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

TECHNICAL PROGRESS REPORT

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DISCLAIMER

ABSTRACT

In this project, fundamental studies were conducted to understand the mechanism of the interactions between polymer/surfactant and minerals with the aim of minimizing chemical loss by adsorption. The effects of chemical molecular structure on critical solid/liquid interfacial properties such as adsorption, wettability and surface tension in mineral/surfactant systems were investigated. The final aim is to build a guideline to design optimal polymer/surfactant formula based on the understanding of adsorption and orientation of surfactants and their aggregates at solid/liquid interface.

During this period, the adsorption of mixed system of n-dodecyl-β-D-maltoside (DM) and dodecyl sulfonate ($C_{12}SO_3Na$) was studied. Along with these adsorption studies, changes in mineral wettability due to the adsorption were determined under relevant conditions. pH was found to play a critical role in controlling total adsorption and mineral wattability. Previous studies have suggested significant surfactant loss by adsorption at neutral pH. But at certain pH, bilayer was found at lower adsorption density, which is beneficial for enhanced oil recovery.

Analytical ultracentrifuge technique was successfully employed to study the micellization of DM/$C_{12}SO_3Na$ mixtures. Compositional changes of the aggregates in solution were observed when two species were mixed. Surfactant mixture micellization affects the conformation and orientation of adsorption layer at mineral/water interface and thus the wettability and as a result, the oil release efficiency of the chemical flooding processes.

Three surfactants $C_{12}SO_{3,}$ AOT and SLE3 and one polymer were selected into three different binary combinations. Equilibrium surface tension measurement revealed complexation of polymer/surfactant under different conditions. Except for one combination of SLE3/ PVCAP, complexation was observed. It is to be noted that such complexation is relevant to both

interfacial properties such as adsorption and wettability as well as rheology. Higher activity of the polymer/surfactant complexes is beneficial for EOR.

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INTRODUCTION

Surfactant/polymer flooding is one of the promising techniques to recover residual oil from domestic oil reservoirs, but a major problem in the use of it is the chemical loss during the flooding process due to the adsorption and precipitation in the reservoirs. The aim of this project is to conduct systematic studies on the interactions between polymers and surfactants in the bulk fluids and at mineral/fluid interfaces in enhanced oil recovery systems. It is known that polymers and surfactants can interact with each other to form aggregates or complexes in solutions and at solid/liquid interfaces and such interactions can dramatically affect the performance of the oil recovery processes. It is therefore a major aim also to understand the mechanisms of such aggregation.

During the previous reporting period, we completed the adsorption of surfactant mixtures of dodecyl maltoside and dodecyl sulfonate on mineral surface. Adsorption isotherms along with hydrophobicity determination revealed interesting relationships among adsorption density, wettability and fluid properties. Adsorption tests were conducted with mixtures of sodium dodecyl sulfonate and sugar-based n-dodecyl-β-D-maltoside (DM) on alumina minerals at different surfactant mixing ratios and pHs. Wettability changes of solid surface , determined for the same system suggested formation of water wetted bilayers under certain conditions, which is beneficial to oil recovery. Also, solution behavior of DM/$C_{12}SO_3Na$ mixture was investigated by pyrene probe fluorescence technique and analytical ultracentrifugation to determine the nature of surfactant interactions in the bulk solution. Different types of micellar aggregates were found at different mixing ratios and concentrations.

During this period, we focused on polymer/surfactant interactions in terms of solution properties. Three surfactants and one polymer were selected for the study using surface tensiometry and analytical ultracentrifuge. In the two of the three groups studied, formation of polymer/surfactant complexes was observed, the nature of complexes being depended on the structure of the polymers and surfactants. Equilibrium surface tension results showed that the surface activity of surfactant solution was reduced due to its binding to the polymer, with saturation adsorption at air/water interface shifted with polymer addition to higher concentrations. Critical concentration, below which no visible binding was observed, was also determined. The presence of the polymer also reduced the adsorption of surfactant on mineral surface under certain conditions. It is noted that all the phenomena mentioned above, particularly reduction of adsorption and polymer surfactant complexation leading to changes in sur adsorption and rheology, will 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 ($C_{12}SO_3Na$) of ≥99.0 purity purchased from TCI Chemicals, Japan, sodium bis(2-ethylhexyl) sulfosuccinate (AOT) of purity ≥99.0 (using TLC), were purchased from Fluka. Disodium laureth 3 sulfosuccinate (SLE3) in aqueous solution form, supplied by Rodia, 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.

Polymers

Poly(vinylcaprolactam) (PVCAP) was provided by International Specialty Products Corporation.

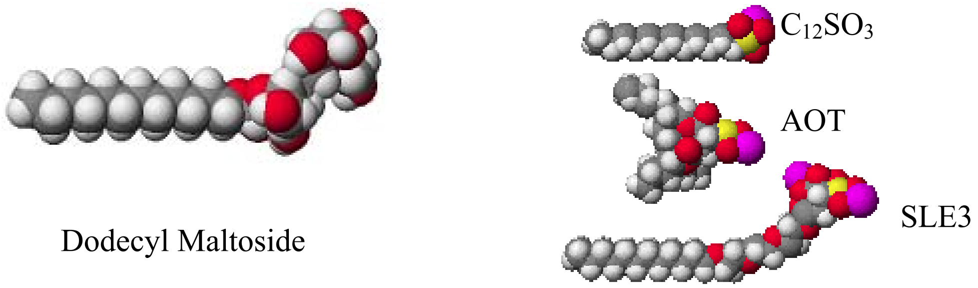
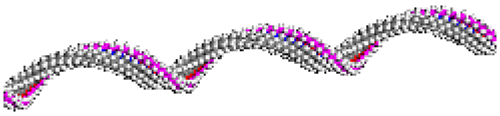


Figure 1 molecular structure of surfactants used during this period.



PVCAP

Figure 2 molecular structure of polymer used during this period.

Mineral Samples:

Solid substrate used during the current period is alumina AKP-50 obtained from Sumitomo. It has a mean diameter of 0.2 μm. And the BET specific surface area of 10.8 m^2/g measured using nitrogen/helium with a Quantasorb system. Its isoelectric point (iep) was determined to be 8.9.

Other Reagents:

HCl and NaOH, used for pH adjustment, 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 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 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 hydrophobicity values were calculated using the equation:

$$Hydrophobicity = \frac{Weight \quad of \quad Particles \quad in \quad Toluene}{Total \quad Particle \quad Weight} \tag{1}$$

Surface tension

The surface tension was measured at 25±1˚C using the Wilhelmy plate technique with a sandblasted platinum plate as the sensor coupled to a Cahn microbalance. The entire assembly was kept in a draft-free plastic cage at a temperature of $25 \pm 0.05\ ^{0}$C. For each measurement, the sensor was in contact with the solution for 30 minutes to allow equilibration.

Analytical Techniques

The residual concentration of the anionic surfactant after adsorption was determined 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 concentration of the individual component surfactant, which were measured by either the two-phase titration or the colorimetric method.

Steady-state Fluorescence Experiments

Steady-state emission spectra were obtained using a Horiba Jobin Yvon Fluorolog FL-1039 spectrophotometer. The samples were excited at 335 nm and their emission between 360 and 500 nm were recorded.

Analytical Ultracentrifuge

A Beckman Optima XL-1 analytical ultracentrifuge with scanning optics with an interference systems was employed to perform sedimentation velocity experiments. The interference optical system provides total concentration by measuring the refractive index difference between the sample cell and the reference cell at each radial position as indicated by the vertical displacement of a set of evenly spaced horizontal fringe. The running condition was set at a motor speed 40,000 rpm, and the temperature at 25^{o}C. Software *Sedfit* developed by Peter Shuck was used to analyze the sedimentation data.

RESULTS AND DISCUSSIONS

1. Surfactant mixture adsorption on alumina

Adsorption of mixed dodecyl maltoside(DM) and dodecyl sulfonate on alumina was measured by depletion technique and the results are shown in figure 3~5. The initial surfactant concentration was maintained at 6 mM. Figure 3 shows that the adsorption density of DM increases with DM ratio but decreases at pH 4. It is known that DM at pH 4 has only 2% adsorption of that at pH 7, but in the presence of dodecyl sulfonate it adsorbs at pH 4 as much as at higher pH due to the hydrophobic chain-chain interaction and neutralization of alumina surface by sulfonate adsorption. Below a ratio 0.60, DM has almost the same adsorption density at pH 4 and 7, but the adsorption decreases sharply due to the absence of deodecyl sulfonate above this ratio. On the other hand, the adsorption density at pH 10 lies below that at pH 7, regardless of the fact that the adsorption isotherms of DM are identical in the pH range of 7~10. The dodecyl sulfonate in the adsorped layer interferes with the packing of DM molecules and thus reduces its adsorption density. The role of packing of surfactant molecules in the aggregate in determining adsorption should be noted.

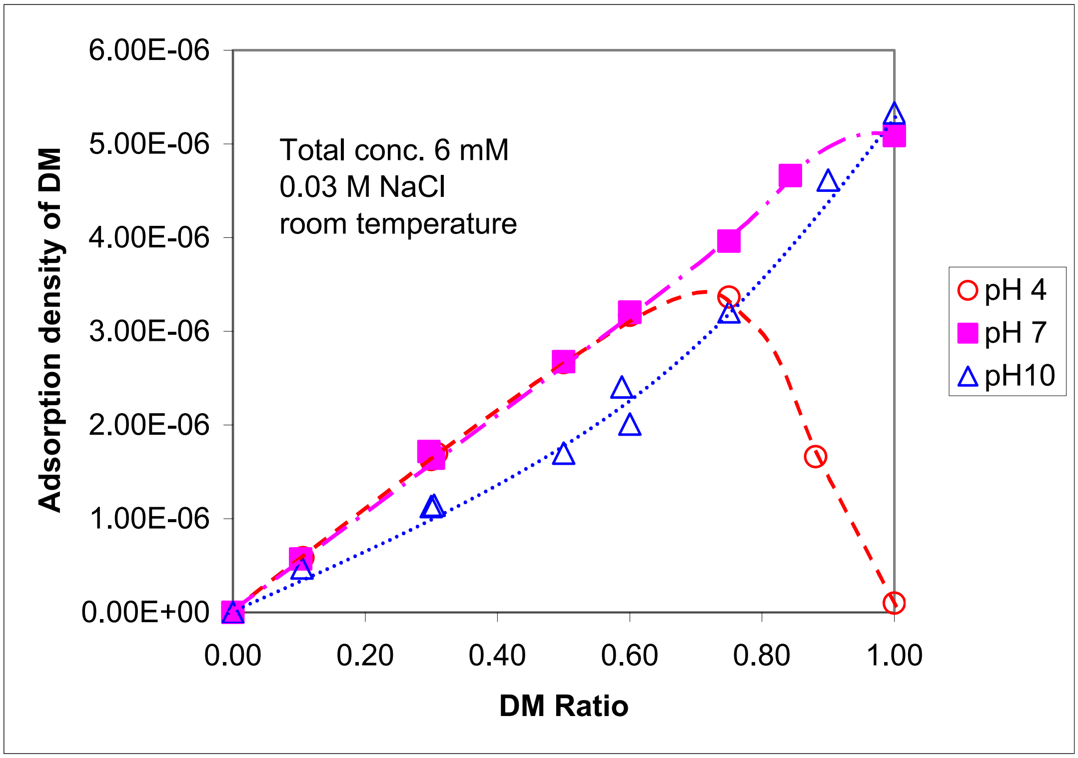


Figure 3 Adsorption of dodecyl maltoside on alumina as a function of mixing ratio at different pH.

Adsorption density of dodecyl sulfonate in the same experimental system was also determined and the results are shown in figure 4. The most significant observation is that dodecyl sulfonate does adsorb on the negatively charged alumina at pH 10 in the presence of dodecyl maltoside in comparison to zero adsorption density of dodecyl sulfonate when present alone. It is proposed that coadsorption takes place due to the hydrophobic chain-chain interaction between dodecyl maltoside and dodecyl sulfonate chains with the nonionic DM oriented towards the alumina and dodecyl sulfonate oriented towards the bulk in order to minimize electrostatic repulsion force between the anionic head group and the negatively charged alumina. The hydrophobicity results discussed below supports the above hypothesis and shows the relevance of such oriented adsorption to controlling mineral wettability. Higher total adsorption at pH 4 than pH 7 is because of the higher the positive charge density on the solid surface at lower pH.

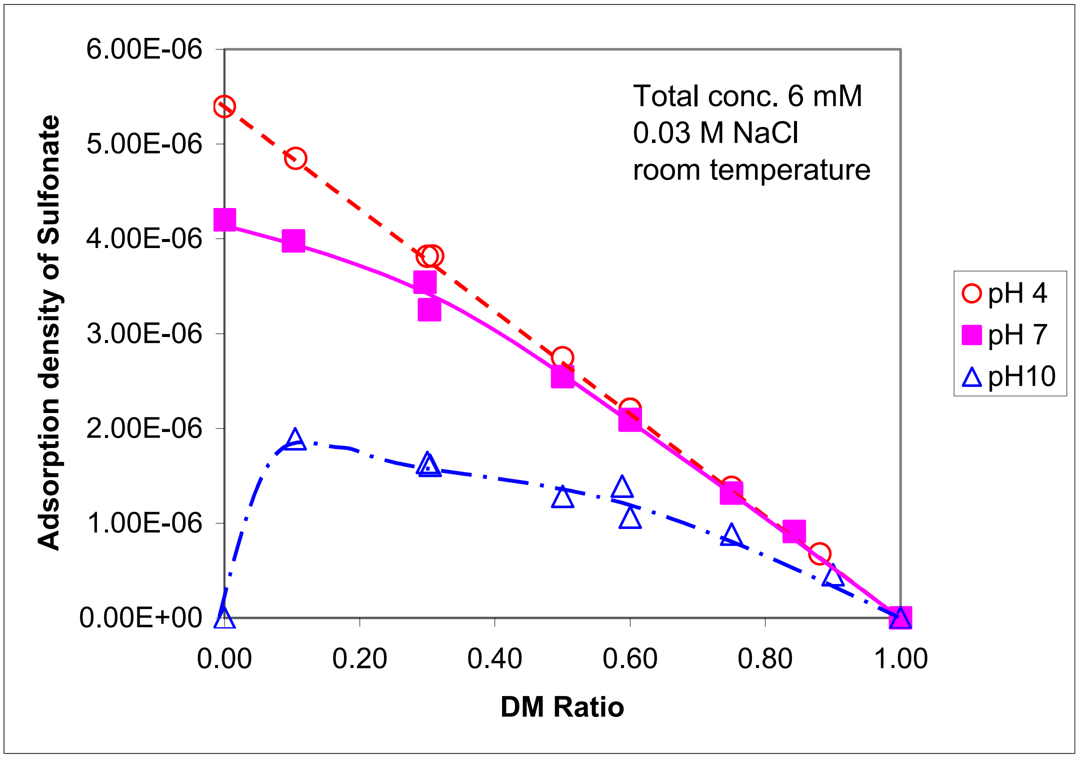


Figure 4 Adsorption of dodecyl sulfonate on alumina as a function of mixing ratio at different pH.

The total adsorption of both surfactants was summed in figure 5. The results reveal how the total adsorption is affected by pH and mixing ratio. At pH 4, adsorption decreases sharply above ratio 0.6, because DM alone has little ability to adsorb. At pH 7, adsorption keeps increasing slowly with DM ratio because DM has a more compact aggregate structure than the dodecyl sulfonate aggregates at water/alumina interface. On the other hand, at pH 10, because dodecyl sulfonate blocks the packing of dodecyl maltoside, the total adsorption is reduced remarkably. Obviously, the total adsorption or each individual surfactant adsorption can be easily controlled by changing the pH and the mixing ratio. This is of importance for enhanced oil recovery. For example, at pH 10, passive dodecyl sulfonate dramatically decreases the adsorption of dodecyl maltoside, which is more expensive than dodecyl sulfonate. Based on the adsorption mechanism and the quantitative analysis, the solution parameters and mixing ratio could be optimized to reduce the cost and improve the performance of surfactant mixtures in oil recovery.

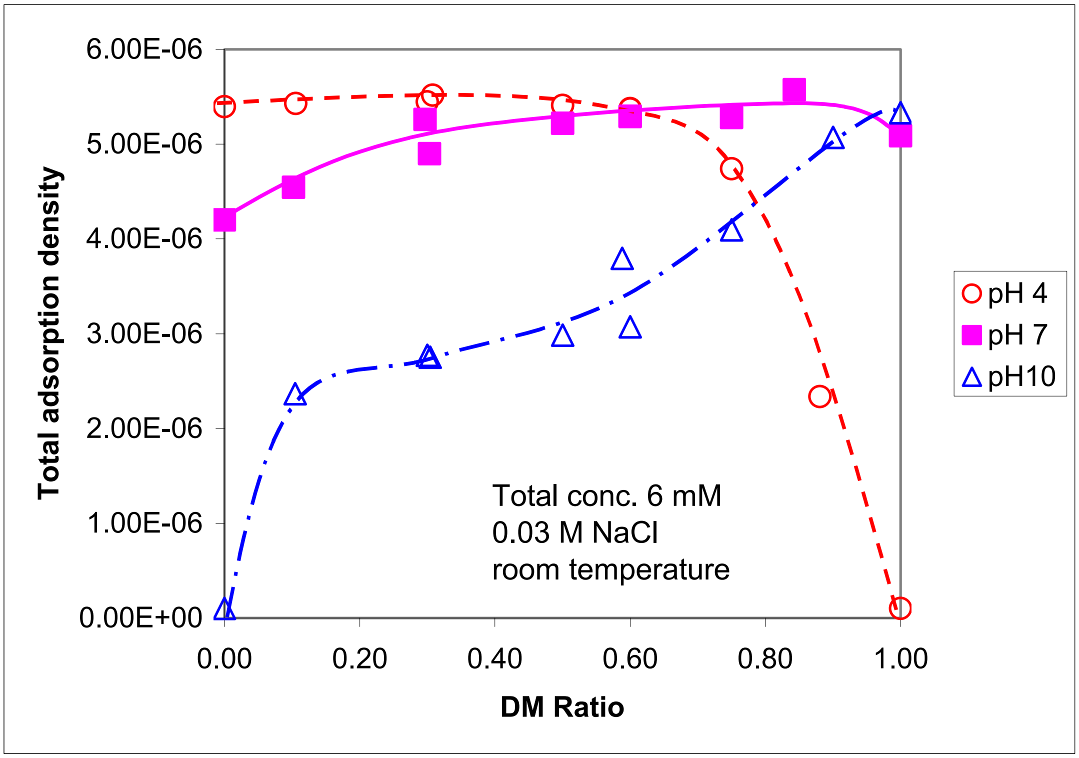


Figure 5 Total adsorption on alumina as a function of mixing ratio at different pH.

2) Hydrophobicity of alumina with mixture surfactant adsorption on surface.

Hydrophobicity of alumina particles with surfactant adsorption on surface was determined by two-phase extraction method. The result is plotted with adsorption density in figure 6~8. The forming of bilayer makes the solid surface hydrophilic at low DM ratio, but, with decrease in adsorption density, alumina particle becomes hydrophobic and reverts to hydrophilic again. At low DM ratio, the solid surface is occupied fully by surfactant molecules, which then forms a bilayer with head groups oriented toward bulk solution and thus make solid surface hydrophilic.

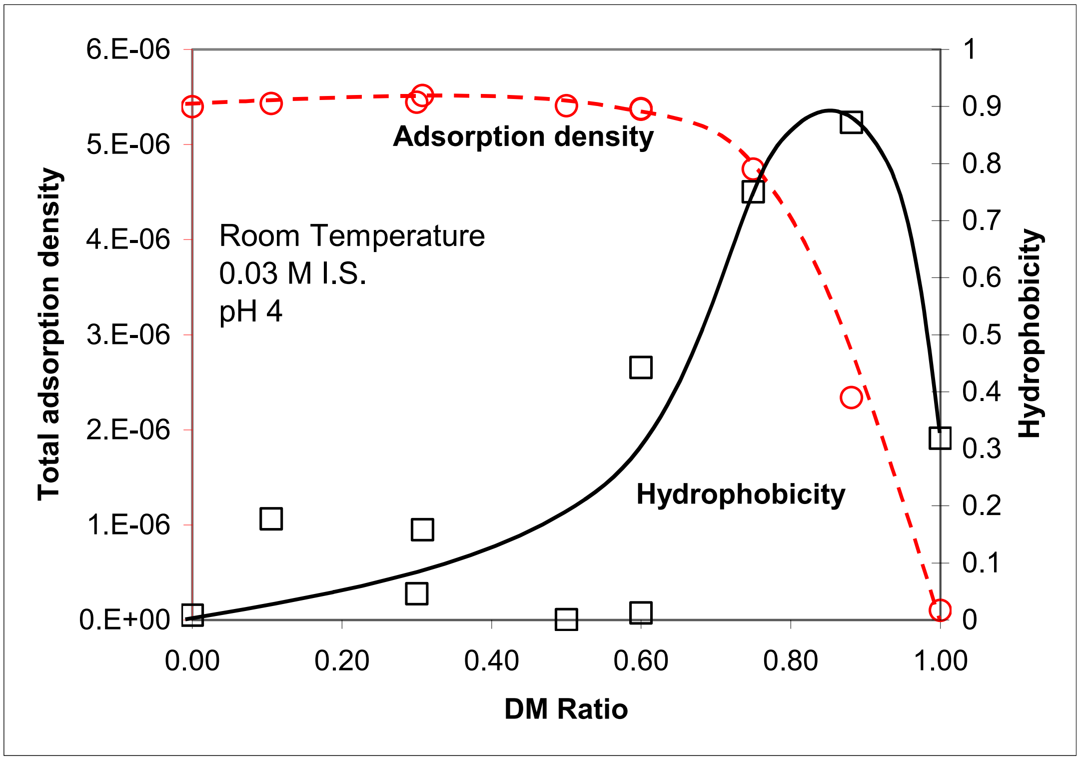


Figure 6 Hydrophobicity of alumina particles with surfactant adsorption at pH4.

Hydrophobicity of alumina particles at different mixing ratios are shown in figures 7 and 8 for pH 7 and 10 respectively. At pH 7, total adsorption density is at a relatively higher level of around 5×10^{-6}mol/L, at which a bilayer should form according to the cross sectional areas of dodecyl maltoside and dodecyl sulfonate as determined from surface tension measurement. In the case of ratio of >0.50, the mineral surface is hydrophilic, which is conducive for the release of trapped oil from the surface of the minerals. Results obtained at pH 10 are shown in figure 8. The total adsorption density is less than 50% of that at pH 7 below a mixing ratio of 0.6, but the mineral surface is surprisingly hydrophilic, which suggests that the head groups of surfactant molecules are orienting towards the bulk solution. This condition is again beneficial for efficient chemical flooding.

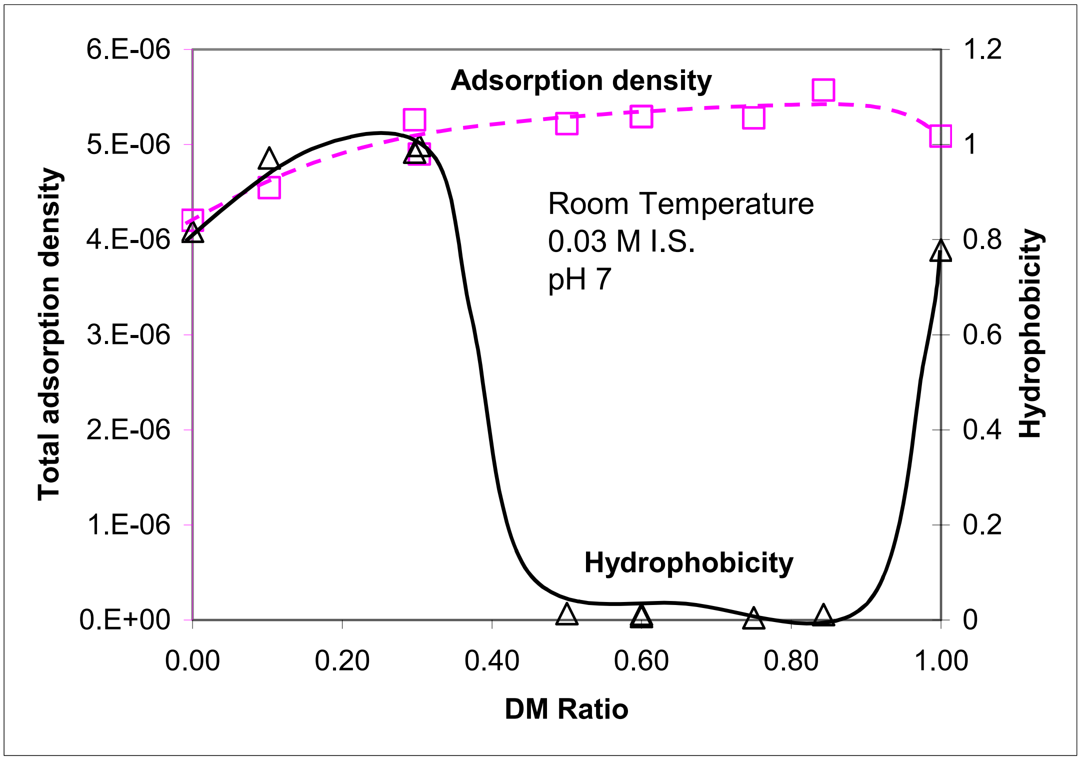


Figure 7 Hydrophobicity of alumina particles with surfactant adsorption at pH7.

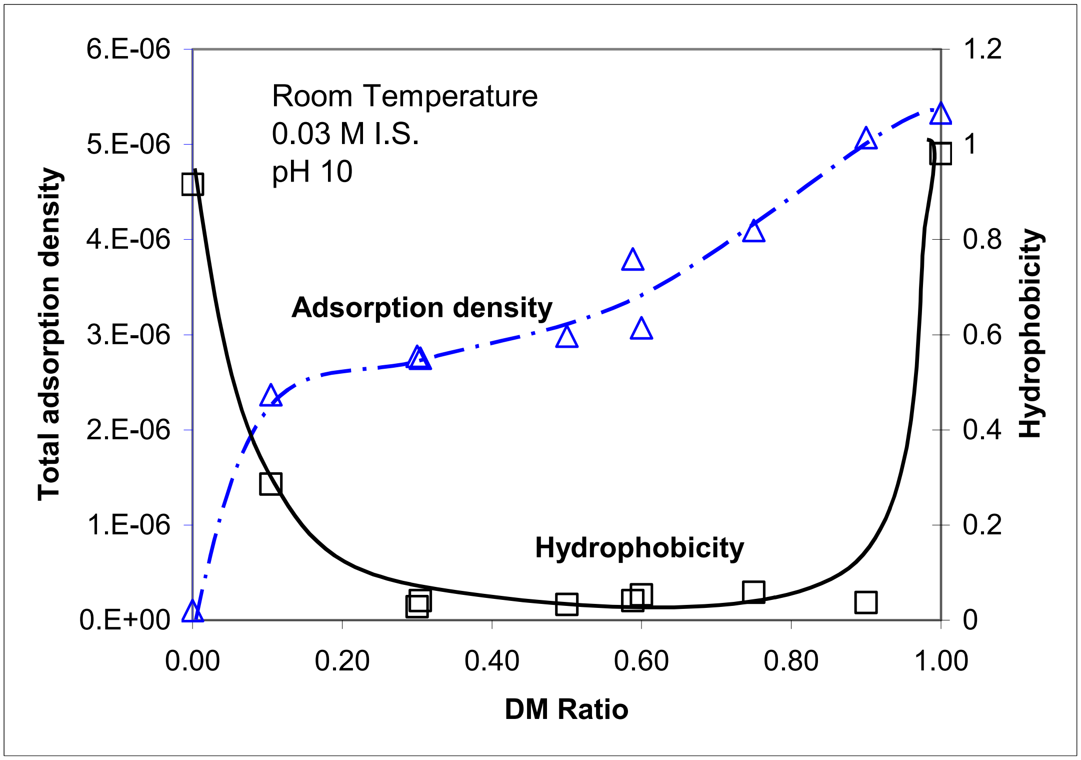


Figure 8 Hydrophobicity of alumina particles with surfactant adsorption at pH10.

3. Surfactant mixture studied by pyrene probe fluorescence spectroscopy

In the previous project periods, fluorescence spectroscopic technique was successfully employed to obtain basic information on the structure of the micelles of mixed surfactants. During this period, dodecyl maltoside/$C_{12}SO_3Na$ mixture system was studied to reveal the mechanism of adsorption and performance. 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 dependency of environment around the probe. This ratio decreases as the polarity increases and can be used to estimate the polarity of the environment and thus detect the presence of surfactant aggregate in solution. The polarity parameter of pyrene is shown in Figure 12 as a function of surfactant concentration. At low concentration for each system, the value of I_3/I_1 ratio corresponds to that of 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.

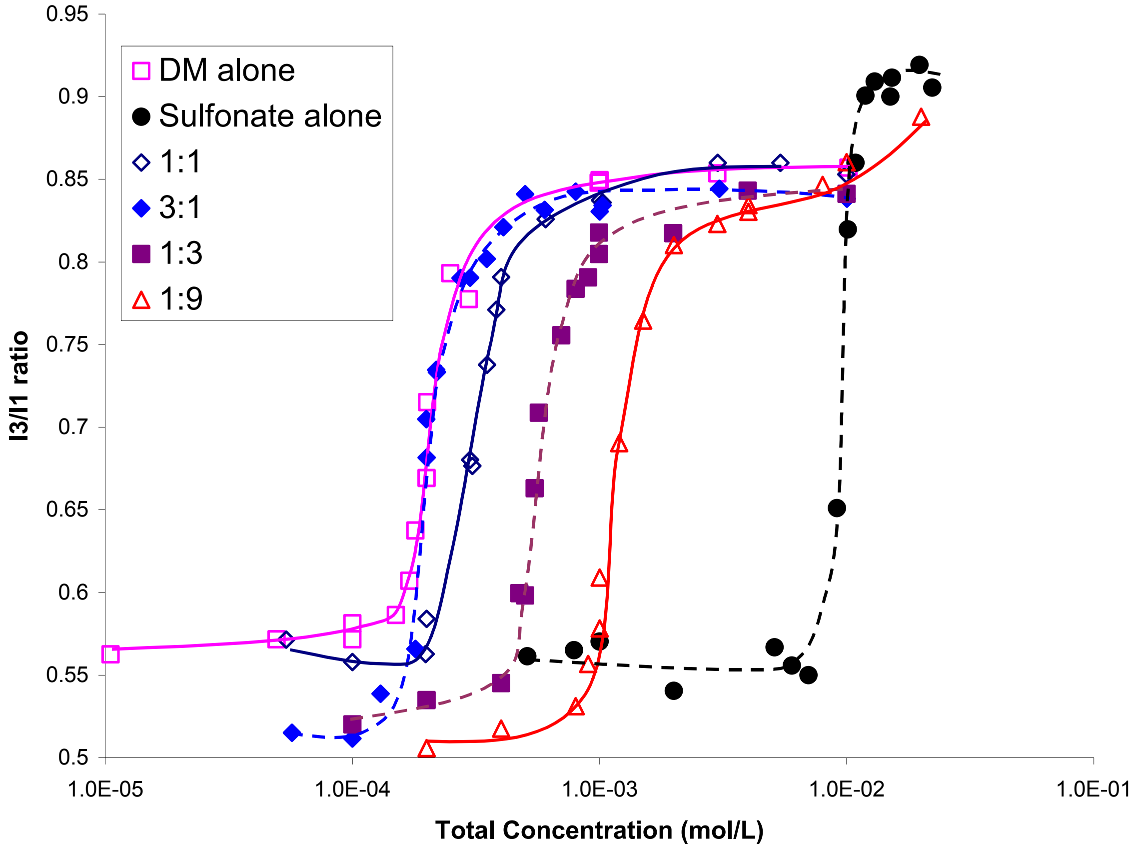


Figure 12 Variation of solution polarity, as indicated by I3/I1 ratio, at different mixing ratios.

The polarity parameter of the pyrene at concentrations higher than cmc provides information on the hydrophobicity and thereby the structure of the micelles. In DM/ C12SO3Na system, I_3/I_1 ratio for $C_{12}SO_3Na$ is higher than that for DM above cmc, suggesting that the core of dodecyl maltoside micelles is more hydrophobic than that of DM micelles, but less hydrophobic than that of pure hydrocarbons. I3/I1 polarity parameter of the micelles decreases with increase in dodecyl sulfonate ratio in the mixtures below a certain concentration. The polarity parameter however increases and gets close to the value of dodecyl sulfonate alone above a certain concentration, at which the transition from dodecyl maltoside rich micelles to dodecyl sulfonate rich micelles happens. 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 difference in surface activity of the components in the mixtures.

4. Polymer-surfactant interactions at air/solution interface

In polymer/surfactant flooding system, the interactions between them control their surface activity and performance. During this period, PVCAP/ $C_{12}SO_3$, PVCAP/AOT and PVCAP/SLE3 were studied by surface tension measurements to understand the micellization of surfactants in the presence of polymers.

Surface tension of C12SO3 with and without 1000ppm PVCAP in 0.03M NaCl medium is plotted in Figure 9 as a function of the surfactant concentration. For the C12SO3 surfactant alone, the surface tension curve yields a cmc of 3 ± 0.2mM. The presence of PVCAP lowered the surface activity even below the cmc of C12SO3, suggesting cooperative binding on the PVCAP polymer. Due to the solubility limit of the surfactant saturation binding above that free surfactant micelles form in the bulk phase could not be reached.

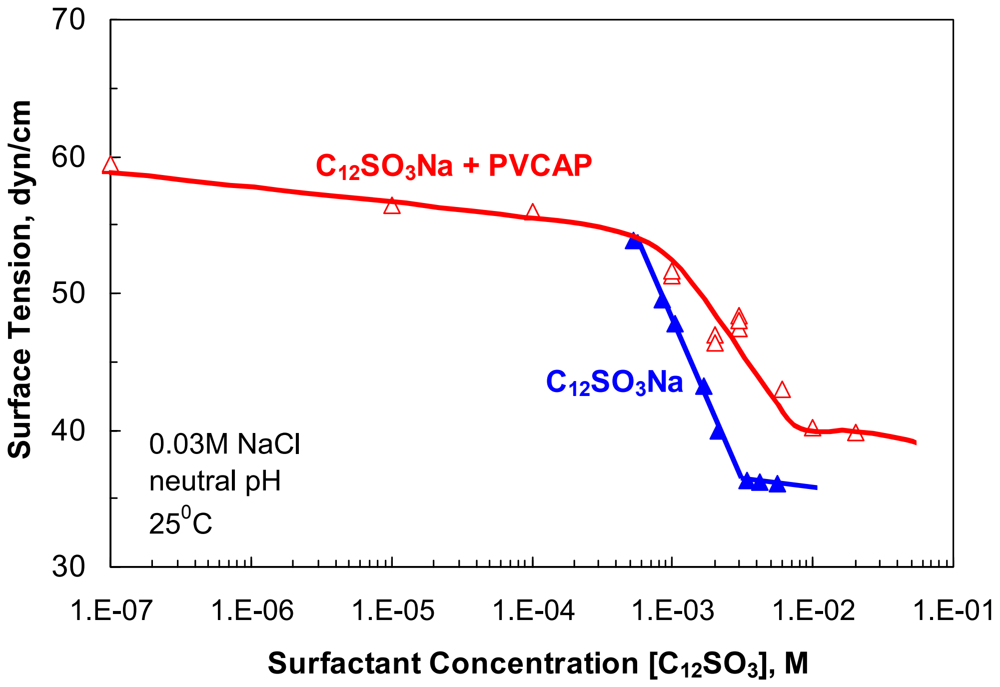


Figure 9. Equilibrium surface tension of C12SO3Na alone(filled triangles) and the corresponding mixtures with 1000ppm PVCAP (open triangles) in 0.03M NaCl.

Similar observations were made for the surface tension of branched, AOT, in the presence of polymer PVCAP. Binding of AOT to the polymer begins at a concentration below the cmc, resulting in its lower surface activity (Figure 10). Unlike the previous mixture, there is, however no clear point on the surface tension curve indicating the critical aggregation concentration (cac) for AOT in the presence of PVCAP. Decrease of the surface activity is determined by the binding strength of the surfactant on PVCAP. The more the surfactant binding on PVCAP, the greater is the decrease in the surface activity.

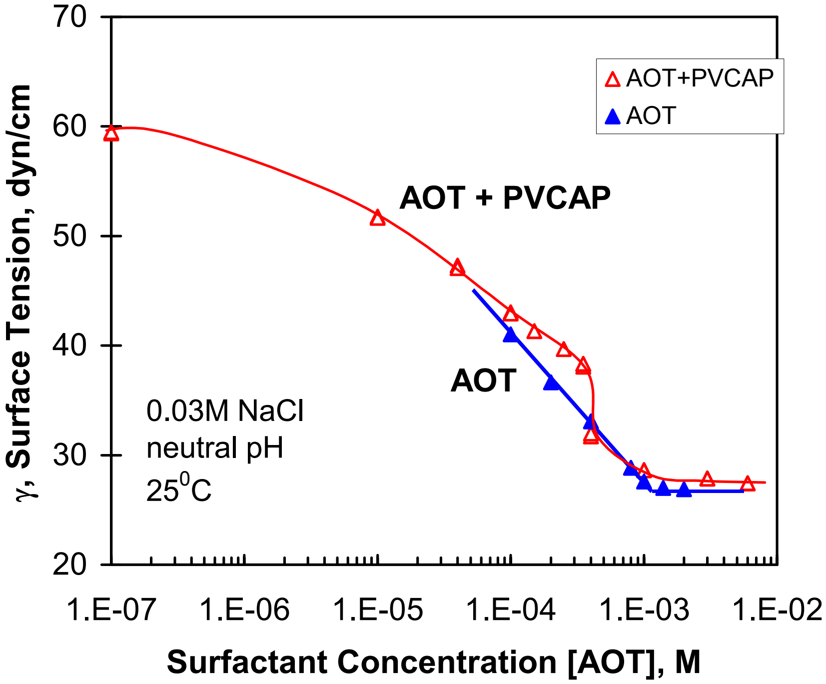


Figure 10. Equilibrium surface tension of AOT alone(filled triangles) and the corresponding mixtures with 1000ppm PVCAP (open triangles) in 0.03M NaCl.

In the case of SLE3 with the insertion of ethylene oxide units and double-charged headgroup, a very different behavior than those of AOT and C12SO3 was observed at concentrations below cmc (Figure 11). The same surface activity was obtained for the mixture and for SLE3 surfactant alone, suggesting absence of any cooperative binding of SLE3 surfactant to PVCAP polymer below cmc. Above the surfactant cmc, a gradual decrease in the surface activity resulted in considerable micellar interaction between SLE3 surfactant and PVCAP polymer. Evidently, for the SLE3, the presence of ethylene oxide units and double-charged headgroup makes the formation of surfactant micelles more favorable than those of polymer-surfactant complexes.

Thus depending on the structure of the surfactant, the polymer-surfactant complexes, as in the case of AOT and $C_{12}SO_{3}$, can be more surface active than the surfactant and act together with the surfactants at the air/aqueous solution interface to reduce the interfacial tension. Such higher surface activity of the polymer-surfactant at water-air interface and therefore possibly at the water-oil interface would be beneficial for enhanced oil recovery.

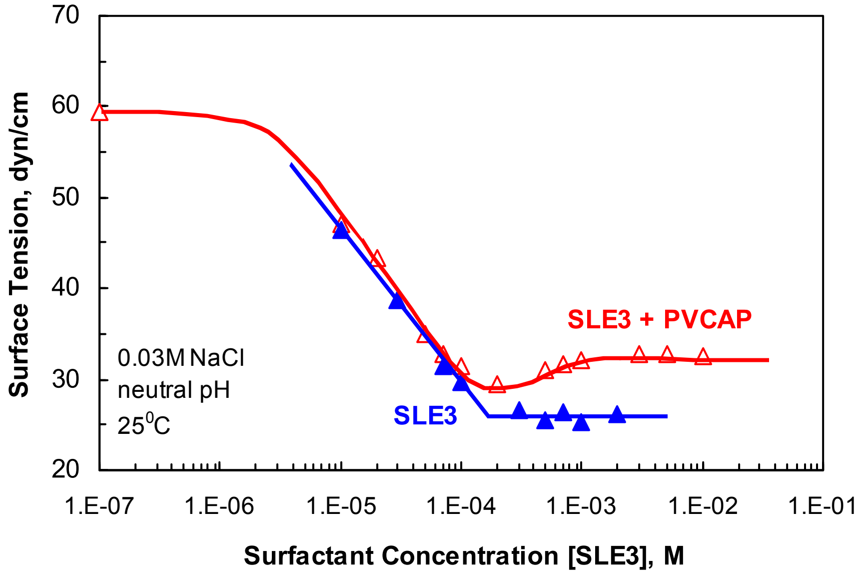


Figure 11. Equilibrium surface tension of SLE3 alone(filled triangles) and the corresponding mixtures with 1000ppm PVCAP (open triangles) in 0.03M NaCl.

5). Micellization of surfactant mixture in solution studied by analytical ultracentrifuge (AUC).

Analytical ultracentrifuge was employed to elucidate surfactant micellar information in terms of aggregate number, micelle size and shape, etc. The experiments were run at 40000 rpm and 25.0 ℃. The sedimentation velocity curves were scanned for 15 hours. Afterwards, the results were analyzed using software. By fitting the velocity curves, the distribution of sedimentation coefficient for DM alone, sulfonate alone and their 1:1 mixture were obtained and shown below. As a nonionic surfactant, DM forms much bigger micelles than dodecyl sulfonate; this is attributed to the electrostatic repulsion among dodecyl sulfonate head groups that limits micellar growth.

Information about micelles of DM/ C12SO3Na system obtained from the analytical ultracentrifuge are summarized in table 1. Interestingly, these two surfactants have very close specific volumes, but form very different micelles. The aggregate numbers are 106, 46.1 and 19.3 for DM, 1:1 mixture and dodecyl sulfonate respectively.

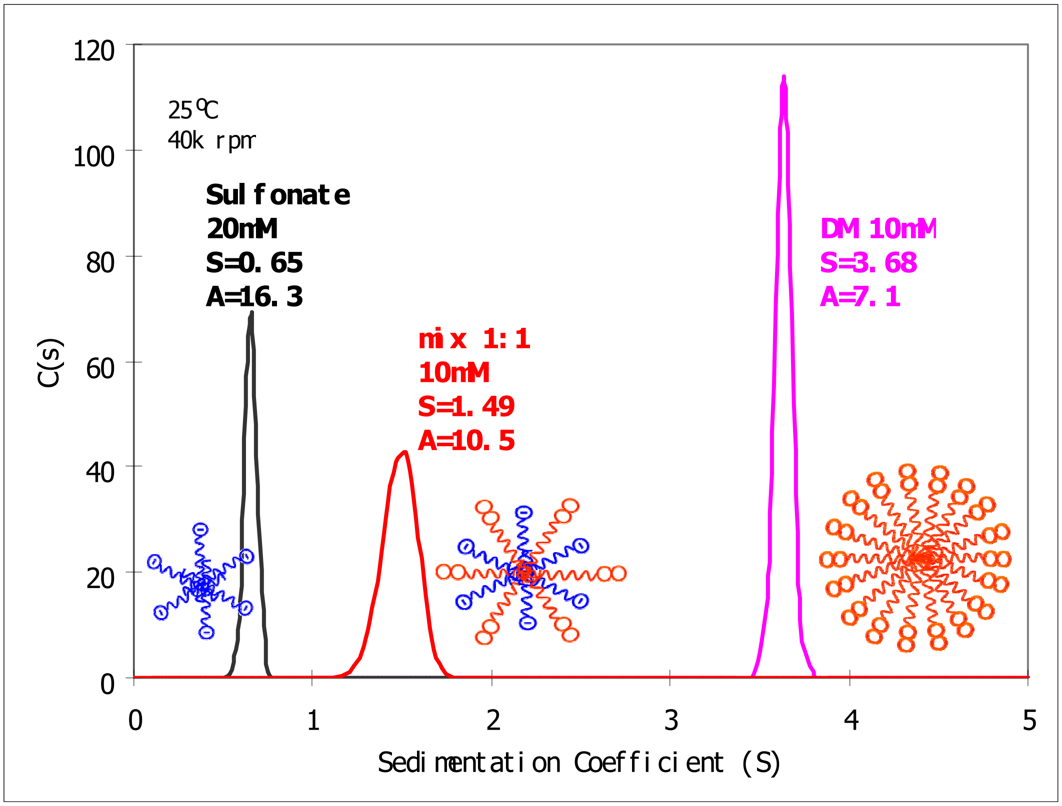


Figure 13 Distribution of sedimentation coefficient of DM/ C12SO3Na system.

Table 1. Parameters of DM/ C12SO3Na system obtained from analytical ultracentrifuge.

DM / Sulfonate	DM alone	1:1 mixture	Sulfonate alone
Specific Volume(ml/g)	0.833	0.830	0.826
S* (Svedberg)	3.68	1.49	0.65
M (g/mol micelles)	54139	18030	5248
Nagg	106	46.1	19.3
Diameter (nm)	5.24	3.62	2.40
Diffusion Coefficient D ($\times 10^{11}$ m^2/s)	8.39	10.13	15.3

SUMMARY AND CONCLUSIONS

Adsorption of surfactant mixtures, wettability changes of minerals and complexation of polymer/surfactant mixtures were investigated during this period to elucidate the mechanisms of interactions from the fundamental point views of molecular structures. Different combinations of polymer/surfactant showed different solution properties.

In surfactant mixture adsorption, active/passive combination was found beneficial to oil recovery. The roles of electrostatic force, hydrogen bonding and hydrocarbon chain-chain interaction were located under different conditions. Our previous results showed the switchablilty between active and passive state triggered by pH changes. At pH 10, the total adsorption density is only 50% of that at other pHs but the bilayer was formed because the head groups of passive dodecyl sulfonate molecules toward water bulk due to the electrostatic repulsion between negatively charged mineral surface and nagative heard group.

Polarity results measured by fluorescence are in good agreement with previous surface tension measurement. The CMC values of surfactant mixtures were also determined from the I3/I1 ratio vs concentration plots. The results showed different microenvironments in different micelles. Dodecyl Sulfonate shows a higher polar micellar core than dodecyl maltoside. In case of mixture, when dodecyl sulfonate molecules dominate in micellar structure, the packing conformation is close to that of dodecyl sulfonate alone.

The surface activity is the same for Disodium laureth 3 sulfosuccinate in the absence and presence of PVCAP because no complex formed between them.

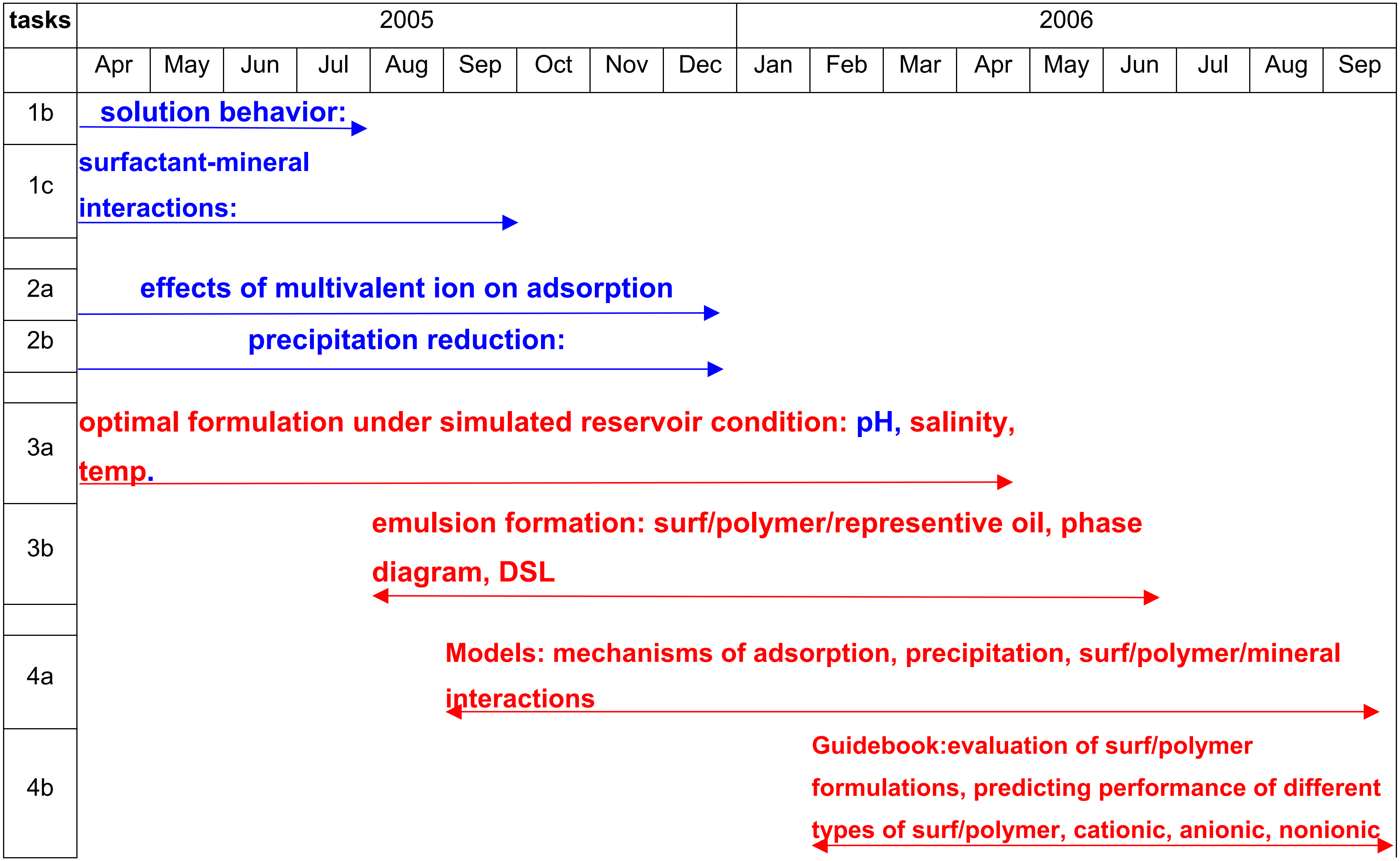
Analytical ultracentrifuge was successfully employed to elucidate the micellar information of DM/ C12SO3Na system. Sedimentation coefficient, aggregate number, diameter of micelles and diffusion coefficient of micelles were obtained for surfactant individuals and mixtures. It was found that micelles in surfactant mixture in middle of individuals.

All these fundamental studied showed the mechanisms of surfactant/surfactant and polymer/surfactant interactions. Based on this information, the design and screen of chemical formula in oil recovery will be optimized.

The polymer/surfactant systems (PVCAP+ C12SO3, AOT, SLE3) showed the polymer-surfactant complexes to be more surface active than the surfactant except for the case of PVCAP / SLE3. Such higher surface activity, that is beneficial for EOR, can thus be obtained by designing the surfactant structure.

DOE Timeline: Mineral-Surfactant Interactions for Minimum Reagent Loss in IOR

tasks	2003			2004												2005		
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar
1a	mineral characterization: SEM, BET, size, surface charge, pzc.																	
1b				solution behaviors: surface tension, interaction, AUC, ultrafiltration, fluorescence for surf/surf mixtures; surface tension, interaction, ultrafiltration for surf/polymer mixtures.														
1c					surfactant-mineral interactions: adsorption, wettability, electrophoresis, SPR for surf/surf mixtures, surf/polymer mixtures.													
2a								effects of multivalent ion on adsorption: adsorption, abstraction, precipitation of surf/surf and surf/polymer mixt in Ca, Fe, SO_4, PO_3										
2b													precipitation reduction: pH, temp, salinity, mixing ratio (surf/surf, surf/polymer)					
3a																optimal formulation under reservoir condition		



1b **solution behavior:**

1c **surfactant-mineral interactions:**

2a **effects of multivalent ion on adsorption**

2b **precipitation reduction:**

3a **optimal formulation under simulated reservoir condition: pH, salinity, temp.**

3b **emulsion formation: surf/polymer/representive oil, phase diagram, DSL**

4a **Models: mechanisms of adsorption, precipitation, surf/polymer/mineral interactions**

4b **Guidebook:evaluation of surf/polymer formulations, predicting performance of different types of surf/polymer, cationic, anionic, nonionic**

Publications and Presentations

1) Shaohua Lu and P Somasundaran, Controllable synergistic or antagonistic adsorption of surfactant mixture on solids, The 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005.

2). Shaohua Lu and P Somasundaran, Mineral wettability control by optimizing adsorption of mixed surfactants, the Fifteenth SPE Improved Oil Recovery Symposium, submitted.

3) Rui Zhang and P Somasundaran Nano-structure of Mixed Surfactant Aggregates in Solution and on Minerals (for poster), the Fifteenth SPE Improved Oil Recovery Symposium, submitted.

4) Puspendu Deo; P. Somasundaran, Conformational Behavior of Hydrophobically Modified Polymers and its effect on the Stability of Emulsions and mineral wettability, the Fifteenth SPE Improved Oil Recovery Symposium, submitted.

5) Review of mineral surfactant interactions talk by P. Somasundaran. Contractor Review Meeting in DOE office, Tulsa. September, 15, 2005.

FUTURE PLANS

For task 1c:

- Investigate interactions of minerals with surfactant-polymers mixtures and at different mixing ratios, in order to select chemicals with minimum adsorption. At the same time, determine wettability change and interfacial potential change of minerals due to surfactants/polymers adsorption. The results will be analyzed to reveal the mechanism of adsorption of various chemicals on minerals. Small angle neutron scattering and reflection studies will be performed if beam time is obtained at the NIST facility instead of Surface Plasmon Resonance as our preliminary tests have shown these techniques can enable us to visualize in-situ adsorbed layer structure at a nano level that no other technique can. Adsorption studies of various chemicals will be used to screen formulations for optimum performances.

For task 2:

- 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 under various conditions will be studied. The effect of polymers on the adsorption of surfactant on various types of miners such as alumina will also be investigated. Adsorption, abstraction and precipitation studies will be conducted to find out optimum formulation to minimize the loss of chemicals due to precipitation.

For task 3:

- Selection of optimal formulations under simulated reservoir conditions: selected experiments will be conducted in the lab under representative reservoir conditions (pH, salinity and temperature) to establish the validity of the optimal processes. Phase diagram of mixtures of representative oil and optimal formulations, possibly mixtures of surfactants and polymers, will be examined to determine the possibility of formation of emulsions in the presence of dissolved multivalent ions from minerals.

For task 4:

- ❖ Develop models to obtain a better quantitatively understanding of the interaction between minerals and surfactants/polymers, the precipitation of chemical reagents due to the dissolution of multivalent ions from the minerals, and the performance of the formulations under reservoir conditions. Based on the models, a guidebook containing optimally desirable chemical combinations will be organized to facilitate the evaluation of formulations of the surfactant/polymers for different reservoir mineral environments in terms of several key parameters.