Adsorption of Sulfonates on Reservoir Rocks

P. Somasundaran, Columbia U.
H. S. Hanna, * Columbia U.

Abstract

Abstraction of Mahogany sulfonate AA™ and recrystallized dodecylbenzenesulfonate by Na-kaolinite, sandstone, and limestone was studied as a function of relevant variables such as pH, ionic strength, and type of inorganic electrolyte added. In most cases, such factors affect not only the abstraction capacity of the solid particles, but also the shape of the abstraction isotherm. Particularly, the inorganic species in the system were found to influence the abstraction and the desorption of dodecylbenzenesulfonate by kaolinite, based upon their size and solvation properties. Thus, appearance of a maximum in this system was related to the predominance of smaller exchangeable "structure-making" ions. Introductions of larger "structure-breaking" ions tends to eliminate such maxima. The role of ions (such as silicate, phosphate, chloride, calcium, sodium, ammonium) are examined and possible mechanisms are discussed. Implications of these observations in developing the capability to control abstraction should be noted.

Introduction

A major problem that affects the efficiency of tertiary oil production by micellar flooding is the loss of surfactants from interaction with minerals and their dissolved components. Trushenski et al. have observed the existence of a retention maximum near the critical micellar concentration range followed by a minimum for the system Berea sandstone/Mahogany petroleum sulfonate-isopropyl alcohol micellar fluid at 110°F (43°C). Similar studies on reservoir rock minerals by Bae et al., Gale and Sandvik, Hill et al., Hurd, and Somasundaran et al. have been discussed earlier. Bae et al. observed the presence of a maximum for abstraction in the systems they investigated. Other recent studies on abstraction on reservoir minerals include those of Malmberg and Smith, Trogus et al., and Lawson and Dilgren. The phenomenon of abstraction maximum and minimum is of much theoretical and practical interest. However, mechanisms of surfactant abstraction in such reservoir/surfactant systems are not yet established fully and as such their abstraction behavior generally cannot be predicted. Also, no fully substantiated reasons exist to account for the presence of the maximum or minimum. Our objective is to study the abstraction behavior of relevant surfactants on reservoir rock minerals under various experimental conditions to understand the mechanisms involved in this interfacial process and to identify conditions under which surfactant retention can be minimized. Results obtained here for the abstraction of recrystallized dodecylbenzenesulfonate by treated kaolinite in various inorganic electrolytes are given with a summary of results obtained previously for the abstraction of certain sulfonates by Berea sandstone, agricultural limestone, and Bedford limestone.

Background

Our previous work clearly has shown that the nature of the abstraction isotherm obtained depends to a large extent on the type of sulfonate used, the morphological and mineralogical characteristics of the rock, and the type of electrolytes present in solution.

*For a definition of the term abstraction, see the section on "Abstraction Procedure."

© 1978 Society of Petroleum Engineers of AIME
Abstraction maxima were obtained for Mahogany sulfonate AA by previously unwetted Berea sandstone (Fig. 1A). Isotherms of dodecylsulfonate (reproduced in Fig. 1B) exhibited only positive slopes, but concentrations studied were restricted to premicellar range because of solubility problems. Increase in ionic strength from adding NaCl increased the abstraction in all cases. Abstraction maximum was sensitive to the amount of NaCl added (Fig. 2). At lower NaCl concentrations, the maximum occurred for Mahogany sulfonate AA/Berea sandstone system; at an intermediate concentration of $2.5 \times 10^{-2}$ mol/dm$^3$ NaCl, the isotherm exhibited a maximum, followed by a shallow minimum; at still higher concentrations, the abstraction maximum was not present. Na$_2$SO$_4$ addition also caused an increase in abstraction, but the effect of this uni-bivalent salt was less than that caused by the addition of the uni-univalent salt, NaCl. Addition of Na$_2$HPO$_4$ depressed the abstraction of the sulfonate under all conditions.

**Abstraction Isotherms of Sodium Dodecylsulfonate, Sodium Dodecylbenzenesulfonate, and Mahogany Sulfonate AA by Two Types of Limestones (Bedford limestone and Agricultural limestone) and Those of Sodium Dodecylsulfonate, Sodium Dodecylbenzenesulfonate, and Aerosol OT by Synthetic Calcium and Magnesium Carbonates Also Exhibited a Maximum Under All Conditions.** The addition of NaCl, Na$_2$SO$_4$, and Na$_2$HPO$_4$ also had noticeable effects on the abstraction of sulfonate by limestones. In this case, mineralogical and morphological characteristics of the absorbent were found to influence the abstraction markedly. The porous type of limestone (Bedford) had a lower abstraction density under natural pH conditions, possibly because of the concentration of the silicates on the surface of the particles after the dissolution of exposed calcite and magnesite and the nonwetting of pores. Interestingly, agricultural limestone was found to abstract more sulfonate than Bedford limestone in the alkaline pH range, possibly because of the activation of the exposed silica on the former by dissolved calcium and magnesium species in this pH range (Fig. 3).

Clearly these results show that the type of inorganic species present in the system plays a major role in controlling the abstraction behavior of sulfonates by mineral solids. To establish the role of each ion clearly and to elucidate the mechanisms involved, however, we must conduct studies on a system comprising purified and well-characterized minerals and surfactants. This study therefore was conducted with sodium dodecylbenzenesulfonate purified by soxhlet-extraction and recrystallization and kaolinite treated with NaCl solutions to produce...
precipitation values obtained using the concentration difference technique is the Gibbs adsorption or surface excess and must be distinguished from total adsorption. Any precipitation in the system, however, also can contribute toward the observed difference in concentration. We attempted to minimize this artifact by resuspending the precipitate (by gentle stirring) that appeared to collect on top of the mineral bed during centrifugation. Nevertheless, any trapping of precipitate inside the mineral bed or its deposit on the mineral particles would lead to values that are higher than those for adsorption alone; the present phenomenon therefore is referred to as abstraction. The value calculated from the

Materials and Methods

Mineral

A well-crystallized sample of Georgia kaolinite obtained from the clay repository at the U. of Missouri was used. The surface area of this sample (as determined by nitrogen adsorption) was 9.8 m$^2$/g. Homo-ionic Na-kaolinite was prepared from this sample as follows: (1) the kaolinite sample was washed repeatedly with water under intense agitation until there was no change in the conductivity of the supernatant water; (2) the solids were repulped with 2M NaCl solution and mixed at a high solid-to-liquid ratio for 15 minutes; the pulp was diluted and remixed for 2 hours, allowed to settle and decanted, and this washing procedure was repeated until a pH of 7 and a constant conductivity of the suspension were reached; (3) the NaCl-treated solids were repulped using 1M NaCl at pH 3, mixed at a high solid-to-liquid ratio, diluted, and washed several times with water until a pH of 7 again was obtained; (4) during the last washing in Step 3, the fine clay particles were separated from the coarse impurities by decantation; and (5) the Na-kaolinite thus obtained was filtered, dried, and stored dry.

Sulfonate

Sodium dodecylbenzenesulfonate (SDDBS) specified by Lachat Chemicals Inc. as 95% active was purified first by drying under reduced pressure over phosphorous pentoxide at 50° to 60°C and then by extraction by dry distilled diethylether in a soxhlet apparatus. The first part of the extract (20 to 30 wt%) was discarded and the latter fraction (30 to 40 wt%) was collected and, after evaporating the diethylether, the residue was recrystallized four times from acetone. A product assaying 98.1% SDDBS and showing no minimum in surface tension/concentration curve was obtained (Fig. 4). Infrared analysis of the purified material indicated the presence of the p-DDBS isomer associated with trace amounts of the o-benzene isomer.

Abstraction Procedure

Abstraction tests were conducted by agitating a known volume of surfactant solution with the desired amount of solids for given times in an incubator maintained at the desired temperature. At the end of the test, a sample of the supernatant solution was centrifuged at 1,500 G (14 715 m/s$^2$) for 20 minutes, and the supernatant was analyzed for the residual concentration of the sulfonate, using the two-phase titration technique with a mixture of dimidium bromide and disulphine blue as indicator. Abstraction of the surfactant is calculated from the difference between initial and final sulfonate concentrations. Note that adsorption in the absence of
concentration differences is called “abstraction,” rather than adsorption. Abstraction by the mineral will include adsorption and precipitation on the mineral, but not the loose precipitate in the bulk solution.

Results and Discussion
Aging of Kaolinite in Aqueous Solutions
Initial tests conducted on the equilibration of dry kaolinite with water at various pH values and ionic strengths showed this process to involve at least two steps. Similarly, abstraction of sulfonate by kaolinite involved a fast and a slow step, the latter possibly caused by slow dissolution of aluminum species from kaolinite during prolonged contact with water and the resulting activation of sulfonate adsorption. Past studies using kaolinite do not appear to have considered the possibility of an intermediate metastable condition. Implication of this on the interpretation of data obtained under metastable conditions should be noted. Furthermore, kaolinite samples, even when stored dry, have been found to undergo changes in abstraction capacity during a period of months.

Effect of pH
The effect of pH on abstraction of sulfonate was marked (Fig. 5). Note that abstraction is given here as a function of pH at constant equilibrium concentration of the surfactant. The sulfonate abstraction by kaolinite is seen to decrease markedly with increase in pH, particularly in the acidic pH range. Anionic dodecylsulfonate ions and micelles can adsorb on kaolinite surface because of either electrostatic attraction of the ions to the positive sites on the kaolinite surface or ion exchange involving either Cl− or OH− ions on the mineral surface, or even chemical interaction in the bulk and solid surface between the sulfonate ions and multivalent cations.

Electrostatic Adsorption. As for most oxide and silicate minerals, H+ and OH− ions are considered to be potential-determining ions for kaolinite. Thus, with a decrease in pH, the number of positive sites on the kaolinite particles is expected to increase and, thereby, can lead to an increase in adsorption of the anionic sulfonate. While this mechanism can explain the results obtained at low pH values, it cannot account for abstraction equivalent to the 12 to 25% surface coverage obtained above neutral pH, and therefore suggests the possibility for the presence of other mechanisms.

Ion-Exchange Process. Information on the nature of ion-exchange possibilities can be obtained by analyzing the data obtained for pH changes in a kaolinite/dodecylbenzenesulfonate system at various pH values. In the present case, while the final pH of the system in the acidic range was always higher than the initial value (pH of 3.1 shifted to ~ 4.6), the opposite was true in the neutral and alkaline pH range (pH values of 7 and 11 shifted to ~ 6.5 and ~ 9.6, respectively). These observations can be explained in terms of the amphoteric character of the terminal aluminum ions on the kaolinite surface. In the acidic pH range, the sulfonate ions can exchange with the surface OH− ions, leading to an increase in the pH of the solution. Such a mechanism has been suggested earlier by Muljadi et al.17 for the adsorption of phosphates on clays. The increase in pH obtained here, however, accounts for only an 8% surface coverage by dodecylbenzenesulfonate, in contrast to the abstraction equivalent to the 45 to 100% surface coverage actually obtained. The decrease in pH in neutral and alkaline solutions is discussed next.

Interaction with Multivalent Ions. These differences can be accounted for by taking into consideration the possible dissolution of the octahedral aluminum from the edges of kaolinite particles:

\[
\frac{1}{2}Al_2Si_2O_5(OH)_4(s) + \frac{1}{2}H_2O \rightleftharpoons Al^3^+ + H_4SiO_4 + 3OH^- \quad pK = 38.7.
\]

The dissolved Al^3+ and its hydroxy complexes can be expected to react with the bulk surfactant species to form aluminum sulfonate complexes that can easily adsorb on kaolinite surface. Precipitation of aluminum sulfonates in bulk solution is another possibility that must be investigated.

The drop in the pH of the clay suspension from 11 to 9.5 can be attributed to the formation of aluminate ions, which is accompanied by OH− consumption as shown by the following reaction,18

\[
\frac{1}{2}Al_2Si_2O_5(OH)_4(s) + \frac{1}{2}H_2O + OH^- \rightleftharpoons Al(OH)_4^- + H_4SiO_4 \quad pK = 5.7.
\]

Sulfonate can adsorb in this case by exchanging with the aluminate ions. Surface coverage expected from this ion-exchange reaction is 7 to 8% of the monolayer coverage, which is close to the observed 12% under alkaline pH conditions. Ion exchange therefore can be considered a major possible
mechanism under alkaline pH conditions. The role of aluminum species and the change in their relative concentrations on pretreatment of the kaolinite in controlling the adsorption and precipitation of sulfonate in fact can be significant. For example, even though the area occupied by the positively charged terminal-edge groups on kaolinite does not exceed 2 to 5% of the total available surface area,\textsuperscript{19} the actual coverage obtained for sulfonate corresponds to a closely packed monolayer under acidic pH conditions. Such coverage can be made possible by the generation of secondary positive sites owing to specific adsorption of $\text{Al}^{3+}$ ion and its complexes to the basal negative kaolinite crystal. The data given in Fig. 6 show clearly that the dissolved aluminum species in the acidic pH range are mainly $\text{Al}^{3+}$. Such $\text{Al}^{3+}$ species can be expected to cause increased adsorption as well as precipitation of dodecylbenzenesulfonate on mineral particulates below pH 6. Above about pH 8, $\text{Al(OH)}_4^-$ will predominate, and these ions will minimize adsorption of similarly charged sulfonate. Similar suggestions also were made by Wayman,\textsuperscript{21} and Swartzen-Allen and Matijevic,\textsuperscript{22} who have considered the possibility of reactions of such aluminum complexes as $\text{Al}_6\text{(OH)}_{15}^3+$, $\text{Al(OH)}^2+$, $\text{Al}_2\text{(OH)}_5^4+$, and $\text{Al}_3\text{(OH)}_6^3+$ with sulfonates.

**Effect of Salinity**

For the study of the effect of salinity on the sulfonate abstraction by kaolinite, we chose NaCl as the supporting electrolyte for the following reasons: (1) there is only limited specific adsorption of $\text{Na}^+$ and $\text{Cl}^-$ ions on kaolinite,\textsuperscript{22} (2) Na salts often are used in preflushing experiments, and (3) $\text{Na}^+$ is one of the major dissolved ionic species in underground waters. We found during these experiments that the addition of salt also will produce a decrease in the pH of the suspension because of the ion exchange between the surface $\text{H}^+$ ions on kaolinite and added $\text{Na}^+$ ions. The units respectively for $10^{-2}$ and $10^{-1}$ M NaCl solutions initially at about pH 6 to 8 certainly will have their own effect on the adsorption of sulfonate on the mineral. Therefore, to evaluate the real effect of ionic strength alone, tests were conducted by maintaining the pH at the desired value throughout the experiment. A summary of the results obtained is presented in Fig. 7 as a function of pH at two constant equilibrium surfactant concentration levels. These results show that abstraction of sulfonate by kaolinite is enhanced, but only slightly, by an increase in ionic strength. Further increase in ionic strength produced salting out of the surfactant. Much larger effects of ionic strengths reported in the past must be attributed partly to simultaneous changes in pH and the resulting increase of surface acidity of the clay mineral because it is clear from a comparison of data given in Figs. 5 and 7 that pH effect is of a larger magnitude under these conditions and because pH seldom is reported as being constantly monitored during tests. Note at this point that the surface state of kaolinite is much more complex than that expected on the basis of its ideal crystal lattice structure. Buchanan and Oppenheim\textsuperscript{20}
negatively charged mineral surface and the anionic sulfonate and thus, in effect, enhances the possibility for its adsorption on this mineral.

So far, we have examined the effect of a general increase in ionic strength on adsorption. In the next sections, we will discuss the role of the type of electrolyte used.

**Effect of Uni-Univalent Electrolytes**

Abstraction isotherms of dodecylbenzenesulfonate by Na-kaolinite in various uni-univalent electrolytes at three pH values (natural pH of ~ 6.5, 9.4, and 4.5) are given in Figs. 8 through 10. The type of electrolyte used affects both the extent of abstraction and, most interestingly, the shape of the isotherm. Distinct maxima appeared on the abstraction isotherms obtained in 10^{-1} M NaCl, KCl, and NH_4COOCH_3 solutions. On the other hand, no such maximum was obtained in 10^{-1} M NaNO_3 and NH_4Cl solutions. This novel observation on the dependence of the appearance of the abstraction maximum on the type of inorganic ions is discussed later.

We also observed similar reactions at electrolyte concentrations of 10^{-2} M. In 10^{-2} M NH_4NO_3, NH_4Cl, KCl, and NaCl solutions, a limiting abstraction of about 1.7 \mu mol/cm², corresponding to 30 to 40% of a compact, vertically oriented monolayer coverage, was obtained under natural pH conditions. Increase of electrolyte concentration...
yields nearly a monolayer limiting coverage. Increase of pH to ~ 9.4 does not alter the shape of the isotherms, but does decrease the limiting abstraction to 12% of the monolayer in 10^{-2} M electrolytes and to 26 and 80% of a monolayer in 10^{-1} M NaCl and 10^{-1} M KCl, respectively. In acidic solutions, on the other hand, both the shapes and the limiting abstractions are different from those obtained under other pH conditions.

In 10^{-2} M electrolytes, the maximum abstraction obtained corresponds to nearly that of a bimolecular layer. The dependence of the abstraction on the pH and the ionic strength was discussed earlier. As far as the effect of the type of inorganic ion is concerned, the uni-univalent electrolytes increase the abstraction of sulfonate by kaolinite under various pH and ionic-strength conditions in the order: NaOH < NaCl < NH_{4}COOCH_{3} < NH_{4}Cl < NH_{4}NO_{3} < HCl < KCl. Thus, monovalent cations increase the abstraction in the order Na^{+} < NH_{4}^{+} < K^{+}, while anions increase it in the order CH_{3}COO^{-} < Cl^{-} < NO_{3}^{-}. These results generally agree with those of Wayman^{21} for the adsorption of alkylbenzenesulfonate on kaolinite, illite, and montmorillonite, and of those of Mortensen^{24} for the adsorption of anionic polycracylic acid on kaolinite.

Most clays are known to show affinity for cations in the order Li^{+} < Na^{+} < K^{+} < NH_{4}^{+} < Rb^{+} < Cs^{+} < Ag^{+}. This also is the order of increasing hydrated-ion radius. Selectivity of the clays for the ions is considered to depend on physicochemical properties of the system, such as hydration characteristics of the solid surface species and the ions.^{16,25} Both the surface and bulk species affect the structure of water. Enhanced adsorption is expected of those ions that induce the same type of structural changes in water as the surface because they can accommodate themselves more easily in the aqueous environment of the interfacial region in such a case. Inorganic ions have been reported widely to produce alterations in water structure, with the effect found to increase in the order Li^{+} < Na^{+} < K^{+} < Cs^{+} for cations and Cl^{-} < Br^{-} < I^{-} for certain anions. Thus, while K^{+} is considered to cause a breakdown of the water structure and thus facilitate self-diffusion of water molecules, Na^{+} is believed to induce a more coherent structure for the water. This interpretation is supported further by Konta and Borovec^{26} for the adsorption of water by homo-ionic kaolinites. Relative capacities of adsorption were found to increase in the order NH_{4}^{+} > Mg^{++} > K^{+} > Na^{+} natural kaolinite > Li-kaolinite. Clay itself is considered to induce a more coherent structure in water. Higher activation energy observed for movement of ions in water containing clay, compared with that in water without clay, is attributed to formation of such a coherent water structure around clay platelets. Inorganic ions that can affect the water structure around the clay particles also can be expected to affect the mobility and concentration of an adsorbing ion such as Na-dodecylbenzenesulfonate. Structure-breaking ions such as K^{+} and NH_{4}^{+} therefore can be expected to cause a larger increase in the adsorption of sulfonate on clay than other ions, which they indeed do as observed here. An increase in ionic strength generally also can be expected to contribute toward increased adsorption because activation energy for ion mobility and self-diffusion of water generally decrease with any increase in electrolyte concentration.^{27,29}

The effect of the inorganic ions also is partly the result of the differences in their capacity to exchange with the ions of the clay and their effect on other system properties, such as critical micelle concentration and micelle charge and size.

Effect of Uni-Bivalent Electrolytes

Results obtained for the effect of uni-bivalent electrolytes (Na_{2}SO_{4}, Na_{2}CO_{3}, Na_{2}HPO_{4}, and Na_{2}SiO_{3}) on the abstraction of dodecylbenzenesulfonate by Na-kaolinite at various pH values are given in Figs. 11 through 13. For comparison, results obtained for the effect of NaCl also are presented.

In contrast to Cl^{-}, addition of SO_{4}^{2-} produces less abstraction under low-surfactant concentration conditions, possibly because of specific adsorption of sulfate ions leading to an increase in the negative charge of the clay particles. Above the critical micelle concentration, SO_{4}^{2-}, however, produces higher abstraction than Cl^{-}, owing possibly to the structure-breaking effect of the former on adsorption of micelles. No abstraction maximum is obtained in sulfate solutions.

Effect of addition of phosphates and silicates is most interesting in that the abstraction can be nearly eliminated, even with small additions. Note also that the effect of phosphate is different in acidic and

![Fig. 11](image-url)
alkaline solutions in that in the former case no abstraction maximum was obtained. This difference largely results from differences in the nature of phosphate species present under various pH conditions. While a significant amount of phosphate will be present in the form of structure-breaking H₂PO₄⁻ under acidic pH conditions, structure-making HPO₄²⁻ will predominate under alkaline pH conditions. An interesting possibility in the clay/phosphate system is the formation of new crystalline phases composed of AlPO₄ salts on the mineral surface. Appearance of such phases should be of significance when determining the sulfonate abstraction by the solid.

In contrast to NaCl, introduction of Na₂SiO₃ produces decreased sulfonate abstraction under all conditions of pH and ionic strength. Reduced abstraction is related partly to the decrease of free aluminum species, expected when silicates are introduced into solution. Silicates will react with aluminum to form aluminum silicate complexes in the solution and possibly on the mineral surface. This also should result in a decrease in the available sites for sulfonate abstraction. Note that in the alkaline region, negligible abstraction and, in some cases, even negative abstraction is indicated. This reagent thus appears to hold some promise as a sacrificial agent for actual applications, particularly because it perhaps can aid in mobility control.

The effect of addition of Na₂CO₃ was investigated only in the alkaline range, owing to the instability of this salt under other pH conditions. Simple abstraction isotherms without any maximum were obtained under all conditions. Also, the abstraction was limited under all conditions to about 8 to 12% of monolayer coverage.

In summary, certain uni-bivalent electrolytes such as Na₂SiO₃, Na₂HPO₄, and Na₂CO₃ can cause little abstraction of sulfonate by kaolinite. Evidently, a detailed investigation of the effect of these salts when controlling the abstraction of sulfonates by reservoir rock systems would be useful.

Effect of Bi-Univalent Electrolytes

Introduction of Ca(NO₃)₂ or Mg(NO₃)₂ to the kaolinite/dodecylbenzenesulfonate system resulted in higher sulfonate abstraction than those observed in NaCl solutions. Tests were conducted in this case at 10⁻² M and 3 x 10⁻² M ionic strengths since considerable precipitation of dodecylbenzenesulfonate salts often occurred under higher ionic-strength conditions. Observed enhancing effects of Ca and Mg species on sulfonate abstraction agrees with the reported effects of such ions on the electrochemical properties of mineral particles. These bivalent ions can adsorb specifically on negatively charged particles and can reduce their negative interfacial potential and even reverse it. Such alterations in potential making the mineral less negatively charged can indeed lead to increased adsorption of the anionic sulfonate. In addition to this, adsorption of sulfonate in the form of complexes such as CaDDBS⁺ also must be accounted for...
as a possible mechanism by which the bivalent ions act. Figs. 14 and 15 indicate that maximum abstraction is about two to three times higher in the presence of small calcium nitrate than that in the presence of magnesium nitrate. This is related directly to calcium sulfonate's solubility being lower than that of magnesium sulfonate.

**Desorption of Sulfonate From Kaolinite Surface**

We began desorption studies because the nature of desorption definitely can help us understand the mechanisms involved when controlling adsorption of surfactants. Desorption experiments were conducted by stagewise dilution of the mineral/surfactant system that was pre-equilibrated at desired pH, ionic strength, etc. The variables, such as solid-to-liquid ratios, pH, and ionic strength, were maintained at constant values throughout the test. Abstraction-desorption results obtained at pH values of ~ 4.6 and ~ 6.6 in 10^{-2} M NaCl solutions are given in Fig. 16. The data given in Fig. 16 indicate that the systems do exhibit hysteresis, and equally important, that the isotherms do exhibit a maximum in the same concentration range where abstraction maximum was obtained. The latter observation clearly supports the possibility that the abstraction maximum obtained is a true maximum, not an experimental artifact. Note that the maximum abstraction density obtained during desorption depends on the maximum surfactant concentration that the mineral had come in contact with before any dilutions. When such maximum precontacted surfactant concentration is near the concentration corresponding to maximum abstraction density, the desorption isotherm does not differ significantly from the abstraction isotherms.
At higher maximum precontacted concentrations, hysteresis is significant.

Mechanism of Dependence of Abstraction and Adsorption Maxima on Inorganic Electrolytes

Suggested explanations in the literature for the observed maximum include decrease or changes in surfactant monomers concentrations, desorption of surface micelles, surface contamination, and micellar exclusion from the interfacial region owing to stronger electrostatic repulsion between the particles and highly charged micelles than the former and singly charged monomers. Alteration in the solid properties such as effective surface area, owing to changes in particle morphology on excessive surfactant adsorption of plugging of the surface pores by surfactant aggregates, also has been suggested as a possible reason for the above adsorption phenomenon.

From our study of the effect of electrolytes on the abstraction by kaolinite, we found that the appearance of the abstraction maximum depends not only on the ionic strength, but also on the type of cations and anions present in the system. None of these mechanisms, except possibly the morphological alterations of the mineral particles, however, can account for the dependence of the presence of the abstraction maximum on the type of inorganic ions present in the solutions.

An important factor is the possible role of the properties of water associated with a solid surface and the influence of inorganic ions on these properties when determining the adsorption of surfactant ions and micelles on that surface. Thus, in the case of a surface that does not have much influence on the structure of water around it, the adsorption process can be expected to proceed normally, reaching a limiting value at high concentrations of the surfactant. On the basis of Husted and Low's results, who observed that the diffusion constants for ions through clay gels is 30% lower than in water, clay particles can be considered to induce a structured region around them as well as inside them between platelets, through which the movement of ions, and, more severely, that of aggregates, will be restricted. Certain ions, however, can cause the breakdown of such structures. Wang reported the structure-breaking properties of simple ions to increase in the order $\text{Cl}^{-} < \text{Br}^{-} < \text{I}^{-}$. Thus, $\text{Cl}^{-}$ ions have the least tendency to disturb the structure of the water around the clay particles and can accommodate themselves better in the structured water region than ions of larger diameter, such as $\text{I}^{-}$. In the case of cations, the tendency to break the structure increases in the order $\text{Na}^{+} < \text{K}^{+} < \text{NH}_{4}^{+}$ and in the case of anions, a more complete series is given by the order $\text{COO}^{-} < \text{HPO}_{4}^{2-} < \text{Cl}^{-} < \text{NO}_{3}^{-} < \text{SO}_{4}^{2-}$. We see from examining the above series that the presence of both $\text{Na}^{+}$ and $\text{Cl}^{-}$ ions is compatible with a structured water region. Because transport and accommodation of surfactant aggregates such as micelles in such a structured water region can be less favorable energetically than those in bulk water, micelles usually are excluded under such conditions. Even though monomers could continue to adsorb even above critical micelle concentration, the negative adsorption of micellar aggregates can lead to a reduction in the surface excess of the total surfactant above the critical micelle concentration. On the basis of these considerations, both $\text{Na}^{+}$ and $\text{Cl}^{-}$ ions usually are responsible for the observed maximum in abstraction from NaCl solutions. In contrast to NaCl, NH$_4$NO$_3$ with both the cation and anion as structure breaking, facilitates adsorption of the micelle (in addition to the monomer), and the adsorption isotherm in this case has no maximum. In this regard, note that only in larger concentrations of these electrolytes (than those of ions released from clay) can we observe their effects. Also, the effects of alkali or acidic added to adjust the pH and of the change of ionic size caused by hydrolysis reactions under different pH conditions must be taken into account. Thus, magnesium ions possibly can act as structure-breaking ions in the alkaline pH range because of their presence as hydroxy complexes (Fig. 15).

On the basis of the above considerations, the presence of the abstraction maximum and its dependence on the type of inorganic ions present in solution can at least be attributed partly to the incompatibility of micellar-type aggregates with the structured water around the particles and the resulting exclusion from the interfacial region. On the other hand, the differences in ion-exchange properties of various inorganic ions would result in varying amounts of ions, which on release from clay can cause surfactant precipitation. Thus, the larger ions such as ammonium can be expected to undergo less exchange than the smaller ones and, hence, to cause less precipitation. Abstraction of precipitated complexes by the particles at lower concentrations and their possible solubilization in the surfactant micelle at higher concentrations also can produce an abstraction maximum, which would depend on the nature of the electrolyte present.

Conclusions

1. The nature of the abstraction isotherm obtained for sulfonates depends on the type of sulfonate used as well as on the morphological and mineralogical characteristics of the mineral.

2. Equilibration of kaolinite with water and abstraction of sulfonate by kaolinite involves both fast and slow steps. The implications of the presence of an intermediate metastable condition during equilibration on the past mechanistic interpretations should be noted.

3. The effect of pH on abstraction was marked because of possible adsorption of aluminum complexes on kaolinite in acidic solutions.

4. The effect of a tenfold increase in ionic strength on abstraction of dodecylbenzenesulfonate by Na-kaolinite is limited. Effect of pH changes that invariably accompany changes in ionic strength must be recognized. However, salinity did have a marked
effect on the abstraction of Mahogany sulfonate AA by Berea sandstone.

5. The effect of inorganic electrolytes depends markedly on the type of cation and anion used. An abstraction maximum is obtained only in inorganic electrolyte solutions composed of (water) "structure-making" ions. No such maximum is obtained when there is a predominance of "structure-breaking" ions.

6. Exclusion of micellar aggregates from the structured interfacial region around the particles (owing essentially to their incompatibility with this region, and other phenomena that depend on sulfonate solubility, micellar composition, etc.) can contribute toward the presence of abstraction maximum. Structure-breaking ions facilitate transport and accommodation of surfactant aggregates, eliminating the possibility for such exclusion.

7. Selection of reagents such as Na2SiO3 on the basis of the above considerations and their role in decreasing the abstraction of sulfonate are noted.

Acknowledgments

Support of the National Science Foundation (ENG-76-08756) and Amoco Production Co., Chevron Oil Field Research Co., Exxon Research and Engineering Co., Gulf Research and Development Co., Marathon Oil Co., Mobil Research and Development Co., Shell Development Co., Texaco Inc., and Union Oil Co. of California is gratefully acknowledged.

References


32. Corrin, M. L.: "Adsorption of Long-Chain Electrolytes