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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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Objective

The aim of this contract is to elucidate the mechanisms underlying adsorption and surface precipitation of flooding surfactants on reservoir minerals. Effect of surfactant structure, surfactant combinations and other inorganic and polymeric species and solids of relevant mineralogy will also be determined. 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/desorption of tetradecyl trimethyl ammonium chloride (TTAC) and sodium dodecyl sulfate (SDS)/octaethylene glycol mono n-decyl ether ($C_{12}EO_8$) surfactant mixtures at the kaolinite-water and alumina-water interfaces was studied during this quarter. The microstructure of the adsorbed layer was investigated using spectroscopic techniques.

Effect of the hydrocarbon chain length of octaethylene glycol mono n-alkyl ether (C_nEO_8) type nonionic surfactants on the adsorption of 1:1 mixtures of sodium dodecyl sulfate (SDS)/ C_nEO_8 at the kaolinite/water interface was studied. The adsorption of SDS was enhanced by the presence of $C_{10}EO_8$ but this effect was not as significant as those by $C_{12-16}EO_8$. Interestingly, once the hydrocarbon chain length of the nonionic surfactant exceeded that of the SDS (12) there was no further enhancement of SDS adsorption. The results are explained in terms of hydrocarbon chain-chain interaction and shielding of the

chains from a hydrophilic environment.

Aggregate size of 1:1 mixtures of SDS/ $C_{12}EO_8$ adsorbed at the alumina-water interface was measured using dynamic pyrene fluorescence spectroscopy. Presence of the nonionic surfactant in the mixed aggregate with the anionic sodium dodecyl sulfate (SDS) reduced the electrostatic repulsion and increased the total aggregate size. The SDS aggregate at the interface was smaller than the $C_{12}EO_8$ aggregate for similar adsorption densities.

Changes in the microstructure of a tetradecyl trimethyl ammonium chloride (TTAC) adsorbed layer during adsorption and desorption were probed using fluorescence spectroscopy. TTAC aggregates at the alumina-water interface are not as tightly packed as TTAC micelles in bulk solution. Also it was found that TTAC adsorption on alumina is not completely reversible. More interestingly, it was observed that the nature of the adsorbed layer was altered upon dilution.

Adsorption of surfactant mixtures at solid-liquid interfaces

Results reported during the previous quarter indicated that with increasing hydrocarbon chain length of the nonionic surfactant C_nEO_8 ($n=10,12,14,16$) the adsorption on kaolinite increased but there was only partial coverage of the kaolinite surface (θ varied from 0.11 to 0.19). During this reporting period, the adsorption of 1:1 mixtures of sodium dodecyl sulfate (SDS) and octaethylene glycol mono n-alkyl ether (C_nEO_8) mixtures at the kaolinite-water interface was studied. It is interesting to note from figure 1 that the isotherms for the adsorption of SDS are identical when the hydrocarbon chain length of the

nonionic surfactants, octaethylene glycol mono n-alkyl ethers ($C_{12}EO_8$, $C_{14}EO_8$, $C_{16}EO_8$), is equal to or longer than that of the anionic SDS (C_{12}).

Figure 1: Effect of nonionic surfactant hydrocarbon chain length on the adsorption of sodium dodecyl sulfate (SDS) from 1:1 SDS/ C_nEO_8 mixtures. 0.03 M NaCl, pH 5.

When the hydrocarbon chain length of the nonionic surfactant is shorter ($C_{10}EO_8$) than that of the anionic SDS, however, a different isotherm is observed. The presence of the anionic SDS enhances the adsorption of the nonionic C_nEO_8 (figure 2) and the isotherms are shifted to lower concentration region as compared to the adsorption isotherms of C_nEO_8 in the absence of any SDS (figure 3).

Figure 2: Effect of nonionic surfactant hydrocarbon chain length on the adsorption of C_nEO_8 ($n=10,12,14,16$) from its 1:1 mixtures with SDS. 0.03 M NaCl, pH 5

Figure 3: Effect of hydrocarbon chain length (C_nEO_8) on the adsorption of nonionic surfactant on kaolinite. 0.03 M NaCl, pH 5.

This is an indication of strong hydrophobic interaction with the coadsorbing anionic surfactant and a schematic description of the interactions is provided in figure 4. When the hydrocarbon chain length of the nonionic surfactant is equal to or longer than that of the anionic SDS, the hydrocarbon chains of SDS are equally shielded from the hydrophilic environment by the hydrophobic chains of the coadsorbing nonionic surfactant.

Figure 4 Schematic presentation of the effect of nonionic surfactant hydrocarbon chain length on the adsorption of the anionic sodium dodecyl sulfate (SDS). a) Nonionic surfactant hydrocarbon chains longer than that of SDS; b) Nonionic surfactant hydrocarbon chain length equal to that of SDS; c) Nonionic surfactant hydrocarbon chain length shorter than that of the SDS, partially exposing SDS hydrocarbon chains to aqueous solution or the hydrophilic ethoxyl chains of the nonionic surfactant.

The identical residing environment then leads to a common isotherm for SDS adsorption on kaolinite (figure 1). When the hydrocarbon chain of the nonionic surfactant is shorter than that of the anionic sodium dodecyl sulfate (SDS), part of the SDS hydrocarbon chain is exposed to the hydrophilic environment (aqueous solution of the hydrophilic ethylene oxide chain of the nonionic surfactant). The residing environment for SDS hydrocarbon chain is thus less hydrophobic and therefore the isotherm is less shifted to the lower concentration region than in the previous case.

Fluorescence Probing of Mixed-surfactant Adsorbed Layers

As reported earlier, fluorescence spectroscopy could not be conducted at the kaolinite-water interface since kaolinite quenched the fluorescence signal from pyrene. Instead fluorescence probing of the adsorbed layer was performed for adsorption on alumina.

In earlier reported studies, pyrene monomer fluorescence was used to describe the micropolarity of the adsorbed layer. In addition to monomer fluorescence, another aspect of pyrene fluorescence, viz. excimer formation, can be exploited to determine the size of surfactant aggregates (micelles, hemimicelles, etc). An excimer is formed when a pyrene molecule in its excited state (P^*) interacts with a pyrene molecule in its ground state (P) according to the reaction:

The excimer formed (PP^*) decays to the ground state by emitting a photon:

In the presence of pyrene molecules in a fragmented media (such as when surfactant micelles, hemi-micelles, etc are present) the decay of pyrene fluorescence can be fitted to the following model¹ based upon a Poisson distribution of probes in surfactant (or hydrophobic) aggregates:

¹ R. Zana, in Surfactant Solutions: New Methods of Investigation, Surfactant Science Series, R. Zana (ed), Vol. 22, Marcel Dekker, New York, 1987.

$$I_t = I_0 \exp [-k_o \cdot t + n (\exp\{-k_e t\} - 1)] \quad (3)$$

where I_0 is the fluorescence emission intensity at the desired wavelength at time $t=0$, k_o the monomer decay rate constant, k_e the excimer formation rate constant, and n the average number of pyrene molecules in a surfactant aggregate. At long times, there is no excimer formation and the fluorescence decay profiles represent the decay due to monomeric emission. Therefore equation 3 reduces to:

$$\ln \left(\frac{I_t}{I_0} \right) = -n - k_o \cdot t \quad (4)$$

and extrapolation to $t=0$ gives n . With a knowledge of n , the aggregation number of the hydrophobic aggregate in which the pyrene molecules reside can be evaluated from the following:

$$\begin{aligned} N_{agg} &= \frac{n \cdot [C_i - CMC]}{[Py]} && \text{for micelles} \\ &= \frac{n \cdot [C_i - C_r]}{[Py]} && \text{for adsorbed layer} \end{aligned} \quad (5)$$

where C_i is the initial total surfactant concentration, CMC the critical micelle concentration, $[Py]$ the pyrene concentration and C_r the total residual surfactant concentration.

Using this procedure the aggregation number of a 1:1 SDS/ $C_{12}EO_8$ mixed adsorbed layer was determined and the numbers so obtained are reported in figure 5 along the adsorption isotherms. It is seen that for SDS adsorption, the aggregation number initially increases and then remains relatively constant in region II. These results are similar to

those obtained by Chandar et al².

Figure 5: Total adsorption of sodium dodecyl sulfate (SDS) and 1:1 SDS/C₁₂EO₈ mixtures on alumina and aggregation numbers of surfactant.

The aggregation number for the adsorption of a 1:1 SDS/C₁₂EO₈ mixture is larger than that for pure SDS adsorption at a similar adsorption density. It is also seen from Table I that the aggregation number for a 1:1 SDS/C₁₂EO₈ micelle is larger than that of SDS micelles. Clearly, the reduction in electrostatic repulsion between SDS ions due to the presence of the nonionic C₁₂EO₈ is an important reason for the observed increase in the aggregation number for 1:1 SDS/C₁₂EO₈ mixtures in the adsorbed layer or in micelles. As a result of screening of electrostatic repulsion, the adsorption of sodium dodecyl sulfate (SDS) should

² P. Chandar, P. Somasundaran and N.J. Turro, *J. Coll. Interf. Sci.*, 117, 1987, 31.

Table I Aggregation number (N_{agg}) of Surfactant micelles, 0.03 M NaCl, 25°C

SURFACTANT	CONC. (kmol/m ³)	k_o ns ⁻¹	k_e ns ⁻¹	n	N_{agg}
Sodium dodecyl sulfate (SDS)	8.0×10^{-2}	0.0064	0.024	0.88	91
Octaethylene glycol mono n-decyl ether (C ₁₂ EO ₈)	2×10^{-3}	0.0059	0.015	0.53	109±9
1:1 SDS/C ₁₂ EO ₈	8.6×10^{-3}	0.0066	0.012	0.84	165±3

be energetically enhanced. This is indeed seen from figure 6.

Figure 6: Isotherms for individual surfactant adsorption on alumina from 1:1 SDS/C₁₂EO₈ mixtures.

Since the mixed aggregates consist of both the anionic sodium dodecyl sulfate (SDS) and the nonionic octaethylene glycol mono n-decyl ether (C₁₂EO₈), it is interesting to determine the aggregation number for each surfactant in the mixed aggregates. This can be done by

knowing the adsorption density of each component in the mixed adsorbed layer. It is seen from Table II that at low adsorption densities, the aggregation number of the nonionic octaethylene glycol mono n-decyl ether ($C_{12}EO_8$) species is lower than that of the anionic SDS. As the adsorption increases, however, the hydrophobic chain-chain interaction becomes more important and the aggregation numbers of each surfactant become similar to each other.

Table II Surfactant aggregation number (N_{agg}) for the adsorption of 1:1 SDS/ $C_{12}EO_8$ mixture on alumina: 0.03 M NaCl, pH 6.5, 25°C

ADS. (kmol/m^3)	SURF./PY	k_o	k_e ns^{-1}	n ns^{-1}	SDS	N_{agg} $C_{12}EO_8$	TOTAL
1.1×10^{-7}	157	0.015	0.18	0.68	61	46	107
2.3×10^{-7}	173	0.013	0.055	0.77	72	61	133
3.2×10^{-7}	179	0.01	0.015	0.79	74	67	141
6.2×10^{-7}	187	0.0079	0.011	1.60	82	77	158
1.9×10^{-6}	194	0.0071	0.0055	0.86	85	83	168

It is to be noted that the aggregation number for SDS in the mixed adsorbed layer is lower than that for pure sodium dodecyl sulfate (SDS) adsorption. This can be explained by considering the surface heterogeneity. Since the surface consists of energetic patches³ for SDS adsorption and the nonionic $C_{12}EO_8$ does not adsorb on alumina by itself, the aggregate size should be largely limited by the finite size of the energetic patches for SDS adsorption.

³ J.H. Harwell, J.C. Hoskins, R.S. Schechter and W.H. Wade, *Langmuir*, 1, 1985, 251.

In the case of 1:1 SDS/C₁₂EO₈ adsorption, part of the SDS ions will be displaced by the nonionic C₁₂EO₈ in order to reduce electrostatic repulsion between the SDS ions, the aggregation number of SDS is decreased.

Adsorption/Desorption of Cationic Surfactant at the alumina-water interface

Studies conducted during the first year indicated that cationic tetradecyl trimethyl ammonium chloride (TTAC) adsorbed significantly at the alumina-water interface when the alumina was negatively charged. Adsorption was found to be completely reversible at the high adsorption densities but at lower adsorption densities there appeared to be some hysteresis. Fluorescence spectroscopy was used this quarter to probe the adsorbed layer and changes therein during desorption.

As mentioned in previous quarterly reports, pyrene monomer fluorescence is sensitive to the medium in which pyrene resides. In hydrophobic environments, the ratio of the intensities of the first and third peaks (I_3/I_1) on a pyrene emission spectrum is higher than when pyrene is in a hydrophilic environment. The value for I_3/I_1 is 0.5-0.6 in water, 0.8-0.9 in surfactant micelles, and >1 in nonpolar solvents. Since this ratio can be used to characterize the polarity of environments, it can be termed as the *polarity parameter*.

The adsorption isotherm of TTAC on alumina is plotted in figure 7. Changes in the polarity parameter of pyrene at the alumina-water interface and in the supernatant are also shown in the figure. It is observed that pyrene goes to the alumina-water interface in a narrow TTAC concentration range which corresponds to a sharp increase in adsorption on the adsorption isotherm. From this it is evident that pyrene is solubilized in TTAC

Figure 7: Adsorption isotherm of TTAC on alumina and corresponding changes in pyrene monomer fluorescence from alumina-water interface and supernatant

aggregates at the alumina-water interface. However once TTAC micelles form in the supernatant, pyrene is preferentially solubilized into the micelles and does not go to the alumina-water interface in spite of the presence of TTAC hemimicelles. This result is interesting considering that in the alumina-SDS system, pyrene is preferentially solubilized in hemi-micelles at the alumina-water interface rather than SDS micelles in the supernatant⁴. Aggregates of TTAC at the alumina-water interface are not as tightly packed and pyrene prefers to be in micelles once they are formed. Supernatant solutions of varying residual concentrations along the isotherm were diluted with pyrene solution of the desired ionic strength and the slurry conditioned for 15 h. The procedure was repeated several times. Pyrene emission spectra were then obtained from the alumina-water interface to gain an insight into the microstructural changes of the adsorbed layer upon dilution. The results are plotted in figure 8 along with the polarity parameter for pyrene dissolved in TTAC solutions of similar concentrations. Pyrene reports the presence of hydrophobic aggregate at the alumina-water interface. The value of the I_3/I_1 ratio decreases at lower concentrations but hydrophobic aggregates are detected at concentrations lower than were detected during adsorption (see figure 7). It should be mentioned that there will be some contribution to the spectrum obtained from the slurry by pyrene in the supernatant. However for the residual concentrations studied there should be no aggregates in solution as is evidenced from the results in figure 8. Aggregates form in solution only above a concentration of $1.5 \times 10^{-3} \text{ kmol/m}^3$. Thus the hydrophobic environment reported by pyrene must be from the interface.

⁴ Prem Chandar, D.E.S. Thesis, Columbia University, 1987, New York.

Figure 8: Changes in pyrene polarity parameter from the TTAC adsorbed layer on alumina upon desorption from different residual concentrations and in TTAC solutions

The adsorption of TTAC on alumina is not completely reversible especially at the lower concentrations. The fluorescence spectroscopy studies provide support to the results from adsorption and electrokinetics reported previously. This aspect merits further investigation.

Future work:

1. Adsorption of surfactant mixtures at the alumina-water interface.
2. Calorimetry.
3. Effect of ethylene oxide chain length of C_nEO_n on SDS/ C_nEO_n mixture adsorption.

Problems:

The study of thermodynamic parameters of surfactant adsorption and aggregation is behind schedule because of a problem with the microcalorimeter. Since the equipment is not manufactured in the United States the spare parts have to be ordered from Sweden and has created a slight delay.

Publications

1. A. Sivakumar and P. Somasundaran, "Adsorption of alkylxylene sulfonates on alumina: a fluorescence probe study", *Langmuir*, **10**, 1994, 131-134.

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