⁂Effect of Quaternary Ammonium Substitution of Hydroxyethylcellulose on Binding of Dodecyl Sulfate

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ABSTRACT

The binding behavior of sodium dodecyl sulfate (SDS) to quaternary ammonium substituted hydroxyethylcellulose (cationic cellulose) of varying degree of substitution was studied by the following measurements: binding isotherms of SDS to cationic cellulose, dye solubilization of the cationic cellulose/SDS complex, partial molal volume of each cationic cellulose, and spin-lattice relaxation time of SDS protons in the course of binding. Binding isotherms showed features similar to that observed for the globular protein/SDS system. The molecular processes of complex formation between cationic cellulose and SDS is discussed based on these results.

INTRODUCTION

The excellent conditioning property of quaternary ammonium substituted hydroxyethylcellulose, i.e., cationic cellulose, when used in hair shampoo, has recently been an area of wide interest. It is well known that cationic cellulose will form a complex with anionic or ampholytic surfactants (1). The complex is solubilized in shampoos, compositions of which contain fairly large amounts of surfactants. When shampooing, dilution occurs and the complex which is separated from solution deposits on the hair. The deposited thin film of complex has excellent conditioning properties. For example, the hair brushes smoothly. Without an anionic or ampholytic surfactant, cationic cellulose may not develop its conditioning property.

In this study, we investigated the course of complex formation of a typical anionic surfactant, sodium dodecyl sulfate, with cationic cellulose of various degree of cationic substitution.

EXPERIMENTAL

Materials

Cationic cellulose was prepared by the reaction of hydroxyethylcellulose, which has 1.8 hydroxyethyl residues/anhydro-glucose unit and a molecular weight of 1.3×10^5 as measured by intrinsic viscosity, with 2,3-epoxypropyltrimethylammonium chloride (2). An aqueous solution of crude reaction products was purified by dialysis with cellulose membrane until chloride ion was not detected by $AgNO_3$. Then the solution was freeze-dried. The degree of cationic substitution was measured by colloidal titration using PVSK and toluidine blue as indicator (3). Table I shows the degree of cationic substitution of the prepared cationic cellulose. The degree of the substitution is expressed by the number of quaternary ammonium residues/anhydro-glucose unit.

Pure sodium dodecyl sulfate (SDS) was prepared from dodecyl alcohol with chlorosulfonic acid and was recrystallized twice from ethyl alcohol.

Measurements

Binding isotherm. Binding isotherms of SDS to each cationic cellulose were measured by the equilibrium dialysis technique using Visking cellulose membrane (type 27/32). Visking tube was immersed in 2% sodium hydroxide solution for 15 min and rinsed thoroughly by deionized water. It was further soaked in 1.5% SDS aq. solution for 15 hr, and finally rinsed again by deionized water. Twenty mL of aqueous solution, which contained cationic cellulose and SDS, was poured into the dialysis tube. After the open ends of the tube were sealed tightly, it was placed in a 50-mL glass-stoppered cylinder containing 20 mL of pure water, and was shaken in a thermostated water bath (25 C) until the concentration of SDS in the outer aqueous phase reached equilibrium. It took ca. 10-20 days to attain equilibrium. The SDS concentration was determined by Epton's titration method (4). The amount of SDS bound to cationic cellulose was calculated from the relation:

$$[\text{bound SDS}] = [\text{SDS}]_{\text{initial}} - 2[\text{SDS}]_{\text{equilibrium}},$$

where $[\text{SDS}]_{\text{initial}}$ is the initial concentration of SDS in the dialysis tube and $[\text{SDS}]_{\text{equilibrium}}$ is the equilibrium concentration of SDS in the outer aqueous phase.

Dye solubilization. Dye solubilization properties of the cationic cellulose/dodecyl sulfate complex was colorimetrically measured using Yellow OB (1-o-tolylazo-2-naphthylamine) dye. The detailed procedure is almost the same as that seen in the literature (5). Reagent-grade Yellow OB was used after recrystallization from ethyl alcohol. The Yellow OB crystal was added in excess to the aqueous solution containing cationic cellulose and SDS, and the solution was shaken gently in a glass-stoppered tube for 24 hr. The excess crystal was filtered from solution using a 0.45-μ Millipore filter. After the filtrate was diluted with 1:1 mixture of alcohol and water, the concentration of solubilized Yellow OB was determined colorimetrically.

Partial molal volume. The partial molal volume measurement was done by the following procedure. The density of the solution and the solvent (water) were measured pycnometrically. Apparent molal volume, V_Φ, was calculated from the density data using the well known equation (6):

$$V_\Phi = \frac{1000}{m \cdot d \cdot d_O}(d_O - d) + \frac{M}{d},$$

where M, m, d_O, and d are the molecular weight and molality of cationic cellulose (mol/kg), density of solvent and of solution, respectively. The obtained values of V_Φ for each

TABLE I

Quaternary Ammonium Substituted Hydroxyethyl Cellulose

Degree of cationic substitution α	Number of cationic residues/cellulose molecule
0	0
0.05	28
0.15	83
0.23	126
0.29	160
0.36	200

cationic cellulose were plotted as a function of the square root of the concentration of cationic cellulose. Partial molal volume was obtained by linear regression to zero concentration.

Relaxation time. The spin-lattice relaxation time (T_1) measurement of SDS protons in D_2O solution was made on a Varian XL-200 spectrometer in the FT mode, using the $180°$-τ-$90°$ pulse sequence.

RESULTS AND DISCUSSION

Binding Isotherms

As shown in Figure 1, no dodecyl sulfate was bound to hydroxyethylcellulose. This is the case for cationic cellulose with a degree of substitution of zero. When the degree of substitution exceeds 0.05, all curves show similar patterns. This pattern is similar to that observed in the system of globular proteins and sodium dodecyl sulfate (7). The amount of bound dodecyl sulfate seems to attain equilibrium in the region of its critical micelle concentration (cmc) of 8 mM.

Figure 2 expresses the results in Figure 1 in a different manner. The vertical axis is now mol/unit mol. As indicated in Figure 2, the molar ratio of bound dodecyl sulfate to the quaternary ammonium residues can be plotted on the same curve in the case where the degree of substitution is 0.23 or above.

When the degree of substitution is 0.05, the binding isotherm does not rise with an increase in dodecyl sulfate concentration.

The isotherm may be represented by two distinct regions. The initial part of the isotherm shows a Langmuir-type binding pattern, in which the binding ratio of dodecyl sulfate to quaternary ammonium residue is found to be roughly 1 mol/unit mol, regardless of the cationic substitution degree. This result indicates that an electrostatic interaction is dominant in this concentration region.

The isotherm rises further with an increase of dodecyl sulfate concentration beyond the Langmuir range. A multimolecular binding of dodecyl sulfate as observed at the higher concentration range suggests that the interaction in this region is hydrophobic in nature.

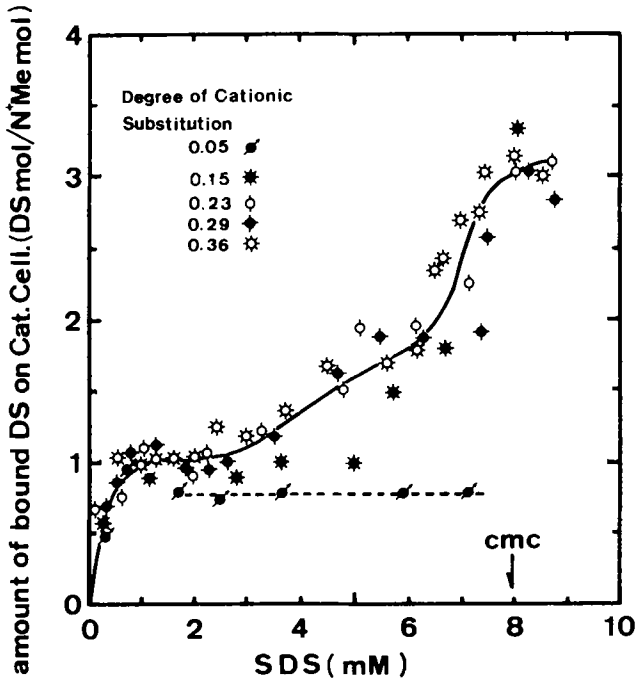

FIG. 2. Binding isotherms of dodecyl sulfate on cationic cellulose.

When the concentration of SDS exceeds 1 mM, separation of the complex from solution was observed. At a concentration of ca. 6-7 mM, the complex was resolubilized and the solution became clear.

By magnifying the initial part of Figure 1, Figure 3 is obtained. We applied Langmuir's binding isotherm to these curves. Langmuir's equation is expressed as:

$$\frac{C}{X} = \frac{C}{a} + \frac{1}{a \cdot b},$$

where the symbols are defined as X = amount of dodecyl sulfate/bound unit mol of ammonium groups of cationic cellulose (mol/mol); C = concentration of dodecyl sulfate (M); a = amount of bound dodecyl sulfate at saturation

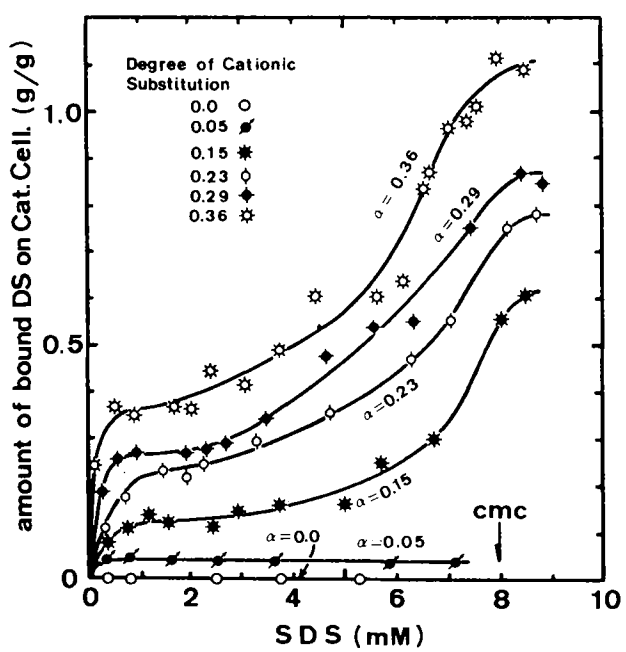

FIG. 1. Binding isotherms of dodecyl sulfate on cationic cellulose.

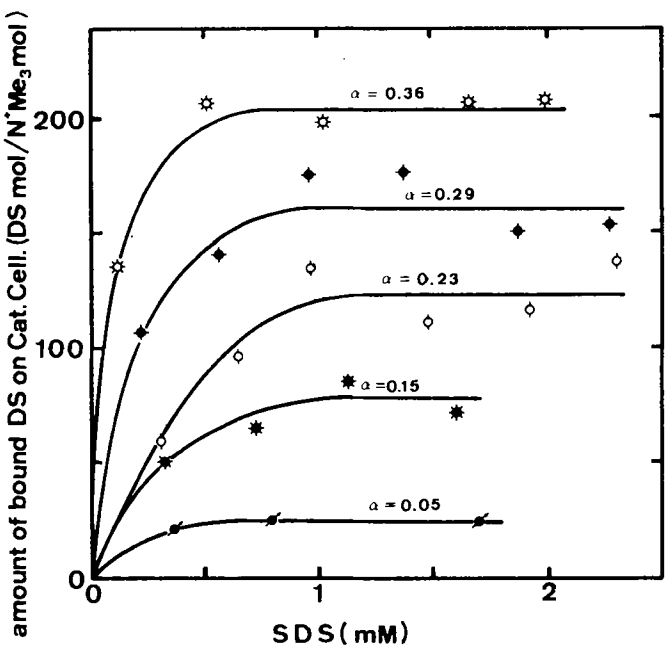

FIG. 3. Binding isotherms of dodecyl sulfate on cationic cellulose.

TABLE II

Effect of Cationic Substitution Degrees of Hydroxyethylcellulose on Binding Characteristics of DS

Degree of cationic substitution	(*a*) Amount of bound DS/NMe_3 of cationic cellulose (mol/mol)	(*b*) Binding coefficient (M^{-1})
0.05	1.1	3.8×10^3
0.15	1.0	3.3×10^3
0.23	1.0	4.0×10^3
0.29	1.1	6.3×10^3
0.36	1.1	1.1×10^4

(mol/mol); and b = binding coefficient of Langmuir Constant (M^{-1}); plots of C/X vs C gave straight lines. The value of a and b thus obtained are given in Table II. The amount of bound dodecyl sulfate at saturation is ca. 1. Further, the binding coefficient gradually increases when the degree of substitution is above 0.23. This result indicates that the interaction between bound dodecyl sulfate molecules takes place at about this degree of substitution. A sudden increase of the binding coefficient over a certain cationic degree of substitution is in accord with the variation of the binding isotherm in the range of multimolecular binding, as shown in Figure 2.

Dye Solubilization

It has been reported that cationic cellulose and sodium dodecyl sulfate complexes are able to solubilize oil-soluble dyes at concentrations one order of magnitude below the cmc of dodecyl sulfate (8).

Therefore we reexamined the solubilization of oil-Yellow OB by complexes of cationic cellulose with various degrees of substitution. As shown in Figure 4, pseudo-micelle formation is observed prior to hydrophobic binding of dodecyl sulfate.

In the dotted line region of Figure 4, the complexes separate from solution. Since the separated complexes showed pale yellow color, one can assume that a solubilization phenomena occurred in this region.

Partial Molal Volume

The influence of degree of cationic substitution on partial molal volume of cationic cellulose was examined. The quantity of quaternary ammonium residues in a unit volume of cationic cellulose solution was obtained from the number of cationic residues/molecule divided by the partial molal volume.

TABLE III

Effect of Cationic Substitution Degrees on Partial Molal Volume of Hydroxyethylcellulose

Degree of cationic substitution	Partial molal vol (mL/mol)	N^+/unit vol (mol/mL)
0	75	–
0.05	79	0.35
0.15	84	1.0
0.23	90	1.4
0.29	93	1.7
0.36	99	2.0

As shown in Table III, both the partial molal volume of cationic cellulose and the number of quaternary ammonium residues in a unit volume of cationic cellulose increased uniformly with the degree of cationic substitution. We already knew that the binding of dodecyl sulfate to cationic cellulose differs from the point of 0.23 substitution, however, the results in Table III do not agree with this. Therefore, we assume the occurrence of a cooperative interaction between cationic cellulose and dodecyl sulfate.

The relationship of the binding coefficient to the number of quaternary ammonium residues/unit volume is plotted in Figure 5. Cooperative binding of cationic cellulose with dodecyl sulfate seems to be accelerated when the number of quaternary ammonium residues of cationic cellulose is above its critical density, which may be ca. 1.5 mol/mL.

Spin-Lattice Relaxation Time of SDS Protons in the Course of Binding

It has been reported that the molecular assembly of dodecyl sulfate bound to globular proteins has a similar

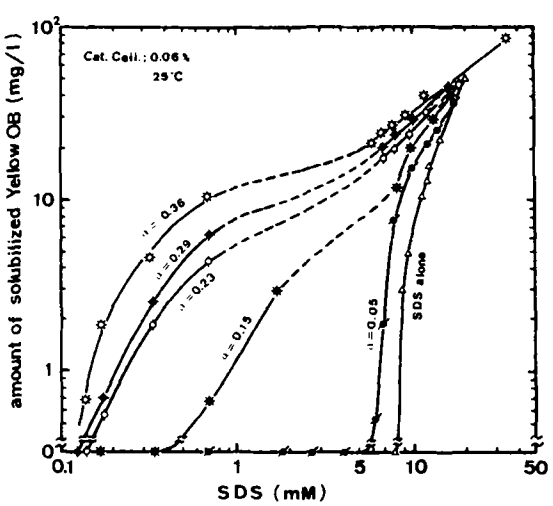

FIG. 4. Effect of cationic substitution degree of cationic cellulose to the dye solubilizing properties of dodecyl sulfate/cationic cellulose complex.

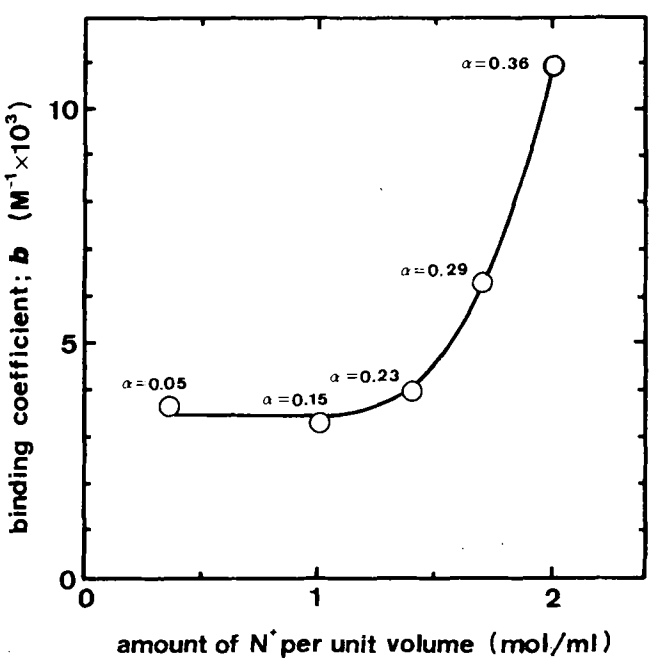

FIG. 5. Effect of cationic substitution degree on binding coefficient of dodecyl sulfate.

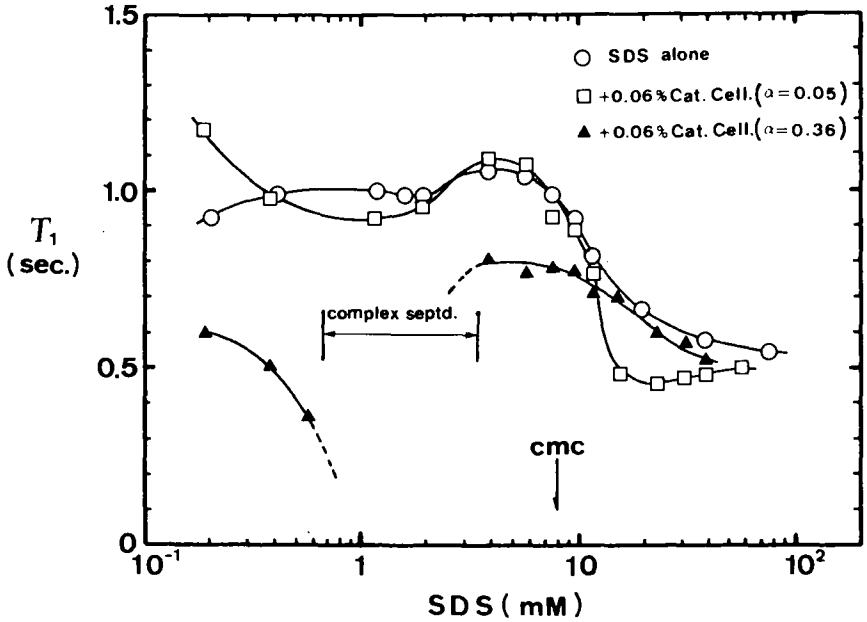

FIG. 6. T_1 of $(CH_2)_n$ protons of dodecyl sulfate in D_2O (26 C).

structure to that of SDS micelles (9). Consequently, as measured by FT-NMR, methylene protons of dodecyl sulfate bound to proteins have a similar spin lattice relaxation time (T_1) to that of dodecyl sulfate micelles.

Figure 6 shows the spin-lattice relaxation time (T_1) of methylene protons of dodecyl sulfate in the presence and absence of cationic cellulose. In the presence of cationic cellulose with a high degree of substitution, T_1 of the methylene protons at a relatively low surfactant concentration is very similar to that of SDS in the micellar state. On the contrary, in the presence of cationic cellulose with a low degree of substitution, where a cooperative binding isotherm was not shown, T_1 of the methylene protons is almost identical to the behavior of dodecyl sulfate itself.

This result suggests that cationic cellulose with a high degree of substitution can form a complex in which a hydrophobic interaction has cooperatively occurred.

In Figure 7, tentative explanation was made on the molecular processes of complex formation. In the absence of dodecyl sulfate, shown in stage 1, cationic cellulose assumes a stretched structure because of the repulsive force among the charged quaternary ammonium groups. Stage 2 shows that all cationic groups of cationic cellulose are saturated with bound dodecyl sulfate anions. The hydrophobic region, like the interior of the micelles, also appears in this stage which makes the complex precipitate as a so-called hydrogel. The molecular processes may well be compared to that of phase separation. Stage 3 shows the unfolded feature of cationic cellulose molecule on which dodecyl sulfate molecules are bound in excess at or above cmc. The speculation is supported by the finding (1) that the direction of electrophoretic movement of cationic

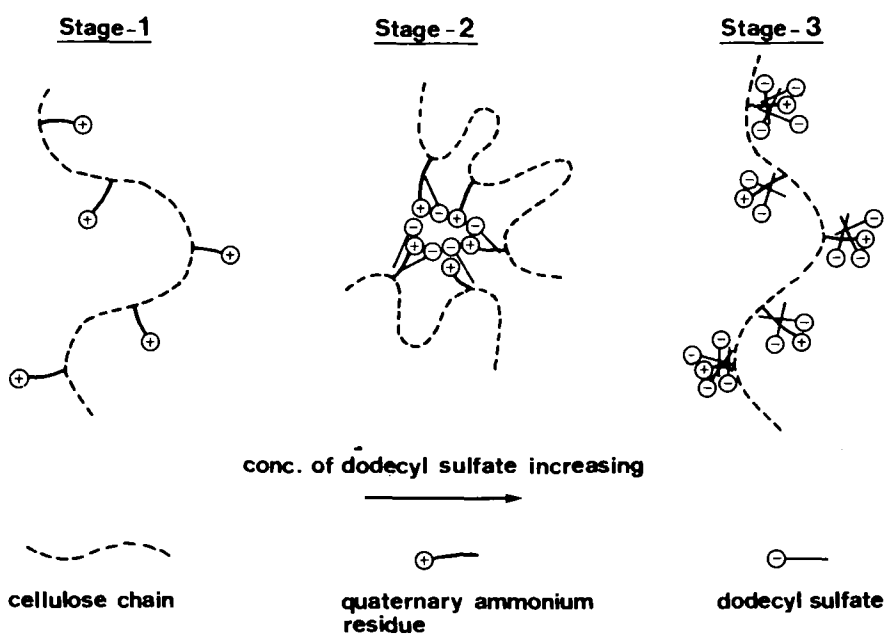

FIG. 7. Proposed structure of dodecyl sulfate/cationic cellulose complex.

cellulose is reversed when SDS is added to the environment at high concentration.

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Separation and Estimation of Anionic Surfactants by Thin Layer Chromatography: I. Mixtures of Sodium Dodecylbenzenesulfonate, Sodium Dodecyl Sulfate and Sodium Dodecanesulfonate

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ABSTRACT

The conditions for separation and quantitative determination of anionic surfactants such as sodium dodecylbenzenesulfonate, sodium dodecanesulfonate and sodium dodecyl sulfate by thin layer chromatography (TLC) were investigated. Analytical results for mixtures of 2 or 3 components under optimal TLC conditions were in satisfactory agreement with known values. The absolute errors and variation coefficients both were within ca. 4%.

INTRODUCTION

Microscale analytical methods using colorimetric analysis have been described by Abbott (1), Longwell and Maniece (2) and others. Analytical results from these methods show only the total content of methylene blue active substances (MBAS) and, therefore, the values of individual substances are not obtained.

In this paper, the conditions for separation and quantitative determination of sodium dodecylbenzenesulfonate (LAS), sodium dodecanesulfonate (SAS) and sodium dodecyl sulfate (LS-Na) by TLC were investigated. Quantitation of mixtures of 2 or 3 components was done under optimal conditions.

EXPERIMENTAL

Preparation of Sodium Dodecylbenzenesulfonate

Forty g of *n*-dodecylbenzene (purity = 99.4%) was placed in a 300-mL, 4-necked, round-bottomed flask equipped with a stirrer, a separatory funnel, a thermometer and a glass tube connected to an aspirator. Twenty percent oleum (60 g) was added under vigorous stirring, keeping the reaction temperature at 20 C. After the temperature had been raised to 50 C in a water bath, the mixture was stirred for 10 min and neutralized with 30% sodium hydroxide. The product obtained was dried and extracted with 95% ethyl alcohol and petroleum ether repeatedly to remove inorganic salts and nonreactive oily materials. By 2 repetitions of recrystallization from ethyl alcohol, white crystals of sodium dodecylbenzenesulfonate (6.0 g) were obtained. The purity of the crystals using the *p*-toluidine method was 97.5%. The IR spectrum of the LAS, which was run in potassium bromide, is shown in Figure 1.

Preparation of Sodium Dodecyl Sulfate

Dodecyl alcohol, 46.6 g (purity = 98.5%) was placed in a 3-necked flask fitted with a stirrer, a thermometer and a separatory funnel. Concentrated sulfuric acid (49.0 g) was added by drops from the funnel under vigorous stirring at temperatures below 30 C. After the reaction was complete, the product was neutralized with 35% aqueous sodium hydroxide. After drying, the product was extracted with 95% ethyl alcohol, then with petroleum ether to remove inorganic salts and nonreactive oily materials. White, scaly crystals of sodium dodecyl sulfate (9.2 g) were obtained by repeated recrystallization from ethyl alcohol. The purity of the crystals using the *p*-toluidine method was 98.6% .The IR spectrum of the LS-Na, which was run in potassium bromide, is shown in Figure 2.

Preparation of Sodium Dodecanesulfonate

A procedure similar to the method of Reed and Tartar (3) was done and the purity of the product by *p*-toluidine method was 97.9%. The IR spectrum of the SAS in potassium bromide is shown in Figure 3.

Thin Layer Chromatography

Preparation of TLC plates. A slurry of the adsorbent was applied to a glass plate (5 x 20 cm, 20 x 20 cm) resulting in an application of 0.25 mm thickness. The adsorbent layers were placed in a well-ventilated oven, activated by heating and stored over silica gel in a desicator before use.

Samples were weighed precisely and dissolved in ethyl alcohol/water (1/1, v/v) to prepare 0.50% solutions. The solutions (0.6-3.0 μL) were applied using a microsyringe