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STATUS REPORT

# POLYMER-SURFACTANT INTERACTIONS ASSOCIATED WITH APPLICATION OF SURFACTANT-ENHANCED ALKALINE FLOODING

By

Troy R. French and Charles B. Josephson

Work Performed for
U. S. Department of Energy
Under Cooperative Agreement DE-FC22-83FE60149

**National Institute for Petroleum and Energy Research**
IIT Research Institute • P.O. Box 2128
Bartlesville, Oklahoma 74005-2128 • (918) 336 - 2400

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Project BE4B, Milesone 5, FY93

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Thomas Reid, Project Manager
Bartlesville Project Office
U.S. Department of Energy

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IIT Research Institute
National Institute for Petroleum and Energy Research
Box 2128
Bartlesville, Oklahoma 74005
918 336-2400

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# POLYMER-SURFACTANT INTERACTIONS ASSOCIATED WITH APPLICATION OF SURFACTANT-ENHANCED ALKALINE FLOODING

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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. 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.

During FY93, light-scattering experiments were conducted to gain a better understanding of chemical interactions that have adverse effects on the rheological properties of surfactant-enhanced alkaline flooding chemical formulations. Despite technical problems that were encountered, significant observations and conclusions about surfactant-alkali interactions have resulted from the work in this area. If light-scattering measurements are to provide a better understanding of the chemical mechanisms involved in the adverse effects of surfactant-polymer interactions, more research and better instrumentation will be required.

## INTRODUCTION

Surfactant-enhanced alkaline flooding, a technology developed in the past 10 years, is a potentially cost-effective method for recovery of some of the remaining oil resource in the United States.[1,2] Moderately basic alkaline formulations are less reactive with reservoir minerals and facilitate the use of low concentrations of surfactants because surfactant adsorption is reduced in the presence of alkaline agents. Low concentrations of surfactant are effective for mobilizing residual oil when moderately basic alkaline chemicals, such as sodium carbonate and sodium bicarbonate, are added to the formulation.[2] Polymer is usually used for mobility control during chemical flooding 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. The chemistry of interaction between aqueous surfactant and polymer is an area of continuing research that is of interest to the petroleum industry.[3-7]

## DISCUSSION

The chemical interactions that can occur during surfactant-enhanced alkaline flooding are complex. Some of the parameters influencing interactions are pH level, ionic strength, polymer properties, cosurfactant (alcohols) properties, and surfactant properties. At least six types of surfactant-polymer complexes have been described, 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.[3-7]

The severity of the effect of interaction on rheology was demonstrated in FY92.[8] Experiments were performed with chemicals that included the surfactant and polymer system that are proposed for a field test conducted in Hepler (KS) oil field under the SGP program. Mixtures were formulated with water from a water supply in Hepler field. Rheology and pH of mixtures were periodically monitored for extended periods of time. The adverse rheological effect of polymer-surfactant interaction is shown graphically in Figs. 1 and 2, which 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%.

On the other hand, the presence of crude oil can reduce the adverse effects of polymer-surfactant interaction on rheology, as does an increase in pH. The rates of change in apparent polymer viscosity for polymer-surfactant-oil mixtures are shown in Figs. 3 and 4. Figures 3 and 4 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 that for the previously discussed 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%.

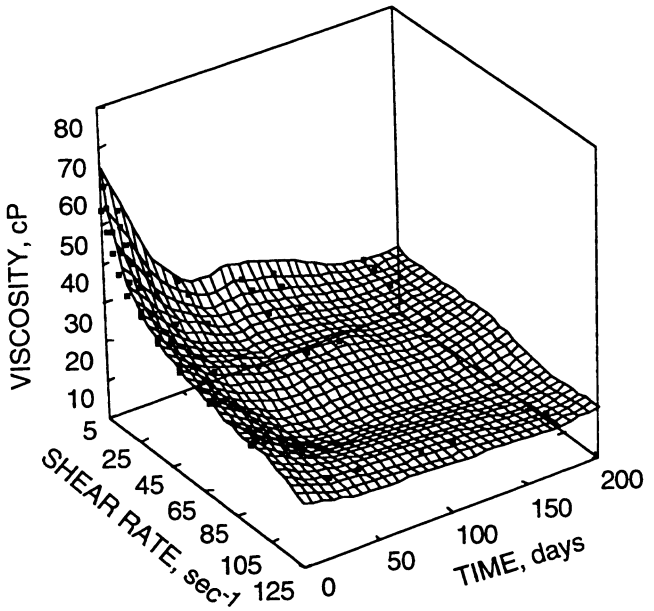


FIGURE 1. - Viscosity of 2,000 ppm Alcoflood 1135 polymer and 0.5% Chevron XP-100 surfactant in 0.4% NaCl, pH 7.04, 23° C.

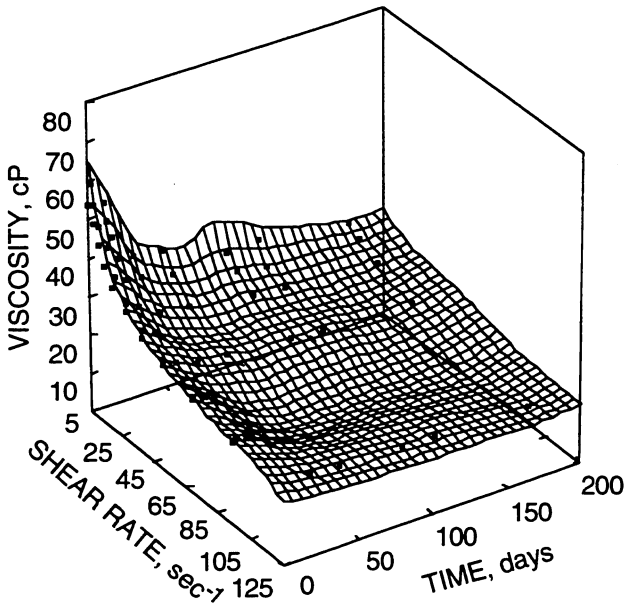


FIGURE 2. - Viscosity of 2,000 ppm Alcoflood 1135 polymer and 0.5% Chevron XP-100 surfactant in 0.4% NaCl, pH 10.70, 23° C.

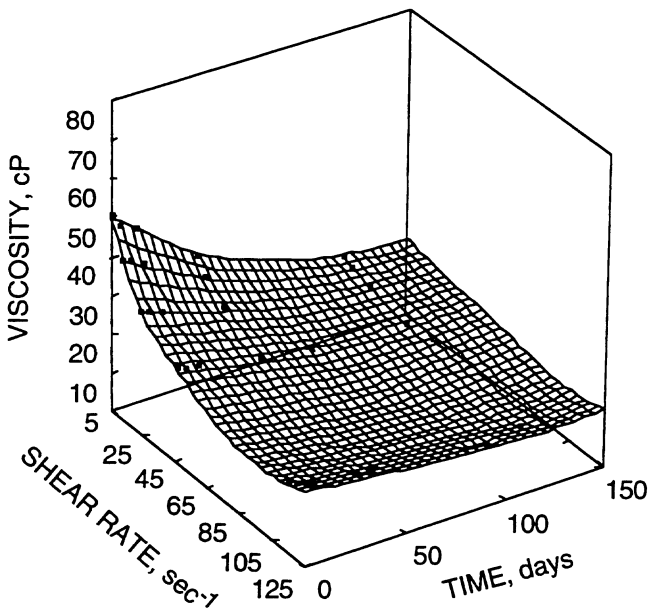


FIGURE 3. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, 0.5% Chevron XP-100 surfactant, and 0.1% Hepler (KS) crude oil in 0.4% NaCl, pH 7.07, 23° C.

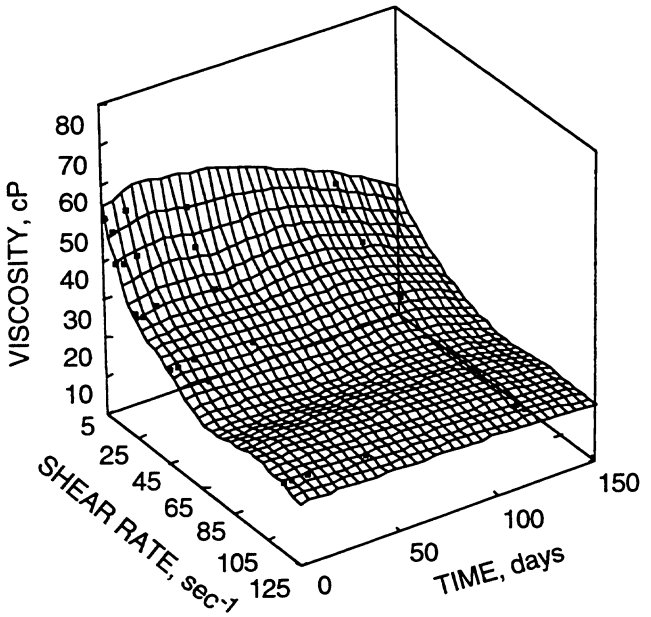


FIGURE 4. - Viscosity of 2,000 ppm Alcoflood 1135 polymer, 0.5% Chevron XP-100 surfactant, and 0.1% Hepler (KS) crude oil in 0.4% NaCl, pH 10.73, 23° C.

The effects of interactions between polymers and surfactants on rheology were shown to be significant, and so far, no satisfactory way has been found to mitigate these effects. Therefore, during FY93, experiments were conducted in order to gain a better understanding of chemical interactions that have adverse effects on the rheological properties of surfactant-enhanced alkaline flooding chemical formulations.

The most useful tools for the study of radiation scattering by polymers in solution have been light and neutron scattering.[9] The power of small-angle neutron scattering to provide information is becoming increasingly recognized; unfortunately, this technique is not available at NIPER at this time. The instruments that are available to us are a C. N. Woods Model 6000 light scattering instrument and a C. N. Woods Model RP-600 differential refractometer. These instruments were purchased by the U. S. DOE in 1978.

Light-scattering measurements were commenced on solutions of Chevron CF-100 surfactant. This surfactant is of particular interest because it is being proposed for use in a field project being conducted under the SGP program. The planned procedure was to be light-scattering measurements of surfactant, polymer, and finally surfactant/polymer mixtures. The results of several measurements conducted with surfactant are shown in Table 1. Notice in Table 1 that $\Delta n \times 10^6$ is less than or equal to 100 in each of the measurements. The highest measured value is lower than the lowest calibration value recommended by the manufacturer of the instrument, as shown in Table 2. The uncertainty of this measurement leads to inaccuracy in calculating Hc/t. An accurate value for Hc/t is necessary to calculate the apparent molecular weight:

$$1/M = Hc/t - 2Bc \qquad (1)$$

**Table 1. Light-Scattering Measurements with CF-100 Surfactant, 436 nm, 23° C**

| Surfactant Conc., g/mL X $10^4$ | $\Delta n \times 10^6$ | Hc/t X $10^8$ |
|---|---|---|
| 1.00 | 13 | 1.47 |
| 3.00 | 68 | 0.76 |
| 5.00 | 100 | 0.70 |

**Table 2. Differential refractometer calibration, 436 nm, 23° C.**

| KCl Conc., g/mLX$10^2$ | $\Delta n$ X $10^6$ |
|---|---|
| 0.37 | 390 |
| 0.77 | 833 |
| 1.50 | 1551 |
| 3.00 | 3133 |
| 4.50 | 4658 |
| 6.00 | 6136 |

where c is the concentration in g/mL, B is a constant (osmotic virial coefficient), and 1/M is reciprocal molecular weight. It was not possible, therefore, to determine the apparent molecular weight of the surfactant because extrapolation of accurate Hc/t values to zero concentration is necessary to calculate molecular weight, as is illustrated in Fig. 5. The only information generated was that the CMC (critical micelle concentration) of this surfactant is apparently between 1 and 3 x $10^{-4}$ g/mL.

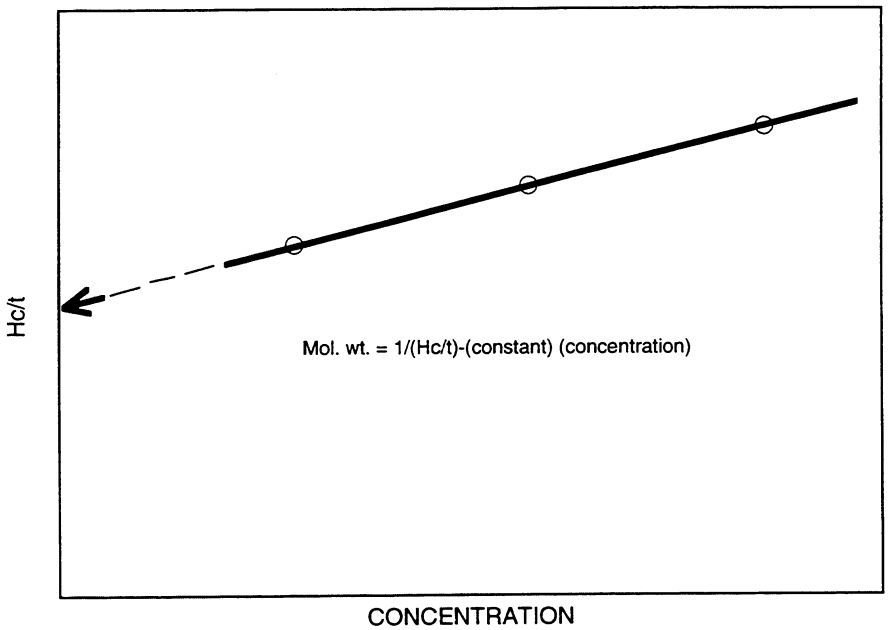


FIGURE 5. - Molecular weight as a function of Hc/t, extrapolated to zero concentration.

After determining that light-scattering measurements conducted with the available instruments and aqueous solutions of surfactant are not useful for this work, the approach was to conduct light-scattering measurements with polymer solutions that contain variable amounts of surfactant. Problems were also encountered in measuring the molecular weights of polyacrylamide polymers. In addition to the insensitivity in measurement of $\Delta n$, the results from light scattering techniques were found to be extremely sensitive to polymer molecule shape, which changes depending on parameters such as extremely small changes in the ionic character of aqueous solutions. The data were reviewed by an expert in light scattering techniques. After review of the data, it was the consensus of opinion that a great deal of additional time is needed to obtain additional data, if indeed, it is possible to do so with the present instrumentation. Therefore, the U. S. DOE Bartlesville Project Office then approved a change in the annual plan that allowed for project BE4B to expend more of its resources on support for the SGP41 field work. That research is reported in the third annual report for that project.

Despite the technical problems that were encountered this year, significant observations and conclusions about surfactant-alkali interactions have resulted from the research in this area during the past 2 years:

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.
9. More research time and better instrumentation are required for light-scattering measurements to provide a better understanding of chemical mechanisms for the above observations and conclusions.

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