

The Role of Mineral Dissolution in the Adsorption of Dodecylbenzenesulfonate on Kaolinite and Alumina

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ABSTRACT

The depletion of surfactants in contact with mineral systems can be due to many phenomena such as adsorption, precipitation with inorganics, or complexation with other chemicals. In many systems containing sparingly soluble oxide or silicates as the substrate, surfactant depletion has been assumed in the past to be solely due to adsorption. In this study, the solubility of kaolinite and alumina is investigated and the contribution of surfactant precipitation with dissolved mineral species is determined.

The solubility of kaolinite is studied as a function of pH, and aluminum was observed to occur in significant amounts under certain pH conditions. Precipitation of dodecylbenzenesulfonate with these dissolved mineral species results in an adsorption maximum in sulfonate micellar solutions. A minimum in residual aluminum concentrations is observed and this coincides with the adsorption maximum. Increase of pH to the alkaline range results in the disappearance of the adsorption maximum. Most importantly, thermodynamic calculations show that incongruent dissolution of kaolinite can occur above pH 4.7 and lead to the formation of a new gibbsite phase which strongly influences the surface properties of the kaolinite, and in turn, the adsorption of dodecylbenzenesulfonate.

Tests were also conducted with alumina and the dissolution of alumina was found to produce similar effects like kaolinite, particularly precipitation of sulfonate and micellar solubilization in the acidic region. Analysis of sulfonate depletion at low pH resulted in almost half of the adsorption being attributed to aluminum sulfonate precipitation. Adsorption, with precipitation isolated, shows the alumina surface to be covered with only a monolayer of the sulfonate.

INTRODUCTION

In investigations of mineral-surfactant interactions, surfactant depletion is usually measured from the difference in solution concentration of the surfactant before and after contact with the substrate and then attributed to the

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Gibbs surface excess or adsorption [3]. The measured losses are usually assumed to be solely due to adsorption, whether physical or chemical, when indeed substantial losses can occur from precipitation. Precipitation of surfactants can arise from interactions with dissolved mineral species, which are often neglected in mineral-surfactant systems studied previously due to the assumed insignificant solubility of substrates [4-6]. Adsorption of surfactants on minerals has been shown in the past to depend on the structure of the surfactant [7] and the type of mineral [8] as well as the physico-chemical properties of solution such as pH [4,6,9,10], temperature [11,12], ionic strength [13-15], and electrolyte [15]. These physico-chemical solution properties can also affect the dissolution behavior of minerals and can result in significant changes in the precipitation behavior of the surfactant.

In this study, the adsorption of dodecylbenzenesulfonate on kaolinite and alumina is investigated. Mineral solubility is simultaneously investigated and the various mechanisms responsible for surfactant loss, adsorption versus precipitation, are isolated.

EXPERIMENTAL

Materials

Dodecylbenzenesulfonate

Samples of dodecylbenzenesulfonate were supplied by Exxon Research and Engineering Co. and specified to contain a mixture of 2 ϕ to 6 ϕ dodecylbenzenesulfonate isomers. The high pressure liquid chromatogram (HPLC) for the sample is given in Fig. 1 where four of the five isomers are detected. Also present is a trace of impurities.

Surface tension results as a function of sulfonate concentration given in Fig. 2 indicate that there is no apparent minimum in micellar solutions with the CMC determined to be 9.7×10^{-5} kmol m⁻³. Calculation of Gibbs adsorption excess results in $\Gamma_{\text{DBS}} = 3.52 \times 10^{-10}$ mol cm⁻² and an area per molecule of 47.2 Å². Considering the sample to be a mixture of branched hydrophobes, the value is in agreement with the values cited in the literature [1].

Kaolinite

A well-crystallized sample of Georgia kaolinite purchased from the clay repository at the University of Missouri was subjected to an ion-exchange treatment described elsewhere [2] to produce the mono-ionic sodium kaolinite (Na-kaolinite) used in this study. BET surface area of the treated sample was determined by N₂ adsorption [Quantasorb] to be 9.8 m² g⁻¹.

DDBS(EX-1)

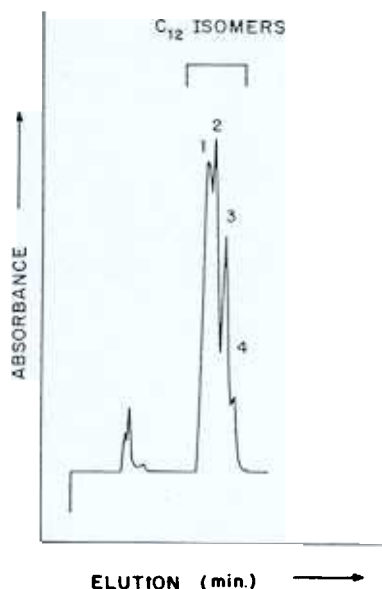


Fig. Analytical liquid chromatogram of synthetic dodecylbenzenesulfonate [DDBS(EX)]

Alumina

Alumina used was a Linde A high purity sample purchased from Union Carbide Corp. BET surface area was determined to be $15 \text{ m}^2 \text{ g}^{-1}$.

Inorganic salts used to adjust ionic strength and pH were of A.R. grade. Triple distilled water was used for all tests.

Adsorption procedure

Adsorption experiments were conducted in centrifuge tubes subjected to wrist-action shaking for 72 h with kaolinite samples and 24 h with alumina samples. At the end of the test, the suspension was centrifuged for 1 h at 2500g and the supernatant was analyzed for residual sulfonate. The adsorption density is calculated from the difference between initial and residual sulfonate concentration.

Analytical methods

Sulfonate concentrations

Sulfonate concentrations were determined either by two-phase titration using dimidium bromide/disulphine blue mixed indicator with $10^{-3} \text{ kmol m}^{-3}$ hexa-

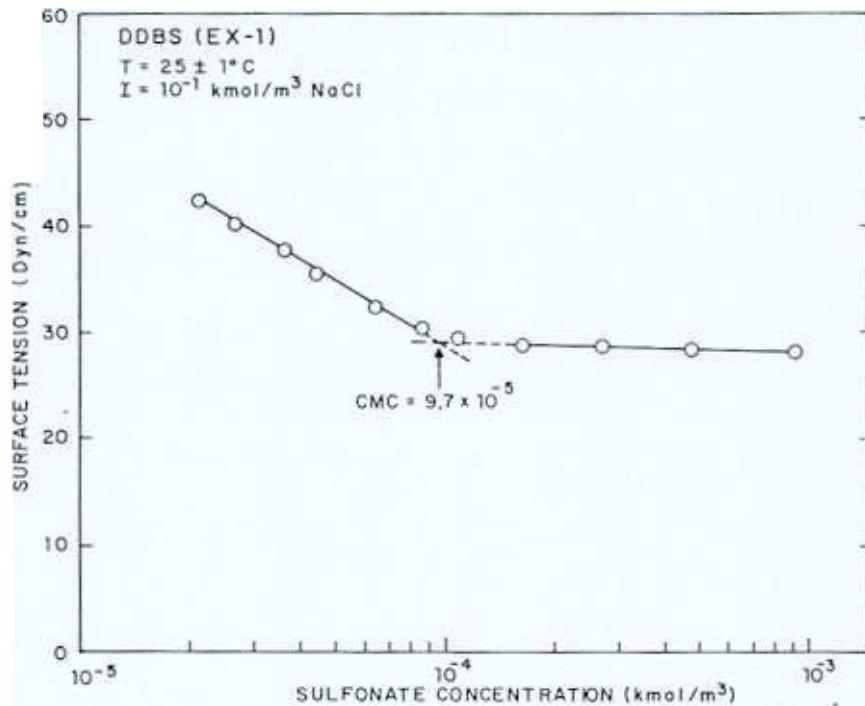


Fig. 2. Surface tension as a function of concentration of DDBS(EX) in $10^{-1} \text{ kmol m}^{-3} \text{ NaCl}$.

decyltributylammonium bromide [16,17], or by UV absorbance at 223 nm. Titrations were conducted for samples of sulfonate concentration greater than $10^{-4} \text{ kmol m}^{-3}$ with optical methods employed for dilute solutions.

Aluminium analysis

Aluminium concentrations were analyzed by colorimetry using Aluminon (aurin tricarboxylic acid) [3] at 527 nm using a Beckman DU-8 spectrophotometer.

RESULTS AND DISCUSSION

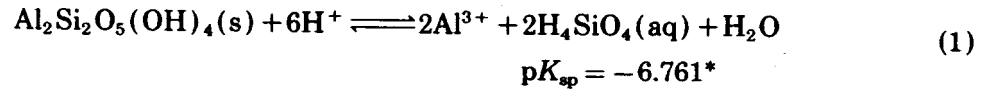
Kaolinite solubility

The interfacial properties as well as bulk reactions of surfactant–mineral systems can be expected to be influenced by the presence of dissolved mineral species. Investigation of surfactant–dissolved species interactions requires a quantitative knowledge of the various ionic species present, the coordinated complexes arising from ion–solution interactions, and the effect of solution properties such as pH and ionic strength on these interactions. Kaolinite sol-

ubility is studied here as a function of pH and modelled with thermodynamic constants and the relevant dissolved species, which can interact with the surfactant to form either soluble complexes or insoluble precipitates, are identified.

Kaolinite solubility equilibria

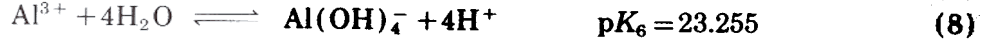
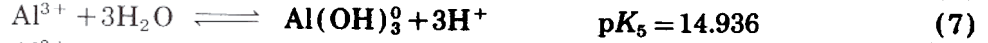
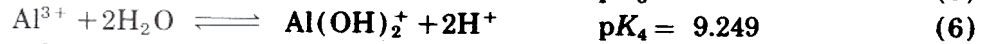
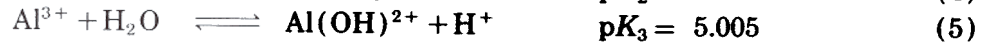
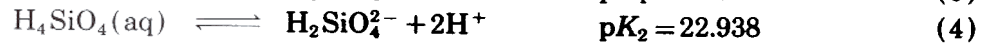
The solubility equilibrium reaction for kaolinite can be written as follows:



Assuming the activities of H_2O and $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ solid to be 1:

$$K_{\text{sp}} = a_{\text{Al}^{3+}}^2 a_{\text{H}_4\text{SiO}_4}^2 / a_{\text{H}^+}^6 \quad (2)$$

The dissolution of kaolinite consumes H^+ while releasing aluminum and silicon species and is therefore pH dependent. The released aluminum and silicon species can also undergo hydrolysis reactions that must be considered:



The above equilibria can be expressed in terms of H^+ , Al^{3+} and H_4SiO_4^0 , grouped in a mass balance equation, and substituted in the simplified solubility product Eqn (2) which results in the following equation:

$$a_{\text{Al}^{3+}} = \frac{K_{\text{sp}}^{1/2} a_{\text{H}^+}^3 (1 + K_1/a_{\text{H}^+} + K_2/a_{\text{H}^+}^2)}{1 + K_3/a_{\text{H}^+} + K_4/a_{\text{H}^+}^2 + K_5/a_{\text{H}^+}^3 + K_6/a_{\text{H}^+}^4} \quad (9)$$

The activity of Al^{3+} can now be computed at each pH with all other species determined once Al^{3+} is known. Kaolinite solubility can also be determined in various supporting electrolyte concentrations by determining the activity coefficients as a function of ionic strength, and then the concentrations of the various species. The activity coefficients are computed using either the Scatchard or the Davies equations.

Due to the possible precipitation of various solid phases, i.e. $\text{SiO}_2(\text{c})$ and $\text{Al}(\text{OH})_3(\text{c})$, other restrictions must be considered in determining the kaolinite solubility. Bulk precipitation can occur under appropriate conditions of pH and H_4SiO_4^0 or Al^{3+} levels as depicted by the following equilibria:

*Equilibrium constants calculated from thermodynamic data gathered in Refs [19-21]

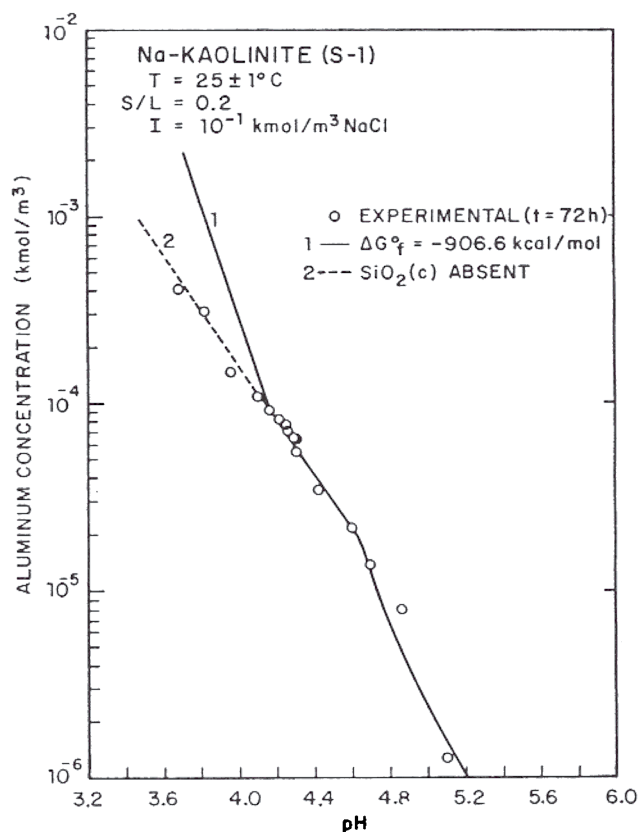
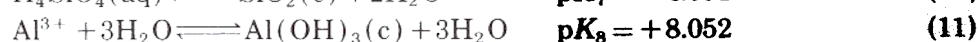
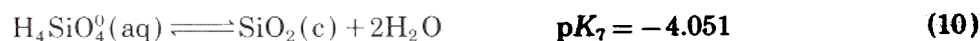


Fig. 3. Total aluminum concentration as a function for pH for Na-kaolinite dissolved in $10^{-1} \text{ kmol m}^{-3} \text{ NaCl}$ for 72 h. Curve 1 calculated considering the formation of both quartz and gibbsite. Curve 2 calculated considering amorphous silica formation rather than quartz.



Experimental determination of kaolinite solubility

Kaolinite solubility was determined at 25°C in $10^{-1} \text{ kmol m}^{-3} \text{ NaCl}$ by contacting 2 grams of Na-kaolinite with 20 cm^3 of electrolyte, centrifuging to separate solids from liquid, and analyzing for aluminum concentration colorimetrically.

The solubility of kaolinite, as measured by aluminum concentrations, is shown in Fig. 3 as a function of pH. The computed total aluminum concentration as a function of pH is also given. A free energy of formation value for kaolinite, ΔG_f^0 , of $-906.6 \text{ kcal mol}^{-1}$ was obtained from curve fitting of the

experimental data (a value well within the range mentioned in the literature [19]). The computed values for Al_T versus pH (curve 1) were obtained, with the precipitation of $Al(OH)_3(s)$ included in the equilibria used to solve the above equations. For pH values less than 4.2, agreement between computed and experimental Al_T values was obtained by omitting the equilibria for quartz formation. Siever [22] has reported the rate of crystallization of quartz to be very slow in the low temperature range with the solubility of amorphous silica representing the upper limit of dissolved aqueous silicic acid. Under the conditions of the solubility tests here, an excellent fit between computed and measured aluminum concentrations resulted when amorphous silica precipitate rather than crystalline quartz was assumed as the solid phase resulting from incongruent kaolinite dissolution (see curve 2 in Fig. 3).

Analysis of the above data leads to the following concerning the kaolinite solubility:

(1) A value of $-906.6 \text{ kcal mol}^{-1}$ for the free energy of formation of kaolinite is appropriate for modelling solubility as a function of pH; this is in agreement with literature values of -906.4 and $-906.1 \text{ kcal mol}^{-1}$ for Georgia kaolinites as determined by Kittrick [23,24].

(2) The solubility results obtained at 72 h indicate a metastable condition since amorphous silica seems to govern kaolinite solubility rather than the slower forming, more thermodynamically stable crystalline quartz.

(3) Formation of gibbsite may result from incongruent dissolution of kaolinite above pH 4.7 and this could produce marked effects on the surface charge characteristics of the suspension.

Based on the above, the concentrations of the species present for kaolinite dissolved in $10^{-1} \text{ kmol m}^{-3}$ NaCl at 25°C were calculated and the resultant species distribution diagram is shown in Fig. 4. Interestingly, the high concentrations of Al^{3+} around and below neutral pH suggest that it can be important in a kaolinite system contacted with anionic surfactants because of the possibilities for either complexation, precipitation, or adsorption activation.

Depletion of dodecylbenzenesulfonate in kaolinite systems

Adsorption isotherms of sulfonates on minerals such as kaolinite have been shown to exhibit special features such as maximum in the critical micelle concentration (CMC) region. The interactions proposed for such behavior have been discussed extensively in the literature [25-29] and in many systems, a combination of interactions are involved. Precipitation of surfactant molecules by inorganic ions and subsequent redissolution of the precipitate in micellar solutions has been identified as a significant factor for surfactant depletion and the appearance of an adsorption maximum. Isolation of the contribution of precipitation to the overall surfactant depletion in a mineral system must be accomplished before actual adsorption mechanisms can be

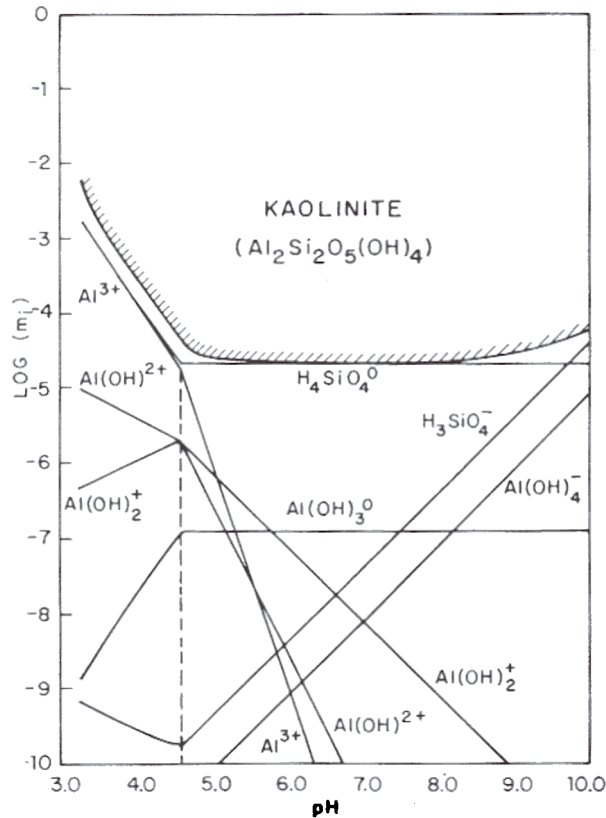


Fig. 4. Dissolved kaolinite species as a function of pH in $10^{-1} \text{ kmol m}^{-3}$ NaCl calculated considering the formation of gibbsite and amorphous silica as a result of the incongruent dissolution of kaolinite.

determined. For the present adsorption studies, sulfonate depletion is measured while simultaneously monitoring the residual aluminum concentrations.

Sulfonate abstraction* and residual aluminum concentrations obtained for kaolinite/dodecylbenzenesulfonate, DDBS (EX), are shown in Fig. 5. An adsorption maximum is not obtained for this surfactant. The CMC of the system as measured by dye solubilization of the sulfonate-kaolinite supernatants was found to be approximately $9.5 \times 10^{-5} \text{ kmol m}^{-3}$, which agrees with the value as determined by surface tension measurements (9.7×10^{-5}) and coincides with the onset of plateau adsorption.

Examination of the sulfonate uptake only would indicate the absence of any aluminum sulfonate precipitation in this system since an adsorption maximum is not obtained. The measured total aluminum in solution can, however, be

*Abstraction includes both adsorption and precipitation of sulfonate.

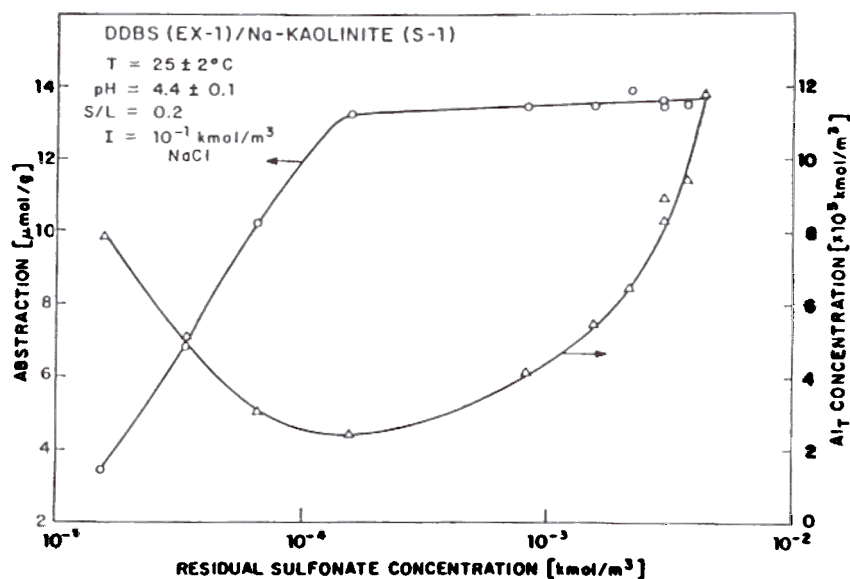


Fig. 5. Abstraction isotherm and measured total aluminum concentrations for the DDBS(EX)-kaolinite system at pH 4.4.

seen to exhibit a minimum near the CMC, indicative of precipitation-redissolution. Evidently, even though some precipitation occurred, the amount of sulfonate precipitated is small compared to that of the sulfonate depleted due to adsorption, and therefore, the adsorption maximum was not detected.

Indeed if precipitation-redissolution of aluminum sulfonate leads to an adsorption maximum, an increase in the level of the dissolved aluminum species should result in higher precipitation levels and a more pronounced maximum. Kaolinite dissolution results in $d \log Al_T / dpH$ of approximately -2 ; therefore a decrease in the system pH should result in enhanced sulfonate depletion due to increased precipitation, in addition to increased electrostatic adsorption. Results of tests at $pH\ 3.7 \pm 0.3$ for the DDBS(EX)/kaolinite system are given in Fig. 6. Lowering the pH from 4.4 to 3.7 resulted in increased sulfonate depletion, and also produced a very sharp adsorption maximum, indicating the increased contribution of precipitation-redissolution in this system. The residual aluminum levels also demonstrated larger changes in the CMC region corresponding to increased precipitation.

The presence of a pronounced adsorption maximum at the lower pH values (with an increase in dissolved aluminum species) clearly supports the hypothesis that the change in aluminum concentration is the result of precipitation-redissolution of aluminum sulfonate complexes. A comparison of the measured aluminum concentration with aluminum depletion is given in Fig. 7

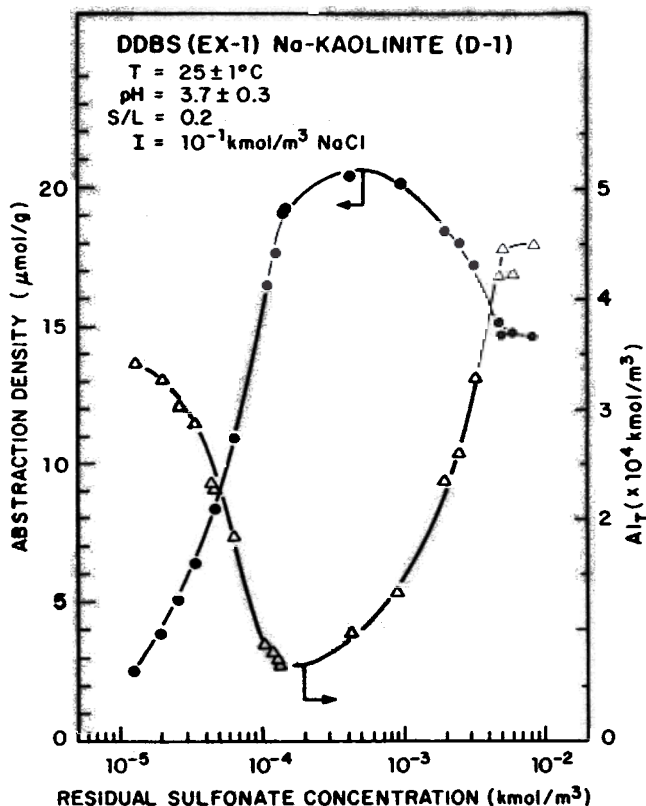


Fig. 6. Abstraction isotherm and measured total aluminum concentrations for the DDBS(EX)-kaolinite system at pH 3.7.

for two different pH levels, with the initial aluminum concentration obtained from tests conducted under the same conditions but in the absence of sulfonate. The system at the lower pH (3.7) not only has a higher measured residual concentrations but also exhibits larger depletion in aluminum concentration as the sulfonate concentration is increased. At pH 3.7, ΔAl_T reaches values of $3.8 \times 10^{-4} \text{ kmol m}^{-3}$ whereas in the case of the system at pH 4.4, ΔAl_T values approach only $9.6 \times 10^{-5} \text{ kmol m}^{-3}$. The contribution of precipitation to overall sulfonate depletion was determined by assuming the precipitate formed to be $\text{Al}(\text{DDBS})_3$. The results are given in Table 1 and show that a residual sulfonate concentration near the CMC ($10^{-4} \text{ kmol m}^{-3}$), the maximum contribution of precipitation is 12% for the system at pH 4.4 whereas the contribution is 30.5% at pH 3.7. Although precipitation does appear to exist in the system at pH 4.4, this was not sufficient to produce an abstraction maximum. However, clearly at these precipitation levels, its contribution must be accounted

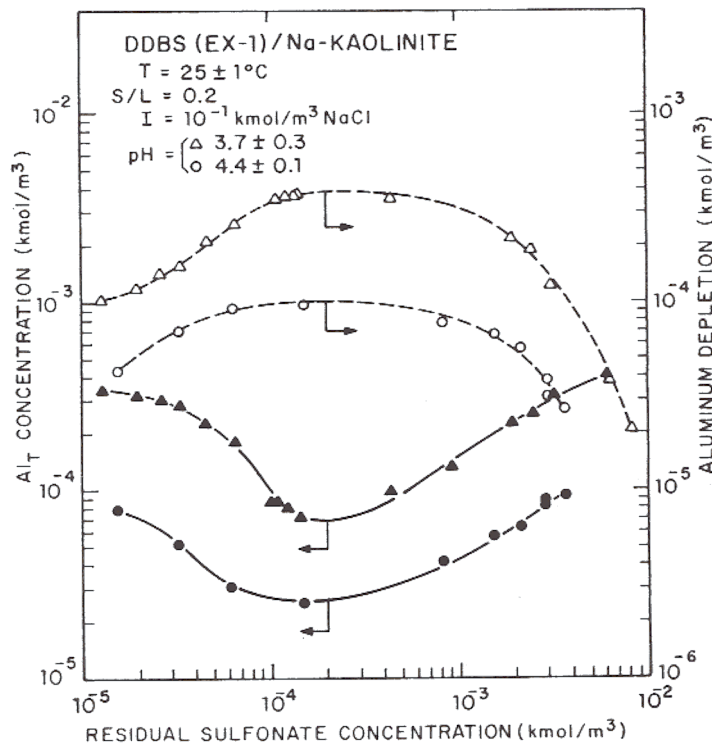


Fig. 7. Comparison of residual concentrations and calculated aluminum depletion for the DDBS(EX)-kaolinite systems at pH 3.7 and pH 4.4.

for at any pH values while developing an accurate understanding of the adsorption phenomenon.

Precipitation of aluminum sulfonate complexes

Precipitation of dodecylbenzenesulfonate with cationic aluminum species will occur if the respective concentrations meet the solubility product requirements. To substantiate the existence of aluminum sulfonate precipitates in the kaolinite system, solubility tests were conducted with solutions of aluminum chloride contacted with dodecylbenzenesulfonate at varying concentration. The results are presented in Fig. 8 as the ratio of the residual to initial concentration as a function of residual dodecylbenzenesulfonate concentration for both the sulfonate and aluminum ions. For both ions, precipitation is evident in the pre-micellar concentration range as the ratios decrease from 1 to < 0.2 , with an

TABLE 1

Contribution of precipitation in the DDBS(EX)-kaolinite systems at two pH levels considering the formation of $\text{Al}(\text{DDBS})_3$.

	pH ^d	
	4.4	3.7
1. Al_T Initial ^a	1×10^{-4}	3.98×10^{-4}
2. Al_T Residual ^c	1×10^{-6}	8.50×10^{-5}
3. Al_T Depletion (1-2)	1×10^{-6}	3.13×10^{-5}
4. DDBS Precipitated ^b	1×10^{-4}	9.39×10^{-4}
5. Total DDBS Depletion ^c	1×10^{-3}	3.08×10^{-3}
6. DDBS Adsorption (5-4)	$\times 10^{-3}$	2.14×10^{-3}
7. Percent Precipitation	12	30.5

^aMeasured in the absence of sulfonate.

^bThree times Al_T depletion.

^cMeasured at residual DDBS concentration of $10^{-4} \text{ kmol m}^{-3}$.

^dConcentration given in kmol m^{-3} .

apparent redissolution in micellar solutions as indicated by the ratios re-approaching 1.0. The minimum in each curve occurs in the CMC region and thus further supports the precipitation-micellar redissolution model. The shape

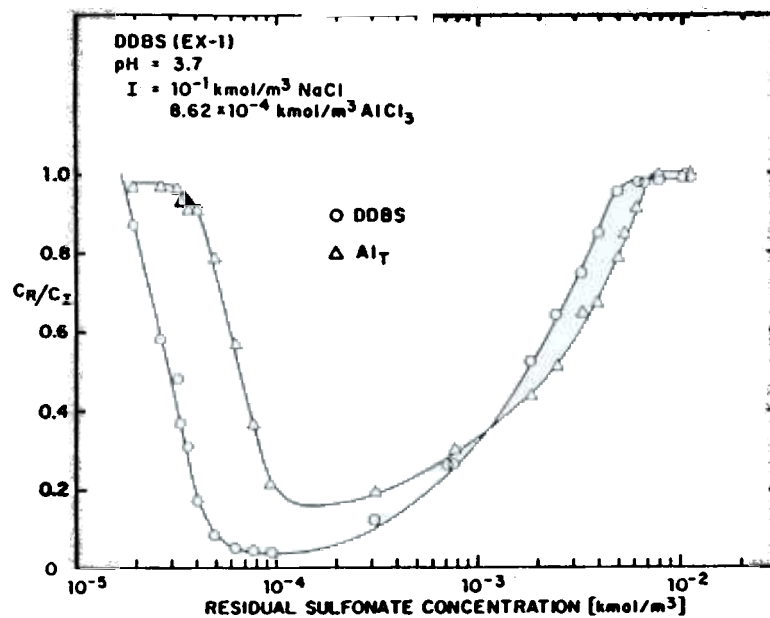


Fig. 8. Ratio of residual to initial concentrations of sulfonate and aluminum versus residual sulfonate concentration for the DDBS (EX)- AlCl_3 system at pH 3.7.

of the curves for aluminum sulfonate precipitation also correlate to the abstraction and aluminum concentration isotherms in Fig. 6; a sharp increase in sulfonate depletion as concentrations approach 10^{-4} kmol m⁻³ DBBS, followed by a gradual decrease in abstraction as DBBS concentrations approach 10^{-2} kmol m⁻³, the same concentration where complete redissolution is evident in the solubility tests. Thus at pH 3.7, it is quite clear that precipitation and subsequent micellar redissolution of aluminum sulfonate is indeed a phenomenon that can contribute to the abstraction maximum observed in this study.

Adsorption of kaolinite at pH levels above point of zero charge

The high abstraction of dodecylbenzenesulfonate on kaolinite at low pH levels resulted from precipitation due to the release of aluminum into solution in cationic form under the acidic conditions studied. Increase of the pH above the PZC of kaolinite into the neutral pH region should result in decreased abstraction of sulfonate due to a reduction in the electrostatic interactions between the kaolinite surface and sulfonate, as well as reduced precipitation owing to a decrease in the cationic dissolved aluminum species.

Results obtained for DBBS (EX) abstraction at pH 7.9 ± 0.2 are given in Fig. 9 and it can be seen that there is no adsorption maximum in this case. At this pH, aluminum was not detectable by colorimetric analysis, but based on the solubility curve in Fig. 4, the aluminum present would predominate as $\text{Al}(\text{OH})_3(\text{aq})$ or $\text{Al}(\text{OH})_4^-$. There should be no sulfonate precipitation under these conditions and the abstraction can be assumed to be just adsorption.

Abstraction tests were also conducted under alkaline pH conditions in order to investigate the role of dissolved anionic aluminum species, if any, on the surfactant abstraction. The results obtained at pH 10.8 given in Fig. 10 suggest the following:

(1) Increase of pH reduces the adsorption of DBBS on kaolinite, as expected, but the magnitude of adsorption is much higher than that expected based on electrostatic considerations (zero adsorption since the PZC of kaolinite is in the pH range 4.5–5.0).

(2) The concentration of dissolved aluminum also increases as the pH is increased but is independent of the residual sulfonate concentration (or adsorption) at this pH.

A question arises as to why sulfonate adsorbs at all at pH levels well above the PZC of kaolinite. At pH 7.9 and 10.8, both the surfactant and the mineral should be negatively charged and the electrostatic driving force for adsorption should be absent. We consider the explanation for the observed behavior to

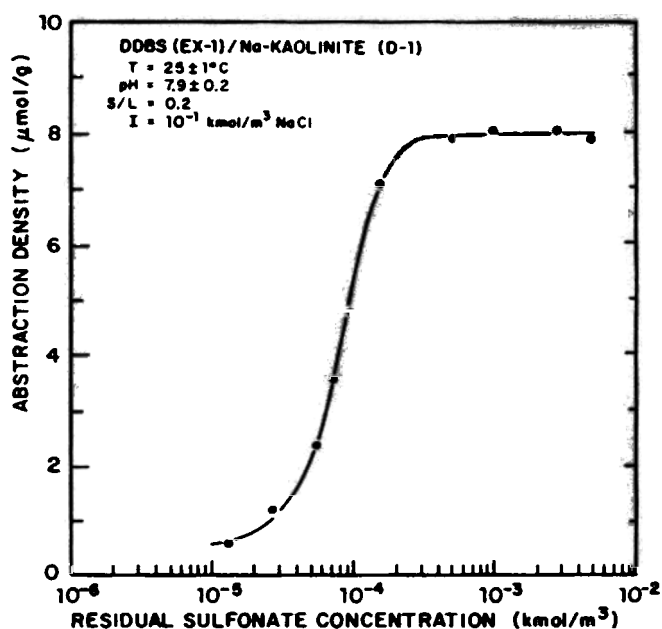


Fig. 9. Abstraction isotherm for the DDBS (EX)-kaolinite system at pH 7.9. Aluminum concentrations were below the detection limit.

reside in the kaolinite dissolution. Above pH 4.7, kaolinite dissolves incongruently to yield gibbsite $[\text{Al}(\text{OH})_3(c)]$ as indicated from solubility calculations and zeta potential measurements. Thus at pH 7.9 and 10.8, gibbsite particles or surfaces can be present in the kaolinite system. Previous studies on gibbsite have reported its PZC to be between pH 8.5 and 9.1 [30,31]; gibbsite surfaces can thus be expected to have a net positive charge at pH 7.9 and provide the necessary coulombic driving force for adsorption of the anionic sulfonate. At pH 10.8, the net surface charge can be expected to be negative but enough positive sites must exist to adsorb the sulfonate molecules since the system is at only a couple of pH units above the PZC of gibbsite. Zero adsorption for alkylarylsulfonate/alumina systems was reported in the literature to occur only above pH 12.5 [32].

Mineral dissolution thus plays an important role in the depletion behavior of dodecylbenzenesulfonate in kaolinite suspensions. Measuring only sulfonate depletion, as is typically done, will not suffice for a thorough understanding of the mechanisms of interaction. Results for the depletion of DDBS contacted with kaolinite as a function of pH is summarized in Fig. 11, and by monitoring the dissolution of kaolinite the following conclusions concerning the mechanisms can be made:

- (1) At acidic pH levels below the PZC (3.7), significant precipitation of the

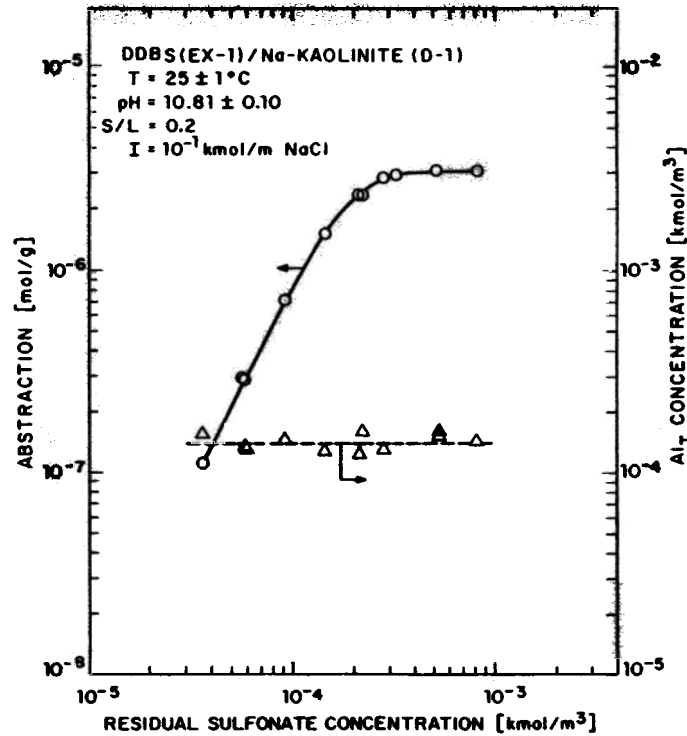


Fig. 10. Abstraction isotherm and measured total aluminum concentrations for the DDBS(EX)-kaolinite system at pH 10.8.

dodecylbenzenesulfonate with cationic dissolved aluminum species occurs and subsequent redissolution of the aluminum-sulfonate precipitates produces an abstraction maximum.

(2) At or near the pH of the PZC (4.4), a reduction in the concentration of dissolved cationic aluminum species results in decreased precipitation such that the adsorption maximum is no longer observed. The contribution of aluminum-sulfonate precipitation still must be accounted for prior to determining actual adsorption densities.

(3) At pH levels above the PZC both in the neutral region (7.9) and the alkaline region (10.8), incongruent dissolution of kaolinite can result in phase transformations to gibbsite such that adsorption occurs at levels governed not only by the surface of the kaolinite, but also by that of gibbsite.

Adsorption of dodecylbenzenesulfonates on alumina

The nature of the dissolved species, as well as the isoelectric point of the mineral, play a significant role in the adsorption of sulfonate on kaolinite.

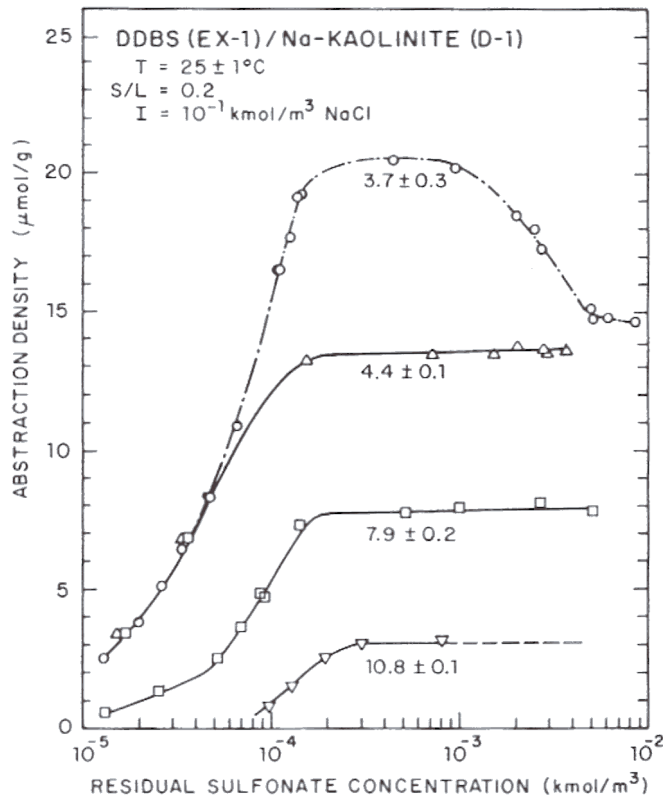


Fig. 11. Summary of abstraction (adsorption) isotherms for DDBS (EX)-kaolinite systems at different pH.

Kaolinite has an isoelectric point reportedly in the pH range 4.5–5.0 [33]. The buffering capacity of the mineral due to its amphoteric nature causes consumption of acid and/or base through interactions of H^+/OH^- ions with the surface hydroxyl groups and results in natural equilibrium pH values in the acidic range. The balance between dissolution and surface charge generation is therefore maintained in the acidic range. This result is important in abstraction tests since the hydrolyzed species of $Al(OH)_n^{3-n}$ in equilibrium with kaolinite are pH dependent with the cationic species predominating in the acidic pH range. For electrolyte solutions under a variety of pH levels contacted with kaolinite, cationic aluminum species can be expected to be present in solution which can complex and/or precipitate anionic surfactants such as DDBS. An alternative aluminum type mineral such as aluminum oxide, Al_2O_3 , has an isoelectric point of pH 9.1 [31]; one can expect the dissolution–surface charge equilibria to be maintained in this alkaline region under natural pH

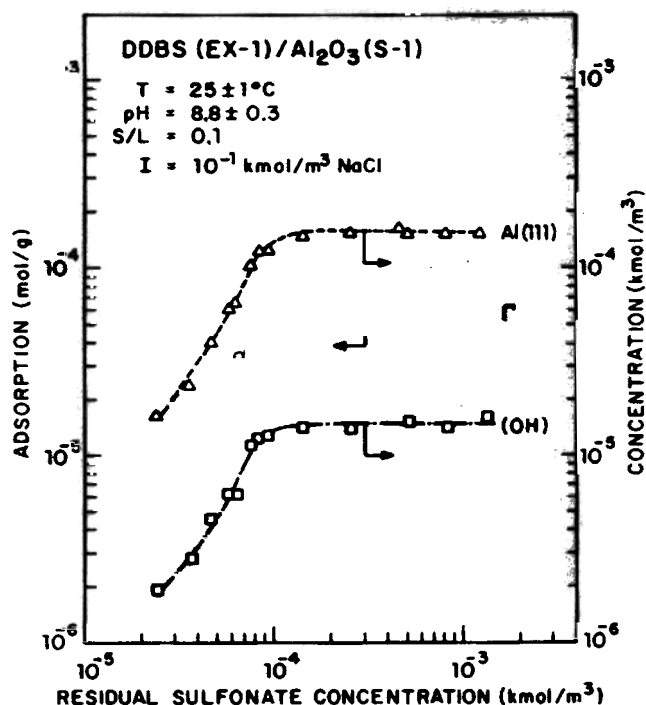


Fig. 12. Abstraction isotherm and measured total aluminum and hydroxyl ion concentrations for the DDBS (EX) - alumina system at pH 8.9.

conditions. The dissolved mineral aluminum species for Al_2O_3 at natural pH will predominate as $\text{Al}(\text{OH})_4^-$ with the secondary species being neutral, $\text{Al}(\text{OH})_3^0$. Owing to its apparent low solubility, alumina substrates have been used in modelling adsorption quite extensively in the past [4-6] but without taking into account the dissolution of the mineral. Only in our previous work has the role of alumina dissolution been identified to play a major role in determining adsorption mechanisms.

The adsorption isotherm and dissolved aluminum concentrations obtained for the DDBS (EX) - alumina system at $\text{pH } 8.8 \pm 0.3$ are shown in Fig. 12. Also indicated in the figure is the change in pH that accompanied the adsorption process as shown by the hydroxyl ion concentration. The major features of this system are:

- (1) The adsorption isotherm exhibits plateau adsorption with the onset of plateau coinciding with the CMC.
- (2) The dissolved aluminum and hydroxyl ion concentrations also exhibit the same behavior as adsorption; an increase with increase sulfonate concentration with plateaus above the CMC.

Clearly, the adsorption process of DDBS at the alumina-water interface

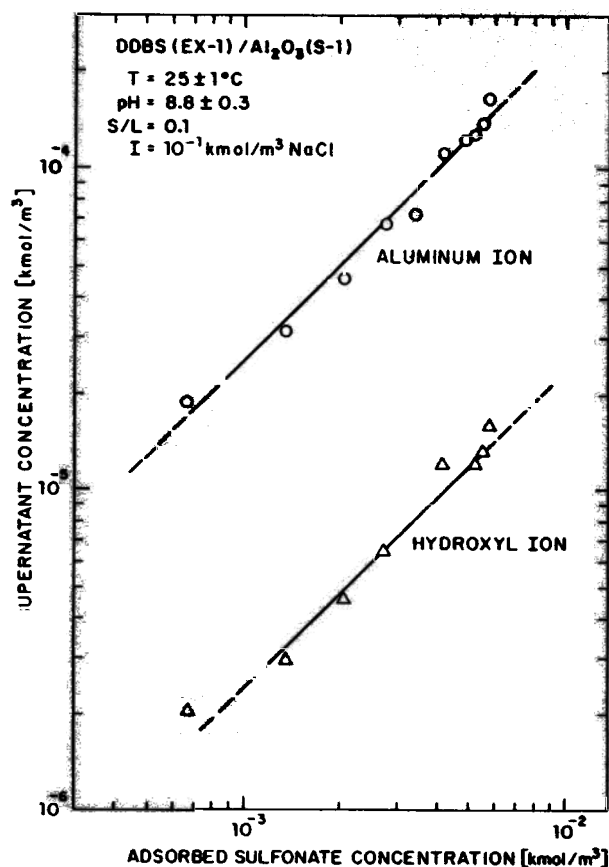


Fig. 13. Measured total aluminum and hydroxyl ion concentrations as a function of the adsorbed sulfonate concentration for the DDBS (EX)-alumina system at pH 8.9.

results in ion exchange between aluminum ions and hydroxyl ions. This can be clearly seen by examining the concentrations of both aluminum and hydroxyl ions as a function of adsorption (Fig. 13). Both ions exhibit log linear relationships with a slope of 1.0. The difference between the sum of the hydroxyl and aluminate ions exchanged with sulfonate may be due to the presence of swamping amounts of chloride ion which can also be expected to undergo an ion-exchange process.

It is to be noted that the kaolinite-DDBS systems at acidic pH levels, the total aluminum concentration does not exhibit a minimum at or near the CMC. This confirms the absence of aluminum sulfonate precipitation in the alumina system since the hydrolyzed species at pH 8.8 are predominantly in the $\text{Al}(\text{OH})_4^-$ form. In the absence of precipitation, an adsorption maximum due to precipitation-redissolution is also not expected as is indeed the case.

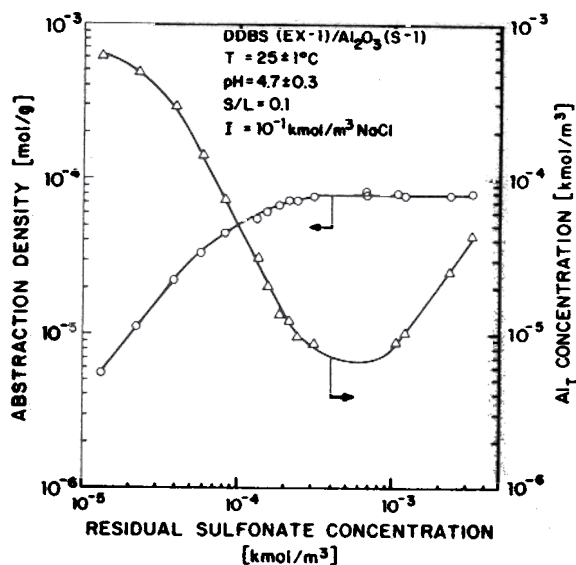


Fig. 14. Abstraction isotherm and measured total aluminum concentrations for the DDBS(EX)-alumina system at pH 4.7.

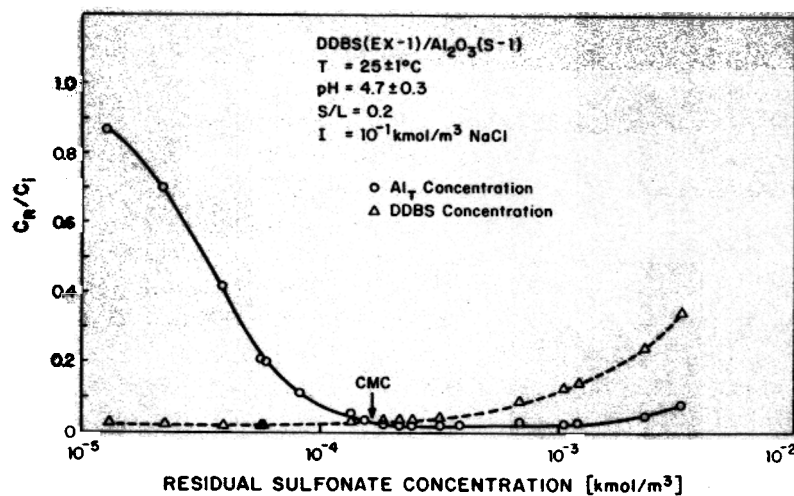


Fig. 15. Ratio of residual to initial sulfonate and aluminum concentrations versus residual sulfonate concentration for the DDBS(EX)-alumina system at pH 4.7.

To further test the role of dissolved mineral species on the depletion of sulfonate, adsorption tests were conducted at acidic pH levels where the dissolved aluminum species are expected to be in cationic form. Abstraction and aluminum concentration results at pH 4.7 are given in Fig. 14. Adsorption maximum is again absent at this pH, although the isotherm does not exhibit the sharp

transition at the CMC observed at pH 8.8. Note that the CMC determined by dye solubilization of the supernatants, however, shifted from 9.5×10^{-5} to $1.26 \times 10^{-4} \text{ kmol m}^{-3}$ DDBS. Interestingly, the aluminum concentration curve is found to exhibit a steep minimum in the CMC region indicative of precipitation–redissolution that was observed for the kaolinite systems. Furthermore, the aluminum concentration in the absence of sulfonate is close to $8 \times 10^{-4} \text{ kmol m}^{-3}$ whereas the residual aluminum concentration at the minimum near the CMC is only $7 \times 10^{-6} \text{ kmol m}^{-3}$; a 100 fold decrease in aluminum concentration occurred due to the presence of sulfonate. Clearly, precipitation of aluminum sulfonate complexes must be occurring to account for such a decrease.

The absence of an adsorption maximum in this system would seem to indicate the absence of precipitation–redissolution. However, if the amount of the precipitate is much more than the concentration of micelles present, redissolution would be minimal and no adsorption maximum would be observed. To examine this possibility, the precipitate formed was assumed to be $\text{Al}(\text{DDBS})_3$, and the contribution of precipitation to the overall sulfonate depletion was determined to be 47% at a residual sulfonate concentration of $10^{-4} \text{ kmol m}^{-3}$, which is near the CMC.

Based on the aluminum depletion one can see that the amount of precipitation occurring under these conditions can be as much as 47% of the overall measured sulfonate depletion. Such high levels of precipitation in the system would require solutions of very high micellar content before significant redissolution occurs; concentrations that may not be practical due to limited sulfonate solubility. This is clearly seen when examining the ratios of residual to initial aluminum and sulfonate concentrations as a function of the sulfonate concentration (Fig. 15). The rate for aluminum concentration decreases initially and then remains quite low for a large increase in sulfonate concentration above the CMC. Only at much higher sulfonate concentrations does the Al ratio begin to increase, indicative of redissolution, but the highest value obtained was still only 0.1. The sulfonate ratio is very low in the premicellar range and it also begins to increase above the CMC, crossing the aluminum ratio curve at the CMC. These results indicate that the redissolution process has begun but the amount of precipitate in the system is rather high compared to the amount of micelles formed. At still higher sulfonate concentrations, the extent of redissolution can again be expected to be significant resulting also in an adsorption maximum.

The investigation of adsorption using alumina has thus clearly helped to confirm that the dissolved species do play an important role in determining the surfactant depletion. In the case of the dodecylbenzenesulfonate–alumina system at pH 4.7, the apparent adsorption plateau was at $8.1 \times 10^{-5} \text{ mol g}^{-1}$ ($5.4 \times 10^{-10} \text{ mol cm}^{-2}$) or 150% monolayer coverage based on the area per molecule of the surfactant. Such multilayer adsorption has been proposed in the literature [5,34] and is the basis for the admicelle adsorption theory of

Harwell et al. [34]. In their studies, the adsorption plateau of an alkylarylsulfonate on alumina was found to increase as the system pH was decreased. At pH values between 2 to 3, the adsorption plateau reached a limiting value and the authors considered this to be the region of saturated adsorption in the form of a bilayer. Thus, the bilayer adsorption theory arises from measurements of sulfonate depletion in a pH region where mineral dissolution is significant but ignored by the authors.

Computation of the contribution of aluminum-sulfonate precipitation for the DDBS-alumina system at pH 4.7 yields an adsorption plateau at 6.0×10^{-5} mol g⁻¹ or 3.9×10^{-10} mol cm⁻², and 111% monolayer coverage. It appears that within the experimental error of the various techniques, sulfonate adsorption on alumina reaches only a monolayer. At pH 8.8, where aluminum-sulfonate precipitation is absent, the adsorption plateau occurs at 5.5×10^{-5} mol g⁻¹ or 3.67×10^{-10} mol cm⁻² which is 104% monolayer coverage. It is clear that only monolayer adsorption on alumina of the sulfonate occurs in both the acidic and alkaline pH regions. If the dissolved mineral species were not monitored, the sulfonate depletion at pH 4.7 would have been attributed totally to adsorption, and subsequently, a conclusion of multilayer adsorption would result. With aluminum species also measured along with the adsorption, sulfonate depletion is shown in this study to be the cumulative result of adsorption and precipitation, with precipitation accounting for as much as 50% of the overall sulfonate depletion. The significance of this composite aspect of the depletion problem in studying adsorption mechanisms is obvious. It is also clear that there is a need for a balance between adsorption, precipitation, and micellization for the adsorption maximum to be observed. Too little or too much precipitation will result in apparent plateau adsorption and can lead to an erroneous interpretation of results.

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