An Electrophoretic Study of the Detergency Process

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Abstract

By using a micro-electrophoresis technique, the electrokinetic behavior of cotton and a clay soil was studied in various surfactant, tripolyphosphate, and carboxymethylcellulose solutions. Correlative soil-deposition studies were also made.

Data are presented which show that double-layer forces of repulsion are not of major importance in preventing the deposition of a clay soil on fabric. However a correlation was demonstrated between soil deposition and adsorption processes which occur at soil-solution and fabric-solution interfaces.

Introduction

A NUMBER OF APPROACHES have been utilized to characterize the detergent process. These have dealt with endeavors to correlate detergency with one or more physical and chemical factors. Recent investigations (1–5) have tried to correlate detergency and electrokinetic phenomena which occur at soil and fabric interfaces during the washing process. Results of these investigations indicate that it would be superficial to suggest that electrical effects predominate in a process of such complexity. Obviously, the electrical charge does not explain the detergent properties of nonionogenic materials. It would seem that the degree of influence of surface electrical conditions on detergency must vary with other events of the wash process. The importance therefore of understanding the electrical conditions of soil and fabric is not that they may determine detergency but that they reflect certain surface or interfacial conditions, which, in turn, determine detergency.

One means of studying the electrical charges on soil and fabric surfaces is electrophoresis. This is the movement in a liquid of a charged particle under the influence of an applied electrical field. Within definite dimensions the speed at which the particle travels is termed its electrophoretic velocity and is proportional to the so-called electrical "double-layer" of that particle. It is the overlapping of these electrical double-layers which give rise to repulsive forces between particles in an aqueous system.

The formation of an electrical double-layer at a solid's surface can be explained as follows. Through ionization or adsorption processes many materials acquire a charge, usually negative, in water. This charge, called the bound or Stern layer, is firmly held at the solid-liquid interface where it attracts ions of opposite charge (counterions) from the bulk of the liquid. Because of thermal movement these counterions are not firmly held but only accumulate at the interface, giving rise to the diffuse layer. For example, the adsorption on a surface of the anion of an anionic surfactant molecule gives rise to the bound portion of the double layer, and the attracted sodium counterion represents the diffuse part. This double layer of charges, bound and diffuse, is responsible for particle movement in an applied electrical field. Thus surface phenomena of importance to detergency, such as adsorption, desorption, or ionization processes which alter the double layer, will be reflected by changes in electrophoretic velocity.

This work was an attempt to characterize soil and fabric surfaces during the washing process by determining their electrical charges as described by electrophoretic velocity measurements under varying conditions of washing. The purpose was to gain further insight into the fundamental mechanisms of detergency. The work was directed toward soil-redeposition phenomena although certain inferences concerning soil removal can be made.

Experimental Section

Preparation of Materials

A white, bleached, unsized Indianhead cotton fabric (Style 405, Testfabrics Inc.) was used for this study. Because electrophoretic measurements are based on the movement of particles suspended in a liquid, it was necessary to reduce the cotton to a particle size sufficiently small to prevent rapid sedimentation. This was accomplished by grinding the fabric in a Wiley Mill, suspending the ground fabric in deionized water, and recovering those particles which passed through a number 400 (37μ) U.S. Standard Sieve. A Millipore Filter (0.45μ pore size) was used for this recovery and subsequent filtrations.

To insure uniform reactivity and reproducibility, the cotton particles were given three successive treatments in 0.1N HCl solutions. After filtration from the final acid treatment they were washed on the filter with deionized water, resuspended, and again filtered. This washing procedure was repeated twice, and the cotton particles were dried at room temperature.

A kaolinite type of clay, Bandy Black (Spink's Clay Company, Paris, Tenn.), was used as the particulate soil. It was given no preliminary treatment.

Test Solutions

The surfactants used in preparation of the test solutions were anionic, sodium dodecylbenzene sulfonate, mol. wt. 348, 98% active (Siponate DS-10, American Alcolac Corporation). Nonionic, ethylene oxide condensate of iso-octylphenol, average mol. wt. 624, 100% active (Triton X-100, Rohm and Haas Company). Carboxymethylcellulose of 95% purity and an approximate molecular weight of 150,000 was obtained from the Hercules Powder Company.

Deionized water with a conductivity of less than 5 μmhos was used in preparation of test solutions. Naturally hard water (10 gpg as $CaCO_3$, 1.71 mM in respect to calcium) was prepared from 23.0 gpg hard well-water by dilution with deionized water. Calcium to magnesium ratio of this well-water was 8:1.

Test solutions were prepared from separate, deionized water-stock solutions of the two surfactants, carboxymethylcellulose and tripolyphosphate. When hard water was used, all materials to be added were premixed. For example, if the desired test solution was to contain anionic surfactant and carboxymethylcellulose in hard water, the correct volumes of stock anionic surfactant and carboxymethylcellulose solutions were mixed and then added to the hard water.

Electrophoretic Velocity Measurements

The equipment used to measure the electrophoretic velocity of the clay and cotton particles (6) is called a "Zeta-Meter" (Zeta Meter Inc., New York). It consists of a Plexi-glas, cylindrical electrophoresis cell, known as a Riddick cell, a variable-voltage DC power output unit, and a stereo-microscope for tracking of the particles. The microscope has paired 20X eye-pieces, one with an ocular micrometer and a special mechanical stage with a polished glass-mirrored-back cell holder. The special stage allows for a reflected-beam lighting technique that creates a dark field effect. Two types of electrodes were used with the Riddick cell, depending on the specific conductance of the suspension under study. For suspensions of low specific conductance (0 to 2,000 micromhos), platinum$^+$ platinum$^-$ electrodes were used. When suspensions of higher specific conductance were encountered, copper$^+$ platinum$^-$ electrodes were used. Accuracy of this equipment, as determined by measurement of the electrophoretic velocity of human erythrocytes in M/15, pH 7.3 phosphate buffer (E.V. = 1.31) was ±6%.

Procedures

Suspensions for electrophoretic velocity determinations were prepared by adding 0.025 g of the ground cotton or 0.125 g of clay to 250 ml of test solution, which had been preheated to 48C. These suspensions were then agitated for 10 min at 68 strokes per minute in a Terg-O-Tometer. After cooling to room temperature, velocity measurements were made. For each test the velocity of 25 to 50 particles was measured and averaged. Temperature and pH of the suspension were then accurately determined.

Electrophoretic velocity has the dimensions of microns/second/volt/centimeter, where volt/centimeter is the drop in voltage per centimeter of cell length. The effective length of the Riddick cell is 10 cm, thus electrophoretic velocity was calculated from the equation:

$$\text{E.V.} = \text{velocity (in microns/second)} \cdot 10/\text{applied voltage}$$

All data were corrected to 25C by the correction factor ±0.98 per degree of difference. In all cases velocity was toward the anode, indicating negatively charged particles.

Because some controversy exists concerning the calculation of *zeta* potential and also because, in general, *zeta* potential is proportional to electrophoretic velocity, test results are reported simply as electrophoretic velocity. However *zeta* potential can be calculated from the Helmholtz-Smoluchowski equation: $\text{Z.P.} = \text{E.V.} \cdot 4\pi \cdot V/D$, where V is the viscosity and D is the dielectric constant of the suspending medium. At 25C this equation reduces to $\text{Z.P.} = 12.85 \cdot \text{E.V.}$ The Helmholtz-Smoluchowski equation is appropriate because of the particle size and solution concentrations used for this study (7).

Soil-deposition tests were conducted in solutions identical to those used in the electrophoretic study. The conditions for these correlative tests were: fabric load, five 4 × 4-inch acid-treated cotton swatches; wash solutions, 500 ml containing 0.5 g of clay at 120C; agitation, Terg-O-Tometer for 10 minutes at 68 strokes per minute. After the 10-minute agitation period the swatches were squeezed by hand to remove excess moisture and then dried in a domestic type of modulated-heat dryer. Reflectance readings of the swatches were then taken on a Gardener Color Difference Meter. For these values the more useful "K/S function" was calculated by using the Kubelka-Munk equation (8). This equation is usually expressed as $K/S = (1-R)^2/2R$, where R is the fraction of incident light reflected, S is the coefficient of light scattering, and K is the coefficient of reflectivity. The K/S ratio is a linear function of the amount of material on a fabric that lowers its reflectance. Thus the higher the K/S value, the more soil is deposited on the fabric.

Results and Discussion

The source of the native negative charge on cotton and clay was of importance to the proper interpretation of the electrophoretic velocity data. Most materials in water, including clay and cotton, acquire a negative charge by ionization of the reactive groups present on their surface or in their structure and by adsorption of a hydrated layer at the solid-liquid interface. The negative charge owing to the hydrated layer is said to arise from a specific orientation of water molecules, which apparently attracts hydroxyl and anions, in general, to the interfacial side of this layer. This gives rise to an adsorption potential (9). The negative charge on clay and cotton in pure water is explained not only by this hydrated layer but also by reactive SiO^-_3 groups in the case of clay particles and by carboxy group ionization in the case of cotton.

Electrophoretic velocity measurements do not give quantitative estimates of adsorption but rather indicate relative degree of adsorption. The velocity of a particle completely covered with an adsorbable material is usually characteristic of the adsorbed material and not of the particle (10). For example, adsorption of anionic material by clay or cotton particles will increase their negative velocities and, if their surfaces are completely covered with the anionic material, their velocities will be approximately equal. The amount of adsorption which occurs is a function of the concentration of the adsorbing material. Complete coverage or maximum adsorption is indicated when the positive or negative velocity of a particle no longer increases with increasing concentration.

Anionic Surfactant Effects

The effect of the anionic surfactant on the electrophoretic velocities of clay and cotton and on soil

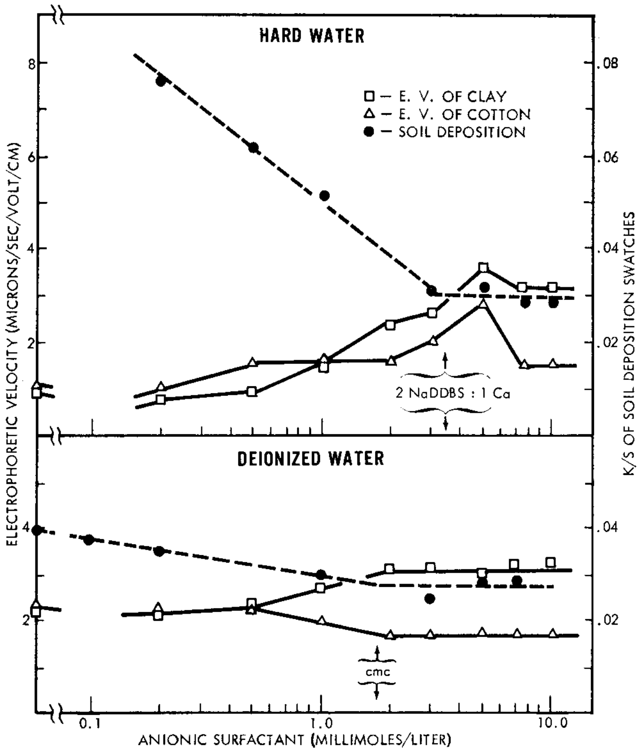

FIG. 1. Electrophoretic velocity and soil-deposition data obtained in anionic surfactant solutions.

deposition is shown in Fig. 1. The velocity-concentration curves for clay particles show slowly increasing negative velocity at low surfactant concentrations, reaching a maximum at the critical micelle concentration (cmc) in deionized water and at a concentration exceeding the surfactant-calcium equivalence point in hard water. Cotton in hard water shows a velocity-concentration curve similar to that of clay. In deionized water however, the velocity of cotton decreases as the anionic surfactant approaches the cmc and shows no change at higher concentrations. This decrease can be explained on the basis of the depressed ionization of the carboxy groups present on the surface or in the cellulose structure. The negative charge added by the anionic surfactant adsorption may not have been sufficient to overcome the loss in the negative charge because of the depressed carboxy group ionization.

The soil deposition-concentration curves of Fig. 1 show decreasing deposition as the anionic surfactant increases, reaching a minimum in deionized water at the cmc and in hard water at a concentration exceeding the surfactant-calcium equivalence point.

For the most part, the rising portions of the velocity curves of Fig. 1, which are attributed to the increasing anionic surfactant adsorption, coincide with the decreasing portions of the deposition curves, thereby suggesting the importance of surfactant adsorption to the prevention of soil deposition.

Another important result, as shown in Fig. 1, is that at high anionic surfactant concentration (7.5 and 10.0 mM) the velocities of clay and cotton and soil deposition in hard water are nearly equal to values obtained in deionized water. Thus the anionic surfactant at sufficient concentration effectively inactivates hardness ions and can function with an efficiency approaching that obtained in deionized water.

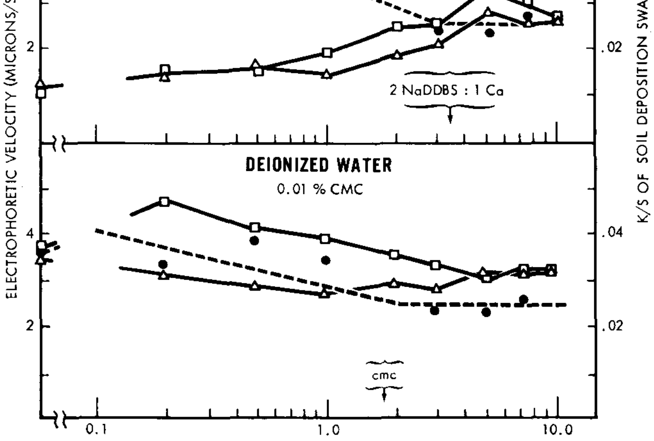

FIG. 2. The effect of 0.01% carboxymethylcellulose on the electrophoretic velocities of clay and cotton and on soil deposition in anionic surfactant solutions.

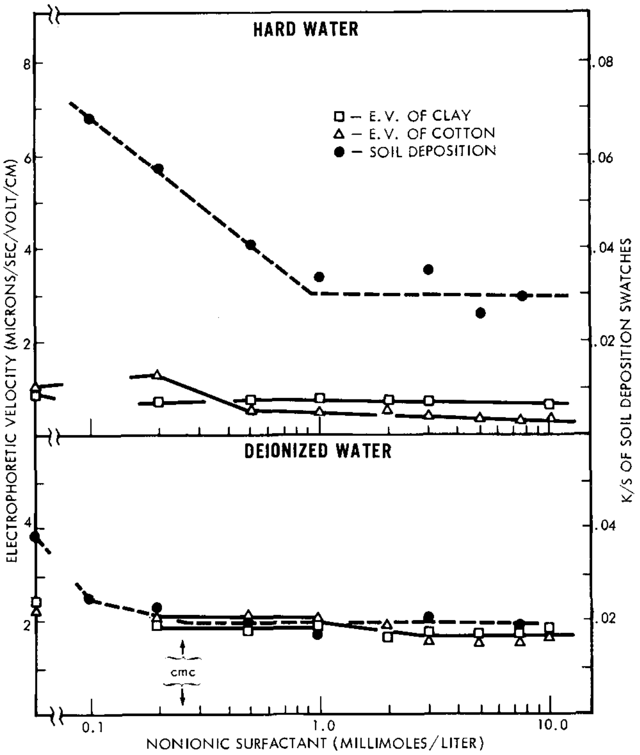

FIG. 3. Electrophoretic velocity and soil-deposition data obtained in nonionic surfactant solutions.

Anionic Surfactant-Carboxymethylcellulose Effects

Fig. 2 illustrates the effect of carboxymethylcellulose on the electrophoretic velocities of clay and cotton and soil deposition in anionic surfactant solutions. Most noticable, at the higher surfactant concentrations in deionized water, is the equalization of the velocities of clay and cotton. This indicates that, at these high concentrations, clay and cotton, because of carboxymethylcellulose adsorption, present nearly identical surfaces to the bulk of the solution.

A comparison of Fig. 2 with Fig. 1 is of interest. In hard water at low surfactant concentration (below the calcium-surfactant equivalence point) the addition of carboxylmethylcellulose considerably decreased soil deposition but had little effect on velocity. In deionized water a reverse situation was true. At low surfactant concentration (below the cmc) the addition of carboxymethylcellulose had only a slight effect on soil deposition but considerably increased velocity. Thus change in soil deposition did not correspond with the change in electrophoretic velocity as brought about by the addition of carboxylmethylcellulose.

Nonionic Surfactant Effects

The curves of Fig. 3 show the electrophoretic velocity and soil-deposition data which were obtained in nonionic surfactant solutions. In hard and deionized water there was a reduction in the velocities of clay and cotton. Although considered nonionic, this surfactant is slightly cationic in its reactions, hence the reduced velocity. The considerably lower velocities in hard water are attributed to reaction with calcium. The calcium forms of clay and cotton are less dissociated; therefore the negative charge resulting from their ionization would be reduced. This demonstrates the inability of a nonionic surfactant to inactivate hardness ions. This is also shown by comparing of soil deposition in hard water with that in deionized water. At no nonionic concentration did

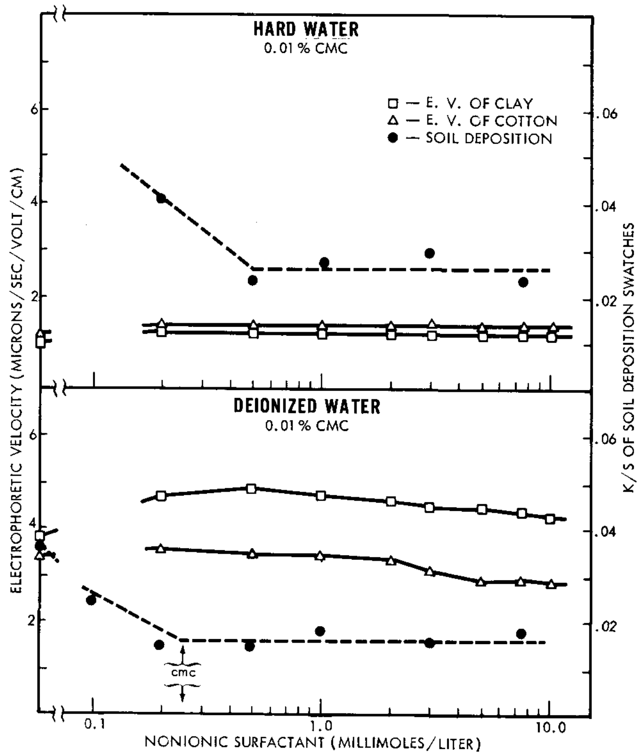

FIG. 4. The effect of 0.01% carboxymethylcellulose on the electrophoretic velocities of clay and cotton and on soil deposition in nonionic surfactant solutions.

hard-water deposition values approach deionized water values.

In considering the data of Fig. 3, it becomes apparent that points of maximum nonionic surfactant adsorption from either deionized or hard water are not obvious. As a result, it cannot be determined whether minimum soil-deposition and maximum nonionic surfactant adsorption coincide as they appeared to do in anionic surfactant solutions.

A comparison of anionic and nonionic surfactant data (Figs. 1 and 3) reveals that minimum soil deposition was obtained at a lower concentration in nonionic than in anionic solutions. This correlates with their respective cmc values. Over-all soil deposition was less in nonionic solutions. This can be explained by differences in the molecular structure of the two surfactants. In general, nonionics have greater "covering" power. Also, the hydrophilic portion of the nonionic molecule is approximately three-quarters of the entire molecule (11) whereas the hydrophilic portion of the anionic molecule is much less. This suggests that the well-covered, hydrophilic surface resulting from nonionic surfactant adsorption presents a greater barrier to deposition than the higher double-layer repulsive forces resulting from anionic surfactant adsorption.

Nonionic Surfactant-Carboxymethylcellulose Effects

Electrophoretic velocity and soil deposition data obtained in nonionic surfactant-carboxymethylcellulose solutions are given in Fig. 4. In both deionized and hard water, carboxymethylcellulose significantly increased the velocities (over velocities obtained in nonionic solutions without carboxymethylcellulose) of clay and cotton. This gives evidence that carboxymethylcellulose is readily adsorbed by both clay and cotton from nonionic surfactant solutions. In deionized water the dependence of carboxymethylcellulose adsorption on the presence of cations (12) is evidently satisfied, in part, by the cationic nature of the nonionic molecule. Equalization of the velocities of clay and cotton did not occur in nonionic-carboxymethylcellulose solutions. This is most noticeable in deionized water solutions.

Soil deposition was lessened by the addition of carboxymethylcellulose but followed the same pattern as in the absence of carboxymethylcellulose.

Several general observations can be made from the electrophoretic velocity and correlative soil deposition curves shown in Figs. 1 through 4. First, there is no consistent evidence of a direct relationship between soil deposition and the double-layer forces of repulsion as described by electrophoretic velocity measurements. Possibly of more importance is an apparent correlation between soil deposition and adsorption phenomena. Evidence of this correlation is shown by the fact that soil deposition did not continue to decrease with increasing surfactant concentration but reached a minimum, in most cases as adsorption appeared to reach a maximum. This agrees with previous work (13), which has demonstrated a similarity between adsorption and detergency curves. An absolute correlation cannot be shown because other factors which result from surfactant or surfactant-carboxymethylcellulose adsorption exert an influence. These factors are related to the degree of hydration and steric effects of absorbed molecules.

As shown by Durham (4) and Lange (5), the most important bonding forces of soil to fabric are the van der Waals polarization forces of attraction. These attractive forces are universal, acting between all ions, atoms, or molecules, and vary in magnitude depending on the material. According to Lange, if one examines the approach to the surface of soil or fabric through a soil-solution or fabric-solution interface, the order would be: the bound layer, the hydrated ends of the adsorbed surfactant molecule, the hydrocarbon chains, and finally the fabric or soil

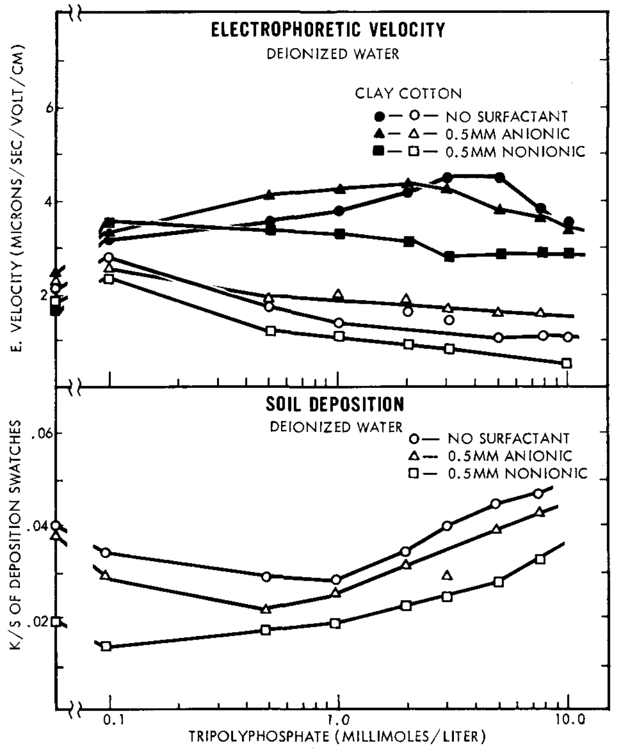

FIG. 5. Soil-deposition and electrophoretic velocity data obtained in deionized water solutions of tripolyphosphate.

surface. Thus the approach is through several different layers; each layer has its own constant for van der Waals attractive forces. It can be assumed that the constants for the hydrated layers (the bound layer and the hydrophilic ends of the detergent molecules) are similar to those of the solution. From this it would appear that forces of attraction between soil and fabric at small distances are less where there is surfactant adsorption to provide a transitional layer between surface and solution. Also, the more heavily hydrated the adsorbed surfactant, the more effective would be the transitional layer.

Tripolyphosphate-Surfactant Effects in Deionized Water

Fig. 5 presents electrophoretic velocity data for clay and cotton in tripolyphosphate and tripolyphosphate-surfactant solutions in deionized water. Correlative soil deposition data are shown also. Two important observations can be made from these data: tripolyphosphate decreased the velocity of cotton and increased that of clay; at the higher tripolyphosphate concentrations, soil deposition was increased.

The velocity data for clay are easily explained. Adsorption of tripolyphosphate and dispersion of clay particles, exposing fresh surfaces of negative charge, accounts for the increase in velocity. Surfactant adsorption accounts for the differences among the individual curves.

The reduced velocity of cotton at all tripolyphosphate concentrations which exceed 0.1 mM is attributed primarily to double-layer compression by increased counterion (sodium ion) concentration. Since cotton does not adsorb the tripolyphosphate anion (14,15) as does clay, it is more sensitive to counterion effects. However, as previously shown, a reduction in the double layer at the surface of cotton does not necessarily cause an increase in soil deposition. For this reason some factor in addition to charge, i.e., double-layer potential was sought to explain the increase in soil deposition. This factor could well be the degree of hydration of the surface of cotton. A decrease in the protective barrier presented by a hydrated layer would allow for greater soil deposition. It is possible that tripolyphosphate acts somewhat as a dehydrating agent for the surface of cotton. The mechanism by which tripolyphosphate functions in this capacity would not be analogous to that of certain salts, which at fairly high concentration can dehydrate an organic surface by a competitive attraction of ions of these salts for solvent molecules.

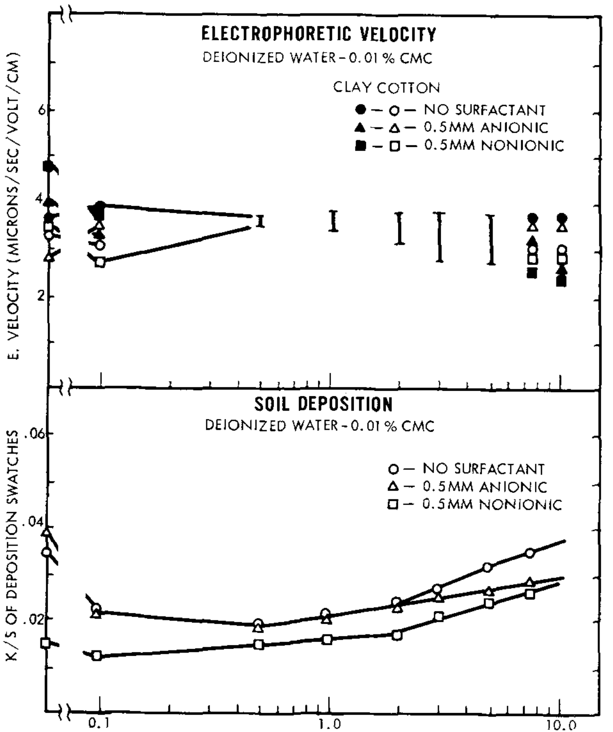

FIG. 6. The effect of 0.01% carboxymethylcellulose on the electrophoretic velocities of clay and cotton and on soil deposition in deionized water solutions of tripolyphosphate.

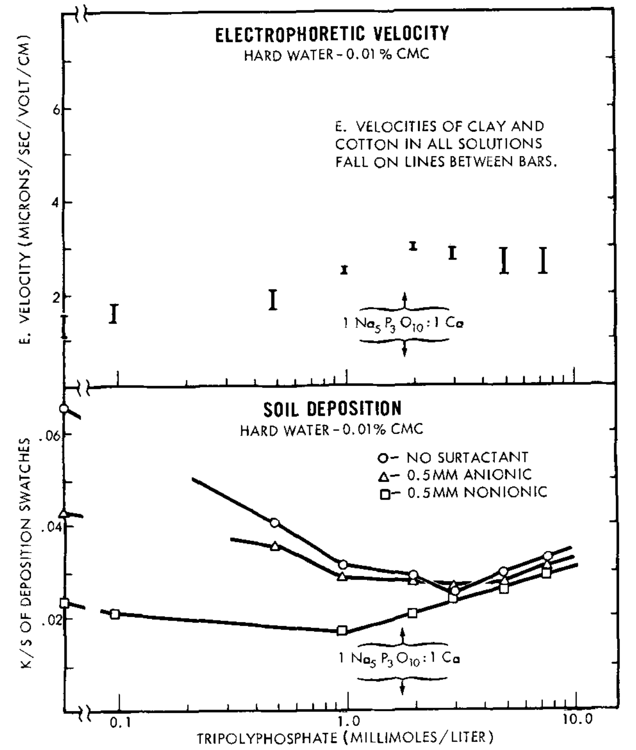

FIG. 7. The effect of 0.01% carboxymethylcellulose on the electrophoretic velocities of clay and cotton and on soil deposition in hard-water solutions of tripolyphosphate.

In contrast, tripolyphosphate appears to be effective at relatively low concentration as evidenced by increased soil deposition. A possible explanation for the action of tripolyphosphate lies in the mode of formation of the hydrated layer. If it is correct, as described by Mattson (9), that water molecules forming the hydrated layer are oriented in such a manner that anions in general are attracted to the interfacial side of this layer, it would seem that the attraction of the large, highly charged polyphosphate anion would disrupt this molecular orientation, thereby destroying the hydrated layer. This effect is not apparent for clay particles because tripolyphosphate is adsorbed by clay.

Soil deposition data of Fig. 5 show that minimum deposition occurred at a different tripolyphosphate concentration, depending on the presence and type of surfactant. The separate curves indicate that some, although perhaps little, surfactant was adsorbed by cotton. This is in agreement with work of Ginn et al. (14), who found less surfactant adsorption in the presence of tripolyphosphate.

Tripolyphosphate-Surfactant Effects in Hard Water

The electrophoretic velocity and correlative soil-deposition test data obtained in tripolyphosphate-

TABLE I

Solutions of Lowest Concentration, Exibiting Minimum Soil-Deposition

	Deionized Water						Hard Water					
	Concentration[a] mM/L	Conductivity µmhos	pH	E. Velocity		Soil deposition K/S	Concentration[a] mM/L	Conductivity µmhos	pH	E. Velocity		Soil deposition K/S
				Clay	Cotton					Clay	Cotton	
No additive	....	7	6.4	2.20	2.21	3.94	....	430	8.7	0.96	1.00	10.6
Anionic	2.0	150	6.7	3.08	1.68	2.80	3.0	500	8.7	2.64	2.03	3.10
Nonionic	0.2	4	6.9	1.88	2.03	2.33	1.0	400	8.6	0.79	0.47	3.00
Anionic + CMC	2.0	170	6.4	3.58	2.92	2.60	3.0	500	8.6	2.50	2.10	2.44
Nonionic + CMC	0.2	25	7.0	4.70	3.55	1.40	0.5	380	8.6	1.31	1.39	2.36
TPP	1.0	490	9.4	3.78	1.42	2.79	2.0	1000	8.6	3.48	1.57	4.01
TPP + Anionic	0.5	320	9.0	4.06	1.91	2.15	2.0	1000	8.6	3.72	1.76	3.30
TPP + Nonionic	0.1	66	7.7	3.55	2.27	1.36	1.0	640	8.7	1.50	0.59	1.86
TPP + CMC	0.5	300	9.1	3.72	3.70	1.98	3.0	1300	8.8	2.88	2.81	2.47
TPP + Anionic + CMC	0.5	340	9.0	3.76	3.66	1.98	3.0	1300	8.7	2.94	2.74	2.61
TPP + Nonionic + CMC	0.1	88	7.4	3.88	2.74	1.23	1.0	650	8.4	2.35	2.42	1.86

[a] Concentrations are for those materials mentioned first. Carboxymethylcellulose was always at 0.01%. Surfactant concentration in tripolyphosphate solutions was 0.5 millimolar.

surfactant solutions, prepared in hard water, are not graphically presented because of their similarity to data obtained in deionized water (Fig. 5). The main difference is a displacement of hard-water data curves in the direction of increasing tripolyphosphate concentration. In all solutions below 1.7 mM ($Na_5P_3O_{10}$ to Ca mole ratio of 1:1) the velocities of clay and cotton were increased whereas soil deposition was decreased. At concentrations exceeding 1.7 mM soil deposition and electrophoretic velocity, test results were quite similar to results obtained in deionized water.

Tripolyphosphate-Surfactant-Carboxymethylcellulose Effects in Deionized and Hard Water

On the basis of data presented in Fig. 6, carboxymethyl cellulose could be called the "great equalizer." The wide divergence in the velocities of clay and cotton shown in Fig. 5 is considerably reduced by addition of carboxymethylcellulose. Cotton and clay, as a result of carboxymethylcellulose adsorption, present similar surfaces to the solutions and thus have similar velocities. This equalizing effect is even more pronounced in hard-water solutions as shown in Fig. 7. A greater adsorption of carboxymethylcellulose in the presence of divalent cations would account for this.

Collected in Table I are pertinent data of those solutions of lowest surfactant or tripolyphosphate concentration in which minimum soil deposition occurred. Data obtained in unaltered deionized and hard water, where deposition was maximum, are included for comparison. A study of these data illustrates the lack of definite correlation between soil deposition and magnitude of the electrical double layer at the surface of clay and cotton or the factors (ionic concentration and pH) which exert an influence on these layers.

The electrophoretic velocity data show that the magnitude of repulsive forces between soil and fabric on account of double-layer interactions do not determine the degree of soil deposition. Of more importance is the presence of adsorbable materials which provide physical barriers to soil deposition rather than electrical forces of repulsion. These barriers, which are transitional layers between the solution and the surfaces of soil and fabric, attenuate van der Waals forces of attraction. Effectiveness of these adsorbed layers in preventing soil deposition appears to depend on the degree of hydration of the adsorbing materials, i.e., nonionic surfactant and carboxymethylcellose, both heavily hydrated, are the most effective.

A possible explanation for the increase in soil deposition in tripolyphosphate solutions may lie in a desorptive action of this builder on the hydrated layer at the surface of cotton. Such an action by tripolyphosphate would allow a clarification of the role played by tripolyphosphate in soil removal as well as in soil deposition. According to Lange (5), the initial step in the detachment of a soil particle from a fiber is a small separation which allows a liquid layer to penetrate between fiber and soil. This wetting or penetration between soil and fiber is not in itself sufficient to cause a complete separation. However, with the addition of tripolyphosphate to the system, it seems quite plausible that tripolyphosphate, by an ability to disrupt or remove a hydrated layer, could complete the detachment of the soil particle from the fiber. This would also point out the importance to detergency of good wetting or penetrating agents. Such agents accelerate the penetration of a liquid layer between soil and fiber.

Detergent builders other than the polyphosphates are notably less effective in improving soil removal. The reason for this may lie in their relative ability to remove or disrupt hydrated layers. This ability would no doubt be dependent on the charge magnitude and charge distribution of the builder anion.

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