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QUARTERLY TECHNICAL PROGRESS REPORT

Title Surfactant Loss Control in Chemical Flooding: Spectroscopic and Calorimetric Study of Adsorption and Precipitation on Reservoir Minerals

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University Columbia University in the city of New York
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Program Manager Prof. P. Somasundaran

Principal Investigator Prof. P. Somasundaran

Contracting Officer's Representative Dr. Jerry F. Casteel
U.S. Department of Energy,
Bartlesville Project Office,
P.O. Box 1398,
Bartlesville, OK 74005.

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Objective

The aim of this project is to elucidate the mechanisms of adsorption and surface precipitation of flooding surfactants on reservoir minerals. Effect of surfactant structure, surfactant combinations and other inorganic and polymeric species will be determined using solids of relevant mineralogy. A multi-pronged approach consisting of micro & nano spectroscopy, microcalorimetry, electrokinetics, surface tension and wettability will be used to achieve the goals. The results of this study should help in controlling surfactant loss in chemical flooding and also in developing optimum structures and conditions for efficient chemical flooding processes.

Summary of Technical Progress

Adsorption of selected individual surfactants on oxide minerals was studied. The aim was to determine the effect of structure on surfactant adsorption at the solid-liquid as well as at the liquid-air interface. Nonionic polyethoxylated alkyl phenols and anionic meta xylene sulfonates (MXS) were the surfactants studied. The position of the sulfonate and methyl groups on the benzene ring of the MXS was varied and its effect on adsorption on alumina was determined. Electrokinetic behavior was also determined along with adsorption in order to determine the role of electrostatic forces in determining the adsorption. In addition, the effect of varying the number of ethylene oxide groups on the adsorption of polyethoxylated alkyl phenols on silica was determined since the ethoxyl groups offer unique opportunities to control adsorption as well as wettability. Effect of pH was studied both because it is a parameter with first order effect and also because pH

effects can help in developing mechanisms.

Interfacial Behavior of Nonionic Surfactants

The study of the effect of the number of ethylene oxide (EO) groups on the adsorption behavior of polyethoxylated alkyl phenols on silica was continued this quarter. The number of EO groups on the surfactants, 10, 15, 20 and 40, offered a wide range. During the first quarter, adsorption of polyethoxylated nonyl phenol with 40 ethylene oxide groups (EO40) was studied using fluorescence spectroscopy, adsorption and surface tension measurements. It was found that the commercial grade EO40 surfactant used was not pure and the bulky surfactant did not form aggregates at the silica-water interface. Subsequent studies were conducted with pure reagents with 10, 15 and 20 EO groups obtained from Nikko Chemicals, Japan.

Figure 1: Polyoxyethylated nonyl phenol surfactant (n: 10, 15, 20, 40).

The purity of the surfactants used is evident from the surface tension behavior of the surfactants shown in figure 2; these measurements were performed on the Fisher du Nuoy ring tensiometer. The surface tension of the commercial grade polyethoxylated nonyl phenol

with 40 ethylene oxide groups (EO40) is also shown for comparison. The minimum in surface tension which is indicative of impurities is detected only for the commercial EO40. There is no minima on the curves for the NP type of surfactants which are more pure than the EO40.

Figure 2: Surface tension of polyethoxylated nonyl phenols with 10, 15, 20 & 40 ethylene oxide groups

It can be concluded from the results in figure 2 that as the number of ethylene oxide groups are increased the surface activity is decreased and the critical micellization concentration (CMC) is also increased. These agree with our earlier results on the

behavior of the nonionic surfactants.

The adsorption isotherms for some polyethoxylated nonyl phenols (NP) on silica are shown in figure 3. With an increase in the number of ethylene oxide groups on the surfactant the adsorption density at the silica water interface is decreased.

Figure 3 Effect of change in number of ethylene oxide groups on the adsorption of polyethoxylated nonyl phenols on silica

The slope of the curve in the pre-adsorption maximum region, which is an indication of cooperative association behavior of the hydrocarbon chains at the solid-liquid interface, decreases as the number of EO groups increases. An increase in the number of EO groups

on the surfactant causes the molecule to become bulky. This will provide steric hindrance to the packing of the molecules into aggregates and as a result the adsorption density will be lower. Future work will focus on characterizing the microstructure of the adsorbed layer in terms of size and mobility of aggregates formed at the interface using fluorescence and electron spin resonance spectroscopic techniques.

The effect of pH on the adsorption of polyethoxylated nonyl phenol with 10 ethylene oxide groups (NP-10) was determined and the results are shown in figure 4. Three different concentrations were studied and the pH was varied from 2.5 to 11.

Figure 4 Effect of pH on the adsorption of polyethoxylated nonyl phenol on silica

Interestingly, there was no effect of pH on the adsorption of NP-10 on silica in the ranges studied. The mechanism of adsorption of ethoxylated surfactants on silica is considered to be hydrogen bonding between the ether oxygen of the ethylene oxide group and the surface silanol groups. As the pH is raised, the number of silanol groups on the silica surface will decrease and the adsorption of NP-10 could have decreased if the mechanism of adsorption was via hydrogen bonding. To explain this behavior the electrokinetic behavior of silica was determined and the results are given in figure 5.

Figure 5: Zeta potential of silica

Silica is negatively charged in the entire pH range studied. By extrapolation, the isoelectric point (IEP) is < 2 . Above pH 4.5 the zeta potential of silica is constant suggesting that there is no change in the charged surface groups above this pH value for this sample. On the basis of this, pH will be expected to have no effect on adsorption of NP-10 on silica above pH 4.5. But from figure 4 it can be seen that the adsorption of NP-10 is constant down to even a pH value of 3. We propose that at pH values higher than the IEP the number of silanol groups ($-\text{SiOH}$) on the surface are very few and there is no significant change in their number to affect adsorption drastically. However, this interesting effect merits further investigation using spectroscopic techniques to probe the interfacial region.

Effect of surfactant structure on adsorption of xylene sulfonates

Studies initiated during the first quarter indicated that the position of the functional groups have a significant effect on the adsorption of alkyl xylene sulfonates: with the sulfonate was in the meta position with respect to the methyl groups (124 MXS), surfactant adsorption on alumina was lower than with the sulfonate in the para position (135 PXS - Para 1). But when the position of the methyl group was changed yet maintaining the sulfonate in the para position (125 paraxylene sulfonate - para2), the adsorption isotherm was identical to that of the para1. This suggested that the position of the methyl groups does not play as important a role as the position of the sulfonate. To examine this aspect further, another structural variation of the xylene sulfonate, orthoxylene sulfonate (OXS) was selected. The structure of the surfactants is shown below.

4C11 2,4 META XYLENE SULFONATE (META)

4C11 3,5 PARAXYLENE SULFONATE (PARA 1)

4C11 2,5 PARAXYLENE SULFONATE (PARA 2)

4C11 4,5 Orthoxylene sulfonate (OXS)

The adsorption behavior of OXS on alumina at room temperature is shown in figure 6. The adsorption isotherm of OXS is different from that of meta and para xylene sulfonates but the adsorption of these surfactants was studied at 43°C and hence the results cannot be strictly compared to isolate the structure effect.

Figure 10: Adsorption of meta xylene sulfonates on alumina

The results in figure 6 indicate that at room temperature OXS adsorbs on alumina only above a certain concentration ($\approx 2 \times 10^{-5} \text{ kmol/m}^3$). In the next quarter, residual concentrations will be measured using alternative analytical techniques (eg. UV

spectroscopy) and the adsorption of OXS will be studied at 43°C to isolate the effect of structure on the adsorption of alkyl xylene sulfonates on alumina.

The surface tension of aqueous solutions of OXS was measured using a du Nuoy ring tensiometer. The results obtained in the absence and presence of salt are shown in figure 7. The surface tension continuously decreases as the concentration is increased in both cases with increased surface activity in the presence of salt.

Figure 11: Surface activity of orthoxylene sulfonate in the absence and presence of salt

This behavior is typical of surfactants at temperatures below their Krafft point. Further experiments will be conducted at higher temperatures to verify this detail.

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