfactant interaction occurred at optimal salinity and below optimal salinity.
5. The magnitude of the interaction was least for non-ionic surfactant and biopolymer.
6. Polymer-surfactant interaction had an adverse effect on polymer rheology.
7. The adverse effect of interaction on polymer rheology was lessened when oil was present.
8. When oil was present, the adverse effect of interaction on polymer rheology was further reduced by increasing pH.

REFERENCES

1. Peru, D.A. *Aqueous Flooding Methods for Tertiary Oil Recovery*. U. S. Patent 4,817,715, April 1989.
2. French, T. R. and T. E. Burchfield. *Design and Optimization of Alkaline Flooding Formulations*. Pres. at the Seventh Joint SPE/DOE Symposium on Enhanced Oil Recovery, Tulsa, OK, April 1990. SPE/DOE paper 20238.
3. Lorenz, P.B. and D.A. Peru. Guidelines Help Select Reservoirs for NaHCO₃ EOR. *Oil & Gas J.*, v. 87, No. 37, Sept. 11, 1989, pp. 53-57.
4. Thornton, S. D. and P. B. Lorenz. *Role of Silicate and Aluminate Ions in the Reaction of Sodium Hydroxide with Reservoir Minerals*. Pres. at the SPE Int. Symp. on Oilfield Chemistry, San Antonio, TX, Feb. 4 - 6, 1987. SPE paper 16277.
5. Dauben, D. L., R. A. Easterly, and M. M. Western. *An Evaluation of the Alkaline Waterflooding Demonstration Project, Ranger Zone Wilmington Field, California*. DOE Report DOE/BC/10830-5 (NTIS Order No. DE87001240), May, 1987.
6. Falls, A. H., D. R. Thigpen, and R. C. Nelson. *A Field Test of Cosurfactant-Enhanced Alkaline Flooding*. Pres. at the SPE/DOE Eighth Symposium on Enhanced Oil Recovery in Tulsa, OK, Apr. 22 - 24, 1992. SPE/DOE paper 24117.
7. Meyers, J. J., M. J. Pitts, and K. Wyatt. *Alkaline-Surfactant-Polymer Flood of the West Kiehl, Minnelusa Unit*. Pres. at the SPE/DOE Eighth Symposium on Enhanced Oil Recovery in Tulsa, OK, Apr. 22 - 24, 1992. SPE/DOE paper 24144.
8. Schuler, P. J., R. M. Lerner, and D. L. Kuehne. *Improving Chemical Flood Efficiency with Micellar/Alkaline/Polymer Processes*. Pres. at the Fifth SPE/DOE Symp. on Enhanced Oil Recovery, Tulsa, OK, Apr. 20-23, 1986. SPE/DOE paper 14934.
9. Krumrine, P. H., J. S. Falcone, Jr., and T. C. Campbell. Surfactant Flooding 1: The Effect of Alkaline Additives on IFT, Surfactant Adsorption, and Recovery Efficiency. *Soc. Pet. Eng. J.*, v. 22, No. 4, August 1982.
10. Krumrine, P. H. and J. S. Falcone, Jr. *Surfactant, Polymer, and Alkali Interactions in Chemical Flooding Processes*. Pres. at the SPE Int'l Symp. on Oil field and Geothermal Chemistry, Denver, CO, June 1-3, 1983. SPE paper 11778.

11. French, T. R. and C. B. Josephson. *Alkaline Flooding Injection Strategy*. DOE Report No. NIPER-563. Sept. 1991.
12. Kalpakci, Bayram. *Flow Properties of Surfactant Solutions in Porous Media and Polymer-surfactant Interactions*. A Thesis in Chemical Engineering, Pennsylvania State University, Nov. 1981.
13. Shuji, Saito. Polymer-Surfactant Interactions. Chapter 15, *Nonionic Surfactants* edited by Martin J. Schick. Marcel Dekker, Inc., New York and Basel, 1987, pp. 881-926.
14. Yang, C. Z. *Adjustment of Surfactant/Polymer Interaction in Surfactant/Polymer Flooding with Polyelectrolytes*. Pres. at the SPE/DOE Fifth Symposium on Enhanced Oil Recovery, Tulsa, OK, April 20-23, 1986. SPE/DOE paper 14931.
15. Trushenski, Scott P. Micellar Flooding: Sulfonate-Polymer Interaction. *Improved Oil Recovery by Surfactant and Polymer Flooding* (Shah, D. O. and Schechter, R. S., Eds.), Academic Press, New York, 1977, pp. 555-75.
16. Nagarajan, R. *On the Nature of Interactions Between Polymers and Surfactants in Dilute Aqueous Solutions*. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 22(2), pp. 33-8, 51-2, 1981.
17. Gao, H. W., T. R. French, and T. E. Burchfield. *Optimal Rheological Characteristics in Dynamic Stability of Polymer Flow Through Porous Media*. Pres. at 1988 AIChE Annual Meeting in Washington D. C., Nov. 27 - Dec. 2, 1988.
18. French, Troy R. *Surfactant-Enhanced Alkaline Flooding Field Project*. DOE Report NIPER-569. Oct. 1991.
19. French, T. R., D. A. Peru, and S. D. Thornton. *Low pH Alkaline Chemical Formulations*. DOE Report NIPER-375, October 1988.
20. Moens, J. and G. Smets. Alkaline and Acid Hydrolysis of Polyvinylamides. *J. Polm. Sci.* Vol. XXIII, 1957, pp. 931-48.

TABLE 1

Observations of Interactions Between Several Polymers, Surfactants, and Brines

Brine	Surfactant	Polymer	Observations
1% NaCl	-	3000 ppm Pusher 500	Clear sol'n
1% NaCl	-	3500 ppm 4800 CX	Hazy sol'n
1% NaCl	-	3000 ppm 4800 CX	Hazy sol'n
1% NaCl	-	1000 ppm 4800 CX	Hazy sol'n
1% NaCl, 0.19N Carbonate mixture	-	3500 ppm 4800 CX	Hazy sol'n
1% NaCl, 0.19N Carbonate mixture	0.25% B-110 0.15% B-105 2.031% 2BA ¹	-	Cloudy sol'n
1% NaCl, 0.19N Carbonate mixture	0.25% B-110, 0.15% B-105, 2.031% 2BA	3500 ppm 4800 CX	Hazy sol'n, thick layer of viscous emulsion at top
2% NaCl	0.25% B-110 0.15% B-105 2.031% 2BA	-	Hazy sol'n, thick layer of viscous emulsion at top that easily disperses
2.5% NaCl, 0.19N Carbonate mixture	0.1% N25-9	2000 ppm 4800 CX	Hazy sol'n-eventually a thin layer of ppt separated
2.5% NaCl, 0.19N Carbonate mixture	0.1% N25-9	2000 ppm 1135	Clear sol'n with trace of ppt
2.5% NaCl, 0.19N Carbonate mixture	-	2000 ppm 4800 CX	Hazy sol'n
2.5% NaCl, 0.19N Carbonate mixture	-	2000 ppm 1135	Clear sol'n
2.5% NaCl, 0.19N Carbonate mixture	0.1% N25-9	-	Clear sol'n
Supply water ²	-	2000 ppm 3230E	Translucent sol'n with thin layer of white opaque, viscous emulsion at top
Supply water, 1.6% NaHCO ₃ , 0.5% STPP	-	2000 ppm 3230E	Translucent sol'n with thin layer of white opaque, viscous emulsion at top
Supply water	-	1000 ppm 3230S	Clear sol'n
Supply water	-	500 ppm 3230S	Clear sol'n
Supply water, 1.6% NaHCO ₃ , 0.5% STPP	0.5% XP-100	1000 ppm 4800 CX	Hazy sol'n, medium layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% XP-100	2000 ppm 3230S	Hazy sol'n, thin layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% XP-100	1000 ppm 3230S	Hazy sol'n, thin layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% CF-100	2000 ppm 4800 CX	Hazy sol'n, thick layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% CF-100	2000 ppm 1135	Hazy sol'n, medium layer of very viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	-	2000 ppm 4800 CX	Hazy sol'n
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	-	2000 ppm 1135	Clear sol'n

TABLE 1 - Continued

Observations of Interactions Between Several Polymers, Surfactants, and Brines

Brine	Surfactant	Polymer	Observations
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% CF-100	-	Translucent sol'n
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% CF-100	2000 ppm 4800 CX	Hazy sol'n, thick layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% CF-100	2000 ppm 1135	Hazy sol'n, thick layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	-	2000 ppm 4800 CX	Hazy sol'n
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	-	2000 ppm 1135	Clear sol'n
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% CF-100	-	Translucent sol'n
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.2% CF-100	2000 ppm 1135	Hazy sol'n, thin layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.1% CF-100	2000 ppm 1135	Hazy sol'n, thinner layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.05% CF-100	2000 ppm 1135	Hazy sol'n, thinner layer of viscous ppt
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	0.5% XP-100	2000 ppm 3230S	Translucent brown sol'n w/ thin layer of dark, visc. ppt and some dark emulsion at top-eventually brown sol'n became clear ³
Supply water, 1.2% NaHCO ₃ , 0.5% STPP	1.0% XP-100	1200 ppm 3230S	Translucent sol'n w/ thin layer of viscous ppt and layer of dark ppt, oil on top ³

1. 2BA is 2-butanol.

2. Supply well water contains 21 ppm divalent cations (2,483 TDS).

3. Sample contains 1000 ppm of Hepler (KS) field crude oil.

TABLE 2

Mixtures of Polymer, Surfactant, and Brines Periodically Monitored for Changes in pH and Viscosity

Nacl conc., %	pH		Surfactant, %	Polymer	Oil, %	Results
	Initial	Final				
0.40	5.74	5.70	—	2000 ppm Alcoflood 1135	—	Slight initial increase in μ , then decreased becoming stable after 50 days. Overall, μ decreased from 46 to 38 cP.
0.40	7.04	7.20	0.5% XP-100	2000 ppm Alcoflood 1135	—	μ decreased sharply for 50 days and continued to decline over entire time interval. Overall, μ decreased from 60 to 19 cP.
0.40	7.07	7.16	0.5% XP-100	2000 ppm Alcoflood 1135	0.1	μ gradually decreased over entire time interval. Very smooth curve. Overall, μ decreased from 50 to 19 cP.
0.40	10.43	8.22	—	2000 ppm Alcoflood 1135	—	Slight initial increase in μ , but relatively stable over entire time interval. Overall, μ decreased from 51 to 44 cP.
0.40	11.00	10.85	0.5% XP-100	—	—	Stable dispersion. $\mu=1.42$ cP@230sec ⁻¹
0.40	10.70	9.16	0.5% XP-100	2000 ppm Alcoflood 1135	—	Very sharp decrease in μ over first 40 days. (There was a slight increase at early time.) μ continued to decrease over entire time interval. Overall, μ decreased from 58 to 27 cP.
0.40	10.73	9.58	0.5% XP-100	2000 ppm Alcoflood 1135	0.1	Very gradual decrease in μ over entire time interval. Very smooth curve. Overall, μ decreased from 52 to 40 cP.
0.58	5.71	6.80	—	2000 ppm Alcoflood 1135	—	Slight initial increase in μ , then decreased becoming stable. Overall, μ decreased from 34 to 22 cP.
0.58	10.53	7.80	—	2000 ppm Alcoflood 1135	—	Slight initial increase in μ , then decreased becoming stable. Overall, μ decreased from 37 to 31 cP.
1.20	5.60	5.58	—	2000 ppm Alcoflood 1135	—	Slight increase in μ at early time, then decreased to a relatively stable value after 60 days. Overall, μ decreased from 21 to 18 cP.
1.20	6.88	7.27	0.5% XP-100	2000 ppm Alcoflood 1135	—	Very sharp initial decrease in viscosity. After 40 days, there was a slight increase in μ . Then μ decreased for remainder of time interval. Overall μ decreased from 25 to 8 cP.
1.20	6.87	7.25	0.5% XP-100	2000 ppm Alcoflood 1135	0.1	Gradual, smooth decrease in μ over entire time interval, except for a slight increase in μ over first 10 days. Overall, μ decreased from 20 to 8 cP.
1.20	10.83	10.55	—	—	—	$\mu = 1.14$ cP@ 230 sec ⁻¹
1.20	10.50	8.33	—	2000 ppm Alcoflood 1135	—	After an initial decrease in μ , μ was relatively stable. Overall, μ decreased from 23 to 19 cP.
1.20	11.06	11.08	0.5% XP-100	—	—	Stable dispersion. $\mu=1.22$ cP@230sec ⁻¹

TABLE 2 - Continued

Mixtures of Polymer, Surfactant, and Brines Periodically Monitored for Changes in pH and Viscosity

NaCl conc., %	pH		Surfactant, %	Polymer	Oil, %	Results
	Initial	Final				
1.20	10.77	9.20	0.5% XP-100	2000 ppm Alcoflood 1135	—	Very sharp initial decrease in viscosity. After 40 days, there was a slight increase in μ . Then μ decreased for remainder of time interval. Overall μ decreased from 24 to 9 cP.
1.20	10.79	9.72	0.5% XP-100	2000 ppm Alcoflood 1135	0.1	Gradual, smooth decrease in μ over entire time interval, except for a slight increase in μ over first 10 days. Overall, μ decreased from 25 to 15 cP.

FIGURE 1. - Interfacial tension between 0.5% Chevron XP-100 surfactant, NaCl, and Hepler (KS) crude oil, 23° C.

FIGURE 2. - Viscosity of non-alkaline mixtures of 2,000 ppm Alcoflood 1135 polymer and NaCl, 11.5 sec⁻¹, 23° C.

FIGURE 3. - Viscosity of alkaline mixtures of 2,000 ppm Alcoflood 1135 polymer and NaCl, 11.5 sec^{-1} , 23°C .

FIGURE 4. - Viscosity of 2,000 ppm Alcoflood 1135 polymer in 0.4% NaCl, pH 5.74, 23°C .

FIGURE 5. - Viscosity of 2,000 ppm Alcoflood 1135 polymer in 0.4% NaCl, pH 10.43, 23° C.

FIGURE 6. - Viscosity of 2,000 ppm Alcoflood 1135 polymer in 1.2% NaCl, pH 5.60, 23° C.

FIGURE 7. - Viscosity of 2,000 ppm Alcoflood 1135 polymer in 1.2% NaCl, pH 10.50, 23° C.

FIGURE 8. - The pH of mixtures of Alcoflood 1135 polymer and Chevron XP-100 surfactant in 0.4% NaCl.

FIGURE 9. - The pH of mixtures of Alcoflood 1135 polymer and Chevron XP-100 surfactant in 1.2% NaCl.

FIGURE 10. - Viscosity of 2,000 ppm Alcoflood 1135 polymer and 0.5% Chevron XP-100 surfactant in 0.4% NaCl, pH 7.04, 23°C.

FIGURE 11. - Viscosity of 2,000 ppm Alcoflood 1135 polymer and 0.5% Chevron XP-100 surfactant in 0.4% NaCl, pH 10.70, 23° C.

FIGURE 12. - Viscosity of 2,000 ppm Alcoflood 1135 polymer and 0.5% Chevron XP-100 surfactant in 1.2% NaCl, pH 6.88, 23° C.

FIGURE 13. - Viscosity of 2,000 ppm Alcoflood 1135 polymer and 0.5% Chevron XP-100 surfactant in 1.2% NaCl, pH 10.77, 23° C.

FIGURE 14. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, and 0.5% Chevron XP-100 surfactant in 0.4% NaCl, pH 10.70, 11.5 sec⁻¹, 23° C.

FIGURE 15. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, 0.5% Chevron XP-100 surfactant, and 0.1% Hepler (KS) crude oil in 0.4% NaCl, pH 7.07, 23° C.

FIGURE 16. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, 0.5% Chevron XP-100 surfactant, and 0.1% Hepler (KS) crude oil in 0.4% NaCl, pH 10.73, 23° C.

FIGURE 17. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, 0.5% Chevron XP-100 surfactant, and 0.1% Hepler (KS) crude oil in 1.2% NaCl, pH 6.87, 23° C.

FIGURE 18. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, 0.5% Chevron XP-100 surfactant, and 0.1% Hepler (KS) crude oil in 1.2% NaCl, pH 10.79 23° C.

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