

MINERAL-SURFACTANT INTERACTIONS FOR MINIMUM REAGENTS PRECIPITATION AND ADSORPTION FOR IMPROVED OIL RECOVERY

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Principle Author: Prof. P. Somasundaran

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Principal Investigator: Prof. P. Somasundaran

Submitting Organization: Office of Projects and Grants
Columbia University in the City of New York
1210 Amsterdam Avenue, Mail Code 2205
Room 254 Engineering Terrace
New York, NY 10027

Contracting Officer's Representative: Sue Mehlhoff
U.S. Department of Energy,
National Petroleum Technology Office
One West Third Street, Suit 1400
Tulsa, Oklahoma 74101-3519

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ABSTRACT

The aim of this project is to delineate the role of mineralogy of reservoir rocks in determining interactions between reservoir minerals and externally added reagents (surfactants/polymers) and its effect on critical solid-liquid and liquid-liquid interfacial properties such as adsorption, wettability and interfacial tension in systems relevant to reservoir conditions. Previous studies have suggested that significant surfactant loss by precipitation or adsorption on reservoir minerals can cause chemical schemes to be less than satisfactory for enhanced oil recovery. Both macroscopic adsorption, wettability and microscopic orientation and conformation studies for various surfactant/polymer mixtures/reservoir rocks systems were conducted to explore the cause of chemical loss by means of precipitation or adsorption, and the effect of rock mineralogy on the chemical loss.

During this period, the adsorption of mixed system of n-dodecyl- β -D-maltoside (DM) and dodecyl sulfonate ($C_{12}SO_3Na$) has been studied. The effects of solution pH, surfactant mixing ratio and different salts on surfactant adsorption on alumina have been investigated in detail. Along with these adsorption studies, changes in mineral wettability due to the adsorption of the mixtures were determined under relevant conditions to identify the nano-structure of the adsorbed layers. Solution properties of $C_{12}SO_3Na$ /DM mixtures were also studied to identify surfactant interactions that affect the mixed aggregate formation in solution. Adsorption of SDS on gypsum and limestone suggested stronger surfactant/mineral interaction than on alumina, due to the precipitation of surfactant by dissolved calcium ions. The effects of different salts such as sodium nitrate, sodium sulfite and sodium chloride on DM adsorption on alumina have also been determined. As surfactant hemimicelles at interface and micelles in solution have drastic effects on oil recovery processes, their microstructures in solutions and at mineral/solution interfaces

were investigated by monitoring micropolarity of the aggregates using fluorescence technique. Compositional changes of the aggregates in solution were observed with the increase in surfactant concentration. The importance of this lies in that the resulting polarity/hydrophobicity change of the mixed micelles will affect the adsorption of surfactant mixtures on reservoir minerals, surfactant/oil emulsion formation and wettability, as a result, the oil release efficiency of the chemical flooding processes in EOR.

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Table 1. Surfactants used and their formulas

Table 2. List of Solids in the Study

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INTRODUCTION

There is a considerable amount of oil trapped, together with water and gas, in reservoirs made up of porous and permeable rocks after the traditional oil production. Surfactant/polymer flooding is one of the promising techniques to recover additional oil from domestic oil reservoirs. In this regard, there is a need for cost-effective reagent schemes to increase the oil recovery. The key criterion for the successful application of techniques using surfactant mixtures is minimal loss of surfactants on reservoir rocks by adsorption and precipitation. To design such optimal systems, a fundamental understanding of the mechanisms of minerals/chemicals interactions is necessary. It is the aim of this project to conduct systematic studies on the role of reservoir minerals in the adsorption and retention of surfactants and polymers on minerals in enhanced oil recovery particularly in the presence of relevant semi-soluble minerals.

It is well known that surfactants can interact to form aggregates in solutions (micelles) and at interfaces (hemimicelles) and these aggregation phenomena can have a drastic effect on oil recovery processes. Such interactions have the potential to minimize the interfacial tension between the oil and the flooding media and to reduce the adsorption of surfactants on reservoir rocks to facilitate oil liberation.

During the previous reporting period, we completed characterization of the minerals of sandstone, limestone, gypsum, pyrite, and kaolinite, for particle size distribution (SEM images) and specific surface area (BET measurements). We carried out adsorption tests with mixtures of C₁₂-C₄-C₁₂ Gemini and sugar-based n-dodecyl-β-D-maltoside (DM) on silica minerals at different surfactant mixing ratios. Along with adsorption study, wettability changes of solid mineral surface were determined. Also, solution behavior of the C₁₂-C₄-C₁₂/DM mixtures was investigated by surface tensiometry and regular solution theory to determine the nature of

surfactant interactions in the bulk solution. Importantly, changes in the mixing ratio in the C₁₂-C₄-C₁₂/DM systems were found to produce marked effects on surfactant adsorption on the minerals. Wettability results indicate bilayer adsorption of the mixtures of DM and C₁₂-C₄-C₁₂ on silica and such adsorption is beneficial for oil recovery.

During this period, surfactant/mineral interactions in terms of surfactant adsorption have been studied for the system of DM and dodecyl sulfonate (C₁₂SO₃Na). The effects of solution pH, surfactant mixing ratio and different salts on their adsorption on alumina have been investigated in detail. The extent of synergistic/antagonistic adsorption on alumina was found to be determined by pH and surfactant mixing ratio. SDS shows stronger interactions with gypsum and limestone than with alumina, due to precipitation of calcium salt of the surfactant on the minerals. Solution properties of C₁₂SO₃Na/DM mixtures were studied to understand surfactant interactions that determine mixed aggregate formation. Surfactant microstructures in solution and at mineral/solution interfaces were investigated by monitoring micropolarity of the aggregates using fluorescence technique. Compositional changes of the aggregates in solution were observed with the increase of surfactant concentration. As indicated above, all these phenomena would impact efficiency of oil recovery processes.

EXPERIMENTAL

MATERIALS

Surfactants

Several typical ionic and nonionic surfactants were selected for this study. During this period, anionic sodium dodecyl sulfonate ($C_{12}SO_3Na$) and cationic dodecyl trimethyl ammonium chloride (DTAC), both of greater than 99% purity purchased from TCI Chemicals, Japan was used as received. Non-ionic sugar-based surfactant, n-alkyl- β -D-maltoside (>95% purity by TLC), from Calbiochem was also used as received. Cationic butane-1,4-bis(quaternary ammonium chloride) Gemini surfactant, represented as $C_{12}-C_4-C_{12}$, has been synthesized by the reaction of 1,4-dichlorobutane and corresponding alkyl dimethyl amines. The purity of the product was confirmed by NMR proton spectrum. These surfactants are listed in table 1.

Table 1. Surfactants used and their formulas

Surfactant	Molecular formula	Molecular Weight
n-dodecyl- β -D-maltoside	$C_{12}H_{25}(C_6H_{10}O_5)_2OH$	510.6
Sodium dodecyl sulfonate	$C_{12}H_{25}SO_3Na$	272.4
Dodecyltrimethylammonium chloride	$[C_{12}H_{25}N(CH_3)_3]Cl$	263.9
Butane-1,4-bis(quaternary ammonium chloride)	$[C_{12}H_{25}N(CH_3)_2(CH_2)_2]_2Cl_2$	553.8

Mineral Samples:

Solid substrates used during the current period are alumina, silica, limestone, and gypsum. Alumina AKP-50 obtained from Sumitomo has a mean diameter of 0.2 μm . The BET specific surface area measured using nitrogen/helium with a Quantasorb system was 10.8 m^2/g and the isoelectric point (iep) was 8.9. Silica obtained from Geltech was of a mean diameter of 0.2 to 0.3

μm , the specific surface area of 12.0 to 12.9 m^2/g and the isoelectric point of around 2. They were used as received. The natural minerals, limestone and gypsum, were obtained from Wards Scientific Corporation. They were ground to fine powder in the laboratory using mortar grinder from Fisher Scientific Co. The BET specific surface areas, measured using nitrogen/ helium with a Quantasorb system were gypsum: 2.64 m^2/g , and limestone: 0.96 m^2/g . Properties for these solids are listed in Table 2.

Table 2. List of Solids in the Study

Name	Structure	Source	Mean particle size (μm)	Specific surface area (m^2/g)	Isoelectric point (iep)
AKP-50 Alumina	Al_2O_3	Sumitomo	0.2	10.8	8.9
Silica (Quartz)	SiO_2	Geltech	0.2 – 0.3	12.2 – 12.9	2
Limestone	CaCO_3	Wards	~ 2	.96	N/A
Sandstone	SiO_2	Wards	~ 2	1.39	2
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Wards	~ 2	2.64	N/A

Other Reagents:

HCl and NaOH, used for pH adjusting, are of A.C.S. grade certified (purity > 99.9%), from Fisher Scientific Co. To study the salt effect on surface tension, micellization and adsorption, salts such as NaCl, CaCl_2 , FeCl_2 , AlCl_3 , Na_2SO_3 , and NaNO_3 from Fisher Scientific Co.; and sodium citrate from Amend Drug & Chemical Company, all of A.C.S. certified, were used as received. Water used in all the experiments was triple distilled, with a specific conductivity of less than $1.5\mu\Omega^{-1}$ and was tested for the absence of organics using surface tension measurements.

METHODS

Adsorption experiments

Adsorption experiments were conducted in capped 20 ml vials. Solid samples of 2 gram were mixed with 10 ml of triple distilled water for 2 hours at room temperature. The pH was adjusted as desired and then 10 ml of the surfactant solution was added, and the samples were equilibrated further for 16 hours with pH adjustment. The samples were centrifuged for 30 min at 5000 rpm and the clear supernatant was then pipetted out for analysis.

Wettability

The samples for determining relative hydrophobicity tests were prepared in the same way as for the adsorption experiment and wettability was determined using liquid-liquid extraction technique. After 16 hours of equilibration, 20 ml of slurry was transferred to a separatory funnel to which 15 ml of toluene was added. The mineral–surfactant–toluene dispersion was shaken for 1 minute manually and then allowed to settle for 1 hour. The bulk of the aqueous phase with hydrophilic solids, as well as the toluene phase with hydrophobic solids, was emptied out of the funnel separately. The two phases containing the solids were evaporated and the weight of the mineral was recorded. The relative percentage hydrophobicity was determined as: (Weight of mineral in toluene phase) / (Weight of mineral in toluene phase + weight of mineral in aqueous phase) * 100%.

Surface tension

Measurements were performed by the drop volume method using a glass syringe, with appropriate correction factors applied. The syringe was calibrated against triple distilled water.

Analytical Techniques

Cationic Gemini residual concentration was determined using a two-phase titration method using an anionic surfactant, sodium dodecyl sulfonate ($C_{12}SO_3Na$), as the titrating solution. The

residual concentration of the anionic surfactant after adsorption was determined also by a two-phase titration method using a cationic surfactant, dodecyl trimethyl ammonium chloride (DTAC), as the titrating solution. Concentration of the sugar-based surfactant after adsorption was determined by colorimetric method through phenol-sulfuric acid reaction. In ionic/nonionic surfactant mixtures, the total residual surfactant concentration after adsorption was obtained by adding the individual component surfactant concentration, which was measured by either the two-phase titration or the colorimetric method.

Fluorescence Experiments

Sample preparation. For fluorescence measurements in solutions, the surfactant solutions were mixed with desired amount of pyrene, to make the final pyrene concentration $\sim 1.0 \mu\text{M}$. Surfactant solutions containing pyrene were shaken overnight at room temperature before taking fluorescence spectroscopy. For fluorescence measurements at solid/solution interfaces, the same adsorption procedure was followed as in the experiments conducted in the absence of probe. Desired amount of pyrene probe from stock solutions containing known amounts of pyrene was added into adsorption sample solution, to make the pyrene concentration $\sim 0.2 \mu\text{M}$. After separating the supernatant and the solid slurry by centrifugation, the solid slurry was taken for direct fluorescence measurements.

Steady-state experiments. Steady-state emission spectra were obtained using a Horiba Jobin Yvon Fluorolog FL-1039 spectrophotometer. A portion of the solid slurry sample from adsorption experiments or surfactant solution sample containing pyrene was transferred to quartz cells, and the samples were excited at 335 nm and their emission between 360 and 500 nm recorded.

RESULTS AND DISCUSSIONS

1. Adsorption of surfactant mixtures

Surfactant mixtures, instead of single surfactant, are invariably used in the chemical flooding technique for enhanced oil recovery. To obtain optimal mineral-surfactant interactions and minimum chemical loss by adsorption in the enhanced oil recovery processes, the effects of solution pH, surfactant mixing ratio and addition of different salts on the mineral-surfactant interactions have been investigated for the mixed systems of anionic dodecyl sulfonate and sugar-based nonionic DM surfactants on alumina.

a) pH effects on DM adsorption

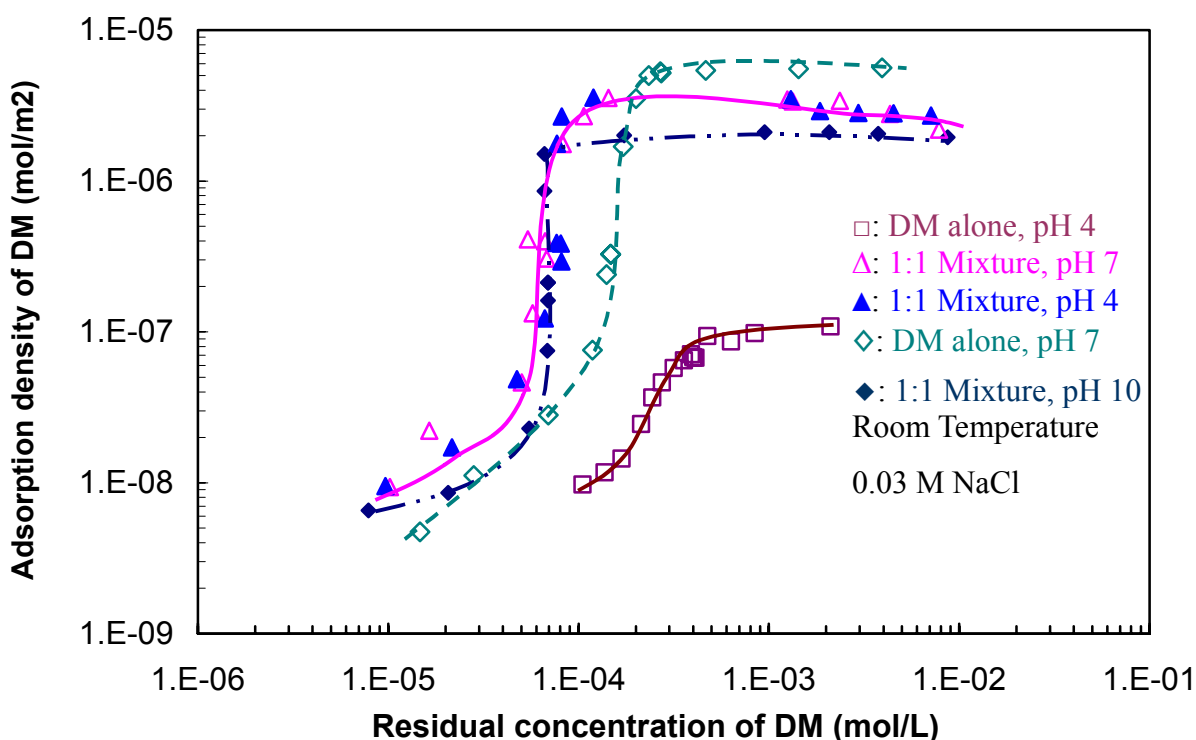


Figure 1. Effects of solution pH on the adsorption of n-dodecyl- β -D-maltoside (DM) on alumina from its mixture with dodecyl sulfonate (C₁₂SO₃Na) compared to DM alone.

The results obtained for the adsorption of n-dodecyl- β -D-maltoside (DM) on alumina from DM alone and from its mixture with sodium dodecyl sulfonate ($C_{12}SO_3Na$) at different pHs are shown in Figure 1. Adsorption of DM at pH 10 from mixtures with sulfonate at a mixing ratio of 1:1 shows much stronger competition between DM and sulfonate in the plateau range. Saturation adsorption of DM from its mixture with sulfonate is less than that in the case of DM alone system. Theoretically, sulfonate with negatively charged head group is not expected to adsorb on alumina at pH 10, due to the mutual electrostatic repulsion. However, the adsorption of DM was affected significantly by the sulfonate at pH 10. Since the adsorption of nonionic surfactant DM does not affect the surface charge of alumina, the driving force for sulfonate adsorption in this case is proposed to be due to hydrocarbon chain-chain interactions between the dodecyl maltoside and dodecyl sulfonate.

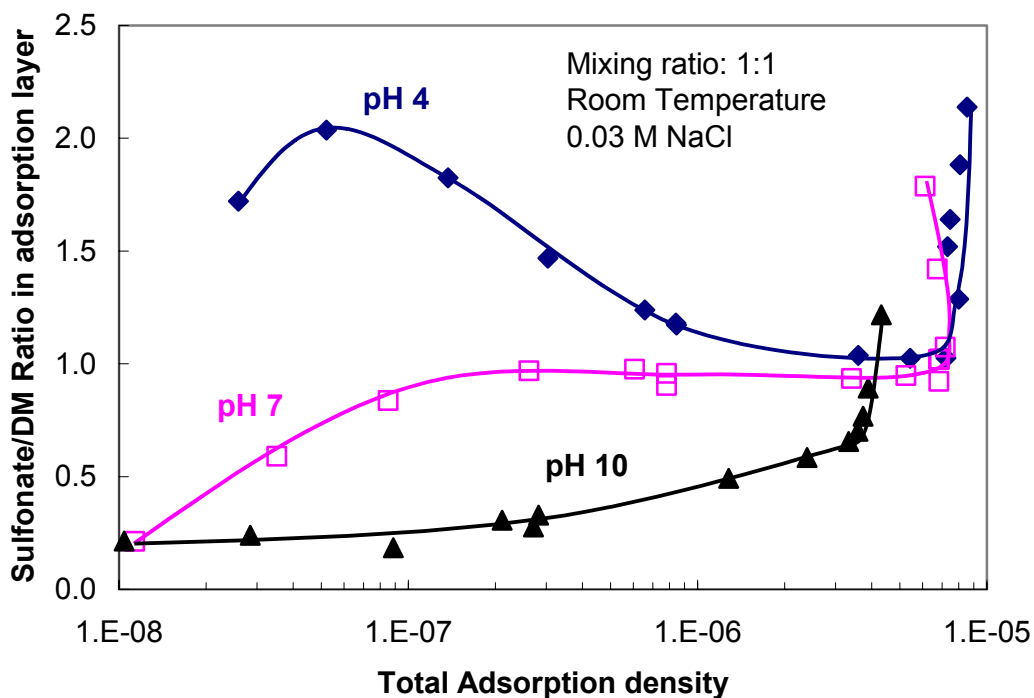


Figure 2. Sulfonate/DM molar ratios in adsorption layer at different pH.

It is apparent that different types of interactions play a part in determining the adsorption of sulfonate/DM mixtures on alumina at different pH. The ratio of sulfonate/DM in the adsorption layer was calculated and is shown in Figure 2 as a function of total adsorption density. Based on our previous studies, it is proposed that hydrogen bonding is the driving force for sugar-based surfactant adsorption on alumina. The driving force for anionic dodecyl sulfonate adsorption usually is electrostatic interaction at low pHs. At pH 4 and 7 (Figure 2), the variation of the sulfonate/DM ratio in the adsorption layer shows a three-stage trend: a steady ratio change at the beginning of mixture adsorption, a flat range with ratio in the adsorbed layer close to the initial ratio in the bulk solution, and a sharp increase of the ratio above saturation adsorption. The changes in the sulfonate/DM molar ratio suggest that different interactions exist between the two surfactants in the adsorbed layer in different adsorption stages. At pH 4, the sulfonate/DM ratio in the adsorption layer is higher than the initial mixing ratio in bulk solution for the whole adsorption range, with the ratio decreasing first, followed by a sharp increase at saturation adsorption. At pH 7 and 10, the sulfonate/DM ratio in the adsorbed layer increases with increase in total surfactant adsorption, suggesting increased hydrophobic chain-chain interactions between dodecyl sulfonate and DM with increase in total surfactant adsorption.

b) Mixing ratio effects on DM/sulfonate mixture adsorption.

The effect of mixing ratio on mixture adsorption is shown in Figure 3 as a function of pH. As discussed before, Interestingly pH shows opposite effect on DM adsorption, when it is adsorbed from a mixture of it with dodecyl sulfonate than from its solution without sulfonate (Figure 3). In these experiments, the initial concentration of DM was fixed at 4×10^{-3} mol/L. From Figure 3, adsorption of DM from its mixtures is much higher than that from DM alone below pH 7, which is due to the neutralization of positive charges on alumina surface by the

anionic sulfonate. DM adsorption is almost the same at mixing ratio of 3:1 as that at 1:1 mixing ratio from pH 4 to pH 7, with much lower DM adsorption observed for 3:1 ratio at pH 3. The increased DM adsorption indicates synergism between dodecyl sulfonate and DM in the pH range of 3 to 7.

On the other hand, in the pH region of 7 to 11, DM adsorption decreases in the presence of sulfonate due to antagonism between the two surfactants. In the case of 1:1 mixture, DM adsorption decreases markedly from pH 7 to pH 11, and in the case of 3:1 mixture, DM adsorption decreases slightly in this pH range. Because of the competition for the adsorption sites on alumina, the more the sulfonate adsorption, the less is the DM adsorption.

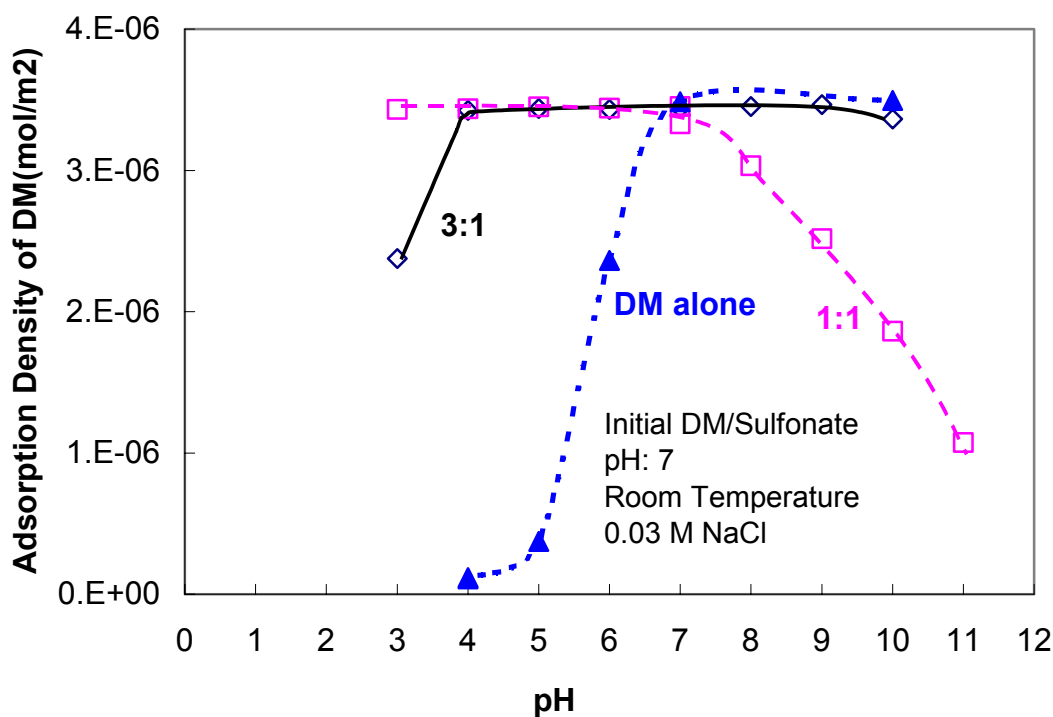


Figure 3. Adsorption of n-dodecyl- β -D-maltoside (DM) from its mixtures with $C_{12}SO_3$ on alumina as a function of pH.

The effect of solution pH on sulfonate adsorption is illustrated in Figure 4. Adsorption

density of sulfonate decreases sharply with increase in pH, and almost no sulfonate adsorption observed above pH 9, due to the alumina being negatively charged. In the case of the 3:1 mixture, even less sulfonate adsorption is observed with the adsorption decreasing only slightly with increase in pH. Clearly, solution pH and surfactant mixing ratio play a major role in determining surfactant/mineral interactions on reservoir rocks. Indeed the adsorption of DM is reduced under saturation conditions at high pH and this is beneficial for the enhanced oil recovery.

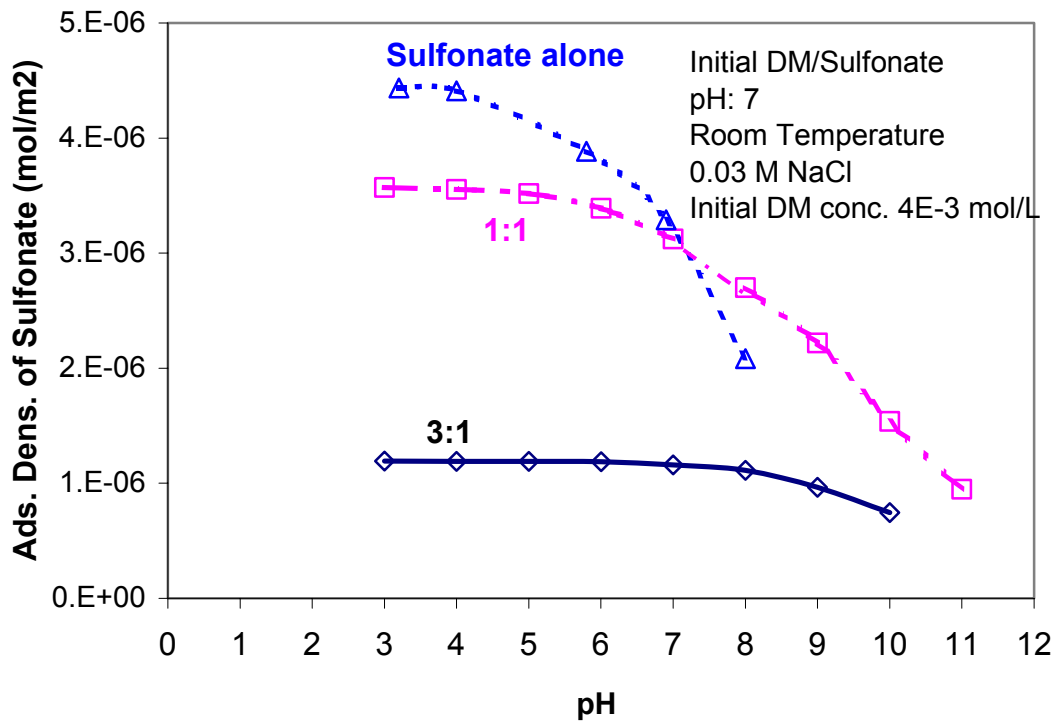


Figure 4. Adsorption of sodium dodecyl sulfonate from its mixtures with DM on alumina as a function of pH.

c) Salt effects on DM adsorption on alumina at low pH

The effects of different salts on DM adsorption on alumina have been studied in search of optimal ionic strength and salt type for minimal chemical loss by adsorption. As shown in Figure 1, DM adsorbs much less at pH 4 than pH 7. The effect of salts on DM adsorption was

investigated to understand the reasons for DM adsorption reduction at low pH. Sodium sulfite increases DM adsorption with maximum adsorption around a salt/DM ratio of 1. In contrast, sodium chloride and sodium nitrate does not enhance DM adsorption.

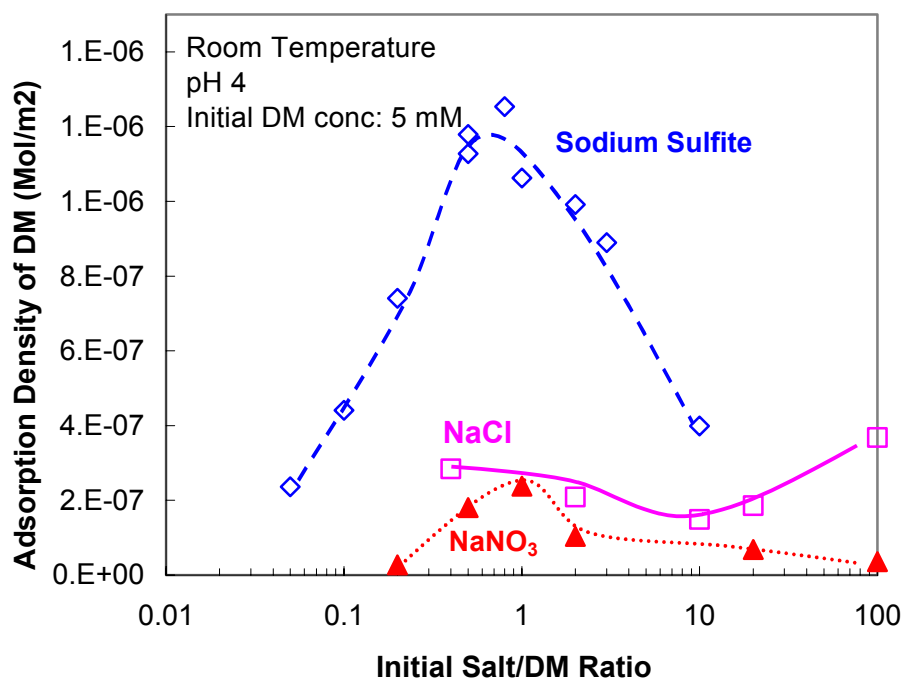


Figure 5. Salt effects on DM adsorption on alumina at pH 4.

d) Wettability of alumina minerals due to the adsorption of surfactant mixtures

Adsorption of surfactants on minerals could dramatically change the wettability of the minerals. Wettability of minerals plays an important role in determining the efficiency of oil liberation from the mineral rocks as well as dispersion of mineral fines in IOR processes. Wettability of alumina in mixtures of anionic dodecyl sulfonate and sugar-based DM surfactants was therefore determined along with the adsorption. The information on changes in relative hydrophobicity of the mineral surface due to surfactant adsorption can also shed light on the orientation of the surfactant species on the solid surface and help to elucidate the mechanisms involved.

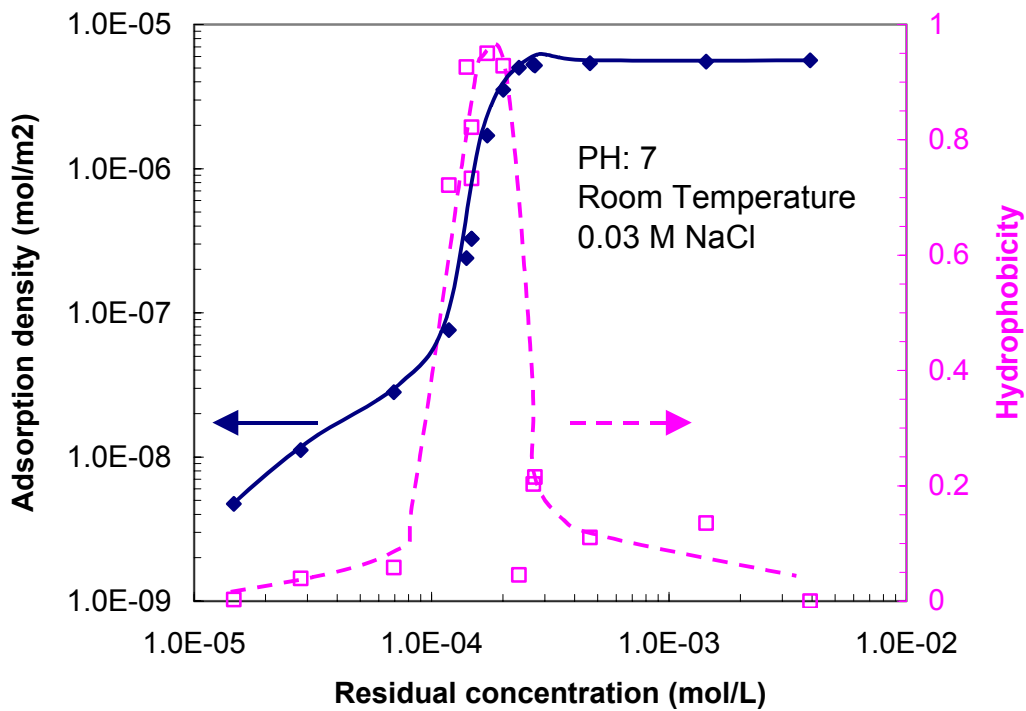


Figure 6. Effects of DM adsorption on hydrophobicity of alumina.

The effect of DM adsorption on the wettability of alumina is illustrated in Figure 6 along with the adsorption isotherm. In the absence of the surfactant, the alumina exhibits complete hydrophilicity. With an increase in the adsorption of DM on alumina, the mineral surface becomes hydrophobic due to the surfactant adsorbing with their hydrophobic tails oriented towards the bulk solution with maximum hydrophobicity around solution cmc. Interestingly, the alumina becomes hydrophilic again at higher surfactant concentrations. The drop in hydrophobicity suggests that additional surfactants orient with hydrophilic groups toward the aqueous phase at higher concentrations, which is as indicated earlier, favorable for good oil sweep.

Similar results were observed for the wettability of alumina due to the adsorption of

$C_{12}SO_3Na/DM$ mixture (Figure 7). Interestingly, the alumina surface becomes highly hydrophobic even at lower surfactant adsorption in this case. Evidently, marked modification of alumina surface could be achieved even at very low mixed surfactant adsorption with hydrophobic groups orienting towards the aqueous phase.

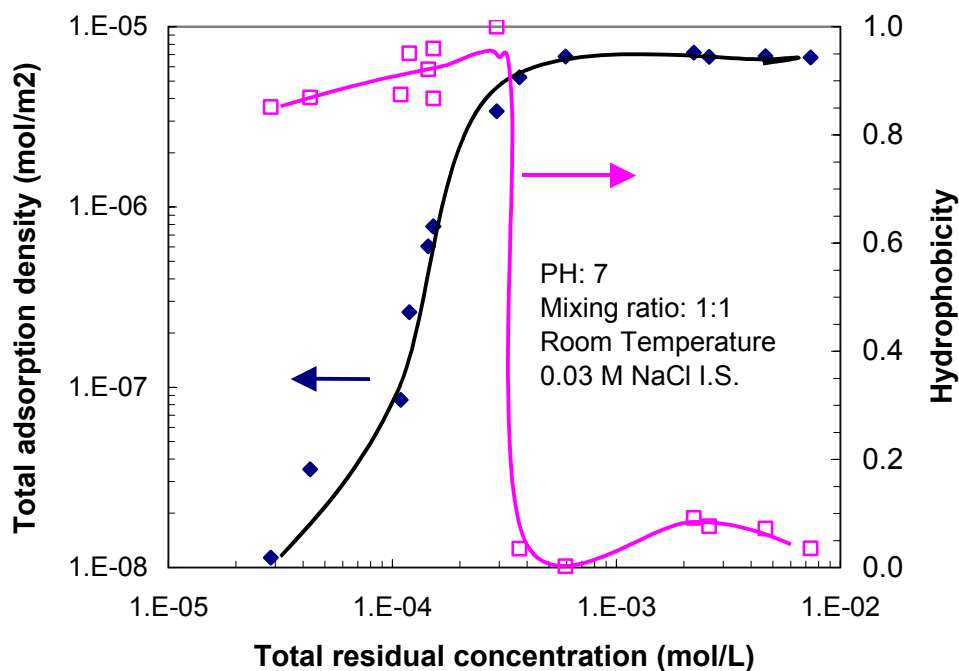


Figure 7. Effects of DM/sulfonate mixture adsorption on hydrophobicity of alumina.

e) Adsorption of sodium dodecyl sulfate on gypsum and limestone.

The role of minerals in determining surfactant/mineral interactions was investigated by determining adsorption isotherms of sodium dodecyl sulfate (SDS) on gypsum and limestone by depletion technique. Very high SDS adsorption was observed in the plateau range on both limestone and gypsum (Figure 8). Compared to SDS adsorption on other minerals such as alumina, the plateau adsorption density on gypsum and limestone were 20 times higher, which is attributed to the surfactant precipitation by the dissolved calcium ions from gypsum and

limestone minerals.

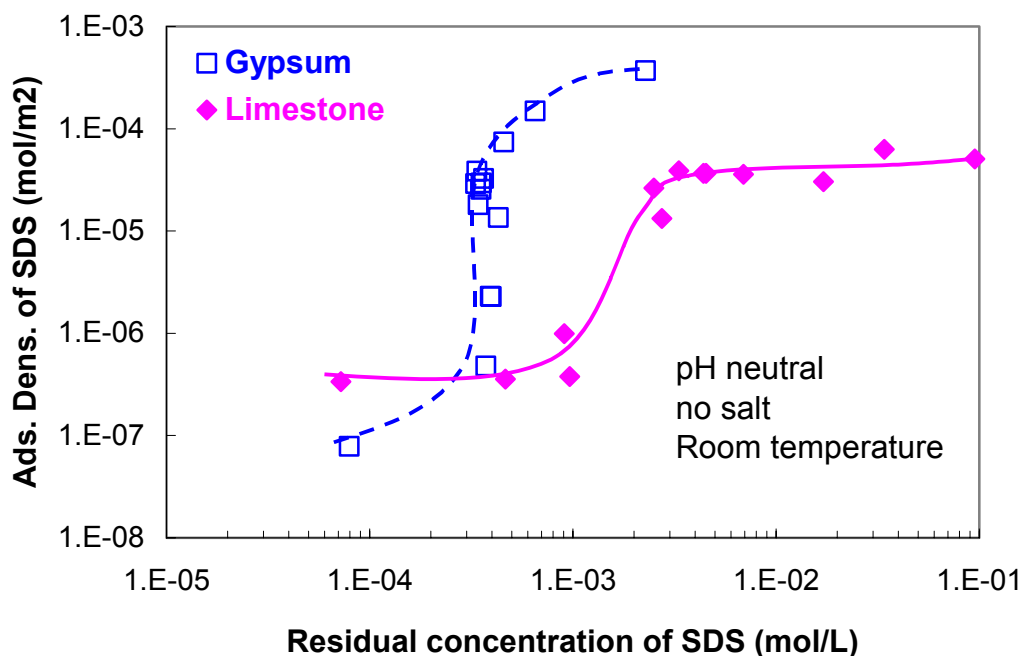


Figure 8. Effects of surface mineralogy on the adsorption of SDS at pH 4.

2. Interactions between DM and dodecyl sulfonate in solutions

Properties, such as surface activity and aggregate formation, of surfactants and their mixtures in solution, will affect the surfactant adsorption. When mixed in solution, surfactants usually show non-ideal mixing and exhibit the so-called synergism/antagonism, depending on the nature of the interactions among the surfactants. Interactions between anionic dodecyl sulfonate ($C_{12}SO_3Na$) and n-dodecyl- β -D-maltoside (DM) in bulk solution were studied during this period by surface tensiometry and results were interpreted using the regular solution theory.

Results obtained for the surface tension of aqueous solutions of $C_{12}SO_3Na$, DM and their mixtures are given in Figure 9. The cmc of the nonionic DM in H_2O is lower than that of $C_{12}SO_3Na$, while the mixtures were generally not as surface active as DM alone. Based on the surface tension results, the interaction parameter β was calculated:

$$\frac{X_1^2 \ln(\alpha_1 C_{12} / X_1 C_1^0)}{(1 - X_1)^2 \ln[(1 - \alpha_1) C_{12} / (1 - X_1) C_2^0]} = 1$$

$$\beta = \frac{\ln(\alpha_1 C_{12} / X_1 C_1^0)}{(1 - X_1)^2}$$

Where X_1 is the mole fraction of surfactant 1 in mixed micelles, α_1 is the mole fraction of surfactant 1 in total concentration, C_1^0 , C_2^0 , and C_{12}^0 are cmcs for surfactant 1, 2, and their mixtures.

Table 3 lists the cmc, DM molar ratio in mixed micelles X_1 and interaction parameter (β) for $C_{12}SO_3Na/DM$ mixtures with different mixing ratio. The calculated β parameter lies between -2.2 and -3.2 for the DM/sulfonate system, suggesting medium interaction between dodecyl maltoside and dodecyl sulfonate, which is weaker than the interaction between DM and SDS with β parameter between -3.25 and -4.0 . It was observed that the higher the DM ratio, the greater is the DM molar ratio in micelles and the stronger the interaction between DM and dodecyl sulfonate.

Table 3. Parameters of DM/sulfonate system obtained from surface tension data analysis.

DM / Sulfonate	1:0	3:1	1:1	1:3	1:9	0:1
CMC (M)	0.00018	0.000223	0.00031	0.000544	0.00109	0.0115
X_1		0.9352	0.8872	0.8162	0.7203	
β		-2.9676	-2.7051	-2.4712	-2.289	

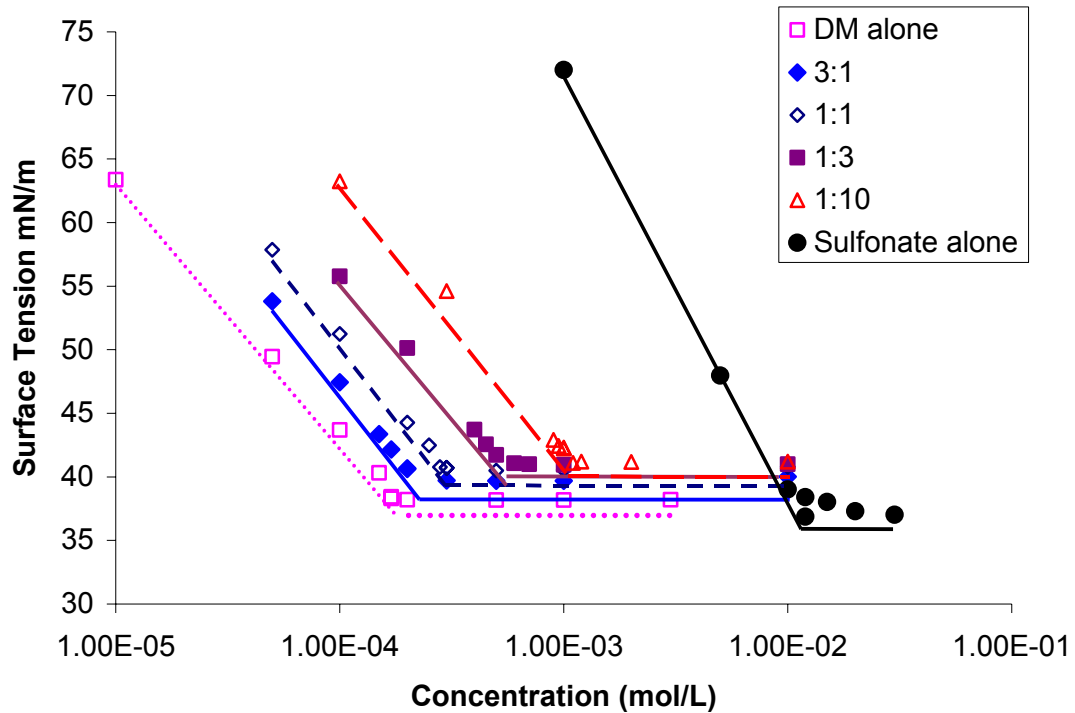


Figure 9. Equilibrium surface tension curves of individual $C_{12}SO_3Na$, n-dodecyl- β -D-maltoside (DM) and their mixtures of varying composition.

3. Fluorescence measurements of polarity change in solutions and at silica surface due to the adsorption of Gemini and its mixtures with DM

Fluorescence spectroscopic technique was used to obtain basic information on the structure of the micelles of mixed surfactants. In fluorescence spectroscopy, the ratio of relative intensities of the I_1 (373nm) and I_3 (383nm) peaks (I_3/I_1) in a pyrene emission spectrum shows the greatest solvent dependency. This ratio decreases as the polarity increases and can be used to estimate the solvent polarity of an unknown environment. The polarity parameter of pyrene is shown in Figure 10 as a function of concentration. At low concentrations, the value of I_3/I_1 ratio corresponds to that for water (0.5~0.6). At certain concentrations, there is a rapid increase in the

value of I_3/I_1 ratio indicating the formation of micelles at this concentration. The cmc of the surfactant obtained from fluorescence tests is in good agreement with those obtained from surface tension measurements (Figure 10).

The polarity parameter of the pyrene at concentrations higher than cmc provides information on the hydrophobicity of the micelles. In $C_{12}-C_4-C_{12}$ Gemini/DM system, I_3/I_1 ratio for DM is higher than that for $C_{12}-C_4-C_{12}$ Gemini above cmc, suggesting that the core of DM micelles is more hydrophobic than that of $C_{12}-C_4-C_{12}$ Gemini micelles, but less hydrophobic than that of pure hydrocarbons. I_3/I_1 polarity parameter of the micelles increases from 0.72 to 0.80 and 0.85 with the increase of DM ratio in the mixtures, indicating that the polarity or hydrophobicity of the micelle core behaves more and more like DM alone (Figure 10). Interestingly, after sharply increasing to its maximum value at concentration just above cmc, the I_3/I_1 polarity parameter of the mixed $C_{12}-C_4-C_{12}$ Gemini/DM micelles showed a gradual decrease with the increase in total surfactant concentration, possibly due to a gradual change in the composition of the $C_{12}-C_4-C_{12}$ Gemini/DM mixed micelles. Compositional change in the mixed micelles has been predicted and observed for many binary surfactant mixtures at concentrations above solution cmc, the extent of the compositional change being determined by the strength of surfactant interactions and the surface activity difference of the components in the mixtures. Since most of the surfactant formulations used in the enhanced oil recovery processes are at concentrations higher than their cmc, the compositional change in the mixed micelles and the resulting polarity/hydrophobicity change of the mixed micelles can be expected to affect the adsorption of surfactant mixtures on the minerals, as well as the oil release efficiency.

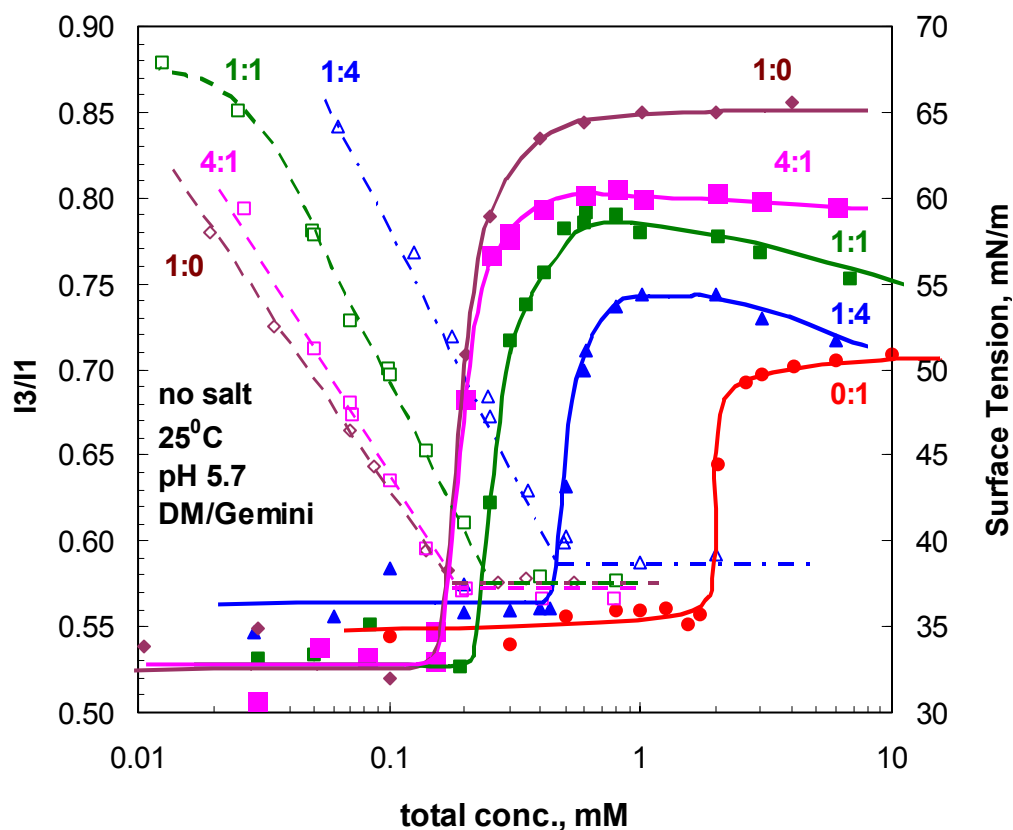


Figure 10. Variation of solution polarity, as indicated by I3/I1 ratio, due to the formation of (mixed) micelles of C₁₂-C₄-C₁₂ Gemini and its mixtures with dodecyl-maltoside (DM) at different mixing ratios. Dashed lines for polarity index, and dotted lines for corresponding surface tension curves.

To understand the nature of observed adsorption, microstructure of the adsorbed layer was probed using fluorescence spectroscopy. Changes in the polarity parameter of pyrene at the silica-water interface and in the supernatant are plotted in Figure 11 along with the adsorption isotherms of C₁₂-C₄-C₁₂ Gemini and its mixture with n-dodecyl- β -D-maltoside (DM). For C₁₂-C₄-C₁₂ Gemini alone, the polarity parameter in the supernatant changes sharply from ~ 0.56 to ~ 0.70 around the critical micelle concentration of the surfactant. At the silica/solution interface, there is a continuous change in the local polarity of the probe from aqueous

environment to a relatively nonpolar, micelle-type environment. This change occurs in a region that is well below the CMC and corresponds to the increase in the adsorption density. It is evident solubilization sites exist for pyrene at the solid/solution interface. Clearly, such aggregation takes place significantly only in Region II and above. In addition, the microenvironment formed by the associated surfactant appears to be similar in nature throughout the entire adsorption isotherm.

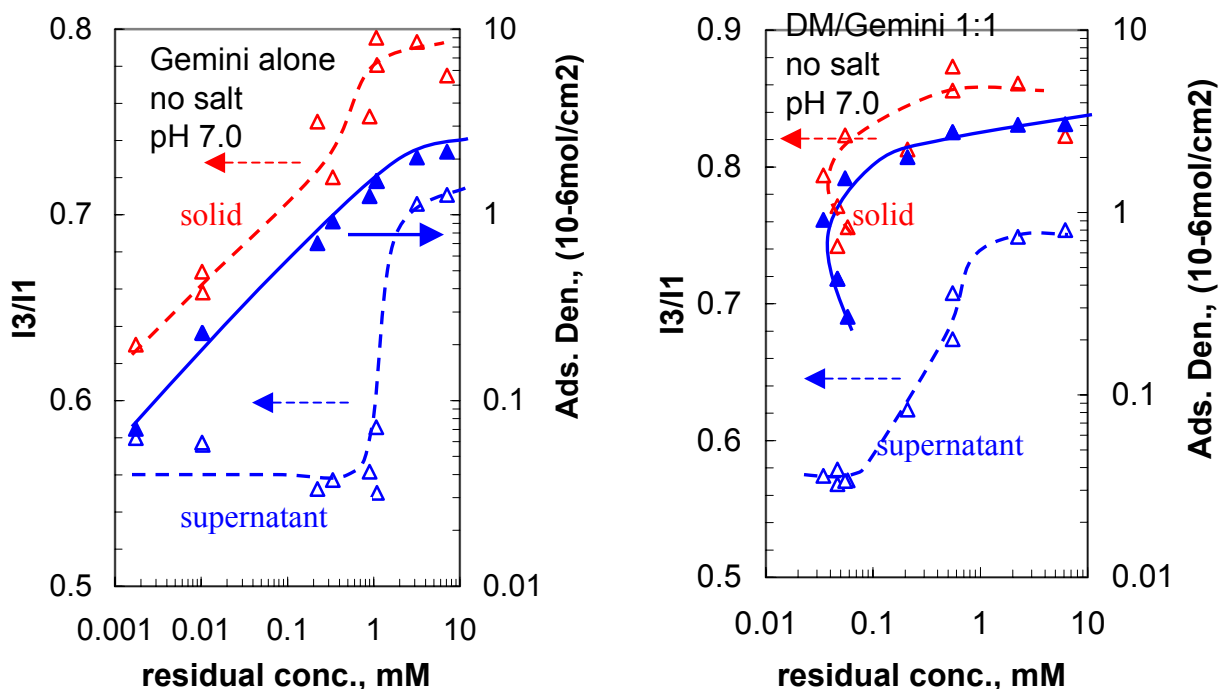


Figure 11. Variation of polarity both at silica/solution interface and in solutions, as indicated by I3/I1 ratio, due to the adsorption of C₁₂-C₄-C₁₂ Gemini and its mixtures with dodecyl-maltoside (DM). Open triangles for polarity index, and closed triangle for corresponding adsorption isotherms.

Similar results were obtained for the 1:1 C₁₂-C₄-C₁₂ Gemini/DM mixtures. Mixed surfactant aggregates form at the silica/solution interface at concentrations below the solution

cmc, with a sharp increase in the total surfactant adsorption. Compared to the abrupt increase of the polarity parameter in the supernatant (Figures 10 and 11a), a steady increase was observed for C₁₂-C₄-C₁₂ Gemini/DM mixtures. This is attributed to the continuous compositional change in the supernatant, which is the result of the difference in adsorption of the two surfactants on silica.

For C₁₂-C₄-C₁₂ Gemini and its mixture with DM, the polarity parameter of the solloids (surface colloids or aggregates) is higher than that of the micelles in the adsorption plateau region. This means that packing of the surfactants at the solid-liquid interface is denser than that in the micelles. This is attributed to the strong hydrophobic chain-chain interaction and inter-penetration of surfactant tails into solloids. Also it is noted that, in the adsorption plateau region, pyrene is present both in the surface aggregates at the solid-liquid interface and micelles in solution. It is reported that in alumina-sodium dodecyl sulfate system, pyrene is preferentially solubilized in solloids at the alumina-water interface rather than in SDS micelles in the supernatant. In contrast, in the alumina-tetradecyl trimethyl ammonium chloride (TTAC) system, pyrene is preferentially solubilized in the micelles than at the solid -liquid interface. It is suggested that the solubilizing power of C₁₂-C₄-C₁₂ Gemini and its mixture with DM solloids is between those of SDS and TTAC.

SUMMARY AND CONCLUSIONS

During this period, surfactant/mineral interactions have been studied for the system of DM and dodecyl sulfonate ($C_{12}SO_3Na$). The effects of solution pH, surfactant mixing ratio and different salts on surfactant adsorption on alumina have been investigated in detail. Solution properties of $C_{12}SO_3Na/DM$ mixtures were also studied in order to determine solution surfactant interactions in the bulk solution.

The extent of synergistic/antagonistic adsorption on alumina is determined by surfactant mixing ratio, solution pH, mineral type etc, and surfactant mixing ratio plays an important role in altering surfactant/mineral interaction by adsorption on reservoir rocks. Indeed the adsorption of DM is reduced under saturation conditions at high pH and thus is likely to be beneficial for enhanced oil recovery.

Adsorption results indicated that there exists stronger interaction between SDS and such minerals as gypsum, limestone than on alumina, because of significant precipitation of the surfactant on the former minerals. From the effect of different salts on surfactant adsorption, it was noted that sodium sulfite shows enhancing effect on adsorption with a maximum DM adsorption around salt/DM ratio of 1, while sodium chloride and sodium nitrate show negligible enhancement on DM adsorption.

Wettability of alumina minerals was monitored along with the adsorption of DM and its mixtures with $C_{12}SO_3Na$. A sharp increase in hydrophobicity of the alumina was obtained, indicating the onset of hydrophobic chain-chain interaction below solution cmc. Around solution cmc, mineral surface quickly changes back to hydrophilic, implying the formation of bilayer adsorption. In this regard, it is to be noted that mineral wettability controls the efficiency of oil liberation as well as dispersion of mineral fines in IOR processes.

Surfactant microstructures in solutions and at mineral/solution interfaces were investigated by monitoring micropolarity of the aggregates using fluorescence technique. Higher polarity of the solloid at solid/solution interface was observed for the system of C₁₂-C₄-C₁₂ gemini/DM mixtures than that of micelles in the solution. Strong hydrophobic chain-chain interaction and inter-penetration of surfactant tails into solloids are attributed to the denser packing of the surfactants at the solid-liquid interface than in micelles. Continuous changes in the polarity of the mixed micelles of C₁₂-C₄-C₁₂ gemini/DM indicated compositional changes of the aggregates in solution with increase in the surfactant concentration. The resulting polarity/hydrophobicity change of the mixed micelles will affect the adsorption of surfactant mixtures on reservoir minerals, surfactant/oil emulsion formation and the oil sweep efficiency of the chemical flooding processes.

Publications and Presentations

1. Somasundaran, P.; Chakraborty, Soma; Qiu, Qiang; Deo, P.; Wang, Jing; Zhang, Rui. “Surfactants, polymers and their nanoparticles for personal care applications”, JCS, (2004), 55(Suppl.), S1-S17.
2. Zhang, Rui; Liu, Chi; Somasundaran, P. “Cooperative adsorption of nonionic surfactant mixtures on hydrophilic surfaces: A simple model”, 229th American Chemical Society National Meeting, San Diego, CA, United States, March 13-17, 2005.
3. Somasundaran, P.; Healy, T.; Ducker, W.; and Zhang, Lei “Adsorption of Surfactants in the Flotation of Minerals”, submitted.

FUTURE PLANS

For task 1:

- ❖ Complete the measurement of solution behavior of cationic C₁₂-C₄-C₁₂ Gemini, DM, anionic alkyl sulfonates and their mixtures (including polymers): micellization / aggregation properties, and molecular interactions. The techniques of ultrafiltration, analytical ultracentrifuge, fluorescence and electro spin resonance (ESR) will be applied on selected systems to identify the size, shape and types of different mixed aggregate species.
- ❖ Complete the interactions of minerals with surfactant-polymer systems: adsorption of mixed systems (C₁₂-C₄-C₁₂ Gemini, DM, anionic alkyl sulfonates and polymer) will be conducted at different mixing ratios, pH and different types of salt, in order to select chemicals with minimum adsorption. Concurrently, wettability change and interfacial potential change of minerals due to surfactants/polymers adsorption will also be determined, and the results will be analyzed for the mechanisms of interactions of various chemicals on minerals. Adsorption studies of various chemicals will be used to screen formulations for optimum performance.

For task 2:

- ❖ Continue determining the effects of dissolved species (multivalent and univalent ions, such as Na⁺, Ca²⁺, Mg²⁺, Fe²⁺, SO₄²⁻ etc.) on the adsorption of selected surfactant systems on minerals: adsorption, abstraction and precipitation studies will be conducted to identify optimum formulation to lessen the loss of chemicals due to the precipitation in the EOR processes.
- ❖ The effects of solution pH, salinity, temperature and types of surfactants and polymers on

the adsorption/absorption of surfactants/polymers will be screened to select optimal working conditions.

For task 3:

- ❖ Selection of optimal formulations under simulated reservoir conditions: selected experiments will be conducted in the laboratory under representative reservoir conditions (pH, salinity and temperature) to establish the validity of the optimal processes.
- ❖ Emulsion formation in the mixed surfactant/oil systems will be studied in the presence of dissolved multivalent ions from minerals.