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 will also be determined. Solids of relevant mineralogy and 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 single surfactant and surfactant mixtures at the kaolinite-water and alumina-water interface were studied during this quarter.

The adsorption of sodium dodecyl sulfate (SDS) and octaethylene glycol mono n-decyl ether ($C_{12}EO_8$) on kaolinite was found to be higher from their mixtures than as single components. This enhanced adsorption was attributed to be due to hydrophobic chain-chain interactions. The effect of pH on the adsorption of single and surfactant mixtures on kaolinite was also elucidated.

Desorption of cationic tetradecyl trimethyl ammonium chloride (TTAC) studied at the alumina-water interface indicated that adsorption was reversible. Electrokinetic measurements supported this observation.

Adsorption of Surfactant Mixtures at Solid-Liquid Interfaces

Adsorption of surfactant mixtures at solid-liquid interfaces is of practical importance for many industrial operations since commercially available surfactants are invariably mixtures of many compounds. However, study of surfactant mixture adsorption at solid-liquid interfaces is very limited. During this reporting period, the adsorption of ionic-nonionic surfactant mixtures at the kaolinite-water interface was systematically studied.

Isotherms obtained for the adsorption of anionic sodium dodecyl sulfate (SDS) on kaolinite are shown in figure 1. The adsorption of SDS decreases as the pH is increased from 5 to 10. Both positive and negative sites coexist on the kaolinite surface and the number of positive sites will decrease with increasing pH. As a result it can be stated that the adsorption mechanism prevalent here is purely electrostatic. At pH 5, the saturation adsorption is $\approx 1.6 \times 10^{-6}$ mol/m²: using a cross-sectional area of 53 Å² for an SDS molecule, this translates into a surface coverage of roughly 56% which suggests that roughly half the surface is covered by positive sites.

As in the case for the adsorption of sodium dodecyl sulfate (SDS), C₁₂EO₈ adsorption on kaolinite decreases with an increase in pH. An hydrogen bonding mechanism has been proposed for the adsorption of ethylene oxide (EO) groups on oxide surfaces and it can be expected that a similar effect predominates here. Reduced adsorption at higher pH values can be attributed to the deprotonation of the surface hydroxyl groups which will result in a decrease in the number of hydrogen bonding sites available for C₁₂EO₈ adsorption. Using a molecular cross-sectional area of 65 Å² for C₁₂EO₈ in the adsorbed state, the surface coverage at saturation can be estimated to be 12%.

Fig 1: Effect of pH on the adsorption of (A) SDS and (B) C₁₂EO₈ from SDS/C₁₂EO₈ mixtures: 0.03 M NaCl, 25°C

Unlike alumina which does not adsorb ethoxylated alcohols and silica which adsorbs ethoxylated alcohols but not sodium dodecyl sulfate (SDS), kaolinite adsorbs both SDS and C₁₂EO₈ to about the same order of magnitude suggesting that the kaolinite surface exhibits the characteristics of both alumina and silica with respect to the adsorption of these two surfactants.

Adsorption of SDS/C₁₂EO₈ mixtures on kaolinite was conducted at different pH values. The adsorption of sodium dodecyl sulfate (SDS) from the mixtures is shown in figure 1 (a) and that for octaethylene glycol mono-n-decyl ether (C₁₂EO₈) in figure 1 (b). At pH 5, the adsorption of the nonionic C₁₂EO₈ is markedly enhanced by the presence of

the anionic sodium dodecylsulfate (SDS) suggesting cooperative adsorption through hydrocarbon chain-chain interactions in the adsorbed layer. At pH 10, adsorption of the nonionic $C_{12}EO_8$ is suppressed by the presence of SDS, indicating competition between the anionic SDS and the nonionic $C_{12}EO_8$ for the limited number of common adsorption sites available.

Figure 2 Schematic presentation of pH effect on the adsorption of SDS/ $C_{12}EO_8$ mixtures on kaolinite. a) low pH, hydrocarbon chain-chain interaction result in cooperative adsorption; b) high pH, competition for limited adsorption sites on kaolinite suppresses adsorption of ethoxylated alcohol ($C_{12}EO_8$).

The mechanisms of pH effect on surfactant mixture adsorption are schematically presented in figure 2. While hydrocarbon chain-chain interaction between the adsorbed surfactant species is predominant at low pH it is not likely to be as predominant at high pH because the adsorbed surfactant species cannot be

close to each other due to lack of adjacent adsorption sites for both surfactant species. Instead competition from the anionic sodium dodecylsulfate (SDS) for limited common adsorption sites leads to suppression of $C_{12}EO_8$ adsorption.

Fluorescence Probing of Mixed-surfactant Adsorbed Layers

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

As mentioned the 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 of mixtures of sodium dodecyl sulfate (SDS) and octaethylene glycol mono-n-decyl ether ($C_{12}EO_8$) on alumina was studied. The I_3/I_1 values of pyrene obtained for the mixed adsorbed layers are given in figure 3 along the isotherms.

It is seen that the polarity parameter is nearly constant along each adsorption isotherm. This can be explained if the increased adsorption is realized by self-replication of the surfactant aggregates with the overall structure of the aggregate remaining unaltered. The I_3/I_1 values for surfactant micelles are given in Table III. It is seen that the polarity parameter for SDS micelles is lower than that obtained for SDS aggregates at the alumina-water interface (figure 3). The aggregates at the solid-liquid interface are more compact than micelles so that water molecules are more effectively excluded from the hydrocarbon core.

Table III: Polarity parameter (I_3/I_1) values for surfactant micelles in aqueous solution

Surfactant	Concentration studied (kmol/m^3)	C.M.C. (kmol/m^3)	I_3/I_1
SDS	3×10^{-2}	1.5×10^{-3}	0.88
$C_{12}EO_8$	1.0×10^{-3}	1.0×10^{-4}	0.80
1:1 SDS/ $C_{12}EO_8$	2.6×10^{-3}	1.1×10^{-4}	0.85

However, the values obtained for the mixed micelle of SDS and $C_{12}EO_8$ is close to

Fig 3: Polarity parameter of pyrene (I_3/I_1) in the adsorbed layer of 1:1 SDS/ $C_{12}EO_8$ mixtures on alumina

Effect of hydrocarbon chain length of nonionic surfactant on its adsorption

Figure 4 shows the isotherms for the adsorption of the nonionic surfactants C_nEO_8 with different hydrocarbon chain length ($n = 10, 12, 14, 16$) on kaolinite. The isotherms are consistently shifted to the lower concentration region as the hydrocarbon chain length is increased from C_{10} to C_{16} . It can be noticed that the plateau adsorption tends to increase slightly with increase in hydrocarbon chain length. Using a parking area of $9.2 \text{ \AA}^2$ per $(-O-CH_2CH_2-)$ group based upon adsorption on silica, it can be found that the kaolinite surface is only partly covered by the nonionic surfactant.

that obtained at the alumina-water interface suggesting that the presence of the ethoxyl chains of the nonionic $C_{12}EO_8$ could be a key factor in determining the polarity in mixed surfactant aggregates.

Subsequent studies will be directed towards discerning the evolution of the adsorbed layer in greater detail.

Surfactant	Plateau Adsorption mol/m ²	Surface Coverage θ
C ₁₂ EO ₈	2.5 x 10 ⁻⁷	0.11
C ₁₄ EO ₈	3.1 x 10 ⁻⁷	0.14
C ₁₆ EO ₈	4.4 x 10 ⁻⁷	0.19

Fig 4: Effect of hydrocarbon chain length (C_nEO₈) on the adsorption of nonionic surfactant on kaolinite: 0,03 M NaCl, 25°C, pH 5

Subsequent studies will focus on the effect of nonionic surfactant's hydrocarbon chain length on adsorption on kaolinite from 1:1 SDS/C_nEO₈ mixtures.

Adsorption/Desorption of Cationic Surfactant at Alumina-water Interface

Results reported during the third quarter indicated that electrostatic forces were predominant during the adsorption of cationic tetradecyl trimethyl ammonium chloride (TTAC) on alumina. Desorption of TTAC from the alumina surface was studied during this reporting period. The adsorption isotherm of TTAC on alumina was first determined. Supernatant solutions of varying residual concentrations along the isotherm were diluted with water and the slurry conditioned for 15 h. This procedure was repeated several times depending upon the concentration. The results are shown in figure 5. The solid line represents the initial adsorption isotherm.

Figure 5: Desorption of TTAC from alumina: Dilutions from different residual concentrations

It is observed that adsorption is reversible in most cases except at low concentrations.

At low concentrations, it does appear that there is some hysteresis but these could result from experimental error due to loss of material during dilution.

Electrokinetic measurements were also performed on the same samples and from the results seen in figure 6, it does appear that the adsorption of cationic TTAC on alumina is reversible. Further studies will concentrate on spectroscopic characterization of the adsorbed layer.

Fig 6: Electrokinetic measurements of TTAC/alumina system after adsorption and upon dilution from different residual concentrations

Future work:

1. Fluorescence spectroscopy of TTAC adsorbed layer on alumina.
2. Microstructure of mixed SDS/C₁₂EO₈ adsorbed layer.
3. Calorimetry on adsorbed alkyl xylene sulfonate layers.

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