Mechanism of Hysteresis in Sulfonate/Kaolinite Adsorption/Desorption Systems: Chromatographic Separation of Isomers

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Received August 11, 1986; accepted January 12, 1987

The mechanisms of interaction between dodecylbenzene sulfonate and kaolinite are investigated in this study by both adsorption and desorption techniques. While the adsorption isotherm at pH 7.9 exhibits a typical S-shape indicative of conventional physical adsorption forces, desorption tests result in an apparent irreversibility with adsorption densities larger than that of the initial adsorption isotherm—a positive hysteresis. Analysis of the adsorption/desorption supernatants by analytical liquid chromatographic techniques showed strong preferential adsorption of the more hydrophobic dodecylbenzene sulfonate components that result in solutions of totally different distributions than the initial stock surfactant. Initially, the content of trace impurities of low hydrophobicity in the surfactant is of the order of 2% but reaches levels as high as 85% of the residual solution as adsorption of dodecylbenzene sulfonate isomers occurs. Recalculation of the isotherm for adsorption of dodecylbenzene sulfonate isomers only rather than for the total sulfonate results in a shift of the isotherm to much lower concentrations. Dilution procedures used to create the driving force for desorption result in an enrichment of the sulfonate solutions with dodecylbenzene sulfonate isomers; thus hysteresis is observed due to the changes in component distribution of the surfactant solution to comprise only dodecylbenzene sulfonate isomers.

INTRODUCTION

The adsorption of alkylarylsulfonates on oxide and silicate minerals has been studied extensively with the forces of interaction considered to be physical (noncovalent) in nature, i.e., electrostatic, hydrophobic, van der Waals attraction (1-4). Descriptive thermodynamic models based on equilibrium adsorption exist in the literature (2, 5-9); however, a major omission in all the adsorption experiments from which the proposed models originate is the test of adsorption reversibility. Equilibrium adsorption must show reversibility from a thermodynamic viewpoint and further insight into the nature of forces, i.e., chemical versus physical, can be obtained from desorption tests. Our past desorption studies with sulfonate/kaolinite systems have clearly shown hysteresis or irreversibility (10, 11) and precipitation of surfactant with dissolved mineral species (12) has been proposed to account partly for such behavior.

In this study, adsorption reversibility was tested for a sulfonate/kaolinite system under conditions where mineral solubility is minimal. To test adsorption reversibility, the system was perturbed only by dilution and the changes in adsorption density were monitored. Since the use of isomerically pure surfactants at ambient temperature is restricted by solubility, an isomeric blend was used, but chromatographic methods were employed to monitor any changes in surfactant composition. All the system variables were thus monitored so that true adsorption reversibility could be tested.

MATERIALS AND METHODS

Dodecylbenzene sulfonate. Samples of dodecylbenzene sulfonate were supplied by
Exxon Research and Engineering Co. and specified to be a mixture of 2φ to 6φ dodecylbenzene sulfonate isomers. The high-pressure liquid chromatogram (HPLC) for the sample is given in Fig. 1 in which four of the five isomers are resolved. Also present are a trace of more polar impurities which are by-products of the sulfonation process and are believed to be disulfonated material.

Surface tension results given in Fig. 2 as a function of sulfonate concentration show no minimum and yield a CMC of $9.7 \times 10^{-5}$ kmole/m³. Calculation of Gibb’s adsorption excess results in $\Gamma_{\text{DDBS}} = 3.52 \times 10^{-10}$ mole/cm² and an area per molecule of 47.2 Å². Considering the sample to be a mix of branched hydrophobes, this value can be considered to be in agreement with those in the literature (13).

**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 (14) to produce the sodium kaolinite used in this study. BET surface area of the treated sample was determined by N₂ adsorption (Quantasorb) to be 9.8 m²/g.

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

**Adsorption/desorption procedure.** The adsorption/desorption tests involved equilibration of the mineral in the desired surfactant solution and determination of the initial surfactant depletion and therefrom adsorption density by removing a known volume of the supernatant and analyzing for residual concentration. Desorption tests were conducted by adding a diluent adjusted to the system ionic strength and pH at the same volume as that of the supernatant removed. The total volume and thus solid-to-liquid ratio remain constant as the dilution stage is repeated for many cycles with the surfactant concentration monitored at each stage. The adsorption density at each step is calculated from

$$\Gamma_n \text{[mole/g]} = [C_i - C_n] \times \frac{V}{W},$$

where $\Gamma_n$ is the adsorption in moles per gram, $C_i$ is the initial sulfonate concentration, $C_n$ is the residual sulfonate concentration, $V$ is the total solution test volume, and $W$ is the mass of absorbent solids.

$$\Gamma_0 = [C_i - C_0] \frac{V}{W} \ldots \text{initial adsorption.}$$

Let $[C_i - C_1] = \Delta C_1$

$$\Gamma_n = [(C_{r,n-1})\alpha + \Delta C_{n-1} - C_{r,n}] \frac{V}{W}$$

with

$$[(C_{r,n-1})\alpha + \Delta C_{n-1}] = C_{r,n},$$

where $\alpha$ is the dilution factor $[1 - \text{volume removed}/V]$, $\Gamma_0$ is the initial adsorption, and $\Gamma_n$ is the adsorption after $n$ dilutions.

Sulfonate concentrations were determined either by a two-phase titration technique using dimidium bromide/disulfine blue mixed indicator with $10^{-3}$ kmole/m³ hexadecyltrimethylammonium bromide (15, 16), or by UV absorbance at 223 nm. Titrations were conducted for samples of sulfonate concentration greater than $10^{-4}$ kmole/m³ with optical methods employed for dilute solutions.

**Analytical liquid chromatography.** High-pressure liquid chromatographic (HPLC) analysis of the surfactant samples was con-
ducted using a Beckman 344 CRT-based gradient liquid chromatograph consisting of a 421 system controller, two 112 solvent delivery modules, a 165 variable wavelength UV-Vis detector, a 20-μl injection loop, and a Shimadzu data handler/printer. The reversed phase column was composed of 5-μm silica particles bonded with C₁₈ organochlorosilane which coats the silica surface with long-chain hydrocarbon molecules and renders a hydrophobic environment. The mobile phase, filtered through 0.2-μm Millipore filters, was a 60:40 mixture of acetonitrile and 10⁻² kmole/m³ tetrabutylammonium phosphate (TBAP) ion-pairing agent. The mobile phase was chosen based on (i) the low UV cutoff of acetonitrile and (ii) the ability of TBAP to complex with anionics and it allows separation and detection (at 228 nm for phenyl-substituted compounds in this case) of the various surfactant components. In reversed-phase liquid chromatography, components that are more polar favor the mobile phase and elute in the order of decreasing polarity. Less polar compounds favor the stationary phase and elute at longer times.

RESULTS AND DISCUSSION

Adsorption/Desorption Isotherms

Adsorption/desorption results obtained for the dodecylbenzene sulfonate/Na-kaolinite system at pH 7.9 and an ionic strength of 10⁻¹ kmole/m³ NaCl are given in Fig. 3. In agreement with desorption results obtained in the past (10, 11), hysteresis is apparent, although unlike in previous studies, the adsorption densities after the dilution are all larger than the initial values. Interestingly, dilution of the supernatants at residual concentrations greater than CMC results in an increased adsorption. Dilutions which result in supernatant concentrations less than CMC always exhibit a decrease in adsorption (desorption) although at larger densities. This desorption behavior is termed positive hysteresis to differentiate it from that observed in the past where lower adsorption densities were obtained under the tested conditions (negative hysteresis).

At pH 7.9, the computed kaolinite dissolution is at a minimum and the total dissolved aluminum concentration is of the order of 10⁻⁷ kmole/m³. As predicted, precipitation of alu-
Chromatographic Separation of Isomers

Chromatograms of dodecylbenzene sulfonate supernatants are given in Fig. 4 for four residual sulfonate concentrations: (a) below CMC, (b) near CMC, (c) above CMC, and (d) well above CMC. It is clear that significant changes do occur in the component distributions as a result of the adsorption process:

i. For premicellar solutions, a depletion of the C\textsubscript{12} isomers with a corresponding increase in the concentration of polar components occurs. The most hydrophobic isomer (peak 4) is no longer detected.

ii. For solutions near CMC, the ratio of polar impurities to C\textsubscript{12} isomers in the solution is decreased with the most hydrophobic isomer peak still not detected.

iii. Slightly above CMC, the C\textsubscript{12} isomers (peaks 1–3) predominate over the polar impurities in the solution and the fourth isomer peak is again resolved.

iv. Well above CMC, the component distribution is very near to that of the original stock DDBS solution.

The results clearly show the more hydrophobic C\textsubscript{12} isomers (peaks 1–4) to adsorb preferentially resulting in solutions of totally different C\textsubscript{12} isomer distributions, and in some instances, solutions rich in polar impurities. The fraction, $\theta$, of C\textsubscript{12} isomers remaining in the supernatants after adsorption (calculated from the normalized peak areas) is plotted as a function of the total measured residual sulfonate concentration and the results are shown in Fig. 3. Adsorption and desorption (dilution) isotherms for DDBS/kaolinite at pH 7.9 ± 0.2. Diluent is electrolyte at equilibrium pH.
in Fig. 5. The distribution parameter, $\theta$, can be expressed as a function of the residual sulfonate concentration, $C_r$,

$$\frac{1}{\theta} = \left(\frac{1}{C_r}\right)m + b,$$

with $m$ the slope equal to $6.06 \times 10^{-5}$ and $b$ the intercept. The inverse of $b$ is the limiting value of $\theta$ and is 1.0, corresponding to a supernatant containing only $C_{12}$ isomers. The solution to the above expression is also given in Fig. 5. $\theta$ arises from area integration of HPLC chromatograms and the fit of the expression to actual measurements is quite good considering the method's precision to be $\pm 5\%$.

It is to be noted that supernatants contained as much as 85% polar impurities, which if used as residual DDBS concentration in the computation of adsorption, can clearly lead to erroneous conclusions; it becomes essential under such conditions to make the calculations based on $C_{12}$ benzene sulfonate concentration only.

**Fig. 4.** Analytical liquid chromatograms for DDBS/kaolinite supernatants at four residual sulfonate concentrations. pH 7.9 $\pm$ 0.2.

**Fig. 5.** Ratio ($\theta$) of HPLC-analyzed $C_{12}$ benzene sulfonate to total measured concentration versus residual concentration for initial adsorption supernatants.
HPLC Analysis of Desorption Supernatants

Desorption isotherms show significant hysteresis and memory effects: the higher the micellar sulfonate concentration at the origination of the dilution isotherm, the greater the adsorption density in the desorption isotherm (or the larger the hysteresis). HPLC data showed preferential adsorption of certain surfactant isomers. Supernatants generated after successive dilutions of samples at two different initial adsorption residual concentrations were analyzed to study this effect in detail.

A. $C_r = 9.5 \times 10^{-5} \text{ kmole/m}^3 \text{ DDBS}$. Results of HPLC analysis of supernatants after successive dilutions of a DDBS-kaolinite suspension at the above residual concentration are given in Fig. 7. Dilutions can be clearly seen in this case to produce enrichment with respect to the $C_{12}$ isomer peaks; after the third dilution the polar impurity peaks are no longer detected. This change in composition is due to dilution and removal of the polar components at each step along the desorption isotherm and suggests that the polar components do not interact with the mineral to any appreciable degree.

B. $C_r = 5.20 \times 10^{-4} \text{ kmole/m}^3 \text{ DDBS}$. Chromatograms obtained for the case of the residual sulfonate concentration above CMC are given in Fig. 8. Before dilution, the polar

![Image]

**Fig. 6.** Comparison of adsorption isotherms for measured total concentration and (HPLC-analyzed) $C_{12}$ benzene sulfonate concentration for DDBS/kaolinite at pH 7.9.

The adsorption isotherm thus calculated for the $C_{12}$ benzene sulfonate adsorption is given in Fig. 6 along with that for the total sulfonate depletion. The recalculated isotherm based on only $C_{12}$ isomers is shifted to lower residual sulfonate concentrations due to the presence of lower amounts of $C_{12}$ sulfonates in the supernatant than the amount of the total UV-absorbing species measured at 223 nm.

![Image]

**Fig. 7.** Analytical liquid chromatograms for successive dilutions of DDBS/kaolinite supernatants at pH 7.9 ± 0.2 and at an initial residual sulfonate concentration below CMC.

*Journal of Colloid and Interface Science, Vol. 120, No. 1, November 1987*
component peaks are present in small amounts and all four C_{12} isomer peaks are clearly resolved. Upon dilution, the polar component peaks are again found to decrease and to become zero by the sixth dilution. More important is the change in the distribution of C_{12} isomer peaks. Dilution resulted in the depletion of the most hydrophobic isomer (peak 4) as the concentration was reduced to premicellar levels. This increased depletion and the redistribution of isomers account for the increase in adsorption levels (positive hysteresis) observed upon diluting solutions at sulfonate concentrations above CMC.

At the completion of the dilution process, supernatants were observed to be composed of only three C_{12} isomer peaks for both samples. To determine the nature of the actual adsorbed species, the kaolinite was separated from the supernatant by filtration and washed repeatedly with water. The solids were then mixed with methanol in a vial for 10 min and centrifuged, and the supernatant was analyzed by HPLC. The chromatograms of the sulfonate extracted or desorbed from kaolinite samples A and B were very similar and the results are shown in Fig. 9. All four C_{12} isomer peaks are now detected whereas the polar component peaks are not, indicating again that only the C_{12} isomers adsorb on kaolinite with the polar impurity components being inert to the adsorption system. A slight change in the resolved isomer peak distribution between the desorbed sulfonate sample and the stock solution was also evident and a comparison of the component distributions for both samples is given in Table I.
TABLE I

Comparison of Dodecylbenzene Sulfonate Isomer Distributions for Stock (Initial) and Kaolinite Desorbed Surfactant Solutions

<table>
<thead>
<tr>
<th>Isomer peak</th>
<th>Stock DDDBS</th>
<th>Desorbed DDDBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.492</td>
<td>0.385</td>
</tr>
<tr>
<td>2</td>
<td>0.323</td>
<td>0.380</td>
</tr>
<tr>
<td>3</td>
<td>0.162</td>
<td>0.210</td>
</tr>
<tr>
<td>4</td>
<td>0.023</td>
<td>0.024</td>
</tr>
</tbody>
</table>

The fraction of C_{12} isomers comprising the supernatant after each dilution is shown in Fig. 10 along with the original distribution for the two cases discussed above. The fraction of C_{12} isomers goes to 1.0 for both samples but through different pathways; it is these pathways to solutions made up totally of C_{12} isomers that are responsible for the positive hysteresis and memory effects observed in desorption tests. It is clear that the observed hysteresis results from the chromatographic separation of the various isomers during both the adsorption and the desorption processes.

The effect of the chromatographic separation of the isomers during the adsorption and desorption processes was further examined by comparing the desorption isotherms with both the measured adsorption isotherm and the computed C_{12} isomer isotherm based on HPLC data. Results are shown in Fig. 11 and it is clear that hysteresis is due to the desorption isotherms gradually approaching the C_{12} isomer adsorption isotherm. Since removal of part of the supernatant containing the more polar impurities followed by dilution results in enrichment of the supernatant with C_{12} isomers, there is a shift from the measured total sulfonate isotherm to the isotherm based solely on C_{12} isomers and this results in hysteresis. Based on these results, the present adsorption system can in fact be considered to be reversible and the actual adsorption of the surfactant can be determined by tracking the pathways of desorption.

CONCLUSIONS

A multipronged approach was undertaken for elucidating the mechanisms of interaction in a dodecylbenzene sulfonate/kaolinite sys-
tem. Desorption and chromatographic analysis of supernatants along with the conventional adsorption tests yielded information that was required for the understanding of the preferential adsorption/desorption processes responsible for the observed hysteresis. It was clear that erroneous adsorption isotherms can result from single-stage experimentation where only the depletion in surfactant concentration is determined. High-pressure liquid chromatographic analysis of surfactant solutions prior to and after mineral contact showed adsorption of the more hydrophobic dodecylbenzene sulfonate components to occur preferentially and desorption hysteresis to result from a shift in the distribution of surfactant components in equilibrium with solids with successive dilutions. Removal of some of the supernatant followed by dilution produces an enrichment of the solution with respect to the hydrophobic dodecylbenzene sulfonate isomers. Tracking of the desorption pathways and the accompanying changes in the surfactant component distribution in solution has proven to be effective in understanding the processes involved in the adsorption of mixed isomeric systems.

ACKNOWLEDGMENTS

The authors thank Dr. Paul Valint of Exxon Research and Engineering Co. for supplying the surfactant samples. Support of the Department of Energy (DE-AC-79BC-10082), the National Science Foundation (CPE-8201216), Amoco Production Co., Chevron Oil Field Research, Exxon Research and Engineering, Gulf Research and Development, Shell Development Co., Standard Oil Company, Texaco, Inc., and Union Oil Company of California is gratefully acknowledged.

REFERENCES