Interactions in the System: Clay-Detergent-Cellulose

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Abstract

The McBain equation describing detergency was used to study the process

$$\text{cellulose} \cdot \text{clay} + \text{detergent} = \text{cellulose} \cdot \text{detergent} + \text{clay} \cdot \text{detergent},$$

by taking thoroughly purified cotton, montmorillonite swelling clay, and n–$C_{12}H_{25}O(CH_2CH_2O)_{14}H$ as well as other nonionic and anionic detergents. The three binary equilibria which add up to this ternary system were also studied.

X-ray diffraction showed that nonionic detergents sorbed by the clay were intercalated between adjacent, 9.5 Å—thick lattice layers of clay with their chains parallel to these layers, in sheets one or two molecules thick. The process was accompanied by dehydration and proceeded down to low equilibrium detergent concentrations. The deflocculation of sodium montmorillonite suspensions by polyoxyethylated compounds was shown by an increase in turbidity and decreases in viscosity and sedimentation volume. Cellulose sorbed $C_{12}H_{25}O(CH_2CH_2O)_{14}H$ reversibly. Its uptake was considerably less than that of clay on a weight basis but was comparable on an area basis.

Kaolinite and calcium montmorillonite picked up by cellulose from aqueous suspensions were gradually removed by washing with water, following first-order kinetics.

Of the sodium montmorillonite picked up, 0.13 ± 0.01% could not be removed by washing with water. This level of tenaciously retained clay was independent of clay concentration, rate of stirring, and temperature. The ash of fabric treated with sodium montmorillonite was a shrunken replica of the fabric, preserving microscopic details faithfully. This and comparison of the specific surface areas of cotton and sodium montmorillonite indicate that cotton was completely coated with clay to an average depth of three to four lattice layers. The reason for this thickness is that the primary particles in sodium montmorillonite dispersions are packets of three to four lattice layers.

Anionic and cationic detergents removed little or none of the 0.13% sodium montmorillonite. Polyoxyethylated and polyoxypropylated compounds removed part but always left behind at least 0.04%. This is the amount of clay required to cover the cellulose surface completely with a sheet of single, nonoverlapping lattice layers. However, when brought into contact in the presence of nonionic detergents, cellulose retained no sodium montmorillonite at all.

Introduction

A MODEL SYSTEM for detergency comprising the three components cellulose, clay, and polyoxyethylated detergent in water was investigated by studying the interactions in the three binary systems

$$\text{clay} + \text{detergent} = \text{clay} \cdot \text{detergent} \quad [1]$$

$$\text{cellulose} + \text{detergent} = \text{cellulose} \cdot \text{detergent} \quad [2]$$

$$\text{cellulose} \cdot \text{clay} = \text{cellulose} + \text{clay} \quad [3]$$

followed by a study of the ternary system. Addition of Equations 1–3 results in

$$\text{cellulose} \cdot \text{clay} + \text{detergent} = \text{cellulose} \cdot \text{detergent} + \text{clay} \cdot \text{detergent} \quad [4]$$

which constitutes an example of the McBain equation describing the process of detergency (1).

The following considerations dictated the choice of components. Cellulose fabrics, mainly cotton, constitute the bulk of the laundry. Clays are one of the chief constituents of particulate dirt (2) and can be obtained as well-defined, pure species. Chosen were montmorillonite and kaolinite, which are the minerals of the two most abundant clays in nature, bentonite and kaolin. Water and other adsorbates cause the former to undergo intracrystalline swelling, thereby developing an enormous specific surface area. This makes montmorillonite a convenient substrate for determining adsorption isotherms and permits the use of x-ray diffraction to study the configuration of the adsorbed molecules (3).

Of the three classes of detergents, anionic ones are only adsorbed in traces by pure cellulose in the absence of hardness (4) and not at all by sodium montmorillonite (5). Cationic surfactants are readily adsorbed by montmorillonite (6) and by cellulose (7) but are of no practical usefulness as detergents. Nonionic detergents were selected because of their growing importance in commercial formulations and because the physiochemical basis of their mode of action in detergency was largely unknown.

EXPERIMENTAL

Materials

Montmorillonite and kaolinite consist of thin, flat plates. In water, kaolinite plates are approximately 100 times thicker than sodium montmorillonite and 25 times thicker than calcium montmorillonite plates (8,9). A single lattice layer or lamella of montmorillonite consists of a sheet of hydrated alumina sandwiched between two sheets of silica and has a thickness of 9.4 Å. Polar molecules are intercalated between adjacent lamellas, causing the lattice to expand in the *c*-direction. This increases the basal spacing, i.e., the Bragg spacing in the *c*-direction d_{001} by a value $\Delta = d_{001} - 9.4$, where Δ is a measure of the thickness of the layer of inserted molecules (Fig. 1). The density of montmorillonite is 2.83, the specific

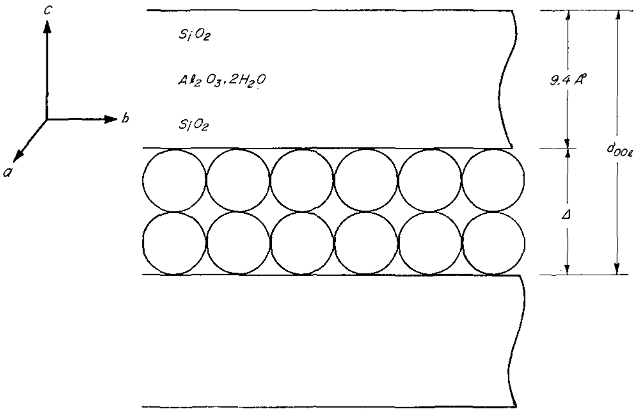

FIG. 1. Cross-section through montmorillonite lattice.

surface area of the expanded lattice 750 m^2/g. This refers to the area in the *a-b* planes. The contribution of the edges of the lamellas is negligible. The base-exchange capacity of the clay, resulting from isomorphous replacement of Si by Al and of Al by Mg atoms, is 0.9 milliequivalent/g; the clay was used in the sodium and calcium form. The source of cotton was an open-weave fabric, which was thoroughly purified to remove all noncellulose constituents (9,10).

The surfactants used were mostly ethylene oxide (EO) adducts of *n*-dodecanol (C_{12}): $C_{12}(EO)_{14}$ (0.066 g/liter), $C_{12}(EO)_{16}$ (0.22 g/liter), and $C_{12}(EO)_{30}$ (0.109 g/liter), and of branched nonylphenol (NPh): $NPh(EO)_{15}$ (0.11 g/liter), and $NPh(EO)_{30}$ (0.42 g/liter) (11,12). Values between parentheses are critical micelle concentrations (cmc). The reason that the cmc of $C_{12}(EO)_{16}$ is larger than that of $C_{12}(EO)_{30}$, despite its smaller EO content, is that the shortest-chain components, which are known to lower the cmc, had been removed from $C_{12}(EO)_{16}$ by molecular distillation (12).

The separate moieties of the detergents, namely *n*-dodecanol, and Carbowax 1000 and 1540 of Union Carbide Chemicals Company, $(EO)_{23}$ and $(EO)_{34}$, as well as a polypropylene glycol of degree of polymerization 13, Pluracol P-710 of Wyandotte Chemical Corporation $(PO)_{13}$, were also used. The water was double-distilled, the temperature was 25.0 ± 0.2C unless otherwise specified.

Methods

For the clay-detergent system, weighed amounts of clay suspensions and of detergent solutions were equilibrated, and clay plus adsorbed detergent was separated in a thermostated centrifuge. The equilibrium concentration of detergent was determined in the supernatant by surface tension and solids content. Most of the adhering solution was removed from the wet sediment by padding between filter paper. The material was then dried completely over phosphorus pentoxide. Carbon analysis of the solid, as well as material balance based on initial weights and equilibrium detergent concentration, were used to determine the amount of detergent contained in the clay-detergent complex. The term "complex" is used to designate clay + sorbed organic material; it does not imply stoichiometric relations. The dry complexes were conditioned over saturated KCl at 26.7C, which provides an atmosphere of 85% relative humidity, and the moisture regain was measured. X-ray powder diffraction diagrams of the complexes (8) were taken at three levels of moisture content: they were dried over P_2O_5, conditioned at 85% relative humidity (5–18% H_2O), and wet sediments blotted between filter paper (43–78% H_2O).

Turbidities of the suspensions were measured with a photoelectric colorimeter using a red, a green, and a blue filter and rectangular 0.25-cm, 1.00-cm, and sometimes 5.00-cm quartz cells. Viscosities were measured at 28.0 ± 0.1C with Cannon-Fenske viscometers, neglecting the kinetic energy correction. Sedimentation volumes were measured at 22.2 ± 0.5C in cylindrical 120-cm high, glass tubes with 3.6-cm inside diameters and with 1,200 cm^3 of suspension.

To hasten the attainment of equilibrium in the system cellulose-detergent, the fabric was chopped up in a Wiley mill fitted with a 20-mesh screen to an average fiber length of 0.45 mm. The amounts of detergent sorbed by cellulose during the adsorption and desorption experiments were calculated by material balance from the equilibrium concentrations of detergent. The latter were determined by surface tension and by a modified cobalt-blue colorimetric method (10).

The clay-cellulose system was studied by treating cotton swatches, each measuring 10 cm^2 and weighing 1 g, or chopped fiber with clay suspensions of different concentrations in a Terg-O-Tometer, using 1250 cm^3 volumes in the 2-liter beakers. Since the bath:cloth ratios were 100:1 or higher, the initial and equilibrium concentrations of the clay suspensions were practically the same, i.e., the clay pick-up by cotton did not significantly lower the clay concentration. After treatment with clay suspensions, the swatches were washed in the Terg-O-Tometer with fresh portions of water. Before each wash cycle, the swatches were briefly swirled in fresh water to remove most of the mechanically retained liquor. A few swatches were removed after each wash cycle and ashed to determine the amount of retained clay. Reflectance measurements for assessing the amount of retained solid dirt are unreliable even for highly pigmented solids such as carbon blacks, especially in the presence of detergents, owing to changes in the degree of dispersion of the pigment (13).

Carboxylated cellulose was prepared by static vapor-phase oxidation with nitrogen dioxide (14) and analyzed by direct titration and by the calcium acetate method (9). The carboxylic acid groups were left in the hydrogen form or transformed into the sodium, calcium, or ferric salt.

Results

The System: Clay-Nonionic Detergent

Structure of Dry Complexes. Three values for Δ were found in dry complexes of sodium montmorillonite with $C_{12}(EO)_{14}$ and $C_{12}(EO)_{30}$ (Table I). At very low detergent contents, the Δ value of 0.2–0.3 Å indicates that adjacent lamellas practically touched each other. As the detergent content increased, the (001) peaks in the diffraction patterns became asymmetrical and finally split, indicating the presence of two basal spacings which corresponded to the Δ values of 0.2 and 4.3 Å. Between 0.12 and 0.20 g

TABLE I

Montmorillonite Complexes of $C_{12}(EO)_{14}$

g Detergent/ 100 g clay	Δ of Complex, Å		
	Dry	Conditioned[a]	Moist[b]
Sodium clay			
0	0.2	6.0 (22.6)[c]	9.6 (100)[c]
1.33	0.3	6.1 (21.4)	9.6 (300)
2.84	0.3[d]	5.8 (20.0)	
6.38	0.2[d]	5.4 (17.1)	9.9 (333)
12.2	4.2	6.7 (14.1)	8.8 (256)
17.9	4.3	8.3 (11.3)	
18.1	4.3	8.3 (10.9)	8.5 (357)
18.2	4.4	8.3 (11.0)	
22.6	4.5[e]	8.3 (9.1)	
25.9	8.4[d]	8.4 (8.2)	8.5 (285)
28.2	8.2[d]	8.5 (7.2)	8.4 (256)
39.9	8.3	8.4 (5.7)	8.4 (256)
58.1	8.4	8.4 (7.5)	8.4 (285)
58.7	8.4	(7.6)	8.6 (300)
65.5	8.3	8.4 (8.4)	8.4 (285)
68.6	8.3	8.5 (9.1)	
Calcium clay			
0	0.2	6.1 (25.9)	9.5 (86)
27.7	7.9	8.7 (9.5)	
30.0	7.7	8.9 (9.3)	9.2 (50)
30.2	7.9	9.0 (9.2)	9.4 (73)
30.2	7.7	9.2 (9.1)	9.5 (69)
$C_{12}(EO)_{14}$		(30.7)	

[a] At 85% relative humidity.

[b] Centrifuged sediment, blotted with filter paper.

[c] Figures in parentheses represent percentage of moisture content, based on weight of dry complex.

[d] Mixed with pattern of single-layer complex.

[e] Mixed with pattern of double-layer complex.

detergent/g clay, $\Delta = 4.2 \pm 0.1$ Å. At higher detergent contents, a second basal spacing appeared, corresponding to $\Delta = 8.4$ Å. From 0.30 g detergent/g clay to the highest detergent content measured, 0.70 g/g clay, Δ remained constant at 8.4 ± 0.1 Å.

The Δ value of 4.2 Å equals the cross-sectional diameter of a paraffin or polyethylene glycol chain, and the Δ value of 8.4 Å is exactly twice as large. This indicates that the detergent chains intercalated between adjacent clay lamellas lie flat and parallel to the lamellas, i.e., in the *a-b* plane. At lower detergent contents, a single layer of detergent molecules is inserted between adjacent lamellas (single-layer complex), whereas there are two layers at higher detergent contents (double-layer complex), as shown schematically in Fig. 1. At intermediate detergent contents, the x-ray patterns indicate the presence of zero plus single and of single plus double-layer complexes.

A close-packed, completed double-layer complex would contain

$$(\tfrac{1}{2})\ (7.5 \times 10^{6}\ \mathrm{cm}^2/\mathrm{g\ clay})\ (8.4 \times 10^{-8}\ \mathrm{cm})\ (1.08\ \mathrm{g\ det/cm}^3) = 0.34\ \mathrm{g\ det/g\ clay} \qquad [5]$$

provided the density of the adsorbed detergent is the same as the bulk density, namely, 1.08. The pure diffraction pattern of the double-layer complex was reached at 0.30 g detergent/g clay, in good agreement with the calculated value. No further lattice expansion took place at higher detergent content, even though enough detergent was adsorbed to form quadruple-layer complexes. This indicates that detergent adsorbed in excess of double layers was not inserted in regular fashion between adjacent clay lamellas. It was probably occluded in voids and interstices, e.g., between overlapping clay plates, and will be referred to as interstitial detergent.

The two polyethylene glycols and the polypropylene glycol had sorption limits of 0.25 ± 0.01 g glycol/g clay; the corresponding Δ values were 8.1 and 8.6 Å. The glycols, which do not associate into micelles, were not adsorbed in excess of double-layer complexes, whereas the detergents were adsorbed in amounts at least twice as great. This indicates that interstitial detergent is most likely in the form of micelles or hemimicelles. In the case of calcium montmorillonite, even the detergents had a sorption limit of 0.32 g/g clay.

Since dodecanol is insoluble in water, clay was treated either with the bulk liquid or with its solutions in aqueous ethanol and aqueous dioxane. Single-layer complexes with $\Delta = 3.9$ and 4.8 Å were obtained with sodium and calcium montmorillonite respectively.

Effect of Moisture. The difference in the Δ values of the third and second column in Table I equals the lattice expansion which the dry complexes undergo when conditioned at 85% relative humidity; the difference between the Δ values of the fifth and third column equals the further expansion in the presence of excess moisture. Since a single layer of water molecules is 3.0 Å thick (3) and amounts to 11 g/100 g clay, it is seen that the zero-layer complexes of sodium montmorillonite pick up two layers of water molecules between adjacent lamellas on conditioning at 85% relative humidity and a third when quite wet. Single-layer complexes insert a single layer of water molecules on conditioning but undergo no additional swelling when wet.

The double-layer complexes of sodium montmorillonite have a constant Δ value of 8.4 Å at 0, 5–10 and 250–300% water content, indicating that water causes no lattice expansion whatsoever. This remarkable behavior implies that when the detergent was adsorbed by the clay, it divested itself of its water of hydration—two water molecules per ether link (15)—and displaced the water of hydration of the clay, all in the presence of excess water.

The double-layer complexes of calcium montmorillonite and $C_{12}(EO)_{14}$ were slightly swollen by moisture: the Δ values increased by 0.8–1.5 Å at 85% relative humidity and by an additional 0.3–0.4 Å when wet. These lattice expansions are insufficient to accommodate a single layer of water molecules between adjacent clay lamellas and most likely resulted from hydration of the Ca^{++} countercation, which binds considerably more water than Na^{+}.

The double-layer complexes of sodium montmorillonite with $(EO)_{23}$ and $(EO)_{34}$ did not swell on conditioning at 85% relative humidity, but the Δ values of the wet complexes exceeded those of the dry complexes by 1.5 Å. The double-layer complexes of calcium montmorillonite with the two polyethylene glycols increased Δ by 2.5–3.3 Å when going from the dry to the conditioned state and again when wet. The double-layer complexes of sodium and calcium montmorillonite with polypropylene glycol, however, were not at all affected by moisture. This is the result of the greater hygroscopicity inherent in the polyethylene glycols, which picked up 57% moisture at 85% relative humidity compared with 5.8% for the polypropylene glycol.

The moisture regain of sodium montmorillonite—$C_{12}(EO)_{14}$ complexes on conditioning (fourth column of Table I) decreased regularly with increasing detergent content to an interpolated minimum of 5.1% at the composition of the double-layer complex, but thereafter increased with increasing detergent content. If one assumes that interstitial detergent has the same moisture regain as the bulk detergent, namely, 30.7%, the moisture uptake of double-layer complexes with interstitial detergent can be corrected for the moisture uptake of the latter by subtracting 30.7% of the percentage of interstitial detergent from the observed moisture regain and by expressing the remaining moisture as percentage of the weight of the dry complex minus the weight of the interstitial detergent. This reduces the moisture regain of all double-layer complexes to $4.7 \pm 0.4\%$, indicating the validity of the assumption that the interstitial detergent absorbs the same amount of moisture as the bulk detergent.

Adsorption Isotherms. According to the isotherms in Fig. 2, the calcium clay adsorbed $C_{12}(EO)_{14}$ more strongly than the sodium clay at low detergent concentrations, in keeping with the ability of Ca^{++} to form coordinate covalent bonds with ethers (16). Even the sodium clay nearly exhausted the nonionic detergent from dilute solution. Both isotherms undergo a decrease in slope on completion of single-layer complexes, which occurred below the cmc for calcium and at the cmc for sodium montmorillonite. The calcium isotherm approaches the composition of the double-layer complex asymptotically. The sodium isotherm levels off on completion of the single-layer complex: directly above the cmc, detergent molecules evidently preferred association into micelles to sorption onto clay. However, once the second detergent layer began to form, the slope increased and completion occurred readily. There is an inflection point in the sodium isotherm at the composition of the com-

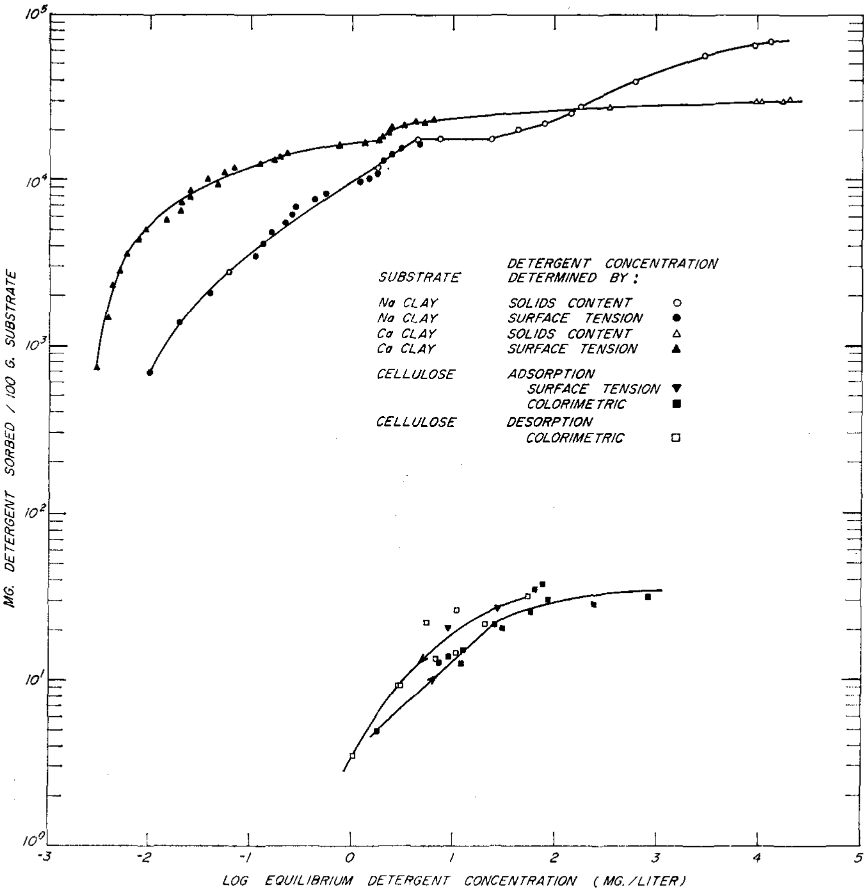

FIG. 2. Adsorption isotherms of $C_{12}(EO)_{14}$ on montmorillonite and cellulose.

pleted double-layer complex. Adsorption of interstitial detergent occurred beyond, but with a smaller slope, forming complexes which contained 0.70 g detergent/g clay or more.

Packing Density of Adsorbed Compounds. The clay acts as a vertical and lateral gage for the adsorbed organic molecules, permitting an estimate of their packing density. The difference between it and their bulk density is a measure of the degree of order in the adsorbed state. The high degree of order in the *c*-direction is attested by the sharp and narrow (001) peaks in the x-ray diffraction patterns of single- and double-layer complexes. The difference between bulk density and density of the adsorbed detergent is therefore a measure of the degree of lateral order, in the *a-b* plane.

For double-layer complexes, the density of the adsorbed detergent ρ was calculated as

$$\rho = \frac{\text{g detergent/g clay}}{(\tfrac{1}{2})\ (7.5 \times 10^6\ \text{cm}^2/\text{g clay})\ (\Delta\ \text{cm})} \qquad [6]$$

It is seen from Table II that increasing EO content results in increasing bulk density and decreasing density in the adsorbed state, i.e., in looser packing of the adsorbed molecules. This is in keeping with the greater flexibility introduced by the ether link into the paraffin chain: the oxygen chain atom has no substituents, whereas each carbon has two hydrogen atoms which hinder the rotation around carbon-carbon bonds. Thus, a greater EO content would result in greater two-dimensional meandering during adsorption. Moreover, stronger binding of the polyethylene glycol moiety to the substrate compared with the paraffin moiety would result in lower surface mobility of the former, making it more difficult to straighten out two-dimensional loops. Alternatively, the permanent dipole of the ether link would restrict the number of sites on the clay surface available for adsorption of the polyethylene glycol moiety since the clay surface consists of an array of oxygen ions, which repel the negative end of the $\overset{\delta+}{C} - \overset{\delta-}{O}$ dipole and attract the positive end. This epitaxial effect could also account for the looser lateral packing with increasing EO content.

TABLE II
Density of Organic Compounds in Bulk and in Double-Layer Complexes

Compound	%EO	Bulk density g/cm³	Density difference[a] %
$C_{12}(EO)_{14}$	76.8	1.08	9.3
$C_{12}(EO)_{30}$	87.6	1.11	16.2
$(EO)_{23}$	100	1.17	29.1
$(EO)_{34}$	100	1.18	28.8
$(PO)_{13}$	....	1.00	23.0

[a] Calculated as 100 (bulk density minus sorbed density)/bulk density.

Deflocculation of Sodium Montmorillonite by Polyoxyethylated Compounds. Nonionic detergents and polyethylene glycols deflocculated suspensions of sodium montmorillonite, as was shown by increased turbidity and decreased viscosity and sedimentation volume.

Transmittance measurements permit to calculate an extinction coefficient K defined by

$$K = \log (I_0/I)/L\,c \qquad [7]$$

where I_0 and I are the intensities of light transmitted by water and by clay suspension, c the clay concentration in g/liter, and L the path length in cm. The values of K, which were reproducible to ±10% or better, are a measure of the degree of flocculation of the clay.

Lambert's law was obeyed by the clay suspensions but *not* Beer's law inasmuch as K increased on dilution. Since the extinction coefficient of suspensions without detergent (K_1) varied with c to the same extent as the extinction coefficient of suspensions with added detergent (K_{12}), the ratio K_{12}/K_1 was independent of c, provided that each pair of suspensions with and without detergent contained the same clay concentration. The ratio was also independent of wavelength.

The extent to which K_{12}/K_1 exceeds unity is a measure of the degree of deflocculation of the clay. Each point in Fig. 3 is averaged from measurements at 0.86 and 1.73 g clay/liter at the three wavelengths. It was possible to use the ratio detergent concentration to clay concentration as abscissa in Fig. 3 because of the nearly quantitative uptake of detergent by clay. Solutions containing the equilibrium concentration of detergent were indistinguishable from pure water according to turbidity and viscosity.

The ratio $K_{12}/_1$, and hence the deflocculating ability of the detergent, rise steeply with an increasing proportion of detergent until the composition of the double-layer complex is reached, at which point they level off. The corresponding plot for $C_{12}(EO)_{16}$ is quite similar to that of Fig. 3, but the polyethylene glycol plot, which reached a maximum at a glycol:clay ratio of 2.9, curved slightly downward at higher composition ratios, indicating the occurrence of limited flocculation. The K_{12}/K_1 ratios for $(EO)_{34}$ decreased with increasing clay concentration.

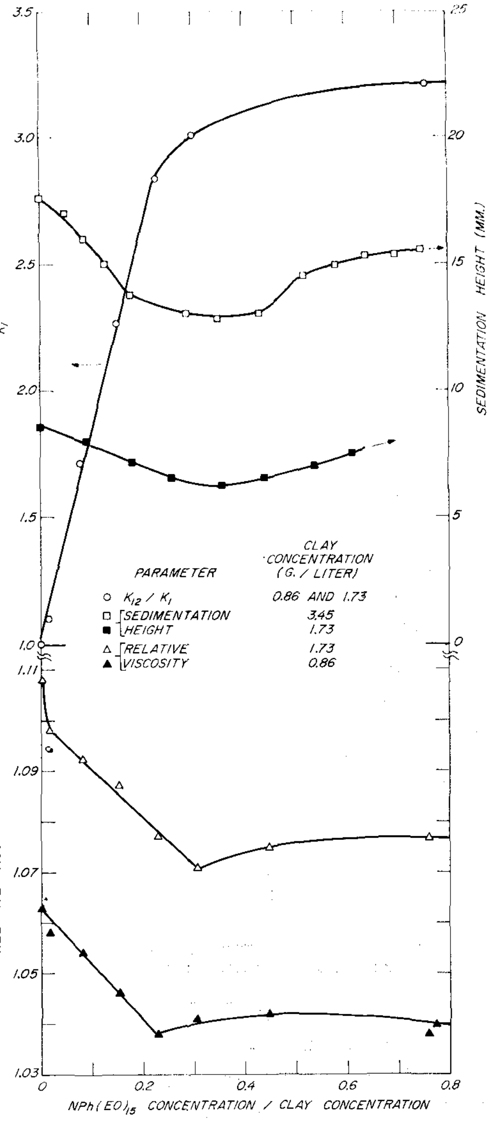

FIG. 3. Reduced extinction coefficients, relative viscosities, and sedimentation volumes of $NPh(EO)_{15}$—sodium montmorillonite suspensions.

Viscosity is expressed as relative viscosity, the ratio of the viscosity of clay suspension to that of water. There was a linear relationship between relative viscosity and clay concentration for suspensions of clay alone as well as for suspensions containing detergent at a fixed detergent:clay ratio. For noninteracting, uncharged spherical particles, the slope of relative viscosity versus volume fraction is 2.5, according to Einstein's equation. For pure clay suspensions, the slope was found to be 177; for suspensions containing $NPh(EO)_{15}$:clay at a constant 0.288:1 ratio, the slope was 125. Thus, the detergent is seen to reduce the structural viscosity of montmorillonite suspensions to a limited extent.

Deflocculation of clay suspensions according to the rheological criterion is also shown in Fig. 3 for two levels of clay concentration. Maximum deflocculation occurred again at a detergent:clay ratio corresponding to the double-layer complex. At higher ratios, slight flocculation occurred. A similar plot was obtained for $C_{12}(EO)_{16}$, but the minimum in relative viscosity for the $(EO)_{34}$-clay system occurred at much higher glycol:clay ratios. This is in keeping with the fact that polyethylene glycol, not being surface-active, is *much less strongly adsorbed not only at the air-water* but also at the clay-water interface.

The minima in sedimentation volume, corresponding to maximum deflocculation, also occurred at the composition of the double-layer complex (Fig. 3).

According to turbidity, viscosity, and sedimentation volume measurements, increasing concentrations of nonionic detergents progressively deflocculated sodium montmorillonite suspensions until the composition of the double-layer complex was reached. At higher detergent concentrations, slight deflocculation occurred according to the turbidity criterion, whereas viscosity and sedimentation data indicated some flocculation.

The initially observed pronounced deflocculation probably consisted in breaking up of stacks of montmorillonite lamellas into smaller stacks or into single, 9.4 Å-thick lamellas by the combined effect of intercalation of nonionic detergent and dilution (3). The primary particles in dilute suspensions of sodium montmorillonite containing no detergent probably consist of stacks comprising three to four lattice layers (17). The slight flocculation at higher detergent concentrations probably resulted in the formation of much looser aggregates than those present in the original suspension, possibly through cross-linking by micelles or hemimicelles of detergent.

The System: Cellulose-Nonionic Detergent

Owing to the fact that polyoxyethylation is a random addition of EO, the detergent used in this system, $C_{12}(EO)_{14}$, has a chain length or molecular weight distribution; 14 is the average number of EO groups per dodecanol molecule. Adsorption by cellulose is likely to fractionate the detergent. If surface activity is the predominant force, molecules of lower EO content would be adsorbed preferentially. The opposite would occur if hydrogen bonding between cellulose hydroxyls and detergent ether links predominated. In either event, the calibration plots of surface tension, or of absorbancy of the cobalt-blue complex, versus detergent concentration established for the original detergent may not be exactly applicable to detergent fractionated by exposure to cellulose. However, it was shown that this introduced only relatively small errors. Determining the detergent concentration by surface tension emphasizes molecules of short polyoxyethylene chains, whereas the cobalt-blue colorimetric method is more responsive to molecules of long polyoxyethylene chains (10). Despite this, concentrations of detergent solutions exposed to cellulose determined by the two methods differed by only 10–30%.

Two detergent solutions were dried after equilibration with cellulose. The degrees of oxyethylation of the residual detergent, determined by an infrared method (11), were 17 and 19 EO per dodecanol, compared with 14 for the original detergent. Therefore, the shorter-chain detergent molecules were adsorbed preferentially.

A similar conclusion can be drawn from the adsorption isotherm (Fig. 2) since the detergent uptake determined by surface tension is greater than that determined colorimetrically. The hysteresis between the adsorption and desorption isotherms determined colorimetrically is at least in part owing to preferential adsorption of the less highly polyoxyethylated detergent molecules. Thus, the adsorption of $C_{12}(EO)_{14}$ by cotton was probably completely reversible. The isotherm levels off near the cmc at a limiting uptake of about 35 mg detergent/100 g cotton.

That value is nearly 1,000 times smaller than the uptake of $C_{12}(EO)_{14}$ by montmorillonite clay (8). The large discrepancy is probably attributable to the fact that the specific surface area of cotton is similarly smaller than the value of 750 m^2/g clay. A value of 0.72 m^2/g cotton has been found by B.E.T. technique, applied to low-temperature nitrogen adsorption (18). Using this figure as the one available to detergent molecules in water, results in an uptake of 0.50 mg detergent/m^2 cotton at the cmc, compared with 0.29 mg detergent/m^2 clay.

The satisfactory agreement between these two values suggests that the detergent molecules adsorbed by cotton have the same configuration as those adsorbed by the clay, viz., that there is a single layer of fairly close-packed chains of unit density lying flat against the substrate. If this is the case, the specific surface area of cotton available to the detergent is calculated as

$$\frac{3.5 \times 10^{-4}\ \text{g det/g cotton}}{(1.0\ \text{g det/cm}^3)\ (4.2 \times 10^{-8}\ \text{cm})} = 0.83 \times 10^{4}\ \text{cm}^2/\text{g cotton} = 0.83\ \text{m}^2/\text{g cotton} \qquad [8]$$

This value agrees well with the B.E.T. nitrogen area, which seems to justify its choice as well as the assumption about the configuration of the adsorbed detergent. Using the B.E.T. nitrogen area of cotton as the one accessible to $C_{12}(EO)_{14}$, could introduce the following two errors. Nitrogen molecules are smaller than detergent molecules and might penetrate into pores too small to admit a detergent molecule. The swelling of cellulose in water increases its specific surface area. The first effect tends to make the nitrogen area too large, the second would make it too small. Apparently these two effects cancelled each other out approximately.

The System: Cellulose-Clay

In the determination of pick-up of sodium montmorillonite from aqueous suspensions by cotton swatches, the problem is the removal of excess suspension, which is held mechanically and by capillarity in the fabric. Plots of clay retention versus concentration in the range of 2 to 27 g clay/liter diverged widely, depending on whether the excess suspension was squeezed out by a rubber-roll wringer or removed by dripping or blotting between filter paper. The three curves had a common extrapolated positive intercept of 0.32 ± 0.02% clay in the fabric at 0 g/liter of clay concentration. This seems to indicate that cotton picked up clay avidly from dilute suspensions until a saturation limit of 0.32% was reached; further apparent increase in clay pick-up at higher concentration resulted merely from an increase in the amount of clay contained in the suspension which was mechanically entrapped by the fabric.

A similar saturation limit is indicated by the fact that the amount of calcium montmorillonite which was retained after a given number of wash cycles was the same for slurry concentrations of 8.0 and 15.0 g/liter, and therefore presumably the true initial pickup from both slurries was the same as well. The extrapolated clay content for zero wash cycles was 0.85%. Clay retention from a 2.0 g/liter slurry was lower (Fig. 4). From the second wash cycle on, the semilogarithmic plots of retained clay versus number of wash cycles or time are linear, indicating that the removal of kaolinite and calcium montmorillonite by washing with water follows first-order kinetics (9).

Removal of sodium clay, however did not go below the constant level of 0.13 ± 0.01%, which was reached after the third or fourth wash cycle (Fig. 4). Further washing with water did reduce the clay content by about 0.003% per wash cycle, but this apparent loss in clay was really owing to loss in cotton lint with a clay content higher than the bulk of the fabric.

This level of 0.13% sodium montmorillonite so tenaciously retained by the fabric was independent of the duration of the treatment with clay suspension between 1 and 3 hr, of the clay concentration between 0.2 and 26.5 g/liter, and of the rate of agitation (46–

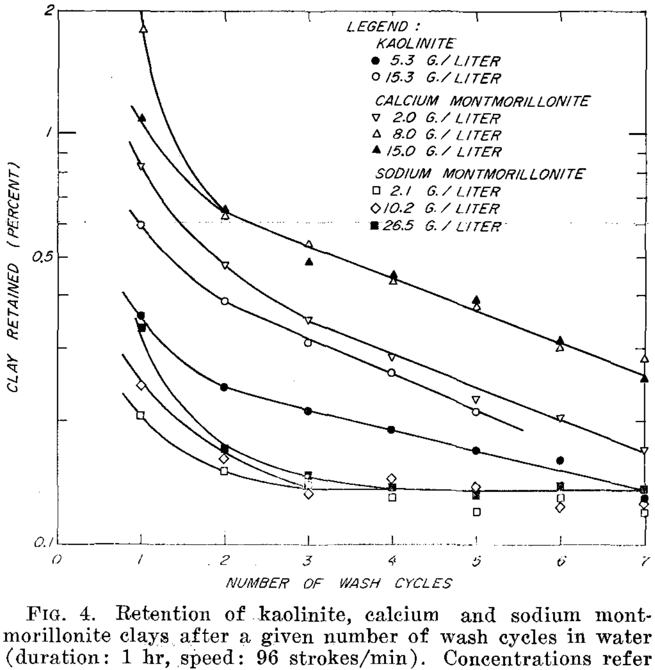

FIG. 4. Retention of kaolinite, calcium and sodium montmorillonite clays after a given number of wash cycles in water (duration: 1 hr, speed: 96 strokes/min). Concentrations refer to clay dispersions used to treat the fabric prior to washing.

155 strokes/min) and temperature (25 or 75C) in both treatment and wash cycles. Chopped fiber reached the somewhat higher constant level of 0.16 ± 0.02% clay after the third wash cycle. Evidently, cutting fibers and destroying the weave exposed additional cotton surface to clay.

Carboxylated fabric containing 0.8 milliequivalent/g in the H^+, Na^+, Ca^{++}, or Fe^{3+} form and 2.0 milliequivalents/g in the Ca^{++} or Fe^{3+} form retained 0.14–0.18% clay, based on silica analysis of the ash after the fourth or fifth wash cycle. This amount of retained clay is only slightly larger than the 0.14% level which was found for the nonoxidized blank fabric, and at least part of the difference is most likely attributable to greater swelling of the carboxylated fabric in water, especially in the alkaline sodium montmorillonite suspensions.

The question to which this experiment was addressed, namely, whether more clay can be retained by carboxylate/silicate salt bridges involving common Ca^{++} or Fe^{3+} ions between cellulose surface and clay particles (9), was answered in the negative. Carboxylate groups are introduced into cellulose by bleaching; they exist in the Ca^{++} and possibly also in the Fe^{3+} form.

Appearance of Fabrics Treated with Clay and of Their Ashes. Electron micrographs of fabric treated with clay suspensions and washed three times were obtained by surface replication. Kaolinite could be seen as discrete particles averaging 0.35 μ in diameter, which covered only a fraction of the cellulose surface. Cellulose containing 0.13% sodium montmorillonite was indistinguishable from clean cellulose, indicating that the clay covered its surface completely with a thin, pliable, and uniform layer which molded itself to the cellulose surface and reproduced all its details.

The ash of fabric treated with kaolinite preserved only the bare outline of the weave whereas the ash of fabric treated with sodium montmorillonite was a faithful if shrunken replica of the fabric, preserving its finest microscopic details down to loose ends and frayed fibrils.

The amount of sodium montmorillonite needed for complete coverage of cotton with a clay layer consisting of single, nonoverlapping lamellas 9.4 Å thick, lying flat against the fibrils, is calculated below. It is assumed that cotton fibers consist of solid cylinders with an equivalent diameter of 16.6 μ, and a density of 1.55 g/cm³. This results in an external specific surface area of 1.55 × 10³ cm²/g, which is, of course, much smaller than the combined external and internal area used previously. The clay content is

$$\frac{1.55 \times 10^3 \text{ cm}^2\text{/g cotton}}{(\frac{1}{2})\ (7.5 \times 10^6 \text{ cm}^2\text{/g clay})} = 4.1 \times 10^{-4} \text{ g clay/g cotton} = 0.041\% \qquad [9]$$

This value is three to four times smaller than the tenaciously retained 0.13% clay found for fabric or the 0.16% found for chopped fiber; the reason is that the primary particles of sodium montmorillonite in dilute suspensions are stacks three to four lamellas thick rather than single lamellas.

The following picture agrees with all available facts. Cotton fabric picks up 0.32% sodium montmorillonite from aqueous suspensions. On washing with water, the clay particles on the cotton surface are deflocculated just as dilution has been found to deflocculate clay suspensions, reducing the clay layer to primary particles consisting of stacks of three to four lamellas which remain lying flat on the cotton surface. They completely cover it with a nearly coherent film (19), amounting to 0.13% by weight of cotton. These stacks probably have a thickness of about 46 to 65 Å, of which 28–38 Å is attributable to clay proper and 18–27 Å to water layers three molecules thick, intercalated between adjacent lamellas. The average diameter of these aggregates, obtained from electron micrographs of dilute, dried, and shadow-cast dispersions, is 0.2 μ. Extremely thin and interspersed with water, these stacks are quite flexible and thus follow and replicate the topography of the cotton substrate faithfully. When the cotton is burned, the infusible clay remains behind, preserving the surface characteristics of the cotton fibers.

The reason that carboxylate groups did not produce higher clay retention is that they, together with the rest of the fiber surface, were completely covered with a montmorillonite layer three to four lamellas thick, which was not removed by water and which shielded them from contact with clay particles in suspension.

The following considerations show why kaolinite was gradually removed mechanically by washing with water, whereas there was a layer of sodium montmorillonite which could not be washed off. Kaolinite platelets are between 10 and 30 times thicker than stacks of three to four lattice layers of sodium montmorillonite with their interspersed water. Being therefore considerably stiffer, they cannot establish as intimate a contact with the cellulose substrate as the montmorillonite particles, so that the forces of adhesion per unit area of clay are much smaller for kaolinite. Furthermore, the specific surface area of kaolinite, i.e., the area per unit weight of clay available to make contact with cotton, is approximately 100 times smaller than that of sodium montmorillonite in the form of stacks of three to four lamellas. Finally, since the kaolinite particles are much thicker than those of montmorillonite, they protrude more above the cotton surface into water and are therefore subject to stronger hydrodynamic stresses during agitation.

The System: Cellulose-Clay-Detergent

Fabric containing 0.13% sodium montmorillonite which cannot be washed off with water constitutes a convenient means for assessing the ability of detergents to remove clay, since any reduction in the amount of retained clay during further washing is caused by the detergent. Swatches were treated in succession for 2 hr with 9 g/liter suspensions of sodium montmorillonite, four times for 1 hr with water, once for 3 hr with the detergent solution to be tested, and four times for 1 hr with water to remove loosened clay. Ash contents were determined after the third and fourth wash cycles. Blank swatches were treated similarly except that water was used instead of detergent solutions. Clay removal was calculated as percentage, based on the clay content of the blank (zero percentage removal). Reproducibility was within ±8% clay removal (20).

Of the compounds tested, EO and PO addition products were the most effective clay-removers, regardless of whether they were surface-active or not. This is in keeping with their strong adsorption by montmorillonite and with their ability to deflocculate its suspensions.

The highest removal observed was 60–70%, or about two-thirds of the 0.13% clay. Since the original coat of clay covering the cellulose fibrils consisted of stacks of three to four lattice layers, it is seen that polyoxyethylated compounds, by virtue of their ability to intercalate between adjacent lattice layers and to break up their stacks, removed the top two to three layers of montmorillonite. However, these compounds did not penetrate between the bottom lattice layer of clay and the cellulose substrate but left the cotton covered with a single lattice layer. In view of its location and high ion exchange capacity, this 0.03–0.04% of residual clay can cause fabric discoloration by picking up heavy metal ions and vagrant dyes from wash liquors.

As is seen in Table III, the ability of NPh(EO)$_{30}$ to remove two-thirds of the clay was largely independent of pH except in an acid medium, where montmorillonite exists in the hydrogen form and the ether link probably acts as a Brönsted base, tying up the ion exchange sites and probably promoting flocculation. Clay removal was also independent of temperature, and the effectiveness of NPh(EO)$_{30}$ was just as great below as above the cmc (0.042%), except at a very low concentration.

Anionic detergents, and cationic detergents and other quaternary compounds were ineffective in removing clay but for opposite reasons. The former interact little if any with cellulose (4) or with montmorillonite in the absence of hardness (5). Therefore, although they removed no clay, they did not interfere with clay removal by nonionic detergents. Quaternary compounds are strongly adsorbed by cellulose (7), and even more strongly by montmorillonite. They are bound to the clay by ion exchange and Van der Waals forces, render it hydrophobic, and coagulate its suspensions (6). Therefore, these compounds removed no clay and also prevented polyoxyethylated compounds from doing so (Table III).

Some of the polyhydroxy compounds were effective, some were ineffective. A polymer which forms insertion complexes with montmorillonite (polyvinyl alcohol) and one which forms only peripheral complexes, i.e., which is only adsorbed at the edges of the lamellas (20) (methyl vinyl ether/sodium maleate copolymer) were both effective in removing clay. The effectiveness of the organic solvents may consist in disrupting the water structure. In this connection, it is noteworthy that aqueous dioxane removed the most clay at a composition close to a maximum in partial molal volume of water in the binary system water-dioxane (21).

The ineffectiveness of the condensed phosphates strengthens the picture of sodium montmorillonite platelets lying flat on the cellulose substrate; little adhesion was contributed by the edges. In the absence of di- and polyvalent cations, the ability of the phosphates to deflocculate clays is due to their interaction with positively charged edges of clay lamellas, reversing the charge and thus eliminating edge-to-face association. The removal of calcium montmorillonite, however, was aided by sequestering agents. Washing cotton swatches containing calcium montmorillonite with solutions of ethylene diamine tetraacetic acid (2 Na, 0.20%, pH = 4.9) or of sodium tripolyphosphate (0.50%, pH = 10.0) removed one-third more clay than washing with water (20). Moreover, the two sequestering agents reduced the clay level to the 0.13 ± 0.01% value characteristic of sodium montmorillonite, indicating that they may have converted the calcium clay to the sodium form.

Antiredeposition Properties of Nonionic Detergents. While the previous section dealt with the effect of nonionic detergents on clay which had been retained by the fabric, it was also of interest to examine the retention by the fabric of clay pretreated with deter-

TABLE III

Clay Removal from Cotton by Chemicals

Material	Concentration %	pH	% Clay removal
Tridecyl alcohol(EO)$_{15}$	0.30	5.6	58 ± 5[a]
n-Octadecanol/n-hexadecanol(EO)$_{15}$	0.30	6.8	61 ± 6
NPh(EO)$_{30}$	0.005	6.0	28
	0.025	5.9	62
	0.10[b]	6.6	57 ± 5
	0.75	6.9	63
	0.10(75C)[c]	5.9	53
NPh(EO)$_{30}$ Na$_2$B$_4$O$_7$	0.10 2.0	9.2	58
NPh(EO)$_{30}$ Sodium acetate 0.1N + acetic acid 0.1N	0.10	4.6	57
NPh(EO)$_{30}$ HCl 0.05M + potassium acid phthalate 0.05M	0.10	2.6	12
80% EO-20% PO Condensate (MW = 8750)	0.30	6.2	49
(EO)$_{23}$	0.75	6.7	62
	2.0	6.2	64 ± 8
	2.0(75C)[c]	6.4	60
(EO)$_{400}$	2.0	6.1	48
(PO)$_{13}$	2.0	6.5	49
Polyoxyethylene sorbitan monooleate	0.50	6.7	32 ± 4
	0.50(75C)[c]	6.7	59
Sucrose monopalmitate	0.50(75C)[c]	6.1	11
Sodium palmitate	0.50(75C)[c]	10.7	29
Sodium oleate	0.30	10.1	16
Sodium N-methyl N-palmitoyl taurate	0.70	6.9	10
Sodium dodecylbenzene sulfonate	0.30	6.8	0
Sodium n-dodecyl sulfate	0.30	6.3	3
Di-isobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride	0.30	5.6	0
Dicoco dimethyl ammonium chloride	0.30	6.3	8
n-Octadecanol/n-hexanol(EO)$_{15}$ Dicoco dimethyl ammonium chloride	0.30 0.15	6.0	0
(EO)$_{23}$ Di-isobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride	2.0 0.30	5.8	4
n-Octadecanol/n-hexadecanol(EO)$_{15}$ Sodium dodecylbenzene sulfonate	0.30 0.15	7.9	50 ± 4
(EO)$_{23}$ Sodium dodecylbenzene sulfonate	2.0 0.30	7.2	70
Sorbitol	5.0	6.1	12
Pentaerythritol	5.0	6.8	0
Glycerin	5.0	6.2	42
Ethanol	20	7.2	48
Acetone	20	6.9	42
Dioxane	10	4.1	35
	20	4.2	0
	68	5.7	6
Acetamide	20	5.1	0
Dimethylformamide	20	7.5	36
Furfuryl alcohol	20	4.0	24
Tetrahydrofuran	20	6.7	53
Pyridine	1.0	7.4	10
Urea	5.0	7.0	16
	33	7.1	18
Tetrasodium pyrophosphate	5.0	10.6	16
Sodium tripolyphosphate	5.0	10.1	9 ± 3
Sodium hexametaphosphate	5.0	6.4	9 ± 2
Ethylene diamine tetraacetic acid, disodium salt	0.2	4.8	0
Sodium tetraborate	2.0	9.2	2
Sodium chloride	15.0	6.9	0
Guanidine hydrochloride	1.6	3.9	2
Guanidine carbonate	1.7	11.1	1
Polyvinylpyrrolidone (MW = 40,000)	0.5	4.0	50
Polyvinylpyrrolidone Sodium bicarbonate	0.5 0.2	8.3	72
Polyvinyl alcohol (MW = 14,000)	0.5	6.5	47 ± 7
Methyl vinyl ether/maleic anhydride copolymer, sodium salt (MW = 180,000)	0.5	10.2	42

[a] The ± sign precedes the range.

[b] The cmc is 0.042%.

[c] Temperature of detergent wash cycle; all other wash and rinse cycles at 25–27C.

gent. When swatches were treated with a suspension containing 3.0 g/liter sodium montmorillonite and 1.0 g/liter NPh$(EO)_{30}$ which had been prepared 15 hr earlier, there was no clay at all retained after the first wash cycle, and probably none was ever picked up by the fabric. Evidently the layer of detergent adsorbed on clay and on cellulose plus its hydration shell proved too great a barrier for effective adhension of clay to cellulose. This shows that the nonionic detergent is a far better antiredeposition agent for the clay than carboxymethylcellulose (22).

Depending on the order of addition in the system cellulose-clay-nonionic detergent, sodium montmorillonite can become attached permanently to the cellulose, or it may never be taken up. This makes it useless to determine the equilibrium constant for Equation 4.

The System: Clay-Anionic Detergent

Sodium montmorillonite adsorbed neither sodium n-dodecyl sulfate nor sodium n-decane sulfonate either below or above their cmc's. Calcium montmorillonite adsorbed both detergents, but metathesis, leading to the precipitation of some calcium alkyl sulfate and sulfonate, complicated the situation.

The x-ray diffraction patterns of calcium montmorillonite treated with detergent solutions and dried contained two sets of (001) reflections. One corresponds to unmodified clay ($\Delta = 0.2$ Å), and its Δ value on exposure to 85% relative humidity also increased to 6.2 ± 0.2 Å. The other set corresponds to Δ values of 20.28 ± 0.05 Å and 17.50 ± 0.08 Å for sodium dodecyl sulfate- and decane sulfonate-treated clay respectively. The corresponding Bragg spacings did not increase on exposure to 85% relative humidity. These Δ values are equal to the fully extended chain lengths of $C_{12}H_{25}OSO_3^-$ and $C_{10}H_{21}SO_3^-$ respectively, indicating that the molecules of adsorbed anionic detergent are intercalated between adjacent lattice layers of clay in a fully extended state, with their chain axes perpendicular to the *a-b* plane of the layers. This is in contrast with cationic (6) and nonionic detergents discussed above, which are inserted with their chains lying in the *a-b* plane of the clay layers.

Based on the relative intensities of the two sets of (001) reflections, on the area per calcium ion, on carbon and sulfur analysis of the complexes, and on the fact that sodium montmorillonite did not adsorb any anionic detergent, a two-stage adsorption process seems indicated for calcium montmorillonite (5). The first detergent molecules to enter the lattice, prying adjacent layers apart, are bound as anions to the calcium counterions at the exchange sites of the clay. They are in an extended, upright position, being arranged in an irregular head-to-head and head-to-tail fashion to match the exchange sites. Detergent molecules subsequently adsorbed are in the clay lattice as sodium alkyl sulfate or sulfonate. They are not bound to the clay by calcium bridges but cluster around those detergent anions which are being associated with them by Van der Waals attractive forces between hydrocarbon chains. The second sorption stage proceeds until the detergent monolayers become condensed.

Absence of interaction between sodium montmorillonite and the two anionic detergents is also indicated by the fact that the detergents did not change the turbidity of suspensions of that clay. This is in contrast with nonionic detergents which deflocculated the clay suspensions, increasing their turbidity as shown above, and with cationic detergents, which flocculated the suspensions and thereby decreased their turbidity (6).

The System: Cellulose-Anionic Detergent

Most of the early work on the adsorption of anionic detergents by cotton contains spurious results owing to the presence of noncellulosic impurities. Cotton freed of waxes and proteins was found to adsorb neither alkyl sulfates (23) nor alkylbenzene sulfonates (24) unless polyvalent cations were present (25). Another set of experiments showed a minute uptake, up to 20 ppm sodium decane sulfonate and 60 ppm sodium dodecyl sulfate (4).

In view of the lack of interaction of anionic detergents with sodium montmorillonite and with pure cellulose, it is easy to understand why they removed none of the clay from the fabric.

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