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

TECHNICAL PROGRESS REPORT

Reporting Period Start Date:	03/31/2004
Reporting Period End Date:	09/30/2004
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Date Report Issued:	October 30, 2004
DOE Award Number:	DE-FC26-03NT15413
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DISCLAIMER

ABSTRACT

Significant surfactant loss by adsorption or precipitation on reservoir minerals can cause chemical flooding processes to be less than satisfactory for enhanced oil recovery. This project is aimed towards an understanding of the role of reservoir minerals and their dissolved species in chemical loss by precipitation or adsorption of surfactants/polymers in enhanced oil recovery. Emphasis will be on the type and nature of different minerals in the oil reservoirs. Macroscopic adsorption, precipitation, wettability and nanoscopic orientation/conformation studies for aggregates of various surfactant/polymer mixtures on reservoir rocks systems is planned for exploring the cause of chemical loss by means of precipitation or adsorption, and the effect of rock mineralogy on the chemical loss.

During this reporting period, the minerals proposed in this study: sandstone, limestone, gypsum, kaolinite and pyrite, have been characterized to obtain their particle size distribution and surface area, which will be used in the analysis of adsorption and wettability data. The effect of surfactant mixing ratio on the adsorption of mixture of C_{12}-C_4-C_{12} Gemini surfactant (synthesized during last period) and sugar-based nonionic surfactant n-dodecyl-β-D-maltoside (DM) has been studied. It was discovered that even trace amounts of Gemini in the mixture is sufficient to force significant adsorption of DM. DM adsorption on silica increased from relatively negligible levels to very high levels. It is clear form analysis of the results that desired adsorption of either surfactant component in the mixtures can be obtained by controlling the mixing ratio, the total mixture concentration, pH etc. Along with these adsorption studies, changes in mineral wettability due to the adsorption of Gemini/DM mixtures were determined under relevant conditions to identify the nano-structure of the adsorbed layers. With increasing total surfactant adsorption, the silica mineral undergoes a wettability change from hydrophilic surface to hydrophobic and then revert to hydrophilic surface. The hydrophilic-hydrophobic transition point is determined also by surfactant mixing ratio. The corresponding solution behavior of mixed systems has been studied, and interaction parameters between the component surfactants have been determined, in comparison with the surfactant interactions at solid/liquid and liquid/liquid interfaces. Mineral surface modification due to the adsorption of mixed surfactants of DM and Gemini under optimal conditions, can be employed to control the mineral wettability to facilitate oil liberation in improved oil recovery processes.

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INTRODUCTION

High energy demand around the world and soaring oil price make it imperative to devise efficient oil recovery techniques. Surfactant/polymer flooding is one of the promising techniques to recover additional oil from domestic oil reservoirs. The key criterion for the successful application of techniques using surfactant mixtures is minimal loss of surfactants on reservoir rock by adsorption or 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 semi-soluble minerals that are prevalent in reservoirs.

Surfactants/polymers can interact to form aggregates in solutions (micelles) and at interfaces (hemimicelles) and these aggregation phenomena can have drastic effects on oil recovery processes. Such interactions have the potential to minimize the interfacial tension between the oil and the flooding media to facilitate oil liberation and, at the same time, to reduce the adsorption of surfactants on reservoir rocks. It is to be noted that adsorption of surfactants on the minerals is determined by a large number of system variables such as chemical and structural properties of the minerals including solubility and interfacial charge, chemical and physical properties of the solution such as, salinity, hardness, pH and temperature, and the chemical composition and structure of the surfactants.

During the previous reporting period, cationic butane-1,4-bis(quaternary ammonium chloride) Gemini surfactant, symbolized as C_{12}-C_4-C_{12}, has been synthesized for the study of mineral-surfactant interactions. Also characterization of silica and alumina minerals has been performed. Importantly, adsorption behavior of the C_{12}-C_4-C_{12} Gemini surfactant and the nonionic surfactant n-dodecyl-β-D-maltoside (DM) has been investigated. When mixed with C_{12}-C_4-C_{12}, significant synergy is observed for DM adsorption on silica, the major component of the reservoir minerals. In contrast, adsorption of cationic Gemini from the mixture is enhanced or reduced on the oppositely charged silica surface, depending on the mixing ratios and surfactant concentrations. Also the mineral surface charge has been observed to have a major effect on the adsorption of surfactants and their mixtures.

During this period, several other mineral samples, including sandstone, limestone, gypsum, kaolinite and pyrite have been characterized. Solution properties of C_{12}-C_4-C_{12}/DM mixtures were studied to reveal solution surfactant interactions, which affect the mixed aggregation formation and mineral-surfactant interactions. Mineral-surfactant interactions were studied by measuring adsorption as a function of surfactant mixing ratio. Interestingly, a small amount of Gemini in the mixture is sufficient to affect the adsorption behavior of DM drastically: DM adsorption on silica increased more than 50 times with only 1% of Gemini present in the mixture. Most notably, desired adsorption of both surfactant components in the mixtures could be obtained by proper control of the mixing ratio and total surfactant concentration. Wettability results indicate that, with bilayer adsorption of the C_{12}-C_4-C_{12}/DM mixtures, the silica mineral surface changes from hydrophilic to hydrophobic and then back to hydrophilic, with increase in the total surfactant adsorption. Appropriate wettability of reservoir minerals is critical in facilitating oil liberation in improved oil recovery processes. Towards this purpose, characterization of relevant minerals and surfactants is necessary to identify the effects of mineral composition, dissolved species (both mineral particles and multivalent ions), surfactant structure on mineral-surfactant interactions.

EXPERIMENTAL

MATERIALS

Surfactants

Several typical ionic and nonionic surfactants were selected for this study. Anionic sodium dodecyl sulfonate ($C_{12}SO_3Na$) and cationic dodecyl trimethyl ammonium chloride (DTAC), both of greater than 99% purity were purchased from TCI Chemicals, Japan and used as received. Non-ionic sugar-based surfactant, n-alkyl-β-D-maltoside (>95% purity by TLC), from Calbiochem was also used as received. The growing application of sugar-based surfactants (alkylmaltosides and alkylglucosides) has been due to their favorable performance properties and biodegradable nature. 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, as illustrated in Figure 1. The purity of the product was confirmed by NMR proton spectrum. Above surfactants are listed in table 1.

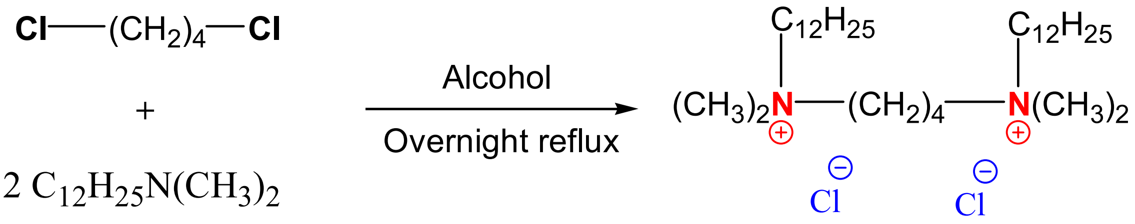


Figure 1. Synthesis of cationic C_{12}-C_4-C_{12} Gemini surfactant.

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_4, and Na_3PO_4 from Fisher Scientific Co.; and sodium citrate from Amend Drug & Chemical Company will be used as received. They are all

A.C.S. certified. 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.

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 dodecylsulfonate	$C_{12}H_{25}SO_3Na$	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:

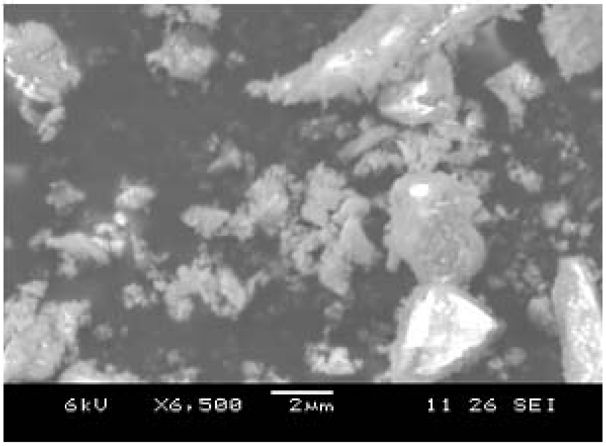
Solid substrates selected for the current study are alumina, silica, Kaolinite, sandstone, limestone, gypsum and pyrite, with the later five minerals characterized during this period. Alumina AKP-50 obtained from Sumitomo has a mean diameter of 0.2 µm. The BET specific surface area measured using nitrogen/helium 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 12.2 to 12.9 m^2/g and the isoelectric point was around 2. Kaolinite with the specific surface area of 23.12 m^2/g and limestone with the specific surface area of 0.96 m^2/g were obtained from the Wards Scientific Corporation. All these solids have relatively homogeneous surfaces and show low solubility in aqueous solutions. They were used as received.

Other natural minerals sandstone, gypsum and pyrite, were obtained from Wards Scientific Corporation in stone form. They were ground to fine powder in the laboratory by using mortar grinder from Fisher Scientific Co. The BET specific surface areas, measured using nitrogen/ helium with a Quantasorb system were sandstone: 1.39 m^2/g, gypsum: 2.64 m^2/g, and pyrite: 0.40 m^2/g. The measured isoelectric point of sandstone was 2. SEM images of these minerals are shown in Figure 2. From SEM images, it can be seen that only kaolinite shows a porous like structure, with the others having crystal-like surfaces. The porous structure of kaolinite results in its higher specific surface area. Properties for these solids are listed in Table 2.

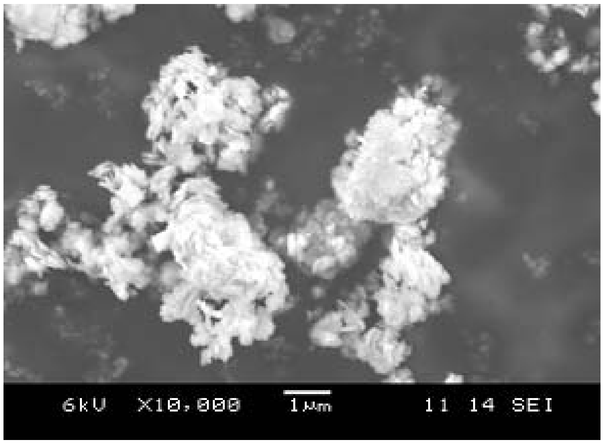
Table 2. List of Solids in the Study

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
Kaolinite	$Al_2Si_2O_5(OH)_4$	Wards	~ 1	23.12	--
Sandstone	SiO_2	Wards	~ 2	1.39	2
Gypsum	$CaSO_4 \bullet 2H_2O$	Wards	~ 2	2.64	N/A
Pyrite	FeS	Wards	~ 2	0.40	N/A

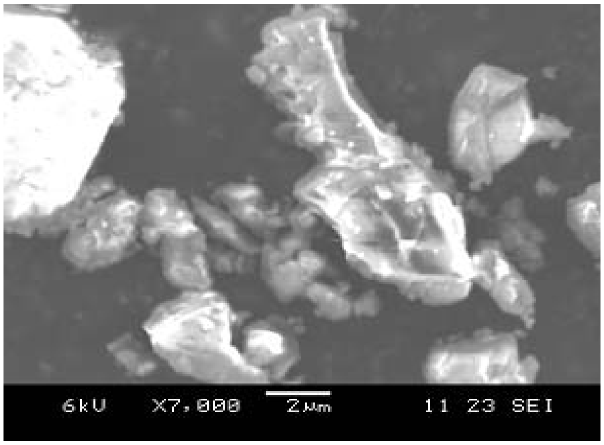
Gypsum



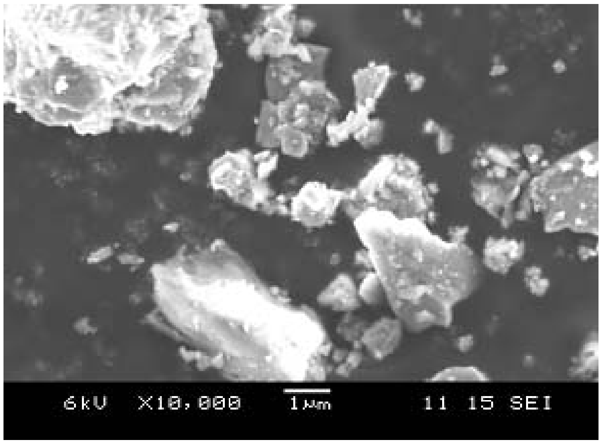
Kaolinite

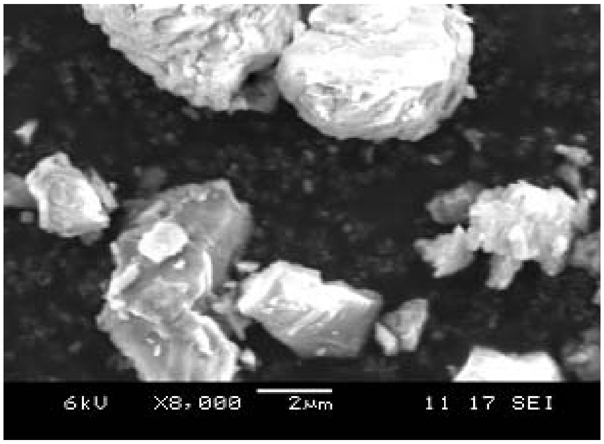


Limestone



Pyrite





Sandstone

Figure 2. SEM images of the minerals gypsum, kaolinite, limestone, sandstone and pyrite in powder form. The appropriate experiment conditions are listed on the images.

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 sample for determining relative hydrophobicity tests was prepared in the same way as that 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 min 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 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%.

Electrokinetics

The electrophoretic mobility of the solid particles (zeta potential) was determined using a Pen Kem Laser Zee Meter. After surfactant adsorption, the sample was diluted with its own supernatant to make a dispersion of suitable solid concentration.

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. Sets of measurements were taken for the aqueous surfactant solutions to ensure appropriate accuracy.

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.

RESULTS AND DISCUSSION

1. Effect of surfactant mixing ratio on the mineral-surfactant interactions at the solid/liquid interface

Surfactant mixtures have long been studied for both theoretical and practical interests. To obtain optimal mineral-surfactant interactions and minimum chemical loss by adsorption in the enhanced oil recovery processes by surfactant/polymer flooding, the effect of surfactant mixing ratio on the mineral-surfactant interactions has been investigated for the mixed systems of Gemini and sugar-based nonionic surfactants on silica.

The results obtained for the total surfactant adsorption on silica at pH 7 from the mixture of cationic C_{12}-C_4-C_{12} Gemini surfactant and n-dodecyl-β-D-maltoside (DM) are shown in Figure 3. DM shows relatively little adsorption on silica, compared to the cationic Gemini, which shows two orders of magnitude more adsorption at pH 7. Adsorption of the mixtures is higher than when present alone in the rising and saturation adsorption ranges, suggesting significant synergistic adsorption. Higher the DM mole fraction in the bulk solution, higher is the total adsorption and lower is the concentration required to reach saturation adsorption. Synergistic participation of DM in mixture adsorption is significant for the mixtures studied and this is clearly seen in Figure 4. At 1:4 Gemini/DM mixtures, the adsorption of dodecyl maltoside on silica from the mixtures is about 100 times higher than that of DM alone and 20 times higher than that from the mixtures with 10:1 Gemini/DM. For 1:4 Gemini/DM mixture, the saturation adsorption density of dodecyl maltoside is about 3.5×10^{-6} mol/m^2 and the surface area per molecule adsorbed is calculated to be 48 Å^2. When compared with the value derived from the surface tension data, this amount of DM surfactant adsorbed on the silica particles is estimated to be just enough to form a theoretical monolayer. A small amount of Gemini apparently acts as anchor molecules for adsorption of DM molecules around them. It would be useful to identify the optimum amounts of Gemini required for the optimal packing of the surfactant molecules in the adsorbed layers under relevant EOR conditions.

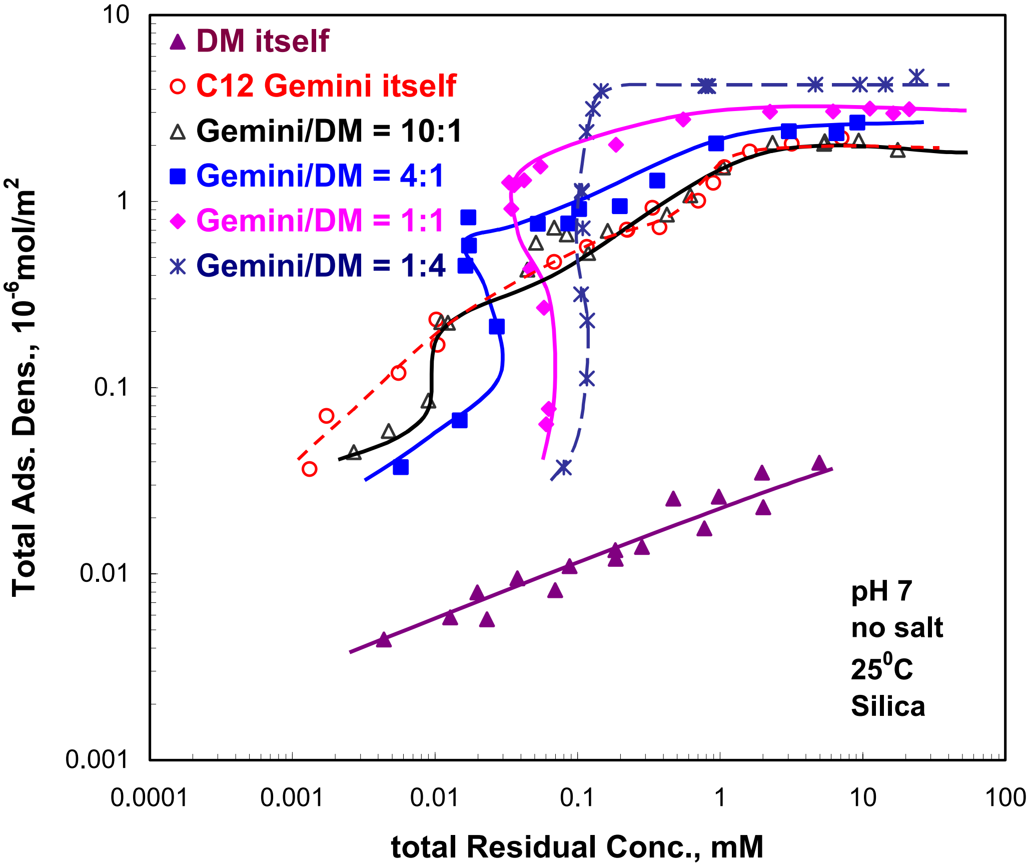


Figure 3. Effect of mixing ratio on total adsorption of mixtures of cationic C_{12}-C_4-C_{12} Gemini surfactant and n-dodecyl-β-D-maltoside (DM) on silica, at neutral pH and no swamping amount of salt.

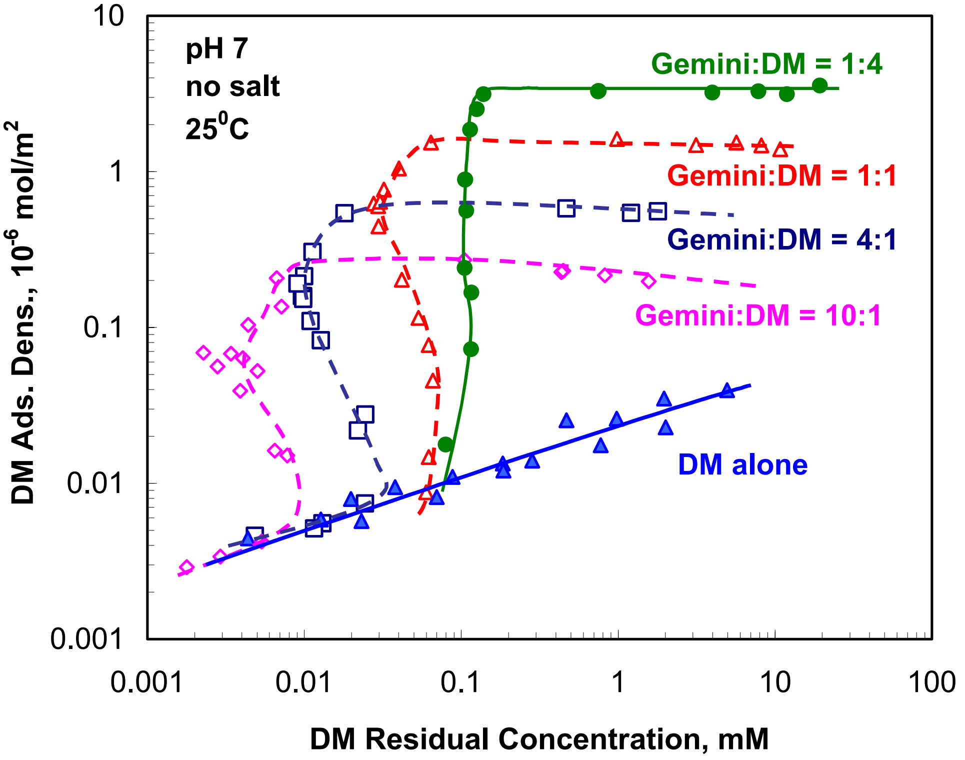


Figure 4. Effect of mixing ratio on the adsorption of n-dodecyl-β-D-maltoside (DM) from its mixtures with cationic C_{12}-C_4-C_{12} Gemini surfactant on silica, at neutral pH and no swamping amount of salt.

In contrast to the increased DM and total mixture surfactant adsorption, the adsorption of cationic C_{12}-C_4-C_{12} Gemini surfactant on silica from its mixture shows synergistic adsorption in the rising part of the isotherm, but decreased saturation adsorption compared to the adsorption of Gemini alone (Figure 5). Higher the DM molar fraction, more is the increase in the rising part of the Gemini adsorption, and higher is the decrease of the Gemini adsorption in the plateau region. This is attributed to the competition by dodecyl maltoside for adsorption sites. This suggests the possibility of obtaining desired interfacial properties by controlling the mixing ratios based on the type of information generated here.

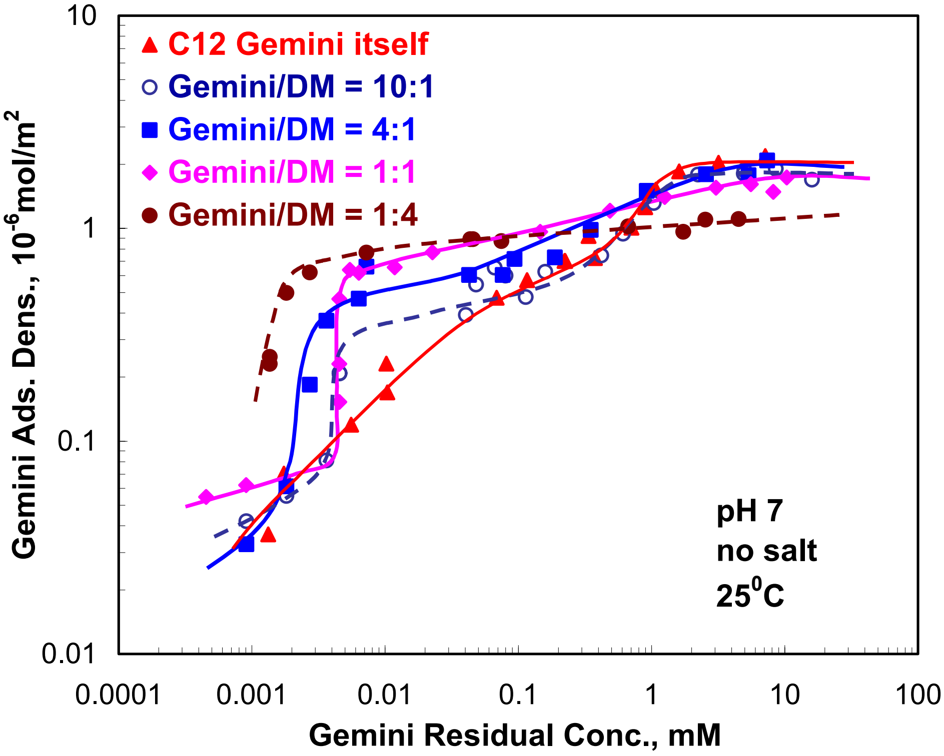


Figure 5. Effect of mixing ratio on the adsorption of cationic C_{12}-C_4-C_{12} Gemini from its mixtures with n-dodecyl-β-D-maltoside (DM) surfactant on silica, at neutral pH and no swamping amount of salt.

As discussed above, change in the mixing ratio in the C_{12}-C_4-C_{12}/DM systems has marked effects on mineral-surfactant interactions, especially the adsorption of DM on silica. The extent of this effect has been further studied by going to extreme mixing ratio conditions, to reveal how effective the surfactant mixing ratio can be. Figure 6 shows the adsorption of n-dodecyl-β-D-maltoside (DM) at such mixing ratio conditions. In Figure 6, the initial Gemini concentrations have been controlled so that at adsorption equilibrium the adsorption densities of Gemini are the same at all mixing ratios. We observed a continuous increase of the DM adsorption on silica with decrease of C_{12}-C_4-C_{12}/DM ratio from 10:1 to 1:100, even though DM barely adsorbs on silica by itself. This drastic increase of DM adsorption in the presence of even very small amount of C_{12}-C_4-C_{12} Gemini has been attributed to the significant hydrophobic chain-chain interaction between DM and Gemini and the formation of mixed aggregates of Gemini and DM on silica surface, with Gemini acting as nucleation sites. Indeed the adsorption of Gemini is reduced under saturation conditions and thus is likely to be beneficial for enhanced oil recovery.

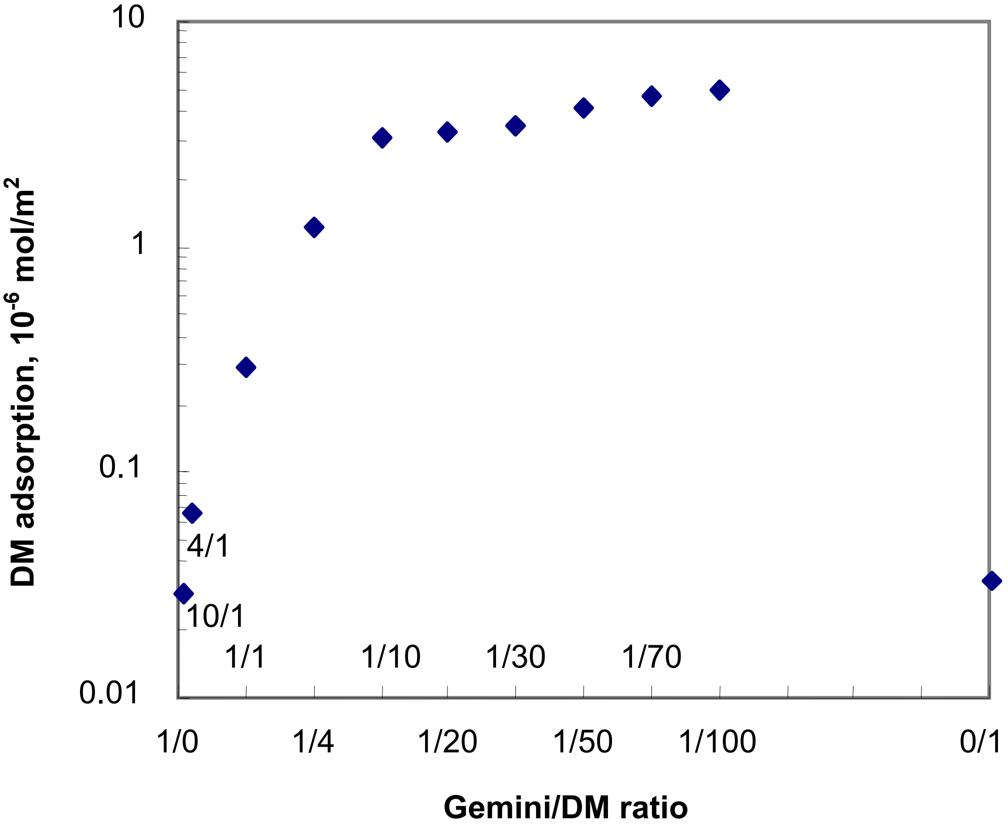


Figure 6. Effect of mixing ration on adsorption of dodecyl-maltoside (DM) from its mixture with cationic Gemini on silica, the adsorption density of Gemini has been controlled to be the same at all ratios.

2. Wettability of silica minerals due to the adsorption of surfactant mixtures

Adsorption of surfactants on silica 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 silica due to the adsorption of the mixtures of cationic Gemini and sugar-based surfactants was therefore determined along with the adsorption measurements.

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. The effect of C_{12}-C_4-C_{12} Gemini adsorption on the wettability of silica is illustrated in Figure 7 along with the adsorption isotherm in both water and 0.03M NaCl media. In the absence of the surfactant, the silica exhibits complete hydrophilicity. With an increase in adsorption of C_{12}-C_4-C_{12} Gemini on silica, the mineral surface becomes hydrophobic due to increasing amount of surfactant adsorbing with their hydrophobic tails oriented toward the bulk solution. The hydrophobicity reaches a maximum and stays constant for a wide range of surfactant concentrations, suggesting that a complete monolayer formation is not necessary to reach maximum mineral hydrophobicity. The drop in hydrophobicity at higher surfactant concentrations suggests that the onset of the chain-chain interaction is causing more and more surfactant to orient with hydrophilic groups toward the aqueous phase. The minimum hydrophobicity of the silica in the plateau region is attributed to the bilayer adsorption, since that can render the silica mineral surface hydrophilic.

It can also be seen from Figure 7, that, C_{12}-C_4-C_{12} Gemini reaches adsorption plateau at much lower concentration in 0.03M NaCl than in water, because of the decreased critical micelle concentration. Decreased cmc also resulted in higher Gemini adsorption density under constant ionic strength conditions in the low residual concentration range, making the silica more amenable to change from hydrophilic to hydrophobic surface. The Gemini concentration for hydrophilic - hydrophobic silica transition is much lower in 0.03M NaCl than in water.

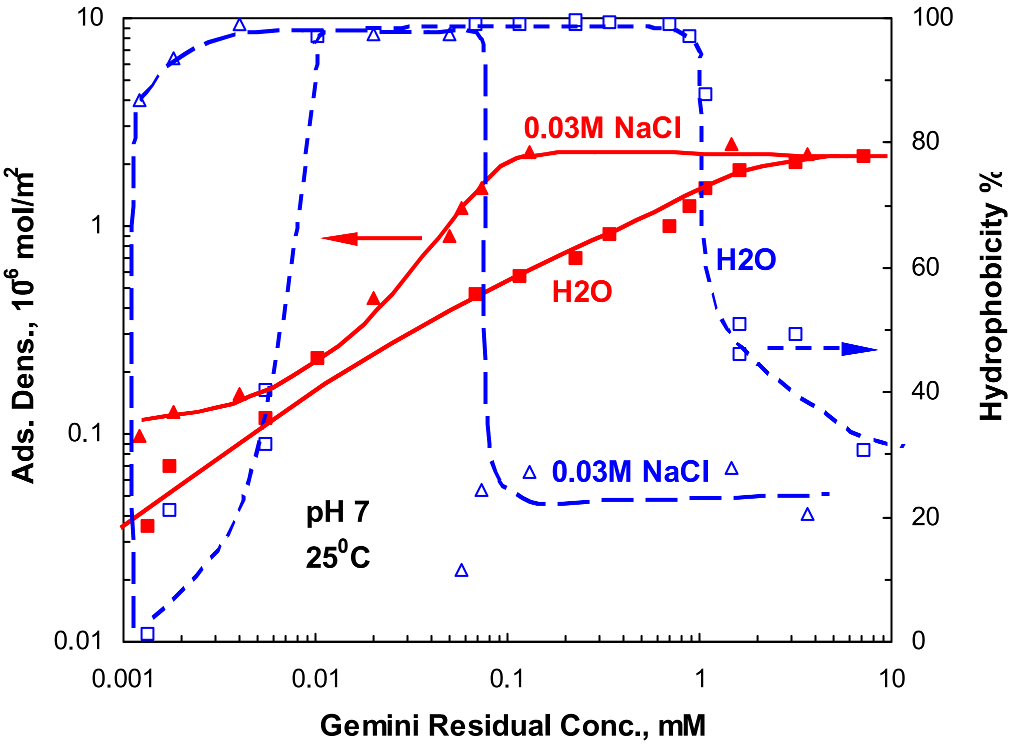


Figure 7. Wettability of silica due to the adsorption of C_{12}-C_4-C_{12} Gemini surfactant at pH 7, 25^0C, in both and 0.03M NaCl and H_2O.

As most commercial surfactants used in enhanced oil recovery processes consist of mixtures of surfactants or polymers, the wettability of mineral solid due to the adsorption of surfactant mixtures is more relevant than the effects of single surfactant. Wettability of minerals has been measured to determine how significantly the co-adsorption of n-dodecyl-β-D-maltoside (DM) and C_{12}-C_4-C_{12} Gemini surfactants would change the wettability of the silica mineral. Figure 8 shows the adsorption isotherms of C_{12}-C_4-C_{12} Gemini on silica from its mixtures with n-dodecyl-β-D-maltoside at different surfactant molar ratio along with the corresponding wettability curves. Similar to the single Gemini surfactant, the wettability of silica changes from hydrophilic to hydrophobic with increase in surfactant adsorption, stays hydrophobic in a wide concentration range and then drops back to hydrophilic due to bilayer adsorption on the silica. It can be seen from Figure 9, that the wettability curve of silica shifts to lower Gemini adsorption density with increase of DM molar ratio in the mixture, indicating significant participation of n-dodecyl-β-D-maltoside in changing the wettability of the minerals. The fact that there is marked synergism/competition in the adsorption of mixtures of n-dodecyl-β-D-maltoside and C_{12}-C_{4}-C_{12} Gemini in different surfactant concentration ranges, offers valuable information to achieve desired mineral wettability by adjusting surfactant molar ratio in the mixture, and total surfactant concentrations.

From the results given in our last report, it is known that electrophoretic property of silica mineral solids is affected only by the adsorption of Gemini but not by that of nonionic DM. Wettability of mineral solids is clearly affected by the total adsorption of both Gemini and DM, and hence it is possible to obtain both desired wettability and electrophoretic property of the mineral solids through the proper selection of surfactant mixtures, their mixing ratio and the total concentration.

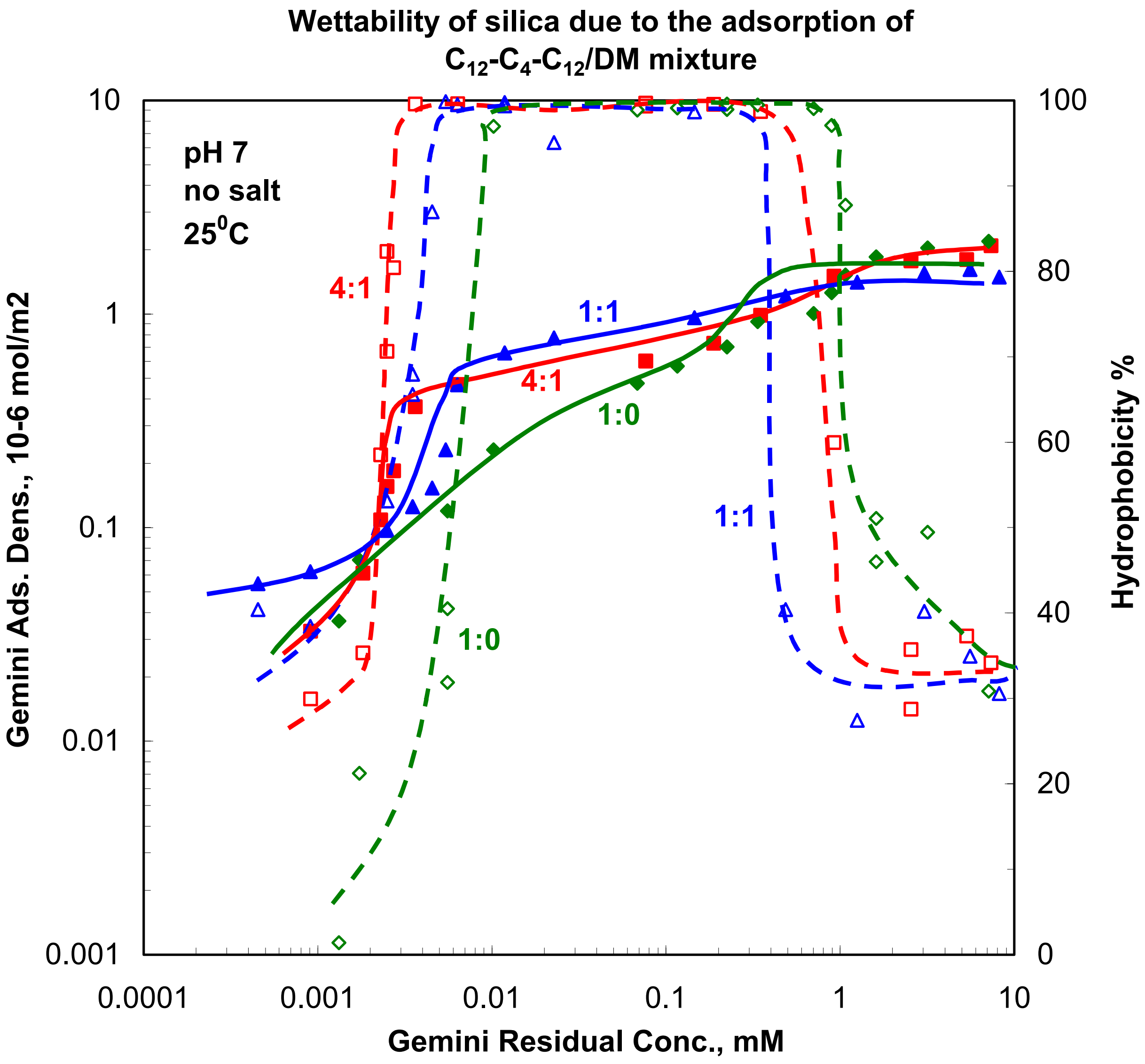


Figure 8. Adsorption of the mixtures of n-dodecyl-β-D-maltoside (DM) and C_{12}-C_4-C_{12} Gemini surfactants on silica and its effects on the wettability of silica at pH 7, 25^{0}C, and no swamping amounts of salt. Solid lines for adsorption isotherms, dashed lines for hydrophobicilty curves.

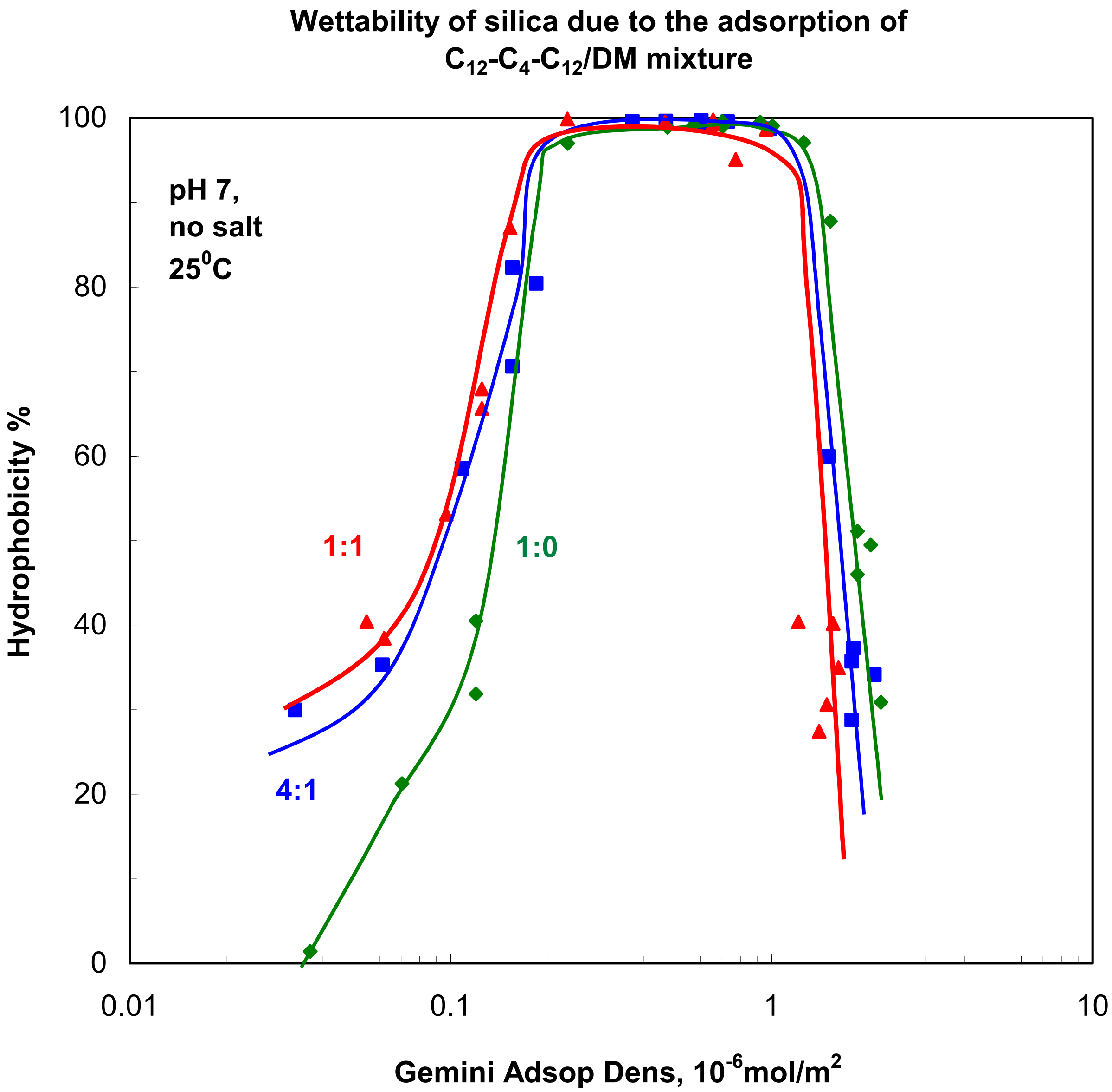


Figure 9. Wettability of silica due to the adsorption of n-dodecyl-β-D-maltoside (DM)/C_{12}-C_4-C_{12} Gemini mixture at pH 7, 25^0C, and no swamping amounts of salt. Gemini/DM molar ratio: 1:1 ▲, 4:1 ■, and 1:0 ◆.

3. Interactions between C_{12}-C_4-C_{12} Gemini and n-dodecyl-β-D-maltoside (DM) in solutions

Mineral-surfactant interactions are dynamic by nature with the adsorbed layers and the bulk phase solution tending towards equilibrium continuously. The behavior of surfactants and their mixtures in solution, such as surface activity and aggregate formation, affect the surfactant adsorption and the mineral-surfactant interactions. When mixed in solutions, surfactants usually show non-ideal mixing and exhibit the so-called synergism/antagonism, depending on the nature of the interactions among mixed surfactants. Interactions between C_{12}-C_4-C_{12} Gemini and n-dodecyl-β-D-maltoside (DM) in bulk solution were studied in this work using surface tensiometry and regular solution theory. Results obtained for the surface tension of aqueous solutions of individual C_{12}-C_4-C_{12}, DM and their mixtures are given in Figure 10. Critical micelle concentrations were determined from the surface tension curves and listed in Table 3. In H_2O, the cmc of the nonionic DM is lower than that of C_{12}-C_4-C_{12} Gemini, while the mixtures are generally not as surface active as DM alone. By regular solution approximation, the interaction parameter (β) for this binary mixed surfactant system was determined to be –1.5, indicating mild interaction between DM and Gemini in solution. Regular solution theory will be applied in the future to correlate changes in monomer concentration of the individual surfactants in the mixtures with their adsorption behavior.

Table 3. Critical micelle concentrations of C_{12}-C_4-C_{12} Gemini and n-dodecyl-β-D-maltoside (DM) mixtures of varying composition

Surfactant mixture mol ratio	cmc (kmol/m^3)
C_{12}-C_4-C_{12} alone	1.75×10^{-3}
4:1 C_{12}-C_4-C_{12} /DM	7.00×10^{-4}
1:1 C_{12}-C_4-C_{12} /DM	4.96×10^{-4}
1:4 C_{12}-C_4-C_{12} /DM	2.50×10^{-4}
1:10 C_{12}-C_4-C_{12} /DM	1.85×10^{-4}
DM alone	1.70×10^{-4}

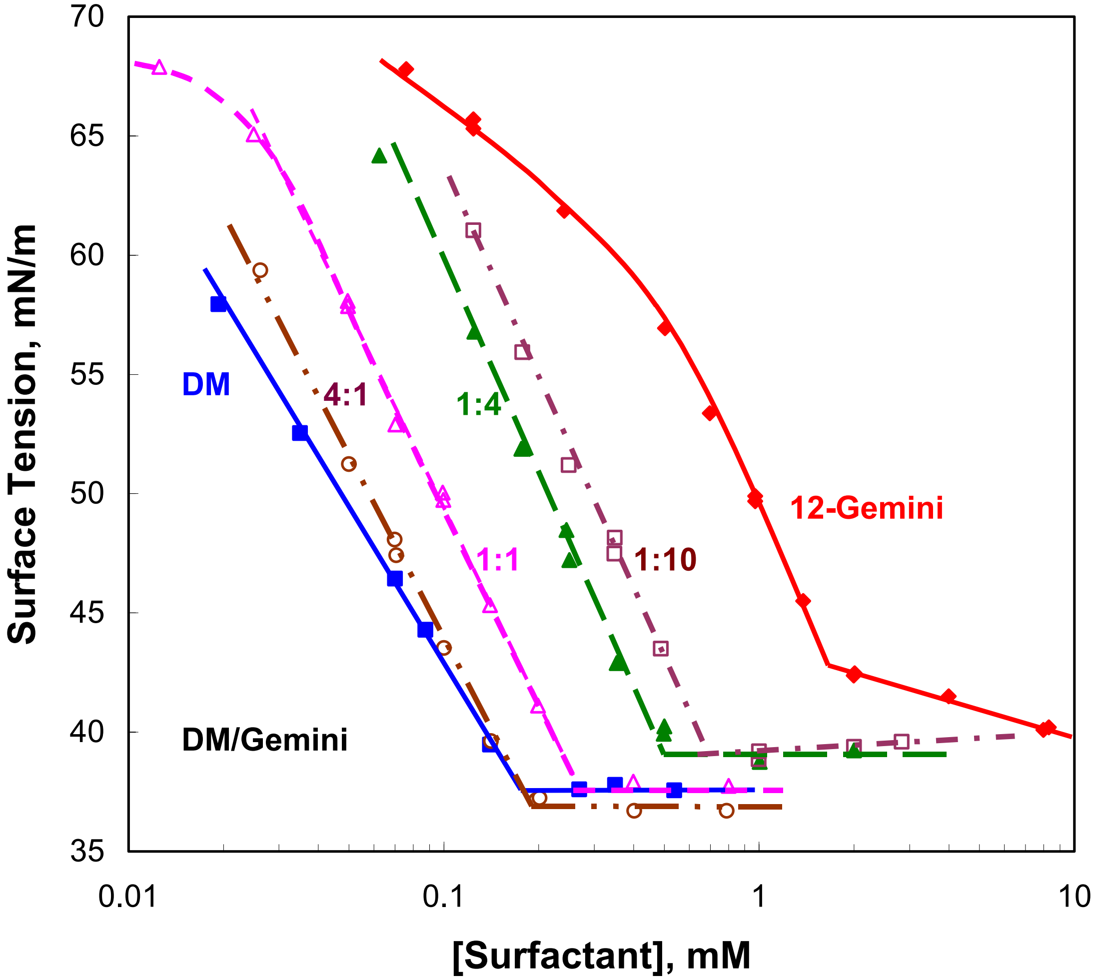


Figure 10. Equilibrium surface tension curves of individual C_{12}-C_4-C_{12} Gemini, n-dodecyl-β-D-maltoside (DM) and their mixtures of varying composition.

SUMMARY AND CONCLUSIONS

During this 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 the mixtures of C_{12}-C_4-C_{12} Gemini and sugar-based n-dodecyl-β-D-maltoside (DM) on silica minerals at different surfactant mixing ratios. Along with adsorption study, wettability change of solid mineral surface was determined. Also, solution behavior of the C_{12}-C_4-C_{12}/DM mixtures was investigated to determine the nature of surfactant interactions in the bulk solution by surface tensiometry and regular solution theory.

Change in the mixing ratio in the C_{12}-C_4-C_{12}/DM systems was found to produce marked effects on mineral-surfactant interactions, in terms of surfactant adsorption on the minerals. At neutral pH, adsorption of DM and C_{12}-C_4-C_{12} from the mixture on silica is very different from those of the individual surfactants. Individual cationic C_{12}-C_4-C_{12} Gemini shows marked adsorption on the silica even at low concentrations. When mixed with DM, an increase in C_{12}-C_4-C_{12} adsorption was observed in the rising part of the isotherm, due to the hydrophobic chain-chain interactions, while in the plateau adsorption region, competition by DM for adsorption sites resulted in decreased C_{12}-C_4-C_{12} adsorption.

Fairly low adsorption of n-dodecyl-β-D-maltoside (DM) alone was observed on silica. However, in the presence of cationic C_{12}-C_4-C_{12} Gemini, even at some very low Gemini/DM ratios, marked synergistic adsorption of DM was observed. This observation is proposed to be the result of the unique molecular structure of C_{12}-C_4-C_{12} Gemini. The presence of the double hydrophobic chain in the cationic C_{12}-C_4-C_{12} Gemini produces a much stronger hydrophobic chain-chain interaction in the adsorbed layer. In this case, adsorption of C_{12}-C_4-C_{12} acting as nuclei (anchors) to form mixed aggregates with DM on mineral surface is proposed to be the major factor for the marked adsorption synergy.

The observed synergy was confirmed by the determinations of wettability changes of the silica due to mixture adsorption. Wettability results indicate bilayer adsorption of the mixtures of DM and C_{12}-C_4-C_{12} on silica. Silica mineral has been observed to change from being hydrophilic to hydrophobic and then back to hydrophilic with increase in mixture adsorption. Also, surfactant mixing ratio was found to affect the hydrophilic-hydrophobic transition of silica mineral, due to the synergy/competition in the adsorbed layer. The observed competitive adsorption between DM and C_{12}-C_4-C_{12} on minerals under the condition provides us with valuable information for obtaining reduced surfactant loss for efficient chemical flooding EOR processes. Use of surfactant mixtures with reduced adsorption, particularly in the high concentration (>>cmc) region, is a promising approach to achieve cost-efficient chemical flooding processes since high.

The fact that electrophoretic property of the silica mineral is affected only by the adsorption of Gemini but not by that of nonionic DM, but wettability of mineral solids is affected drastically by the total adsorption of both Gemini and DM, suggests that it is possible to achieve both desired wettability and electrophoretic property of mineral solids through the proper control of surfactant mixtures, their mixing ratio and the total concentration.

Publications and presentations

1. R. Zhang, L. Zhang and P. Somasundaran, “Study of mixtures of n-dodecyl-β-D-maltoside with anionic, cationic and nonionic surfactant in aqueous solutions using surface tension and fluorescence techniques”, Journal of Colloid and Interface Science, 278, 453-460, 2004.

2. R. Zhang, P. Somasundaran, “Abnormal micellar growth in sugar-based and ethoxylated nonionic surfactant and their mixtures in dilute regimes using analytical ultracentrifugation”, Langmuir, 20, 8552-8558, 2004.

3. P. Somasundaran and Lei Zhang, “Mineral-Surfactant Interactions and Environmentally Benign Surfactants for Efficient Enhanced Oil Recovery”, 8th International Symposium on Reservoir Wettability, Houston, TX, May 2004.

4. R. Zhang, P. Somasundaran, X.Y. Hua and K.P. Ananthapadmanabhan, “Study of Mixed Micellar Growth of Nonionic Surfactants using Analytical Ultracentrifuge”, 78th ACS Colloid and Surface Science Symposium, New Haven, CT, June, 2004

FUTURE PLANS

For task 1:

- Continue measurement of solution behavior of cationic C_{12}-C_4-C_{12} Gemini, DM, anionic alkyl sulfonates and their mixtures (including polymers): micellization/aggregation properties, surface tension and molecular interactions. The techniques of surface tensiometry, 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.
- Interactions of minerals with surfactant-polymer systems: adsorption of mixed systems (C_{12}-C_4-C_{12} Gemini, DM, anionic alkyl sulfonates and polymer) will be conducted at different mixing ratios, 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 to reveal 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^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, SO_4^{2-} etc.) on the adsorption of selected surfactant / polymer 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.
- Reduction of chemical precipitation in the EOR processes: the effects of solution pH,

salinity, temperature and types of surfactants and polymers on the adsorption/abstraction of surfactants/polymers will be screened to select optimal working conditions.

For task 3:

- Selection of optimal formulations under simulated reservoir conditions: relevant experiments will be conducted in the laboratory under representative reservoir conditions (pH, salinity and temperature) to establish the validity of the optimal processes.