The Role of Surfactant Precipitation and Redissolution in the Adsorption of Sulfonate on Minerals

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Abstract
The presence of maxima and sometimes minima in the adsorption isotherms of surfactant on minerals has been attributed to various mechanisms involving micelle exclusion, impurities, surfactant composition, mineral morphology, etc. This study on the precipitation of sulfonates with various inorganic ions (Na, K, NH₄, Ca, Mg, and Al) and the subsequent redissolution when the surfactant concentration is increased shows a precipitation maximum to occur in the same surfactant concentration range where an adsorption maximum is obtained. Simultaneous abstraction, precipitation, and adsorption experiments have been conducted using chromatographically purified dodecylbenzenesulfonate and Na-kaolinite, and the results show the "abstraction vs. surfactant concentration" curves to exhibit a much more pronounced maximum than the real adsorption (abstraction minus precipitation) maximum. We suggest that the total abstraction of surfactant from the solution on contact with mineral phase, usually called "adsorption," is a summation of both the "real" adsorption and precipitation and that the precipitation/redissolution phenomenon is one of the major reasons for the adsorption maxima. Introduction of oil into the system reduces the precipitation because of partitioning of the sulfonate between the oil and aqueous phases. Precipitation and adsorption data are used to derive possible mechanisms for the precipitation/redissolution phenomena.

Introduction
The effect of inorganic electrolytes on the behavior of surfactants in porous media is of considerable interest since reservoir fluids contain significant amounts of various mono- and multivalent inorganic ions. Interaction of these ions with the surfactant in the bulk solution during micellar flooding can lead to surfactant precipitation and to surfactant depletion and possibly even to reservoir plugging.

Precipitation is often observed during adsorption experiments when surfactants are contacted with mineral suspensions due to the presence of inorganic ions that are added to the system or introduced by mineral dissolution. The system made up of kaolinite and alkylbenzenesulfonate investigated in this study showed a complex and interesting behavior involving precipitation followed by redissolution at higher sulfonate concentrations. The phenomena of precipitation and redissolution were found to have a definite influence on the nature of the adsorption or depletion. Note that the latter includes surfactant lost not only by adsorption, but also by precipitation and entrapment.

Adsorption isotherms of surfactants from micellar solutions often exhibit a maximum and sometimes even minimum. The presence of maximum has been attributed in the past to mechanisms involving micelle exclusion from the interfacial region because of electrostatic repulsion or structural incompatibility, the presence of impurities, surfactant composition, adsorbent morphology, etc. None of these mechanisms, however, is substantiated well enough to be considered a confirmed mechanism for surfactant adsorption from concentrated solutions, particularly since there are serious possibilities of experimental artifacts arising from such processes as precipitation and entrapment. Indeed, more than one mechanism can operate in different systems or in the same system under even slightly different conditions. In our studies, the phenomenon of precipitation was responsible to some extent for the amount of adsorption as well as its maximum.

The investigation of the precipitation/redissolution process (in the absence of mineral) can help in developing an understanding of the mechanisms involved. Precipitation experiments were therefore conducted in this study with sulfonate solutions containing different types of ions, namely, sodium, calcium, and aluminum. Kinetics of precipitation was investigated under selected conditions by studying the development of the solutions' turbidity.

From the data, solubility products of the Ca and Al sulfonates are determined. Mechanisms for the redissolution are suggested.

Experimental Procedure
Materials. Samples of sodium dodecylbenzenesulfonate specified to be 90% pure (purchased from Lachat Chemicals) were purified by deoiling, recrystallization, and liquid chromatographic (LC) techniques. Sodium (1-butylcycloctyl)benzenesulfonate (Texas No. 2) purchased...
from the U. of Texas was used as received. Surface tension vs. concentration curves obtained for aqueous solutions of recrystallized and LC-purified dodecylbenzenesulfonate as well as Texas No. 2 (1, butyloctyl)benzenesulfonate obtained with the Wilhelmy plate technique did not exhibit any minimum. The critical micelle concentrations (CMC) determined from the surface tension measurements in the absence of additional electrolyte were approximately $10^{-3} \text{kmol/m}^3$ [$0.84 \times 10^{-5} \text{lbm mol/gal}$] in all cases.

The mineral used in the adsorption experiments was Na-kaolinite, prepared from a well-crystallized sample purchased from the clay depository at the U. of Missouri by the procedure described in Ref. 3.

Inorganic salts used in the precipitation experiments and to adjust the ionic strength and pH were of analytical reagent grade. Hydrocarbons specified to be 99+% pure were purchased from Aldrich Chemical Co. Inc. Triply distilled water was used in all experiments.

Test Procedures. In the adsorption tests, desired amounts of solids first were agitated on a wrist-action shaker for 2 hours in the electrolyte solution. Sulfonate then was introduced into the suspension and further agitated for 72 hours. The suspension was centrifuged at a gravity force of 1,500 for 20 minutes, the liquid above the mineral layer was mixed by inverting the tube carefully, and the supernatant was analyzed for the residual concentration of the sulfonate by the two-phase titration technique using the dimidium bromide/disulfphine blue mixed indicator as described by Powers and Reid et al. Adsorption tests were carried out at $30^\circ \text{C}$ [$86^\circ \text{F}$].

Precipitation of the sulfonate during adsorption experiments by the ions present in the clay supernatant was studied in the following manner. A sample of the supernatant was prepared under conditions similar to those used in the adsorption tests described. Na-kaolinite was equilibrated with the desired electrolyte solution at a solid-to-liquid ratio of 0.2:1 for 72 hours and then the kaolinite was removed by centrifugation for 20 minutes. To avoid any dilution effects, the supernatant was evaporated to dryness and the desired volume of sulfonate solution was added. The test solution then was agitated on a wrist-action shaker for 12 hours and its residual concentration was determined after centrifugation for 20 minutes. Precipitation was calculated from the differences between the initial and final values of sulfonate concentration. In certain cases, the turbidity of the sulfonate/supernatant mixture also was measured.

A Brinkman PC-600 probe colorimeter was used to measure turbidity of the solutions. Equal amounts (5 mL [5 cm$^3$]) of surfactant and inorganic electrolyte solutions were mixed in a test tube and shaken for 10 seconds. The probe was then inserted directly into the 10-mL [10-cm$^3$] sample and the first reading was taken 15 seconds after mixing. The dependence of turbidity on surfactant and/or electrolyte concentration was determined from the values of light transmission or optical density measured 30 minutes after mixing. All turbidity measurements were made at room temperature ($25^\circ \text{C}$ [$77^\circ \text{F}$]).

Results and Discussion

Kinetics of Precipitation. The rate of formation of precipitates depends on experimental conditions such as the concentrations of added surfactant and inorganic electrolytes, the type of ions present, and the degree of stirring. Fig. 1 illustrates the development of turbidity as measured by the optical density of the solutions as a function of time when $10^{-3} \text{kmol/m}^3$ [$0.84 \times 10^{-5} \text{lbm mol/gal}$] (1, butyloctyl)benzenesulfonate solution is mixed with solutions containing various amounts of CaCl$_2$. We observed that at higher concentrations of electrolytes, development of turbidity is rapid and equilibrium is approached in minutes. At lower concentrations, however, the initial rate of the turbidity development is relatively low and an equilibrium is reached only in hours. At very low concentrations of Ca$^{++}$ (<$10^{-4}$ kmol/m$^3$ [<$0.84 \times 10^{-6}$ lbm mol/gal]), precipitate is found to appear only after
was added at constant surfactant concentration also can result from the differences in kinetics of precipitation under various conditions.

The solubility product, $K_s$, of the sulfonate salts was calculated with the help of the turbidity vs. log concentration data and using the following expression relating it to activities of ions.

$$K_s = [a_{M^{m+}}][a_{S^{-}}]^m$$

where $a_{M^{m+}}$ and $a_{S^{-}}$ represent the activities of cation and sulfonated species, respectively. Using the data for the concentrations that correspond to the initial increase in turbidity and the respective activity coefficients calculated using the Debye-Hückel equation, the solubility product was calculated to be $2 \times 10^{-11}$ for calcium and $4 \times 10^{-19}$ for aluminum sulfonates.

Precipitation/Redissolution in Mono- and Multivalent Salt Mixtures. The effect of NaCl addition on calcium sulfonate precipitate that has already been formed in solution is shown in Fig. 6 where transmission of the suspension is plotted as a function of the concentration of NaCl. In the absence of NaCl, addition of $5 \times 10^{-3}$ kmol/m$^3$ [0.42 x 10$^{-3}$ lbm mol/gal] CaCl$_2$ results in almost complete precipitation of $10^{-3}$ kmol/m$^3$ [0.84 x 10$^{-5}$ lbm mol/gal] and $5 \times 10^{-3}$ kmol/m$^3$ [0.42 x 10$^{-3}$ lbm mol/gal] sodium dodecylbenzenesulfonate solutions. As NaCl was added to these systems, turbidity gradually decreased, and finally, at about $5 \times 10^{-2}$ kmol/m$^3$ [0.42 x 10$^{-2}$ lbm mol/gal] of NaCl, a clear solution was obtained.

An explanation for this interesting effect of NaCl becomes evident when the possible role of micellization/solubilization phenomena is examined. For complete redissolution of calcium sulfonate precipitates, as stated earlier, sulfonate is required to be at a concentration that is at least five times that of calcium ($5 \times 10^{-3}$ kmol/m$^3$ [0.42 x 10$^{-3}$ lbm mol/gal]) CaCl$_2$. Since the solution considered here contains only $10^{-3}$ kmol/m$^3$ [0.84 x 10$^{-5}$ lbm mol/gal] sulfonate, it is apparently unable to produce enough micelles to cause redissolution of the precipitate particles. Indeed, the addition of NaCl can be expected to lower the CMC of sulfonate and thus enhance the formation of micelles and cause redissolution of the precipitate. Upon further addition of NaCl, the solubility limit of the sulfonate is exceeded and it precipitates out of the solution. For the present cases, the sulfonate tolerance limit corresponds to approximately 0.3 kmol/m$^3$ NaCl [0.25 x 10$^{-2}$ lbm mol/gal].

The implication of the phenomena of precipitation and redissolution to adsorption is important since adsorption is usually conducted in brine solutions. Release of multivalent ions such as Ca$^{++}$, Mg$^{++}$, or Al$^{+++}$ by the clay in the presence of NaCl can produce precipitation and redissolution regions which can in turn generate apparent maxima or minima in adsorption isotherms. Furthermore, precipitation of sulfonates can conceivably lead to plugging of pores in reservoirs with serious consequences. The potential role of redissolution in such cases deserves investigation.

Precipitation, Abstraction, and Adsorption. Precipitation and redissolution of the previously discussed type can give rise to a maximum in the abstraction (abstraction of surfactant from solution) isotherms and, if precipitation is not totally isolated from adsorption, can generate an apparent maximum in the adsorption isotherm. In the case of clays, a number of mono- and multivalent cations—Na$^+$, Ca$^{++}$, Al$^{+++}$, etc.—can be expected to be present in a supernatant of it and to produce precipitation.

Results obtained for abstraction of as-received and purified sodium dodecylbenzenesulfonate from a solution upon the equilibration of it with homoionic Na-kaolinite are given in Figs. 7 and 8. These isotherms are characterized by the presence of a maximum. The data for sulfonate depletion on contact with the supernatant of a kaolinite suspension as well as the data for the light
transmission of the sulfonate supernatant mixtures before centrifugation also are given in these figures. Various abstraction curves show excellent correlation; both the precipitation and transmission curves exhibit maxima in the concentration region of the abstraction maximum.

The amount of sulfonate that will precipitate because of interaction with dissolved mineral species in the presence of kaolinite need not be precisely equal to that which will precipitate in a supernatant from which kaolinite has been removed because of elimination of the possibility for continuous equilibration of kaolinite with the solution in the latter case. The natural pH values obtained during precipitation tests were slightly higher than those obtained in the abstraction tests, again from lack of continuous equilibration in the presence of kaolinite. Assuming these two effects to be minimal, adsorption isotherm was calculated from the difference between the two isotherms (Figs. 7 and 8).

The adsorption maximum is considerably less sharp, suggesting that the precipitation of sulfonate from interactions with the dissolved mineral species does indeed contribute toward determining the shape of the abstraction isotherm for the system considered here. The resultant adsorption isotherm still exhibits a maximum, even though much less prominent. The presence of such maximum could be attributed to other mechanisms which have been suggested earlier,1-3,13,14 but it is possible that this is caused by the absence of kaolinite during the precipitation process in supernatants. As sulfonate precipitates, when kaolinite is present in the system, and consumes the dissolved mineral species, more ions can be expected to be released from the mineral because of the offset of equilibrium conditions. In the abstraction experiments, precipitation can therefore be higher than what was observed during precipitation experiments. Release of ions can conceivably be higher when the initial precipitation is rapid rather than when it is slow. This can cause the decrease in the abstraction density to be higher in the rapid precipitation region. The observed decrease in precipitation at higher surfactant concentrations can be caused by the solubilization of the precipitate by the micelles which are known to bring into solution otherwise insoluble nonionic organic species.12

Release of mineral species is confirmed by the surface tension measurements made with NaCl solutions and with clay supernatant solutions. With the dissolution of the mineral, ionic strength would increase, and the CMC of the sulfonate solution should decrease. The opposite was observed here (Fig. 9); CMC in the supernatant solution is slightly higher than in the NaCl solution. This is because precipitation of sulfonate had occurred in the supernatant solution. Since precipitation is a competing phenomenon, higher total surfactant concentration will be required for the attainment of CMC.

The effect of addition of oil to precipitating systems is illustrated in Fig. 10. Addition of n-dodecane (10 and 52% by weight with respect to the sulfonate) eliminated precipitation in the low-surfactant-concentration region. Note that precipitation caused by salting out still occurred in concentrated sulfonate solutions.
The elimination of precipitation possibly is caused by partitioning of the surfactant species into the separate oil phase present in the system or the dissolution of the precipitate in the oil that might be present in the form of microemulsion. In the former case, surfactant species can be partitioned between the separate oil and aqueous phases, thus reducing the surfactant concentration in the aqueous phase and consequently reducing the precipitation also. The latter case is similar to the micellar solution discussed earlier. The difference between the two is that microemulsions can form below CMC and, as a result, solubilization can commence at surfactant concentrations below such CMC, thus reducing precipitation and maybe even eliminating it.

It is clear from the discussed results that surfactants of the sulfonate type can undergo precipitation and redissolution on interacting with solutions containing dissolved inorganic ions and that such phenomena can play a major role in producing a maximum in the abstraction isotherms.

Conclusions

1. The study of kinetics of precipitation as a function of electrolyte concentration showed the time for complete precipitation to depend on the sulfonate concentration, with precipitation continuing to take place for hours when the concentration of inorganic electrolyte is low.

2. Monovalent cations such as K\(^+\) caused the precipitation of sulfonates on increasing the sulfonate concentration. Multivalent ions such as Ca\(^{2+}\) and Al\(^{3+}\) also precipitated the sulfonate, but in these cases the precipitate redissolved on further increasing the sulfonate concentration. The concentration at which complete redissolution occurs appears to be a function of the valency of the multivalent ion.

3. The solubility products of the salts of sulfonate were determined from the turbidity measurements; calcium and aluminum dodecylbenzenesulfonates have the solubility products of \(2 \times 10^{-11}\) and \(4 \times 10^{-19}\) respectively.

4. In the studies with solutions containing mixtures of mono- and multivalent ions, addition of even monovalent ions was capable of dissolving bisulfonate precipitates. Addition of NaCl thus caused the redissolution of the calcium sulfonate precipitates. Addition of Na ions is believed to lower the CMC of the sulfonate and give rise to the formation of micelles and in turn to the dissolution of the precipitate in them.

5. Possible mechanisms suggested for the redissolution phenomenon are: solubilization of precipitates by micelles; redissolution by complexation; and redispersion of the coagulated colloids caused by the development of charge resulting from the adsorption of sulfonate. Solubilization by micelles is considered to be the predominant mechanism for the systems studied here.

6. Precipitation of surfactant because of its interaction with dissolved mineral species is confirmed to contribute to the presence of maximum observed in the "adsorption" isotherms. Because of this, it is recommended that precipitation and abstraction experiments be conducted under identical environments to calculate the actual adsorption densities on minerals.

7. Addition of oil was found to reduce (in some cases completely eliminate) surfactant precipitation, possibly because of the partitioning of the surfactant between the oil and the aqueous phases.

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References


SI Metric Conversion Factors

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*Conversion factor is exact.*