

The Adsorption of Calcium Ions to Surfactant Films on Graphon

A. C. ZETTLEMOYER, J. D. SKEWIS, and J. J. CHÉSSICK, Surface Chemistry Laboratory, Wm. H. Chandler Chemistry Laboratory, Lehigh University, Bethlehem, Pa.

Abstract

Previously, the adsorption mechanisms of sodium dodecyl sulfate (NaDS) and of sodium dodecylbenzene sulfonate (NaDBS) onto Graphon (a high area, graphitized carbon black) had been determined. Calorimetric heats of adsorption of the surfactants were also measured using a plastic calorimeter designed to avoid contamination by calcium ions. This work has now been extended to learn the effects of calcium on the Graphon/solution interface.

Radiocalcium adsorption measurements showed that the adsorbed NaDS takes up limiting amounts of one calcium for two DS ions and the chains extend directly from the surface in close-packed array. (In the absence of calcium, the NaDS takes up one of two arrangements with two different lengths of the hydrocarbon chain lying on the Graphon surface). Several lines of evidence indicate that the calcium is tightly bound at the interface. Above the cmc, the micelles compete for the calcium ions. For NaDBS, the arrangement on the Graphon is not altered by the calcium but other results are similar.

Trace amounts of calcium strongly enhance the flocculation of the Graphon. This finding suggested that deposition of the surfactant-coated Graphon onto cotton should be followed as a function of added calcium. It was found that traces of calcium greatly increased the deposition apparently by bridging surfactant on the Graphon to surfactant on the cotton.

Introduction

IT BECAME apparent several years ago in this laboratory that Graphon, a graphitized carbon black of high area (ca. 100 m²/g), was a boon to the study of surface active agents. The heat of immersion of this powder is quite low into water (1), so that the heat evolved is considerably augmented by the adsorption of surface active agents from aqueous solutions. The Graphon surface is almost entirely homogeneous, thus providing adsorption sites of equal low energy. Furthermore, each surface active agent evolves a characteristic amount of heat upon adsorption at the Graphon/water interface (2). That is to say, the wetting tendency of surface active agents can be rated by measuring the heat of immersion of Graphon into their solutions. Measurements were made for a number of different compounds to explore the utility of the method and a detailed study was made of the adsorption characteristics and heats of adsorption of sodium dodecyl sulfate, NaDS, and sodium dodecylbenzene sulfonate, NaDBS (2,3).

A plastic calorimeter, employing two thermistors in a Wheatstone bridge as temperature sensing elements, was designed and constructed to work with surface active agents. All plastic parts were required to avoid traces of alkaline earth ions which were found to effect drastically both the adsorption char-

acteristics and the heats evolved. In addition, a higher sensitivity was required than was available in the simplified heat of immersion calorimeters than in use here (2). As was expected, the final steady state was reached slowly because of the plastic construction, but adsorption is also a slow process. The largest amount of heat evolved by surface active agents so far was that produced by sodium lauryl sulfate (when slightly impure) for which the value is as high as 140 ergs per cm² of Graphon surface. Graphon into pure water evolves only about 30 ergs/cm². Table I lists the values obtained on a number of anionics and nonionics; cationics are only now being explored.

For NaDS, two characteristic heat values were uncovered, the one for low packing on the surface obtained at low concentrations and the other for high packing obtained at high concentrations or with added sodium chloride. On the basis of the adsorbed NaDS rather than on the basis of unit area of adsorbent, the values were 9.5 and 7.6 kcal/mole, respectively. At low concentrations, apparently more of the hydrocarbon chain was interacting with the Graphon surface and less repulsion energy was contributed by the head groups. This conclusion was in accord with the adsorption isotherm studies which followed both the anions and counterions.

The wetting process is certainly one of the important steps in detergency and the Graphon may be regarded as a "model dirt," one of low energy and hydrophobic. Therefore, these heats of immersion allow this vital step to be measured quantitatively. It became of interest, also, to add trace amounts of calcium to the solutions of NaDS and learn its effect on the adsorption isotherms and on the Graphon sols.

The purposes of this paper are to present the effects of the Ca⁺⁺ on the adsorption characteristics of NaDS. The adsorption of NaDBS on Graphon was also monitored in the presence of added Ca⁺⁺; the behavior of this system was the simpler of the two. Radiocalcium was employed to follow the calcium adsorption. In addition, the effects of the calcium on the deposition of Graphon onto cotton were examined.

TABLE I
Heats of Immersion of Graphon in 0.5% Aqueous Solutions of Surfactants

Surfactant	Approx. purity	Heat of immersion $-h_{I(SL)}$ ergs/cm ²	Type
Water.....		32	
Sodium lauryl sulfate ^a	100	116, 20	Anionic
Purified sodium dodecylbenzene sulfonate.....	100	110	Anionic
Sodium dodecylbenzene sulfonate (Santomerse-3) ^b	99	73	Anionic
Monobutyl biphenyl sodium monosulfonate (Areskap-100) ^b	78	Anionic
Monobutyl phenylphenol sodium monosulfonate (Areskap-100) ^b	51	Anionic
Sodium decylbenzene sulfonate (Santomerse-D) ^b	90	47	Anionic
Sulphate ester of an alkyl phenoxy polyoxyethylene ethanol (Alipal CO-436) ^c	68	Anionic
Polyoxyethylated nonyl phenols ^c			
Igepal CO-650.....	99	88	Nonionic
Igepal CO-850.....	99	60	Nonionic
Igepal CO-530.....	99	40	Nonionic

^a Supplied by National Bureau of Standards, Washington, D.C.

^b Supplied by Monsanto Chemical Co., St. Louis, Mo.

^c Supplied by General Aniline and Film Corp., Easton, Pa.

Experimental

In earlier reports the techniques for determining the adsorption isotherms, following both the anions and the sodium counterions, were described (3) and the design of the plastic calorimeter was given in detail (2). These will not be repeated here.

Water purification and storage required special precautions. It was finally distilled from an alkaline permanganate solution through a block tin condenser and collected in leached polyethylene bottles. The specific conductance as used was about 5×10^{-7} mhos/cm.

The adsorption measurements were also conducted in leached polyethylene bottles. The leaching was accomplished by washing with solutions of the surface active agents for two weeks followed by final rinsing with distilled water.

The radioactive calcium-45, listed as Ca-45-P3 was received from the Isotopes Division of the AEC in the form of the chloride. Its specific activity was 2530 millicuries per gram of calcium chloride.

The Graphon, a graphitized carbon black, was produced by the Cabot Company (lot L-340) and had a nitrogen surface area of $95 \text{ m}^2/\text{g}$.

The surface active agents were carefully purified before use until they showed no minimum in the surface tension-concentration curve. The cmc's for the NaDS and the NaDBS were found to be 8.0×10^{-3} and 4.0×10^{-3} moles/liter, respectively, in accord with earlier published results (4).

The adsorption of calcium ions (and of the surface active agent anions and sodium ion) was followed by doping initial concentrations with small amounts of radioactive tracer. Evaporation to dryness in planchets of known area and counting with a Geiger counter allowed both the initial and final concentration to be determined (3b).

The Effects of Calcium Ions on the Adsorption of NaDS to the Graphon/Solution Interface

The adsorption isotherm for NaDS from solutions in pure water onto Graphon possesses two plateaus indicative of two preferred packing arrangements (3). In the loose arrangement, more of the hydrocarbon chain lies on the surface of the Graphon than when packing is closer at high concentrations. The remainder of the chains under the influence of the sulfate groups extend into the solution where a Gouy-Stern electrical double layer of counterions complete the adsorbed film.

Figure 1 illustrates the increased adsorption of NaDS at several initial concentrations caused by adding calcium chloride. At the higher initial NaDS concentrations, there are sharp breaks in the curves showing sudden increases in NaDS adsorption. It is quite unlikely that multilayers form: the second layer would certainly not be hydrocarbon chain against the double layer and double layer somehow oriented against double layer would leave hydrocarbon chains exposed to water. It must be concluded, then, that the increased adsorption is due to reorientation with subsequent closer packing. More will be said about this situation. It should be emphasized, however, that no adsorption of Na^+ or Ca^{++} onto Graphon occurred in the absence of surface active agent.

The calcium ion is also adsorbed to the Graphon/solution interface as shown in Figure 2. The breaks in the curves, showing sudden increases in calcium ion adsorption, correlate with the sudden increases in adsorption of DS^- anions. Another interesting point is the apparent decrease in calcium ion adsorp-

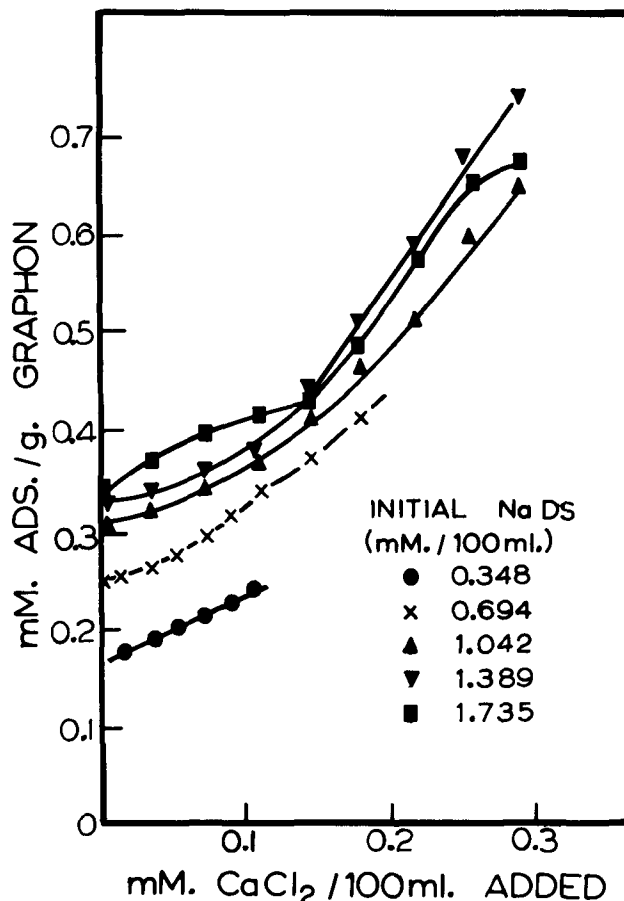


FIG. 1. Adsorption of dodecyl sulfate anions with CaCl_2 added.

tion above the cmc. The micelles apparently compete rather successfully for the calcium.

The ratio of adsorbed calcium ions to adsorbed dodecyl sulfate anions is plotted as a function of added calcium chloride in Figure 3. The curves approach the limit of 0.5 which is the stoichiometric ratio for $\text{Ca}^{++}/\text{DS}^-$. Of course, the calcium ions displace the sodium ions as illustrated in Figure 4. Here, the inflection points result from reorientation of the DS^- anions. At any point where the adsorbed calcium ions and adsorbed sodium ions are equal in number, the equilibrium concentration of Na^+ is 500 times greater than the concentration of Ca^{++} .

The isotherms for the adsorption of calcium ions versus the calcium ion equilibrium concentrations, given in Figure 5, are unusual in that they exhibit

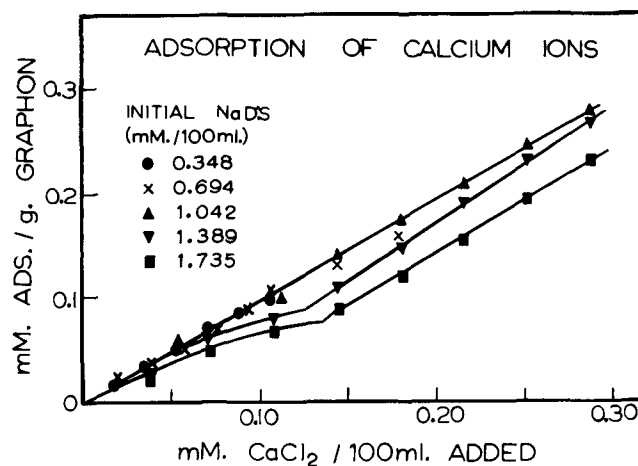


FIG. 2. Adsorption of calcium ions.

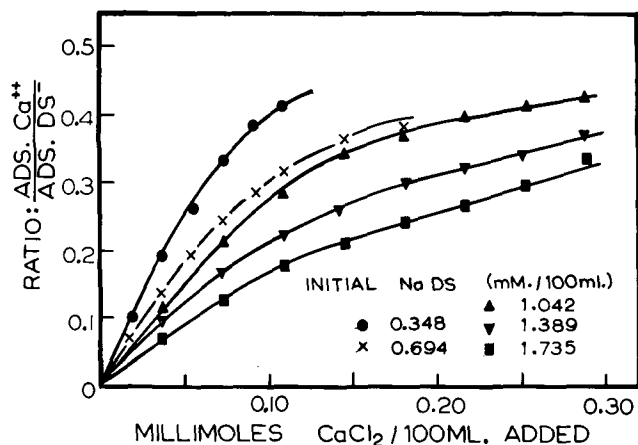


Fig. 3. Ratio of adsorbed calcium to adsorbed DS anions.

sudden reversals in slope at high initial concentrations of NaDS. These reversals are due to reorientation as explained heretofore; more calcium ion is adsorbed at the closer packing.

Finally, the true adsorption isotherms for Ca^{++} as a function of equilibrium concentration of DS^- were extracted from the data. Figure 6 indicates that the Ca^{++} adsorption increases with NaDS concentration until the cmc is reached; in this region there is a sudden decrease again showing the competition for the Ca^{++} provided by the micelles.

These results make it clear that the Ca^{++} affects the adsorption of the DS^- which in turn affects the $\text{Ca}^{++}/\text{Na}^+$ ratio at the interface. Apparently, the adsorption of Ca^{++} reduces the repulsion between the sulfate anions so that closer packing can occur. It is certainly not possible to make the simplifying assumptions van Voorst Vader (5) applied to the thermodynamical development of the situation at the air/surfactant solution interface. Also, the adsorp-

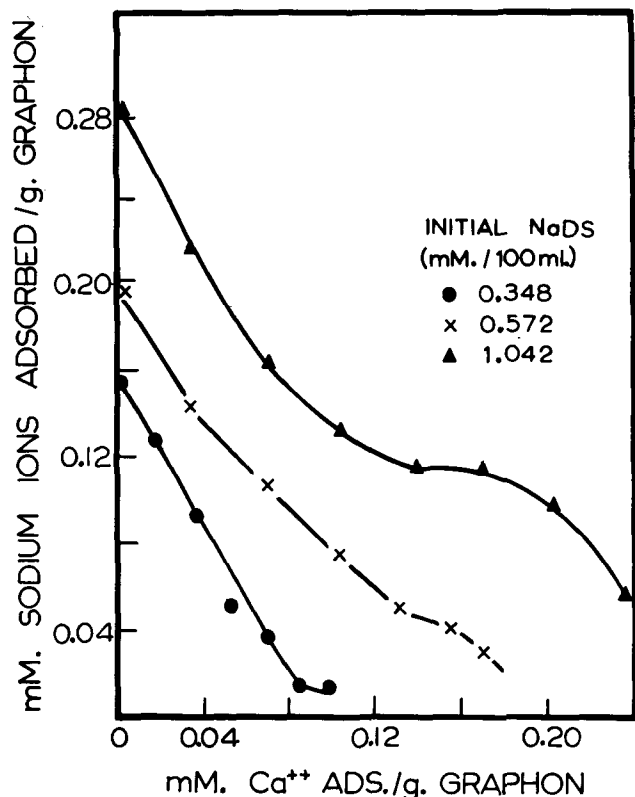


Fig. 4. Adsorption of sodium ions as a function of adsorbed calcium ions.

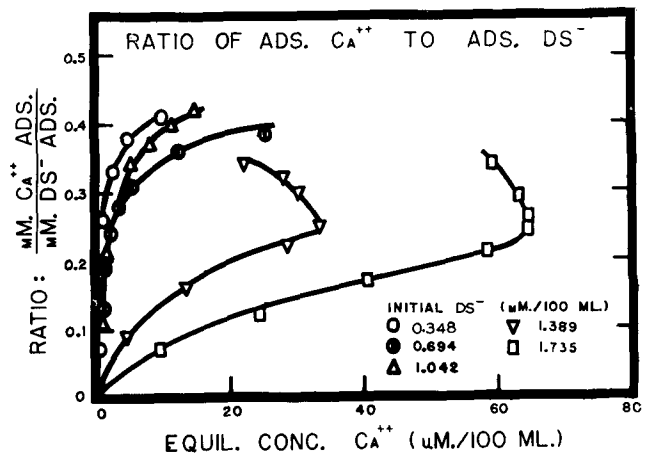


Fig. 5. Ratio of adsorbed calcium ions to adsorbed dodecyl sulfate anions.

tion of hydronium and hydroxyl ions cannot be neglected as suggested by v.d. Tempel (6). In addition, measurements of Ca^{++} adsorption in the cmc region appear to be very sensitive to the micelle formation.

A very simple semi-empirical equation can be set up to fit the adsorption results obtained in the presence of the Ca^{++} . Consider at first that the rate of adsorption will be less dependent on the Na^+ , which is largely in the diffuse layer, than on the DS^- or Ca^{++} . Suppose for the rate of adsorption we write:

$$\frac{dn}{dt} = B_1 (1-\theta) C_{\text{DS}^-} C_{\text{Na}^+}^{1/3} C_{\text{Ca}^{++}} \quad (1)$$

and for the rate of desorption:

$$-\frac{dn}{dt} = B_2 n \quad (2)$$

Here, n is the moles of surfactant anions adsorbed per g, C_{DS^-} is the concentration of unaggregated anions, θ is the fraction of the surface covered, C_{Na^+} and $C_{\text{Ca}^{++}}$ are the solution concentrations of the respective cations, and B_1 and B_2 are constants. Then, setting $\theta = n/n_0$, where n_0 is the maximum value of surfactant adsorption, we obtain the equilibrium equation by equating Equation 1 and 2:

$$n = \frac{C_{\text{DS}^-} C_{\text{Na}^+}^{1/3} C_{\text{Ca}^{++}}}{A + (1/n_0) C_{\text{DS}^-} C_{\text{Na}^+}^{1/3} C_{\text{Ca}^{++}}} \quad (3)$$

A remarkably good fit to the adsorption results was obtained with $A = 30.863 \times 10^{-8}$ and $1/n_0 = 0.1423 \times$

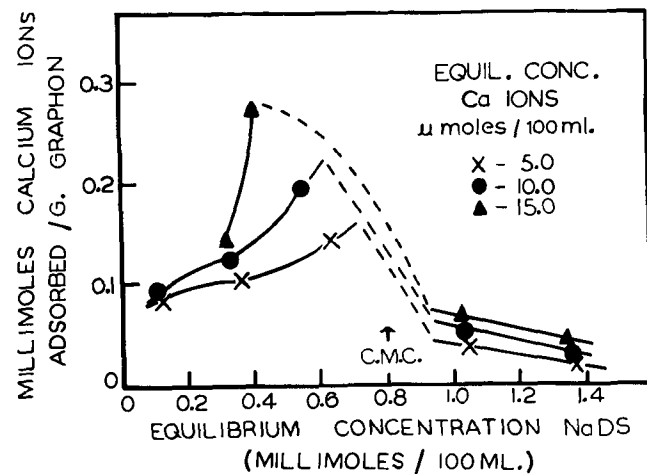


Fig. 6. Adsorption of calcium ions as a function of equilibrium concentration of sodium dodecyl sulfate.

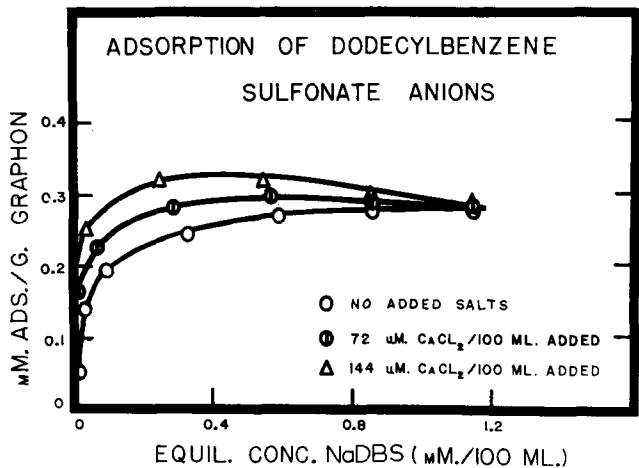


FIG. 7. Adsorption of dodecylbenzene sulfonate anions with CaCl_2 added.

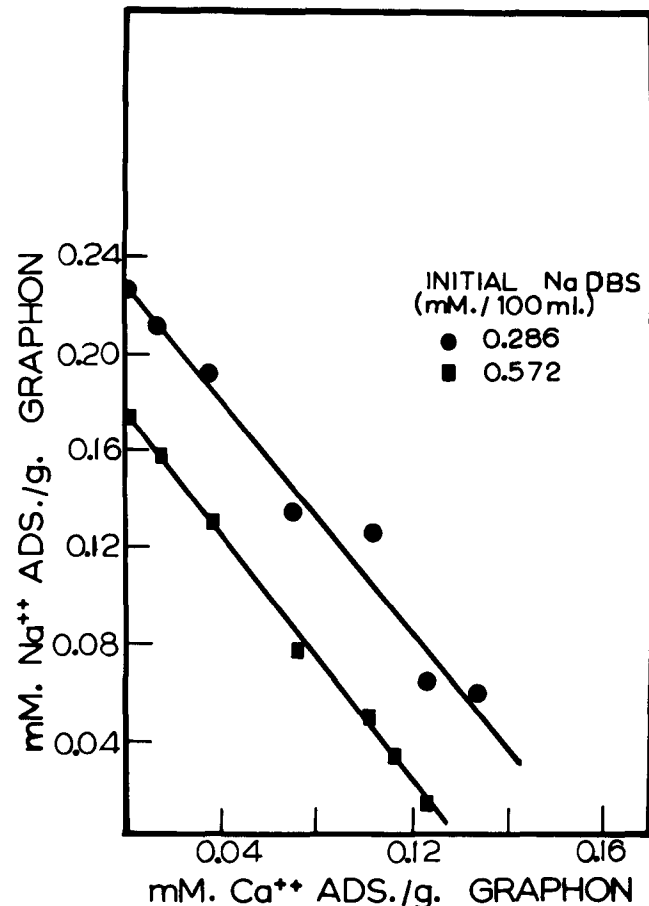


FIG. 9. Adsorption of sodium ions and calcium ions.

10^4 ; the average percent deviation was 1.0, the maximum deviation 1.7%. The limit of adsorption of DS^- in the presence of Ca^{++} was therefore 7.03×10^{-4} moles DS^-/g of Graphon. The corresponding limiting area was 22\AA^2 per anion. It must be concluded that the hydrocarbon chain is essentially pulled off the surface in this state so that the chains are in close-packed array with the polar head groups held close by the adsorbed calcium ions.

The Effects of Calcium Ions on the Adsorption of NaDBS to the Graphon/Solution Interface

The orientation of DBS^- on the Graphon is apparently the same at all equilibrium concentrations; the benzene ring is in juxtaposition to the graphitic surface and part of the hydrocarbon chains and the sulfonate groups extend into the solution (3). Thus, there is no reorientation to complicate the picture and the analysis of the Ca^{++} adsorption succumbs to a simple Langmuir treatment. In other words, the effects of introducing calcium ions are similar.

The increased adsorption of DBS^- caused by the addition of small increments of Ca^{++} is depicted in Figure 7. As for DS^- , the ratios of $\text{Ca}^{++}/\text{DBS}^-$ approach 0.5 with increasing calcium ion concentration as in Figure 8. The displacement of Na^+ by Ca^{++} is shown in Figure 9.

As for the NaDS , the adsorption of NaDBS is also generally affected by the of Ca^{++} so that the situation is complicated. When the initial NaDBS concentra-

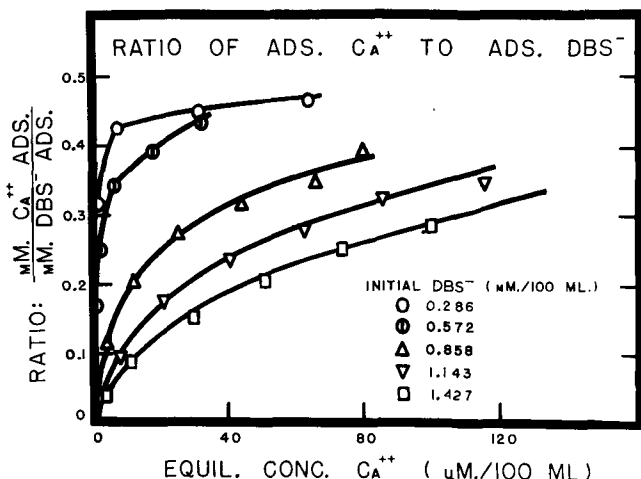


FIG. 8. Ratio of adsorbed calcium ions to adsorbed dodecylbenzene sulfonate anions.

tion was as high as 1.427 mmoles/100 ml, however, the addition of sodium or calcium chloride did not change the DBS^- adsorption. Direct experiments at this initial NaDBS concentration showed the effect of added sodium ions in decreasing the Ca^{++} adsorption. These experiments led to an analytical examination of the limiting ratio of Ca^{++} to adsorbed DBS^- if the Na^+ could be completely eliminated.

To accomplish this analytical task, it was fortunate that the simple Langmuir equation, although naive, fitted the results well. Table II illustrates the fit and gives the extrapolated values for zero Na^+ concentration.

The plot of the last equation extrapolates closely to 0.5 $\text{Ca}^{++}/\text{DBS}^-$ adsorbed at about 250 $\mu\text{moles Ca}^{++}/100 \text{ ml}$ (100 ppm Ca^{++}). The constant 6.6 represents $1/n_m$, the inverse of the monolayer capacity in mmoles

TABLE II
Equations for the Adsorption of Calcium Ions with Varying Amounts of Sodium Ion

Equation	Initial Na^+ concn mmoles/100 ml	Avg % deviation
$n = \frac{C}{1.17 + 6.5C}$	4.85	3.7
$n = \frac{C}{0.89 + 6.7C}$	3.14	4.6
$n = \frac{C}{0.55 + 6.6C}$	1.427 (none extra)	2.3
$n = \frac{C}{0.22 + 6.6C}$ (extrapolated constants)	0 (extrapolated constants)

n = mmoles Ca^{++} adsorbed/g Graphon; C = equil concn Ca^{++} , mmoles, 100 ml.

per g of Graphon. Thus, $1/6.6 = 0.15$ is to be expected since the extrapolated capacity of DBS^- is about 0.3 mmoles/g Graphon.

The heat of adsorption of Ca^{++} to the Graphon/solution interface was also measured by breaking calcium chloride solution into suspensions of the Graphon in the NaDBS solutions. The value of 3.0 ± 0.5 kcal/per mole of Ca^{++} adsorbed was the same as that obtained by adding calcium chloride to concentrated NaDBS solutions from which the $\text{Ca}(\text{DBS})_2$ precipitated. A similar value was also obtained when the concentration was such that the Ca^{++} was merely adsorbed by micelles without precipitation. It is unfortunate that the deviations in all these enthalpy measurements are so large. Current measurements in this laboratory of the heat of double layer formation show that it is often of the order of 0.5 kcal/mole. Consequently, the above heat measurements do not contribute firmly to a definite decision as to whether the Ca^{++} is diffusely adsorbed or adsorbed by chemical binding.

Nature of the Adsorption of Calcium Ions at the Graphon/Anionic Surfactant Solution Interface

It is well established that traces of Ca^{++} profoundly affect the surface active properties of anionics such as foaming properties (7), detergency (8), soil deposition (9), and the stability of emulsions (10). One of the major basic problems regarding systems related to these properties concerns the characteristics of the calcium adsorbed at the corresponding interfaces. Does the calcium interact chemically with the surfactant ions or is it adsorbed in some form of electric double layer? Recent attempts to establish the nature of the interaction are considered indecisive. Thus, van Voorst Vader (5) got rather poor agreement between the total of Na^+ and 2Ca^{++} adsorption versus anionic ion adsorbed at the solution/air interface, but he made his studies in the cmc region where competition with the micelles is a sharply changing factor. The radiotracer studies reported here also suggest that adsorption, at least at the Graphon/solution interface, is more complicated than was recognized heretofore. Schwartz, Martin, and Davis (11) decided that Ca^{++} was adsorbed as the salt CaZ_2 on cotton, but study of their analytical method leaves the question in considerable doubt.

The great influence of trace Ca^{++} in competing for Na^+ at the Graphon/solution interface, the trend toward a $\text{Ca}^{++}/\text{Z}^-$ ratio of 0.5 and the common value of 3 kcal/mole for precipitating $\text{Ca}(\text{DBS})_2$ or for adsorbing Ca^{++} at the Graphon/solution interface, all suggest chemical interaction. The following studies of the effect of Ca^{++} on the deposition of Graphon dispersions in NaDBS solutions onto cotton, at first glance, tend to support this contention. Nevertheless, it must be concluded that the present studies do not completely settle the question. There is a corresponding problem in the adsorption of polar organic molecules onto metal oxides; here the question of chemisorption versus physisorption also remains unsettled. In both problems, the greatest current anticipation is that the interaction can be put on an accurate energy basis. At the present time, it can be said that the Ca^{++} is far less diffusely, hence more energetically, bound than the Na^+ ion.

The Deposition of Graphon onto Cotton in the Presence of NaDBS as Affected by the Addition of Calcium Ions

The results on the studies of the adsorption of Ca^{++} to the Graphon/surfactant solution interface

prompted the further study of the deposition of Graphon onto cotton. It was of interest to learn whether the trace amounts of calcium could influence the deposition to the same degree that Na^+ was displaced. Also, Graphon provides a truly model dirt far simpler than most materials employed heretofore in detergency studies.

The literature contains many reports of investigations of detergency, and almost as many ideas concerning the fundamental nature of deterging processes. In spite of the numerous and varied concepts, it is generally agreed that most cleaning processes consist of the following three steps (12):

- a. Separation of the soil from the material or surface that is being cleaned.
- b. Dispersion of the soil in the deterging medium.
- c. Prevention of redeposition of the soil onto the cleaned surface.

In all these steps, the adsorption of surfactant materials onto the soiled goods or dirt can be considered to be important. Indeed, Reich claims (13) there is no doubt that adsorption of detergents by soil and substratum is fundamental to detergency. For if the surfactant is strongly adsorbed at the surface of the soil and substratum, the adsorption will alter the zeta potentials, the wetting tendencies, the soil agglomerates, etc. However, as Schwartz and Perry point out (14), a vast amount of work has been aimed at evaluating and measuring detergency effects by practical methods rather than by theoretical or academic considerations.

A detailed study of the separation of soil from a substrate that is being cleaned requires consideration of the characteristics of the soil, the characteristics of the surface from which the soil is to be removed, and the characteristics of the bonds or attractions between the soil and the substrate. It becomes almost impossible, therefore, to discuss detergency in completely general terms. To simplify matters, many investigators have studied model systems of cotton fabrics and carbon blacks. These studies have been approached from two directions, one being a study of the degree of removal of carbon black from solid cotton cloth, the other consisting of measuring the amount of carbon black deposited on clean cotton cloth. Although these two approaches are in direct contrast to each other, both are important. In detergency, the dispersion of the soil or prevention of redeposition is neither more or less important than the original separation of soil from fabric.

Goette (15) has discussed the removal of soil from fabric substrates and claims that practical experience and laboratory experiments have clearly demonstrated the influence of particle size on the removability. As the particle size of the soil becomes smaller, the removal of the soil from the fabric becomes increasingly more difficult. When the soil particles are sufficiently small, it becomes impossible to remove them from the fabric even with the best of detergents.

Vitale (16) studied the removal of carbon soil from cotton fabrics in relation to the amount of calcium and magnesium ions in sodium dodecylbenzene sulfonate solutions. Increasing amounts of water hardness had a decreasing effect on the soil removal. These studies correlated with other investigations (17a,b) which have shown that increasing calcium and magnesium ion concentrations had an increasing effect on the deposition of carbon soils to cotton fabrics.

Compton and Hart (18a,b,c) reported the degree

of deposition of carbon black to cotton cloth was directly related to the particle size of the carbon black. For particles sizes below $50 \text{ m}\mu$, the soil deposition was very severe and increased with decreasing carbon black particle size. Above $50 \text{ m}\mu$ in particle size, the soil deposition was much less and was relatively independent of particle size. Compton and Hart concluded that soiling in this system occurred by mechanical entrapment of the carbon particles by irregularities in the cotton surfaces. Of course, van der Waals attraction forces and repulsion forces are also likely to play a role.

In fact, Durham (19) has shown that theoretical considerations of the van der Waals attractions forces, and the repulsion forces arising from electric double layers, leads to a description of a potential energy barrier between two approaching surfaces. The potential energy barrier required to prevent the deposition of a solid particle onto a fabric increases as the particle size of the soil decreases. Thus, the rate of deposition of soil to cotton fabrics should be inversely proportional to particle size and to the interfacial potentials at the soil/solution and cotton/solution interfaces.

These studies, based on observations of model systems, have described the controlling factors of detergency processes but have not explained the observations on the basis of measured properties of the interfacial films. The present series of studies has described the Graphon/surfactant solution interface in some detail; this fundamental approach should explain in a qualitative manner some of the observed factors in detergency. Besides, the surface of the Graphon is far more homogeneous than are carbon blacks so that interactions should be simpler and more reproducible.

Adsorption of ionic surfactants to the Graphon/solution interface results in the formation of an electric double layer. The interfacial potential of this double layer promotes repulsion forces between two approaching particles or between a solid particle and a cotton substrate if the cotton surface is similarly charged. The repulsion forces may be pictured as a potential energy barrier between the Graphon particles and a cotton surface. Hence, the higher the potential energy barrier or interfacial potential, the slower will be the rate of deposition of Graphon particles to a cotton fabric.

These concepts were studied by agitating swatches in dispersions of Graphon in aqueous sodium dodecylbenzene sulfonate solutions containing amounts of calcium chloride. Cotton cloth, obtained as Indian-head desized muslin (Testfabrics, Inc., 54×48 count) was washed well with distilled water before use. The cotton swatches were oscillated in a vertical direction with an amplitude of $\frac{1}{4}$ inch and a frequency of 60 cycles/min for a period of 60 min. A volume of 200 ml of solution was used in each case; the solution contained 0.572 mmoles of sodium dodecylbenzene sulfonate, 6 mg of Graphon, and specified amounts of calcium chloride. The Graphon particles were barely visible in a bench-type photomicroscope, and so the average particle diameter was known to be 0.1μ or less.

After agitating the cotton swatches in the solutions, the cotton fabric was rinsed in distilled water and dried. The relative amounts of Graphon particles deposited on the cotton were determined by comparing the reflectance of light from the cloth before agitation in the Graphon dispersions. This comparison is reported as I , the deposition index, where

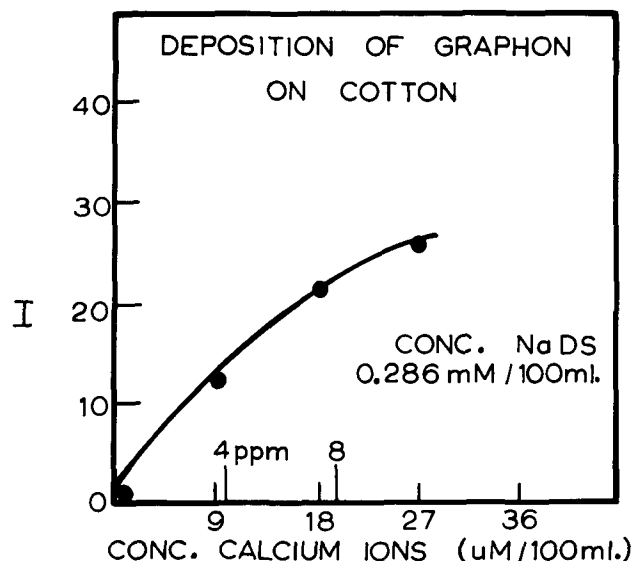


FIG. 10. Deposition of Graphon particles to cotton as a function of calcium ion concentration.

$$I = \frac{\% \text{ Reflectance clean cloth} - \% \text{ reflectance soiled cloth}}{\% \text{ Reflectance clean cloth}} \times 100$$

It is recognized that reflectance and soil deposition do not always parallel each other. For this system, reflectance appears to be a reliable index; the deposition also followed the increased rate of flocculation of the Graphon sols as Ca^{++} was increased.

Figure 10 shows the comparison between measured values of I and concentration of calcium ions in the surfactant solutions. Indeed, an increase in calcium ion concentration caused an increase in Graphon deposition to cotton cloth. This phenomenon is in agreement with the concept of a potential energy barrier existing between the Graphon particles and the cotton substrate. The height of the potential energy barrier is really a function of the number of adsorbed dodecylbenzene sulfonate anions which are not complexed with calcium ions. In Figure 11, the deposition index is plotted in relation to the number of adsorbed surfactant anions which are not complexed by calcium ions, the latter quantity being calculated from earlier adsorption measurements. It appears that this plot is rather basic. The vital effect of trace amounts of calcium is evident.

This brief description of the deposition of Graphon particles to cotton cloth has neglected the properties of the cotton/surfactant solution interface, which are undoubtedly also very important in detergency. In

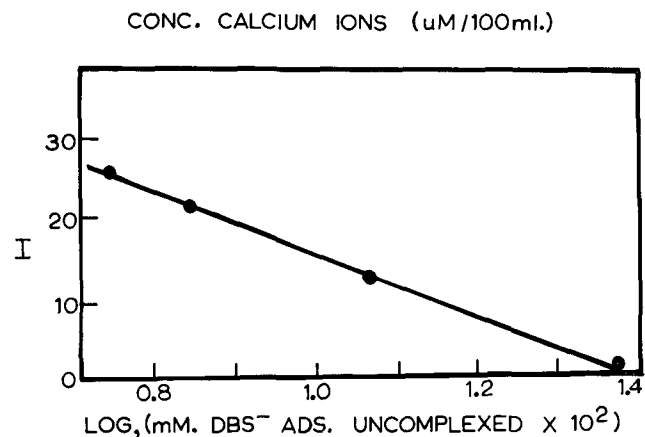


FIG. 11. Deposition of Graphon particles to cotton as a function of the adsorbed dodecylbenzene sulfonate anions uncomplexed with calcium ions.

addition, not all soils would be expected to give rise to the same interfacial properties as Graphon. However, this study has shown that very low concentrations (a few ppm) of calcium ions can have marked effects on the packing of surfactant molecules at the graphite/surfactant solution interface and, moreover, on the attachment of graphite particles to cotton.

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Refining Crude Cottonseed Oil Dissolved in Hexane¹

M. A. ZEITOUN,² W. B. HARRIS, and W. D. HARRIS, Cottonseed Products Research Laboratory, Agricultural and Mechanical College of Texas, College Station, Texas

Abstract

Measurements were made of the surface tensions of mixtures of cottonseed oil and hexane and of their interfacial tensions against water and caustic soda solutions. Attempts were made to study the reaction rate between the two phases. The results show that in caustic refining of hexane miscellas the caustic is readily dispersed into the oil-hexane phase.

Refining losses were found to be lower for miscellas containing less than 70% oil. Concentrations as low as 40% were refined successfully. The losses were inversely related to the viscosity of the solution.

Introduction

IT IS KNOWN that the red color of solvent-extracted cottonseed oil is made more difficult to remove by the heating necessary to evaporate the solvent (1). For this reason the refining of oil dissolved in hexane is of interest to persons operating solvent extraction plants. Literature references indicate, however, that color removal during miscella refining is a major problem. Very little information is given about optimum conditions for refining oil-hexane miscellas.

Mattikow (2) states that decolorizing the oil is not successful when the oil content is less than 77%. Folzenlogen (3) claims that color can be removed from 40% oil miscellas if polypropylene glycol is added as a surface active agent. James (4) indicates that 50% miscella concentration is most effective for neutralization and decoloration. Thurman (5) reports that in a two-step process, 75% miscella refines to a good color and that 50% is almost as

good, providing a surface active agent such as polypropylene glycol is used. A recent patent (6) has been issued covering the use of polypropylene glycol in miscella refining. Cavanagh (7) refines 40% miscella successfully, providing the meats are treated with soda ash prior to removal of the oil. He indicates that even 19% miscella can be refined to a low bleach color, but he does not give the refined color nor the amount of bleaching earth used. Frankel (8) describes a two-step refining process in which 25% miscella yields superior results.

According to James (4), considerable difficulty is encountered in obtaining effective contact between caustic solutions and miscella. Sufficient contact for neutralization of the fatty acids is said to be easy, but the coagulation of phosphatides and the removal of color are said to require better mixing. He indicates that successful mixing can be obtained using surface active agents or mechanical homogenizers.

Some of the physical properties which would affect mixing of caustic solutions and miscella are interfacial and surface tensions, viscosity, and density. No data were found in the literature for interfacial and surface tensions. The viscosities and densities of oil-hexane solutions have been published (9,10,11). These references point out that the reduced viscosity and gravity of miscella solutions make the separation of soapstocks easier. However, no correlations between refining losses and viscosity or density were found.

In this investigation, surface and interfacial tensions were measured for miscella-caustic soda and miscella-water systems. The refining of crude cottonseed oil dissolved in hexane was studied. The variables were the amount of hexane present, the quantity of caustic used, and the concentration of the caustic.

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² Present address: Cairo, Egypt.