# Interaction of an Anionic Surfactant with Hydrous Ferric Oxide Sol[1]

HANS SCHOTT[2] and I. J. KAZELLA,[3]
Research Center, Lever Brothers Company, Edgewater, New Jersey

## Abstract

The effect of sodium dodecyl sulfate (SDS) on positively charged hydrous ferric oxide sols (FOS) was studied by following turbidity and electrophoretic mobility as a function of increasing concentration of added SDS and by determining the adsorption isotherm.

Adsorption of SDS reduced the electric charge of FOS and caused flocculation. Complete precipitation occurred near zero charge. Further increase in SDS concentration resulted in smaller additional adsorption, charge reversal, and redispersion of FOS.

The effect of increasing particle size, resulting from aging or dialysis, on SDS adsorption is discussed qualitatively.

## Introduction

THE INTERACTION between hydrous ferric oxide sols (FOS) and an anionic detergent was studied with a twofold purpose. Rust, as well as colloidally dispersed hydrous oxides of heavy metals naturally occurring in some waters, present a problem in detergency since they may cause discoloration of fabrics during laundry. Thus one purpose in studying the effect of an anionic detergent on one of these colloidal oxides was to gain some insight into their behavior during the washing process.

The work was carried out in neutral media to preserve the positive charge of FOS because, whereas considerable information is available concerning the effect of detergents on negatively charged colloidal particles such as clays and carbon black, little is known about their effect on positively charged colloids. The system therefore duplicates conditions in the rinse cycles of washing machines, where small amounts of detergent carried over via foam or through adsorption by the fabric come in contact with colloidal oxides contained in some waters, with little or no builder present to boost the pH.

The work has broader colloid-chemical significance. Although there is ample information on the effect of nonsurface-active electrolytes on the stability of colloidal hydrous oxides from the work of Weiser and others starting in 1920 (1), relatively little is known about the effect of surface-active electrolytes. The present work contains data on the interaction of sodium dodecyl sulfate (SDS) with FOS as observed by electrophoresis, chemical analysis, and turbidimetry.

## Experimental

### Materials

The FOS was prepared from aqueous solutions of ferric nitrate made up with ACS reagent grade $Fe(NO_3)_3 \cdot 9\ H_2O$ and doubly distilled water to contain 40 ppm of iron. Enough sodium hydroxide was added to give a pH value in the range of 5.2 to 5.5. Although most experiments were performed with such sols containing sodium nitrate, sols from which dissolved electrolytes had been removed by dialyzing them against water inside a bag of gel cellophane were used in others. The results obtained with salt-free sols fell in line with those from nondialyzed sols. The preparation of SDS has been described (2).

### Measurements

Electrophoretic measurements were made in a Northrop-Kunitz micro-electrophoresis apparatus (3) (Arthur H. Thomas Company, Philadelphia, Pa.). Readings were taken in duplicate, at 21.1% and 78.9% depth of the 0.835-mm thick rectangular glass cell. At both stationary levels, several measurements were made before and after inverting the direction of the current. Power was supplied by a 150-v d-c supply. The voltage between the platinum electrodes was in the range between 13 and 21 v, varying usually less than ± 0.5 v during a single run.

Light transmission was measured with an electrophotometer (Model AC, Fisher Scientific Company, Pittsburgh, Pa.), using 1.00-cm square glass cells with the red (650 mμ transmission maximum) or pale green (510 mμ maximum) filter.

To determine the amount of adsorbed surfactant, sols equilibrated for 4 hr at 25C were centrifuged at 25C and 18,000 × g in a Servall thermostated centrifuge, followed by filtration through a Millipore GS filter. The filtrate was analyzed for SDS by titration with a cationic detergent, using the partition of methylene blue as end-point indicator (4). That the 4-hr period was sufficient to attain equilibrium was shown by the fact that the same SDS concentrations were obtained after an additional 17 hr of storage at 25C.

## Results

### Turbidity

Turbidity (or optical density) is defined as the logarithm of the ratio of the intensity of the incident light beam ($I_o$) to that of the transmitted beam (I). Translating turbidity measurements of dispersions into particle size is extremely difficult. For particles which are small compared with the wavelength of light, Rayleigh scattering predominates; the amount of light scattered increases with increasing particle size at constant concentration, and the transmittance ($I/I_o$) decreases as turbidity increases. For suspensions of larger, rather opaque particles, turbidity usually increases with decreasing particle size (5) at constant concentration. However the total scattering coefficient (opacity factor) varies for a given material as a function of particle size, going through a maximum often located at about 5μ (6); therefore, even in the colloidal range, increasing particle size can sometimes result in increasing turbidity at constant concentration, chiefly in the submicron range.

When studying the turbidity of FOS as a function of concentration of added SDS, flocculent particles

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[1] Presented at the Second Middle Atlantic Regional Meeting, American Chemical Society, New York, N.Y., February 1967.

[2] Present address: U.S. Forest Products Laboratory, Madison, Wis.

[3] Present address: School of Dentistry, Fairleigh Dickinson University, Teaneck, N.J.

visible under the microscope and sometimes to the naked eye place the system in the category where transmittance usually decreases with decreasing particle size. Transmittance measurements were made at room temperature with undialyzed sols containing 36 ppm of iron, neutralized to a pH of 5.2, and aged for 16–18 days (see below). Addition of SDS increased the pH to between 5.8 and 6.2, probably owing to the ejection of hydroxyl counterions bound to FOS into the bulk solution by SDS. Thus all experiments were performed considerably below the zero point of charge of FOS, which is at the pH of 8.6 (7). The situation corresponds therefore to the rinse cycle of a washing machine, where detergent carried over, e.g., via foam, interacts with the FOS of the rinse water.

In the range of SDS concentrations of 0.04–0.07 g/liter, corresponding to *zeta* potentials close to zero, coagulation upon SDS addition set in too fast to allow meaningful measurements. Those transmittance values which could be measured, i.e., for sols outside the region of zero *zeta* potential, are listed in Table I. They changed little with time during the period of observation, viz., from zero up to five hours after SDS addition.

The addition of small amounts of SDS produced a flocculent precipitate suspended in the sol and an increase in transmittance, indicating that some aggregation occurred. Larger amounts of SDS, which changed the charge of the sol from positive to negative, caused some deflocculation, reducing the transmittance. There is some evidence that flocculation at low SDS concentration and deflocculation at high SDS concentration become less marked as the sol ages.

The opposite situation, where increased turbidity results from increasing particle size, is exemplified below. In view of some lack of reproducibility observed in measurements of adsorption of SDS on FOS, attempts were made to correlate FOS particle size prior to SDS addition with the extent of SDS adsorption. Part of a dialyzed FOS sol of 100 ppm Fe was gently stirred for several hours until a slight cloudiness, visible to the naked eye under normal illumination, developed. At this point, transmittance readings were made on both portions of the sol after dilution to 80 ppm Fe, using the nondialyzed sol also diluted to 80 ppm as reference, and the adsorption of SDS was then determined at two concentrations. Since the turbidity of sols had been generally found to increase and the SDS uptake to decrease somewhat on aging, both quantities were measured within a single day for all three sols, at the age of 16–18 days.

The results are shown in Table II, where it is seen that the SDS uptake goes up with increasing transmittance. Since the increase in SDS adsorption is evidently the result of decreasing particle size, decreasing particle size resulted, in this case, in increased transmittance or lower turbidity. The turbidity data of Table II were determined at various settings for the transmittance of the nondialyzed reference sol in order to establish that the ratios of the transmittance of the nondialyzed sol to that of the dialyzed sol and to that of the dialyzed and stirred sol were nearly independent of the setting chosen for the reference sol. The apparent extinction coefficients of the three sols, defined as $\frac{1}{Lc} \log \frac{I_0}{I}$, are in the approximate ratio of 1.00:1.03:1.42 (with red filter) and 1:00:1.20:1.70 (green filter) respectively, for the nondialyzed 80 ppm sol, the dialyzed but unstirred 80 ppm sol, and the dialyzed 80 ppm sol rendered slightly cloudy by stirring. As expected, dialysis produced some aggregation, presumably by completing the hydrolysis of the FOS and thus building up particles via increased oxolation (conversion of *ol* to *oxo* groups). Stirring of the dialyzed sol caused additional agglomeration, as witnessed by the slight turbidity visible to the naked eye. These three sols are in the region where the total scattering coefficient, hence the turbidity, increase with increasing particle size.

TABLE I

Turbidity of Hydrous Ferric Oxide Sols[a] as a Function of Concentration of Added Sodium Dodecyl Sulfate

| | % Transmittance | |
|---|---|---|
| g/liter SDS[b] | Pale green filter | Red filter |
| 0.00 | 60.[c] | 60.0[c] |
| 0.02 | 61.8 | 62.4 |
| 0.03 | 62.4 | 63.5 |
| 0.10 | 58.1 | 59.1 |
| 0.60 | 58.0 | 58.5 |
| 1.80 | 58.6 | 59.3 |
| 2.80 | 58.5 | 59.2 |
| 4.50 | 59.3 | 59.8 |

[a] 36 ppm Fe.
[b] Equilibrium concentration of sodium dodecyl sulfate.
[c] Used as reference setting.

TABLE II

Effect of Turbidity of Hydrous Ferric Oxide Sols on Adsorption of Sodium Dodecyl Sulfate

| 80 ppm Sol[a] | 80 ppm Dial. sol[b] | 80 ppm Dial. stirred sol[c] |
|---|---|---|
| | % Transmittance prior to SDS addition<br>Pale green filter | |
| 50 | 46.9 | 38.4 |
| 60 | 56.2 | 46.7 |
| 70 | 64.7 | 53.8 |
| 80 | 74.1 | 61.2 |
| | % Transmittance prior to SDS addition<br>Red filter | |
| 55 | 54.6 | 47.1 |
| 60 | 59.4 | 51.1 |
| 70 | 69.2 | 59.8 |
| 80 | 79.1 | 68.9 |
| | Adsorption, g SDS/g iron<br>at SDS concentration of 0.115 g/liter | |
| 0.133 | 0.097 | 0.044 |
| | at SDS concentration of 0.294 g/liter | |
| ........ | 0.140 | 0.095 |

[a] Nondialyzed sol used as reference for transmittance measurements. Concentrations refer to iron.
[b] Dialyzed sol.
[c] Dialyzed sol rendered cloudy by stirring.

### SDS Adsorption

The 25C adsorption isotherm of SDS on FOS is shown in Figure 1. All points were determined on sols aged 17 ± 3 days. The difference in SDS uptake between nondialyzed, dialyzed, and dialyzed plus stirred sols is probably attributable to differences in specific surface area and particle size.

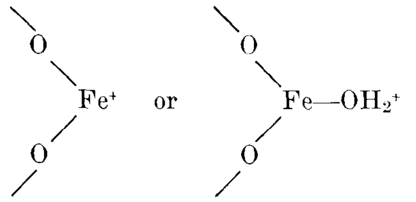
The highest concentration of SDS studied is well below its critical micelle concentration, viz., 2.32 g/liter. In view of the limited range of concentrations covered, it is not possible to classify the isotherm. The highest uptake observed, 0.235 g SDS/g Fe, corresponds to a lower limit of 128 $m^2/g$ $Fe(OH)_3$ for the specific surface area of FOS, assuming a cross-sectional area of 50 $Å^2$ per SDS molecule. At a specific gravity of 3.4, solid spheres of that specific surface area would have an average radius of 69 Å. In view of the large internal area, actual particles are probably much larger, containing pores filled with water.

### Electrokinetic Measurements

The electrophoretic mobilities of three sols are plotted in Figure 2 against the SDS concentration. Each point is the average of at least four measurements, made at the upper and lower stationary level in both directions. The SDS concentrations are equilibrium values; they were determined four hours after SDS addition, and the inital concentrations were corrected for SDS adsorbed by FOS. The differences between the three sols probably originated from differences in initial particle size (degree of agglomeration) or in the extent of hydrolysis. Agglomeration may result in trapped liquid inaccessible to SDS.

The original sols were positively charged. A gradual increase in SDS concentration reduced this charge, decreasing the electrophoretic mobility and rendering the sols less stable. This resulted in increasing flocculation (Table I). When charge and mobility were close to zero, the sols coagulated completely, separating into a reddish-brown flocculent precipitate and a colorless, clear supernatant liquid. At still higher SDS concentrations, the sols became negatively charged owing to adsorption of excess SDS. This produced sols somewhat more deflocculated than the original ones, and considerably more finely dispersed than the sols near the point of charge inversion.

The sols had zero charge in the range of SDS concentration of 0.06 g/liter for the nondialyzed sol to 0.09 g/liter for the dialyzed sol. According to Figure 1, this corresponds to an SDS uptake of 0.09–0.10 g SDS/g Fe or to a molar SDS:Fe ratio of about 1:50. This indicates that about 2% of the ferric iron was in the



form in the original sols. The adsorption isotherm (Figure 1) undergoes a decrease in slope in the range of SDS concentrations where the charge reversal of FOS occurs. This indicates that SDS is adsorbed less strongly on neutral or negatively charged sols than on positively charged ones, as expected.

It is interesting to note that charge reversal, minimum in turbidity, and change in slope of the adsorption isotherm occurred at the same SDS concentration. This is shown in Figure 3, where electrokinetic mobility, slope of the adsorption isotherm, and absorbancy are plotted on the ordinate as a function of the equilibrium SDS concentration for a dialyzed sol. Absorbancy is defined as $\log \frac{I_0}{I}$ where $I_0$ is the transmittance of the sol without SDS and I that of the sol containing the specified SDS concentration.

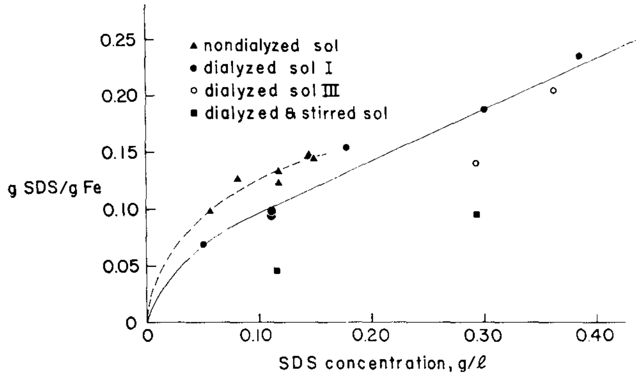


FIG. 1. Adsorption isotherm of sodium dodecyl sulfate on hydrous ferric oxide sols at 25C.

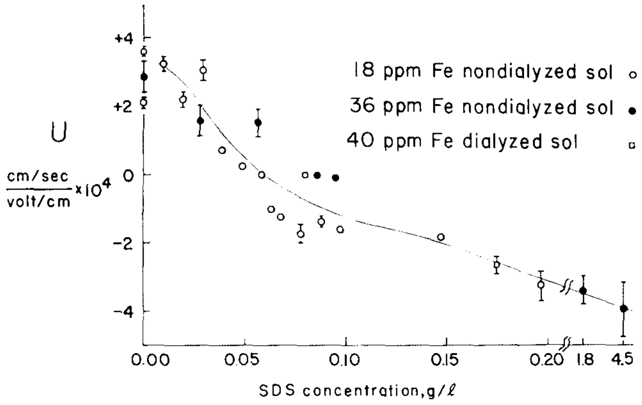


FIG. 2. Electrophoretic mobility U of hydrous ferric oxide sols as a function of sodium dodecyl sulfate concentration. Vertical lines represent standard deviations.

For purpose of comparison, it is interesting to note the electrokinetic properties of another model soil containing iron, namely, a ferric clay. Finely powdered ferric montmorillonite was prepared by metathesis between an aqueous slurry of sodium montmorillonite and ferric chloride solution, followed by comminution through wet ball-milling. It had a negative charge at a slurry pH of 6.4, and the electrophoretic mobility in water as well as in 0.01 N KCl was $(3.33 \pm 0.78) \times 10^{-4} \frac{\text{cm/sec}}{\text{volt/cm}}$. This mobility is similar to that of the positively charged FOS in the absence of SDS.

## Conclusions Regarding Detergency

During the wash cycle, FOS contained in the water represents no special problem since there are two mechanisms to change its charge from positive to negative while preserving its colloidal stability. Builders and sequestrants present in formulated detergents boost the pH of the wash liquor above the zero point of charge of the FOS. Moreover the concentration of anionic detergent is high enough to cause charge reversal and to produce a stable, negatively charged FOS.

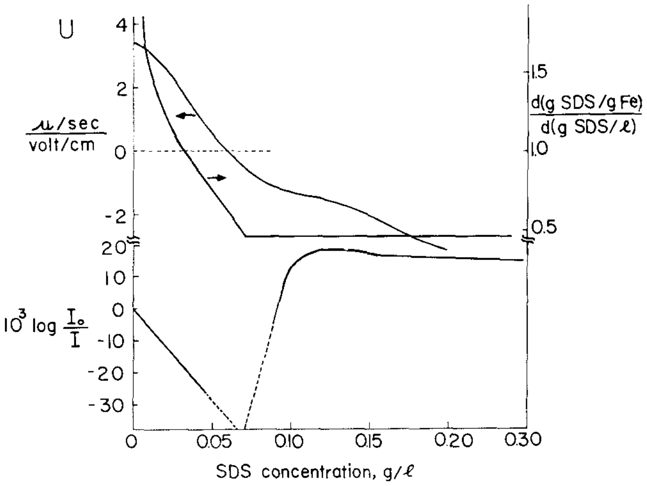


FIG. 3. Electrophoretic mobility U, slope of adsorption isotherm d (gSDS/g Fe)/d (g SDS/liter), and absorbancy $\log \frac{I_0}{I}$ of FOS as a function of SDS concentration.

However, detergent is carried over from the wash cycle to the rinse cycles in two ways not available to builders and sequestrants, namely, via foam, which holds a high concentration of detergent, and through adsorption by the fabric and subsequent desorption. Thus the water in the rinse cycles is neutral since little builder is carried over, whereas the concentration of detergent is of the order which reduces the stability of FOS that may be present. This would cause such FOS to coagulate and, as often occurs in such a situation, to precipitate onto the fabric. In conclusion, discoloration of fabrics in the laundry process by any colloidally dispersed, positively charged heavy metal oxides which may be present in the water takes place during the rinse cycles rather than during the wash cycle.

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