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

TECHNICAL PROGRESS REPORT

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ABSTRACT

The aim of the 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 the 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 will be 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 reporting period, the minerals used have been characterized, for particle size distribution and surface area. Also a series of novel cationic Gemini surfactants: butane-1,4-bis(quaternary ammonium chloride), has been synthesized. The solution and adsorption behavior of individual surfactants, the highly surface-active Gemini surfactant C_{12}-C_4-C_{12}, the sugar-based nonionic surfactant n-dodecyl-β-D-maltoside (DM) and their mixture has been studied. DM alone shows low adsorption on silica because of the lack of any electrostatic attraction between the surfactant and the silica particle. On the other hand, the cationic Gemini adsorbs markedly on the oppositely charged silica surface. Marked synergism has been observed in the case of DM/C_{12}-C_4-C_{12} mixture adsorption on silica. Adsorption of DM from the mixtures increases dramatically in both the rising part and the plateau regions. Adsorption of the cationic Gemini C_{12}-C_4-C_{12} from the mixture on the other hand increases in the rising part, but decreases in the plateau regions due to the competition for adsorption sites from

DM. Desired mineral surface property, that may be obtained using the proper mixtures of DM and Gemini under optimal conditions, can help to control the mineral wettability to facilitate oil liberation in improved oil recovery processes.

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INTRODUCTION

There is 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 under investigation in a number of places. The key criterion for the successful application of techniques using surfactant mixtures is minimal loss of surfactants on reservoir rock 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 drastic effects on oil recovery processes. Our recent work has shown that the aggregation behavior of some surfactant mixtures is quite unusual both in that more than one type of mixed micelles can form and possibly co-exist in the solution. This finding has both theoretical and practical implications. It has potential for applications to minimize the interfacial tension between the oil and the flooding media to facilitate oil liberation and, at the same time, to reduce adsorption of surfactants on reservoir rocks. It is to be noted that adsorption of surfactants, including polymeric ones, on 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 solution such as salinity, hardness, pH, temperature, and the chemical composition

and structure of the surfactants.

During this period, measurements of the properties of the minerals to be used including particle size distribution, surface area and morphologies have been performed. A series of novel cationic Gemini surfactants butane-1,4-bis(quaternary ammonium chloride), symbolized as C_n-C_4-C_n, with *n* indicating the alkyl chain length, have been synthesized for the study of mineral-surfactant interactions. The solution and adsorption behavior of the Gemini surfactant C_{12}-C_4-C_{12} have been studied, along with the nonionic surfactant n-dodecyl-β-D-maltoside (DM). While DM alone shows meager adsorption on silica, the major component of the reservoir minerals, because of the lack of any electrostatic adsorption, cationic Gemini adsorbs significantly on the oppositely charged silica surface. Characterization of typical minerals and individual surfactants would help to identify the effects of mineral composition, dissolved species (both mineral particles and multivalent ions), surfactant types and structures on mineral-surfactant interactions at later study stages.

EXPERIMENTAL

MATERIALS

Surfactants

Several typical ionic and nonionic surfactants were selected for this study. Anionic sodium dodecyl sulfonate ($C_{12}SO_3Na$) of greater than 99% purity and cationic dodecyl trimethyl ammonium chloride (DTAC) 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 structure of n-dodecyl-β-D-maltoside (DM) is shown in Figure 1. The growing applications of sugar-based surfactants (alkylmaltosides and alkylglucosides) have been due to their favorable performance properties, such as good biodegradability and the fact that these surfactants are produced from renewable resources. These surfactants are listed in table 1.

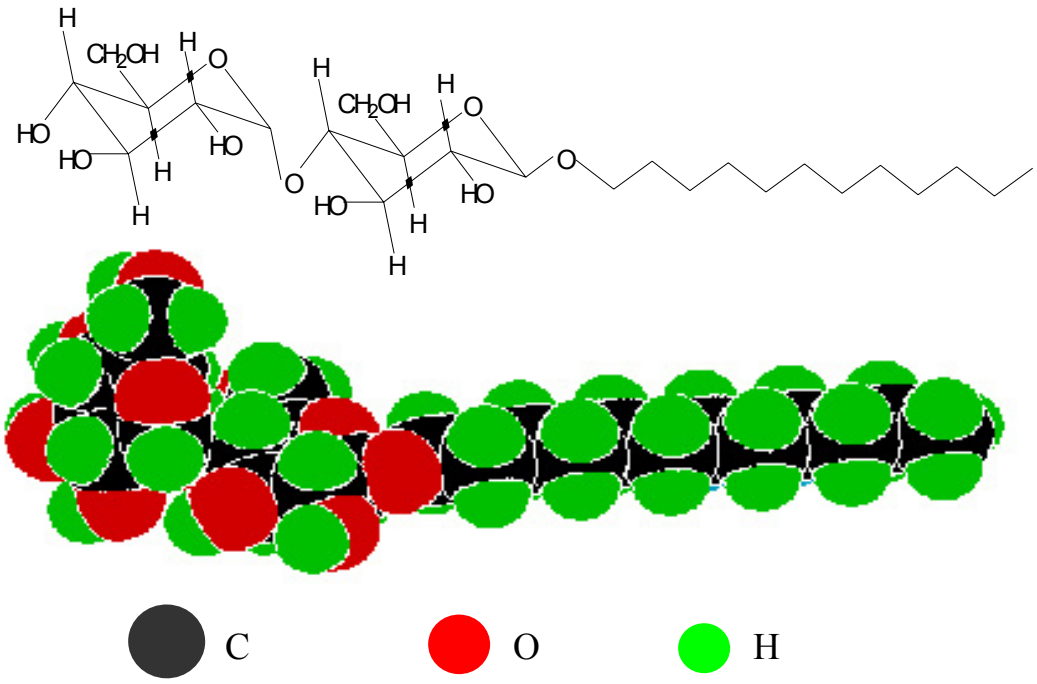

Figure 1. The Chemical Structure and molecular model of Sugar-based Surfactant n-dodecyl-β-D-maltoside (DM).

Table 1. Surfactants to be used and their formulas

Surfactant	Molecular formula	Molecular Weight	Purity
n-dodecyl-β-D-maltoside	$C_{12}H_{25}(C_6H_{10}O_5)_2OH$	510.6	>95%
Sodium dodecylsulfonate	$C_{12}H_{25}SO_3Na$	272.4	>99%
Dodecyltrimethylammonium chloride	$[C_{12}H_{25}N(CH_3)_3]Cl$	263.9	>99%

Synthesis of cationic Gemini surfactants

Cationic Gemini surfactants, butane-1,4-bis(quaternary ammonium chloride), represented as C_{12}-C_4-C_{12} and C_{14}-C_4-C_{14}, have been synthesized by the reaction of 1,4-dichlorobutane with corresponding alkyl dimethyl amines, as illustrated in Figure 2. After solvent evaporation, crude white paste product obtained was recrystalized in THF and then in ethanol/ethyl acetate solvent several times. The purified products were white powder, and were stored in a desiccator under vacuum for the complete removal of the solvent. High purity of the synthesized Gemini surfactants was confirmed by their proton NMR spectrums, as shown in Figure 3. There is only a slight amount of hydroxyl salt in the C_{12}-C_4-C_{12} and C_{14}-C_4-C_{14} Gemini, presumably due to the ion-exchange or replacement reaction with alcohol, and no other impurity was found by NMR in either Gemini.

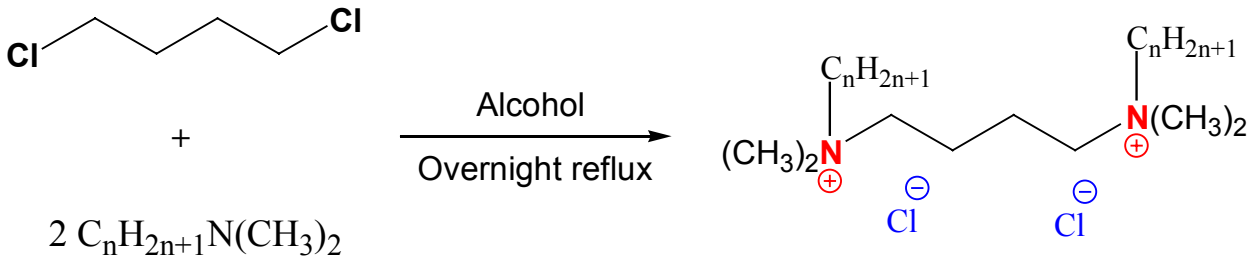

Figure 2. Synthesis of cationic Gemini surfactants C_n-C_4-C_n, n: alkyl chain length.

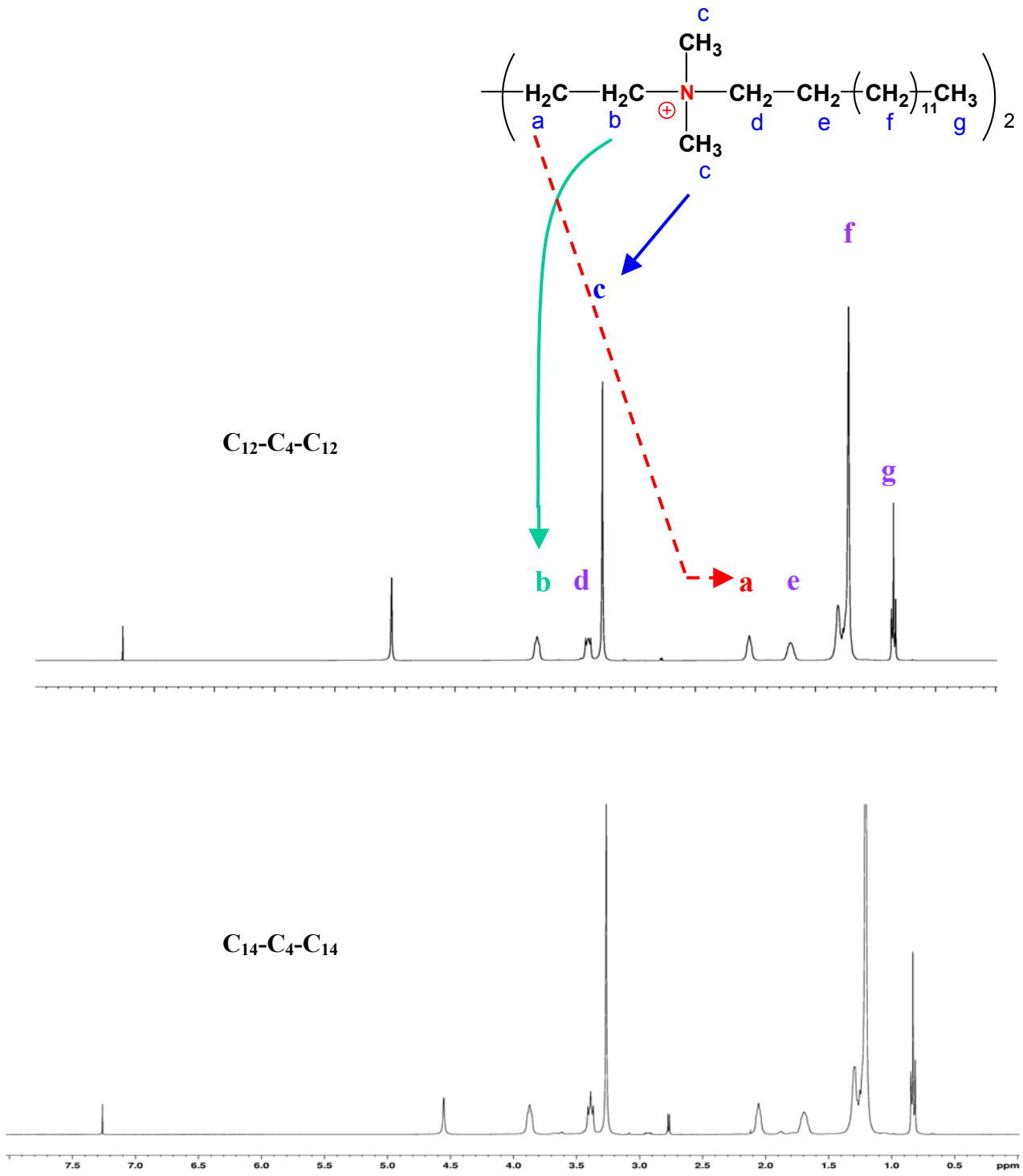

Figure 3. Characterization of synthesized Gemini surfactants C_{12}-C_4-C_{12} and C_{14}-C_4-C_{14}, their ^{1}H NMR spectrums show high purity of the products.

Mineral Samples:

Solid substrates selected for the current study are alumina, silica (quartz), and Kaolinite, which were characterized. Alumina AKP-50 obtained from Sumitomo had a mean diameter of 0.2 μm. The BET specific surface area measured using nitrogen 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 and the specific surface area of 12.2 to 12.9 m^2/g and the iep was around 2. Kaolinite with the specific surface area of 8.2 m^2/g was obtained from the University of Missouri. All these solids have relatively homogeneous surfaces and show low solubility in aqueous solutions. They were used as received. The measured properties for these solids are given in Table 2.

Table 2. List of Solids in the Study

Name	Source	Mean particle size (μm)	Specific surface area (m^2/g)	Isoelectric point (iep)
AKP-50 Alumina	Sumitomo	0.2	10.8	8.9
Silica (Quartz)	Geltech	0.2 – 0.3	12.2 – 12.9	2
Kaolinite	Univ. of Missouri	--	8.2	--

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 LiCl, NaCl, KCl, $CaCl_2$, $AlCl_3$, Na_2SO_4, and Na_3PO_4 from Fisher Scientific Co.; NaBr and NaI from Aldrich Chemical Company, Inc.; 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.

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 clear supernatant was then pipetted out for analysis.

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.

Analytical Techniques:

In adsorption experiments, 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. Adsorption of double hydrophobic chain Gemini and single chain general surfactants

Cationic Gemini surfactant butane-1,4-bis(dodecyl dimethyl ammonium chloride), C_{12}-C_4-C_{12}, with two hydrophobic and two hydrophilic groups in the molecule, could be viewed as a dimer of dodecyltrimethyl ammonium chloride (DTAC), which has a single hydrophobic and hydrophilic group. Figure 4 shows the structural relationship between C_{12}-C_4-C_{12} and DTAC. C_{12}-C_4-C_{12} is more surface-active than DTAC in terms of the micelle formation. The critical micelle concentration of C_{12}-C_4-C_{12}, 1.5mM, is 10 times lower than that of DTAC (20mM), due to the increased hydrophobicity of C_{12}-C_4-C_{12} with two hydrocarbon chains.

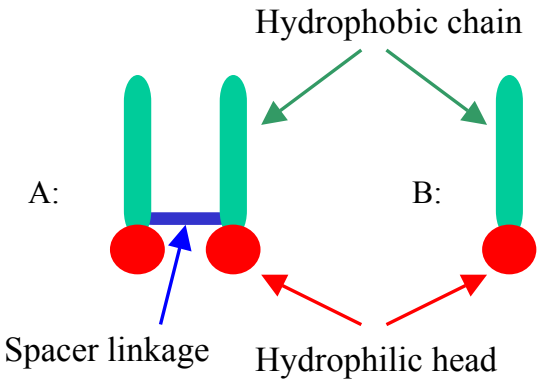

Figure 4. Structure comparison of cationic Gemini surfactant C_{12}-C_4-C_{12} (A) to DTAC (B), C_{12}-C_4-C_{12} is a dimmer of DTAC.

Adsorptions of Gemini C_{12}-C_4-C_{12} and DTAC on silica mineral were measured under the same conditions, and the results obtained are shown in Figure 5. Both C_{12}-C_4-C_{12} Gemini and DTAC reach the same saturation adsorption with approximate bilayer formation around their solution cmcs, because they share the same cross sectional area per hydrophobic chain. Adsorption of Gemini C_{12}-C_4-C_{12} in the low concentration ranges is markedly higher, which is

attributed to the greatly increased electrostatic adsorption of C_{12}-C_4-C_{12} on the negatively charged silica, with the presence of **two** positively charged headgroups in the molecule.

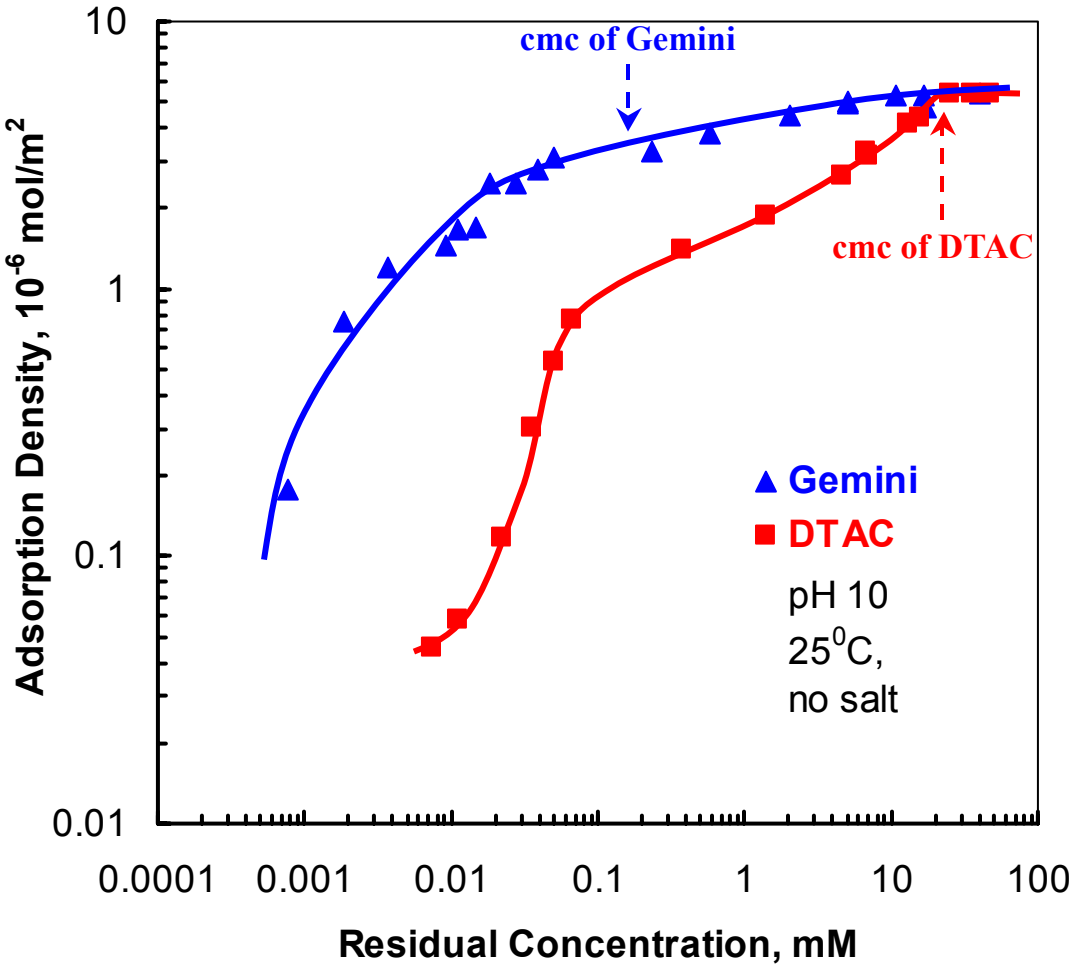

Figure 5. Adsorption of Gemini C_{12}-C_4-C_{12} and single chain DTAC on silica. Both adsorption density and residual concentration values are based on per hydrophobic alkyl chain in the surfactant molecule. For Gemini, there are two hydrophobic chains in every molecule.

2. pH Effect on the adsorption of cationic Gemini surfactant on silica

Figure 6 shows the adsorption of cationic Gemini surfactant C_{12}-C_4-C_{12} at different pH w/o swamping amounts of salt. Clearly, pH has a remarked effect on the adsorption of the cationic Gemini on the negatively charged silica minerals. At pH 4, relatively low adsorption of

C_{12}-C_4-C_{12} on silica was observed, with an S-shaped adsorption isotherm. At neutral pH, the adsorption of C_{12}-C_4-C_{12} on silica increases sharply in the low concentration range, because of the strong mutual electrostatic attraction between the double positively charged headgroups on cationic Gemini and the negatively charged silica surface. Under basic conditions, a sharp increase of C_{12}-C_4-C_{12} adsorption was observed at lower concentrations.

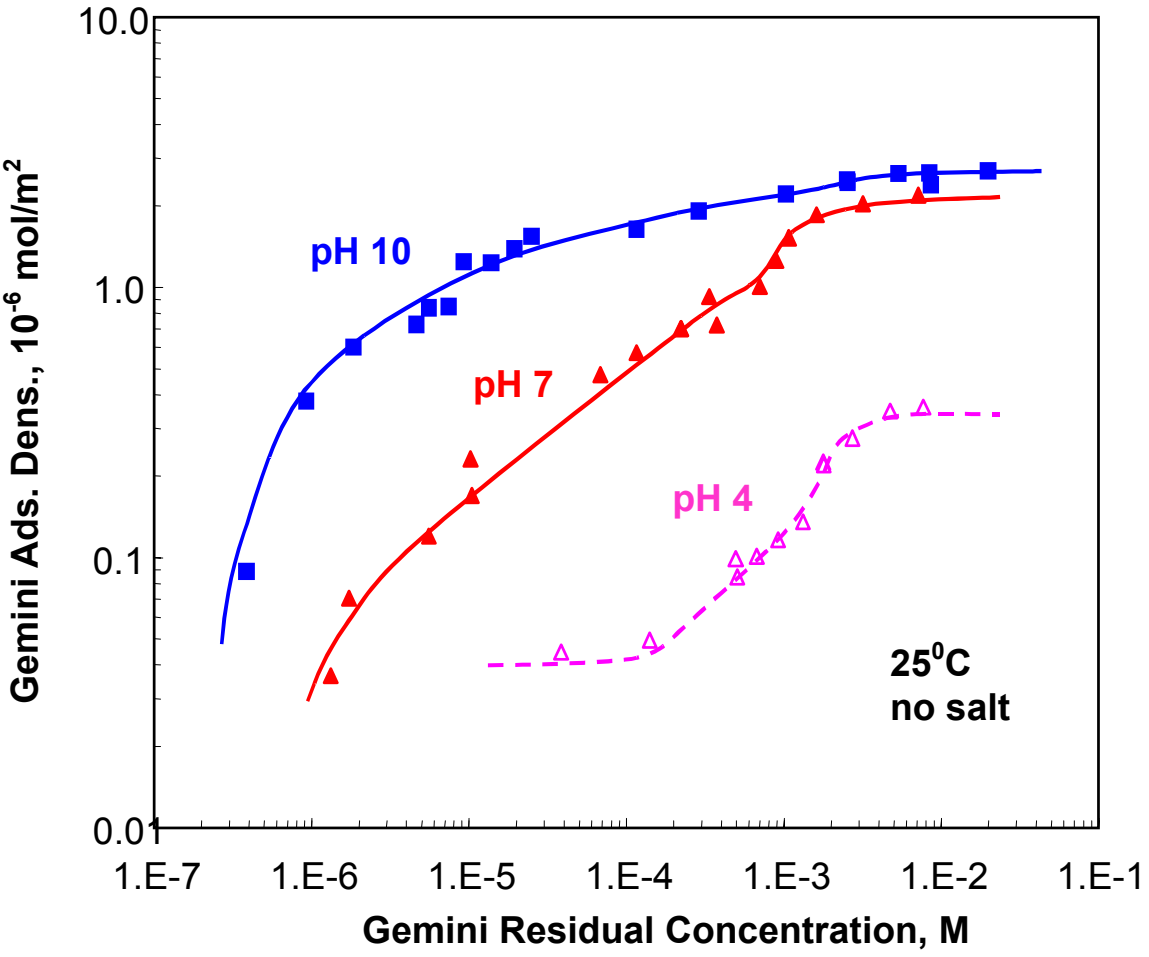

Figure 6. Effects of pH on adsorption of cationic Gemini surfactant C_{12}-C_4-C_{12} on silica at room temperature w/o salt. pH 4 △, pH 7 ▲, and pH 10 ■.

3. Adsorption of the mixtures of Gemini and sugar-based nonionic surfactants on silica

Surfactant mixtures have long been studied for both theoretical and practical interests. We investigated the adsorption behaviors of mixture systems of Gemini and sugar-based nonionic surfactants.

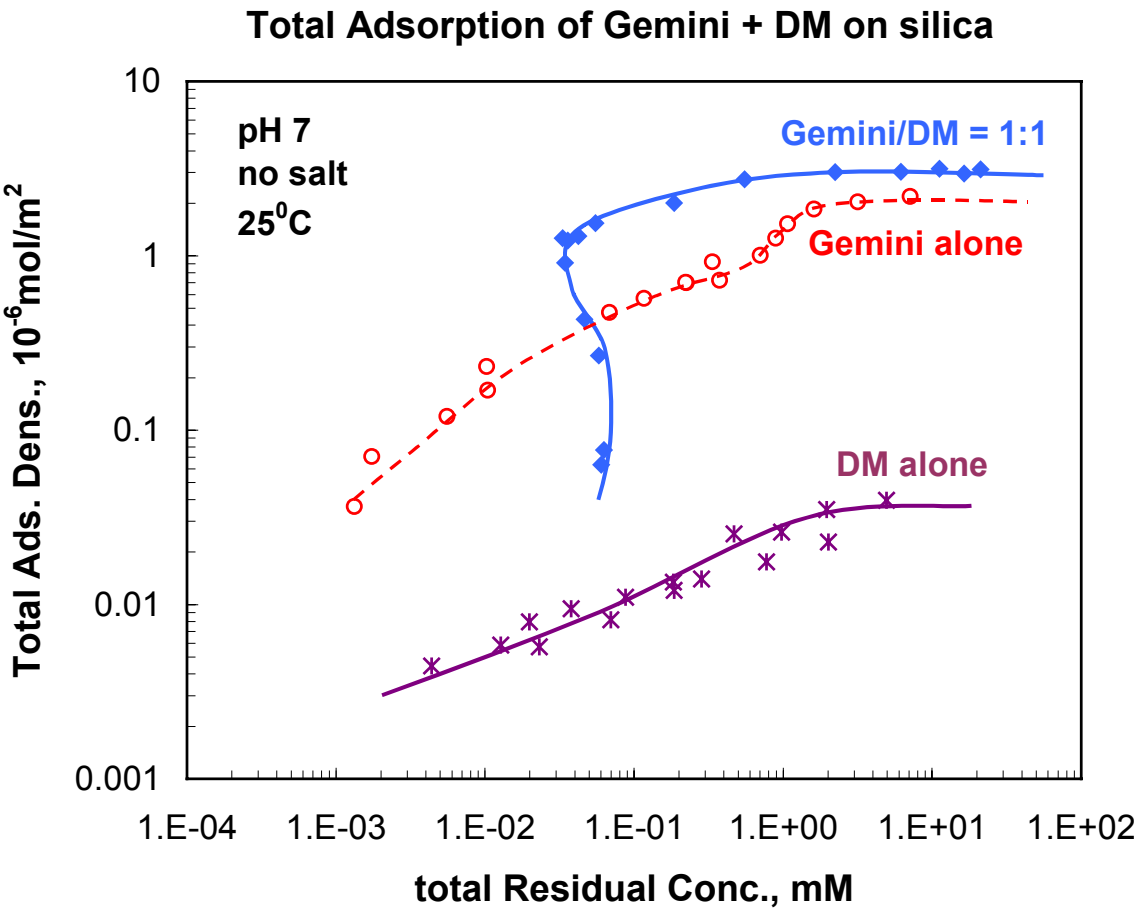

Figure 7. Total adsorption of mixtures of n-dodecyl-β-D-maltoside (DM) and cationic Gemini C_{12}-C_4-C_{12} and on silica, at pH neutral, no swamping amount of salt.

The results obtained for the total surfactant adsorption of both on silica at pH 7 from mixtures of cationic Gemini surfactant C_{12}-C_4-C_{12} and n-dodecyl-β-D-maltoside (DM) is shown in Figure 7. While DM shows negligible adsorption on silica at pH 7, cationic Gemini alone shows appreciable adsorption under this condition. Apparently, in both the rising and saturation adsorption ranges, considerable synergistic adsorption exists. In the mixtures, lower

concentration is required to reach saturation adsorption, because DM shows lower concentration for the formation of aggregates at both the solid/liquid interfaces and the bulk solution. In Figure 8 the adsorption of DM from DM alone is compared with that from its mixture with C_{12}-C_4-C_{12}. With 1:1 Gemini/DM mixtures, the adsorption of DM on silica from the mixtures is 50 times higher than that of the adsorption of DM alone. Significant synergistic participation of DM in mixed adsorption is the major reason for the observed adsorption in this case. The synergy in the mixtures is proposed to result from the marked hydrophobic chain-chain interaction between DM and the adsorbed Gemini C_{12}-C_4-C_{12}. Since cationic Gemini C_{12}-C_4-C_{12} can easily adsorb on the negatively charged silica, adsorbed C_{12}-C_4-C_{12} molecules are proposed to act as nucleation sites for forming mixed aggregates with DM on silica surface, which would greatly increase DM adsorption.

In comparison to the increased DM and the combined mixture adsorption, adsorption of the cationic Gemini C_{12}-C_4-C_{12} on silica from its 1:1 mixtures with DM shows synergistic adsorption only in the rising part of the isotherm and some decreased saturation adsorption compared to the adsorption of Gemini alone (Figure 9). It is to be noted that the observed adsorption decrease in C_{12}-C_4-C_{12} from its mixture with DM meets the requirement of reduced surfactant loss for cost-efficient chemical flooding process. The increased Gemini C_{12}-C_4-C_{12} adsorption in the rising part is again attributed to be the hydrophobic chain-chain interaction between DM and C_{12}-C_4-C_{12}, while the decreased Gemini adsorption in the plateau regions is due to the significant competition of adsorption sites by DM (Figure 8).

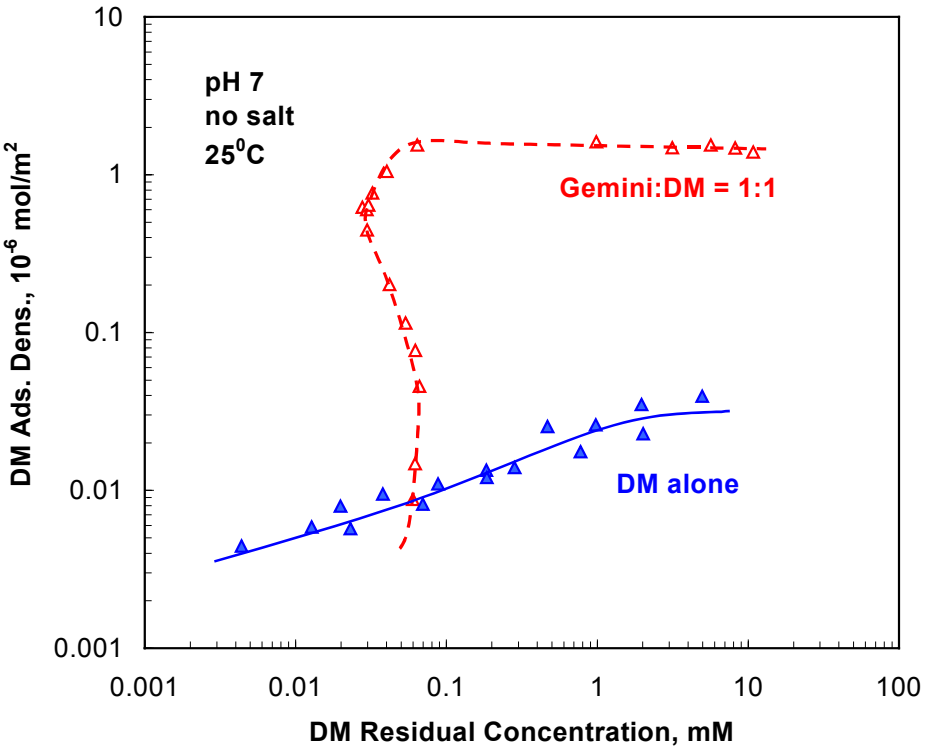

Figure 8. Adsorption of n-dodecyl-β-D-maltoside (DM) from its mixtures with cationic Gemini surfactant C_{12}-C_4-C_{12} on silica, at neutral pH, no swamping amount of salt.

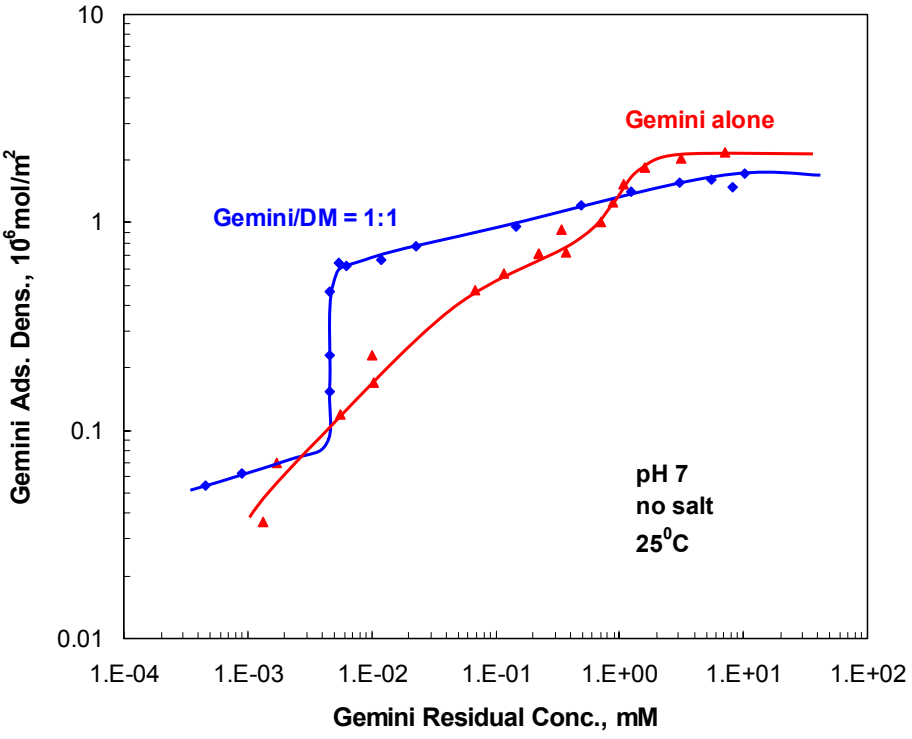

Figure 9. Adsorption of cationic Gemini surfactant C_{12}-C_4-C_{12} from its mixtures with n-dodecyl-β-D-maltoside (DM) on silica, at neutral pH, no swamping amount of salt.

The effect of Gemini/DM mixing ratio on the adsorption of Gemini C_{12}-C_4-C_{12} on silica is illustrated in Figure 10. The residual Gemini concentrations after adsorption at different mixing ratios have been controlled to be the same in the rising part of the adsorption isotherms. A drastic increase in Gemini C_{12}-C_4-C_{12} adsorption has been observed with the increase of DM in the mixtures from DM/Gemini mixing ratio 1:10 to 1:1. Again, clearly the hydrophobic chain-chain interaction leads to significant synergy in adsorption in the rising part. In the plateau region competition for adsorption sites dominates and causes a decrease in C_{12}-C_4-C_{12} adsorption.

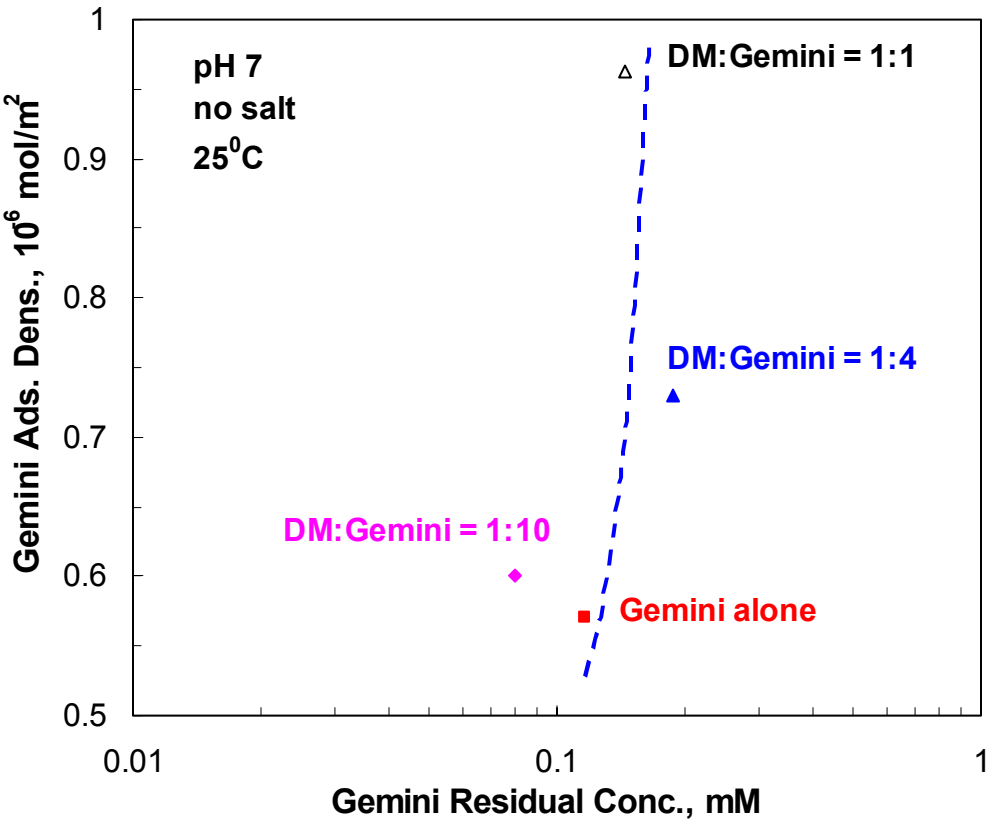

Figure 10. Effect of the mixing ratio on the adsorption of cationic Gemini C_{12}-C_4-C_{12} from its mixtures with n-dodecyl-β-D-maltoside (DM) on silica, at room temperature, neutral pH, no swamping amount of salt.

4. Electrokinetics of silica in the mixtures of cationic Gemini and sugar-based surfactant solution

Surface charge of the minerals is one of the important factors determining the solid/solution interfacial processes such as adsorption and the efficiency of oil liberation from the mineral rocks in the IOR processes. Electrokinetic studies of silica mineral have been carried out during this period along with adsorption. The results obtained are shown in Figures 11 and 12. It is clear from Figure 11, that the zeta potential of silica is not altered significantly by the adsorption of DM surfactant alone, which is in accord with the nonionic nature of n-dodecyl-β-D-maltoside. Figure 11 also shows the zeta potential of the silica surface as a function of the amount of cationic Gemini C_{12}-C_4-C_{12} adsorbed on silica. The zeta potential of silica particles shows the same change with the Gemini adsorption from both individual surfactant solution and its mixture with DM, showing that the adsorption of the cationic Gemini C_{12}-C_4-C_{12} is the reason for the change in electrophoretic property of the mineral. The results show good correlation between the cationic Gemini adsorption and the zeta potential change.

Figure 12 shows the zeta potential change of silica as a function of residual Gemini concentration. The surface charge reversal of silica occurs at lower concentrations in the case of 1:1 DM/C_{12}-C_4-C_{12} mixture than in the case of the cationic Gemini C_{12}-C_4-C_{12} alone (DM adsorption making no significant contribution to the zeta potential change of the silica mineral), suggesting synergy between C_{12}-C_4-C_{12} and DM, with more Gemini C_{12}-C_4-C_{12} from the mixture adsorbed on silica at low Gemini residual concentrations (*i.e.* the rising part of Gemini adsorption isotherm).

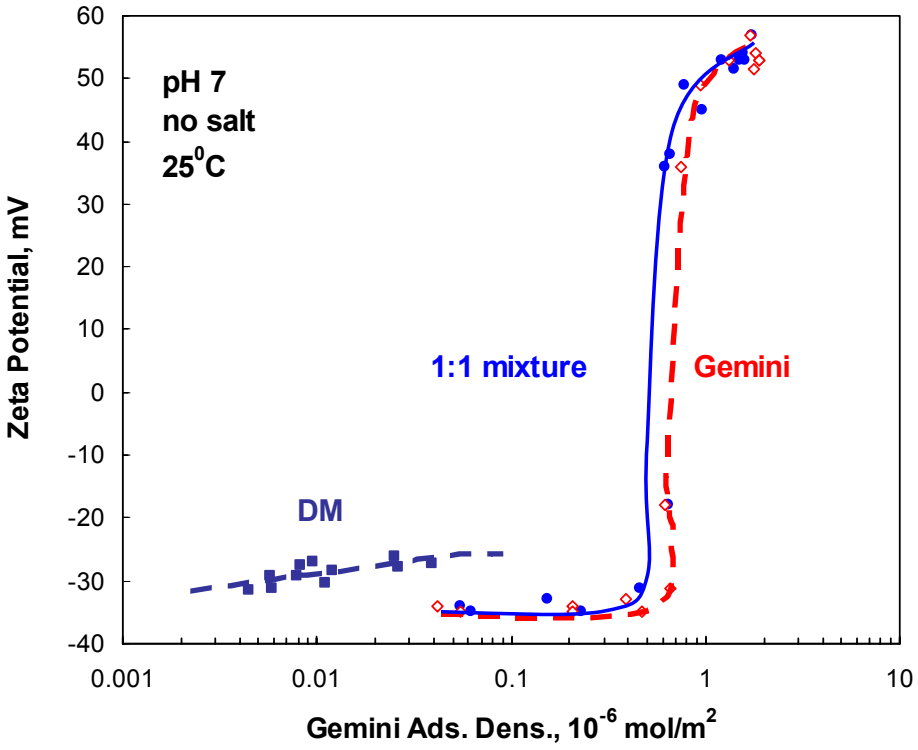

Figure 11. Effect of Gemini adsorption density on the zeta potential of silica due to mixture adsorption, pH 7, 25^{0}C, and no swamping amounts of salt.

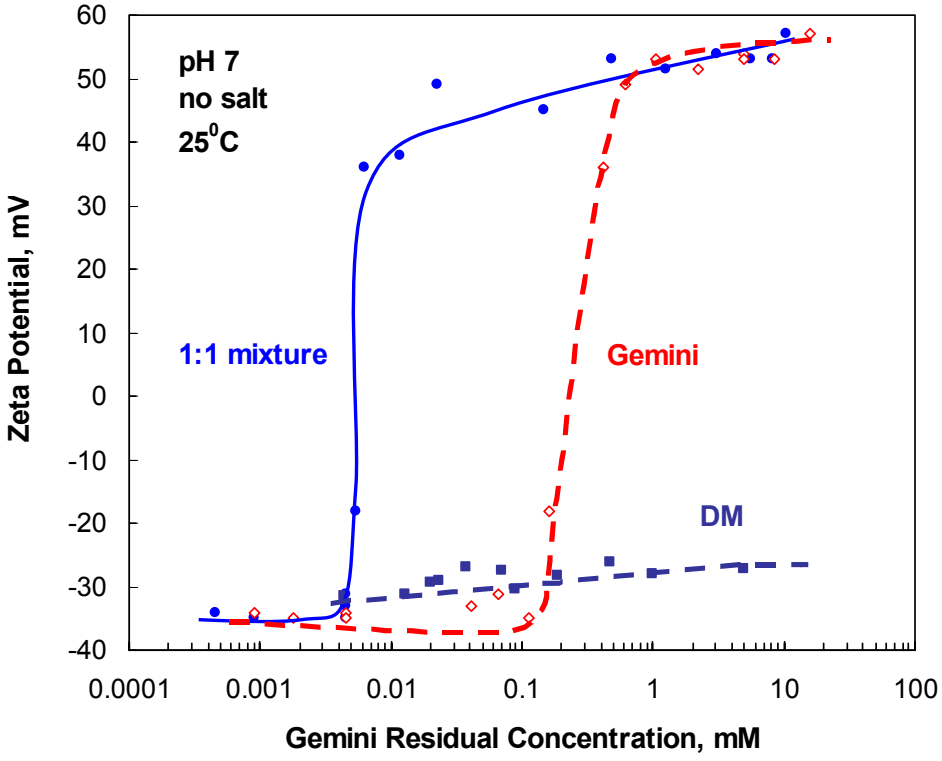

Figure 12. Effect of Gemini residual concentration on the zeta potential of silica due to mixture adsorption, pH 7, 25^{0}C, and no swamping amounts of salt.

SUMMARY AND CONCLUSIONS

During this period, we characterized the properties of the minerals, for particle size distribution and surface area. We also synthesized a series of novel cationic Gemini surfactants: butane-1,4-bis(quaternary ammonium chloride), C_n-C_4-C_n, n indicating the alkyl chain length. Adsorption behavior of individual surfactants (sugar-based n-dodecyl-β-D-maltoside (DM), Gemini C_{12}-C_4-C_{12}) and their mixtures on well-characterized silica mineral have been measured. Electrokinetics of mineral particles after adsorption has also been monitored to help elucidate the mechanisms of surfactant adsorption.

Cationic Gemini C_{12}-C_4-C_{12}, a dimeric form of the single chain surfactant dodecyl trimethyl ammonium chloride (DTAC), shows marked adsorption on the silica even at very low concentrations, compared to DTAC. Solution pH plays an important role on the adsorption of Gemini C_{12}-C_4-C_{12} on silica. Increase in pH increases C_{12}-C_4-C_{12} adsorption density due to the increased electrostatic adsorption of the Gemini on oppositely charged silica.

At pH 7, fairly low adsorption of n-dodecyl-β-D-maltoside (DM) on silica was observed. When mixed with cationic Gemini C_{12}-C_4-C_{12}, a sharp increase in the adsorption of DM, with reversed "S"-shaped adsorption in the rising part of the isotherm occurred. This phenomenon, not observed in the mixtures of DM with corresponding conventional cationic DTAC, is proposed to be the result of the unique molecular structure of Gemini C_{12}-C_4-C_{12}. The presence of the double hydrophobic chain in the cationic Gemini C_{12}-C_4-C_{12} produces a much stronger hydrophobic chain-chain interaction. Meanwhile, adsorption of C_{12}-C_4-C_{12} acting as nuclei (anchors) to form mixed aggregates with DM on mineral surface is considered to be an important factor for the marked adsorption synergy. The observed synergy was confirmed by the measurements of zeta potential change of the silica due to mixture adsorption.

Adsorption of Gemini C_{12}-C_4-C_{12} from its mixtures with n-dodecyl-β-D-maltoside increases in the rising part of the isotherm, due to the same reason mentioned above, i.e. hydrophobic chain-chain interaction. In the plateau adsorption region, competition for adsorption sites from DM resulted in decreased C_{12}-C_4-C_{12} adsorption. 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, appears to be a promising approach to achieve cost-efficient chemical flooding processes since high surfactant content formulations are normally used in EOR.

FUTURE PLANS

For task 1:

- Solution behavior of cationic Gemini C_{12}-C_4-C_{12}, DM and their mixtures (including polymer): surface tension and micellization/aggregation properties, by techniques of surface tensiometry, fluorescence and electro spin resonance (ESR).
- Interactions of minerals with surfactant-polymer systems: adsorption of mixed systems (Gemini C_{12}-C_4-C_{12}, DM and polymer) at different mixing ratios, their corresponding electropheresis tests and wettability measurements.
- Finishing characterization of minerals for sandstone, limestone, gypsum and pyrite.

For task 2:

- Effects of dissolved species (multivalent and univalent ions, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, SO_4^{2-} etc.) on the adsorption of surfactant-polymer on minerals: adsorption, abstraction and precipitation studies.

Publications and presentations

1. R. Zhang, L. Zhang and P. Somasundaran, "Surface tension and fluorescence study of n-dodecyl-β-D-maltoside (DM) with anionic, cationic and nonionic surfactant mixtures in aqueous solutions", Journal of Colloid and Interface Science, accepted.

2. R. Zhang, P. Somasundaran, "Abnormal micellar growth in sugar-based and ethoxylated nonionic surfactant and their mixtures in dilute regimes using analytical ultracentrigation", Langmuir, submitted.

3. P. Somasundaran and Qiong Zhou, "Environmentally Benign Surfactants For Efficient Enhanced Oil Recovery", *Second Joint DOE U.S.-People's Republic of China (PRC) Conference on Clean Energy,* Washington DC, November 2003.

4. Qiong Zhou and P. Somasundaran, "Mineral-Surfactant Interactions and Environmentally Benign Surfactants for Efficient Enhanced Oil Recovery", 8th International Symposium on Reservoir Wettability, Houston, TX, May 2004, accepted.