CHAPTER IV

MECHANISTIC STUDIES OF PARTICULATE SOIL DETERGENCY: I: HYDROPHOBIC SOIL REMOVAL

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4.1 Abstract

The mechanism of particulate soil detergency using aqueous surfactant systems is not well understood. In this research, carbon black (model hydrophobic soil) removal from a hydrophilic (cotton) and hydrophobic (polyester) fabric is studied using anionic, nonionic, and cationic surfactants. The zeta potential, solid/liquid spreading pressure, contact angle and surfactant adsorption of both soil and fabric are correlated to detergency over a range of surfactant concentrations and pH levels. Electrostatic repulsion between fabric and soil is generally found to be the dominant mechanism responsible for soil removal for all surfactants and fabrics. Steric effects due to surfactant adsorption are also important for nonionic surfactants for soil detachment and antiredeposition. Solid/liquid interfacial tension reduction due to surfactant adsorption also aid in detergency in cationic surfactant systems. Wettability is seen to not be an important factor and SEM photos show that entrapment of soil in the fabric weave is not significant; the particles are just attached to the fabric surface. Anionic surfactants perform best, then nonionic surfactants. Cationic surfactants exhibit poor detergency which is attributed to low surfactant rinseability.

Keywords: Detergency, Particulate soil, Carbon Black

4.2 Introduction

This paper is the first in a series, which addresses development of a mechanistic understanding of particulate soil detergency and considers hydrophobic soil removal from polar (cotton) and hydrophobic (polyester) fabrics. Subsequent papers will address hydrophilic soils like ferric oxide and clays. The overall goal is to understand the mechanisms by which surfactants of different types induce particulate soil removal. The basic strategy is to measure a number of fundamental properties such as spreading pressure and surfactant adsorption at the soil/solution and fabric/solution interface, zeta (electrical) potential of soil and fabric, and wettability of solution onto soil and fabric, all as a function of surfactant type and concentration, pH, fabric type, and soil type. These measurements can then be used to interpret detergency results. For example, insight could be gained about the relative importance of interfacial tension reduction as opposed to electrostatic effects on soil removal as well as the importance of redeposition compared to initial soil removal and antiredeposition mechanisms. These systematic investigations should aid in understanding "rules-of-thumb" developed from empirical studies regarding the most effective surfactant type to remove certain soil types from certain fabrics. In this study, carbon black was selected as a model particulate soil and three different types of surfactant were used; sodium dodecyl sulfate (SDS), an anionic surfactant; cetyltrimethyl ammonium bromide (CTAB), a cationic surfactant; and octylphenol ethoxylate (OP(EO)10), a nonionic surfactant.

Laundry detergency can be defined as the removal of unwanted substances (soils) from fabrics. Soil can be classified into four groups: oily soil (usually organic liquid), particulate soil (inorganic solid), solid nonparticulate soil (waxy solids like solidified hamburger grease), and stain formation at a chemical bond between soil and fabric (e.g., wine, blood) [1-3]. Oily soil removal has received much attention in the literature particularly relating detergency to oil/water interfacial tensions and microemulsion formation [4-9]. Stains are mainly removed by the action of enzymes and bleaches, augmented by surfactants. Particulate and solid non-particulate soil removal studies have largely been empirical, in part because fundamental parameters such as soil/solution interfacial tensions are difficult or impossible to measure and correlate to soil removal. Our group has recently published studies of the thermodynamics and kinetics of the soap scum dissolution by surfactant/chelant solutions as an example of mechanistic studies of solid nonparticulate soil removal from hard surfaces [10, 11]. Particulate soils are solid particles deposited mostly from air suspension. Examples of such dust include carbon black, clay, alumina, silica, iron and other metal oxides. Usually, these particulates have a large specific surface area, so oil and greases can co-adsorb very readily, resulting in mixed soils. Particulate soils are difficult to remove because of their rigidification and water insolubility. Moreover, they can redeposit on surfaces that have been cleaned [1].

There are several mechanisms which can be important in particulate soil removal in laundry detergency. When a particle is detached from the fabric, two new interfaces are created (soil/bath and textile/bath) while only one interface is destroyed (soil/textile). The soil detachment is thermodynamically favorable when the sum of the interfacial tensions (IFT) of the two new surfaces is lower than the interfacial tension of the destroyed surface [12].This effect can be quantified by the work required for the particulate soil removal (W) as described by Equation 1, which must be negative in order to favor soil removal.

$$W = [\gamma_{SB} + \gamma_{TB}] - \gamma_{ST} \qquad [1]$$

where γ_{SB} = interfacial tension at soil/bath interface,

γ_{TB} = interfacial tension at textile/bath interface,

and γ_{ST} = interfacial tension at soil/textile interface

Adsorption of surfactant onto the soil and onto the fabric from the bath can reduce these solid/solution interfacial tensions, increasing the thermodynamic favorability of detachment [13]. The electrical potential of the soil and fabric can be affected by surfactant adsorption, leading to the enhancement of soil detachment. Electrostatic and steric stabilization of dispersed soil particles following detachment are important antiredeposition mechanisms and can be affected by surfactant adsorption [3]. A theory for particle removal from the fabric surface, based on the DLVO theory of colloidal stability, was developed by Lange [14]. Zeta potential is generally used as a representative of electrostatic repulsion force [14-18]. This has led to attempts to correlate soil removal with the zeta potential of the fibers and soils in the wash liquid. Since most textile fibers and soil particles are negatively charged in aqueous solutions, the magnitudes of the charges of both surfaces are further increased by the adsorption of anionic surfactants [15]. The repulsive forces between the similar charges of fiber and soil contribute to the detachment of soil [16] and also prevent soil redeposition [17]. The correlation between the zeta potentials to the particulate soil detergency was observed by Harris [18]. In contrast to anionic surfactants, cationic surfactants can cause a decrease in washing effectiveness and even below that observed with pure water. Significant soil removal then occurs only at high surfactant concentrations, at which a complete charge reversal takes place on both fabric and soil [19]. The effectiveness of both anionic and nonionic surfactants was found to exhibit little difference in removing particulate carbon, as reported by Grindstaff [12]. The removal of surface adhered particles by surfactants and fluid motions was studied by Batra et al. [20]. Their work included the effects of the adsorption of ionic surfactant, the critical hydrodynamic force (a minimum force required to detach the particle from the fabric) as well as the influence of zeta potential and the Hamaker constant. They found that anionic surfactant increases the magnitude of zeta potentials of fabric and soil which decreases the critical hydrodynamic force and reduces the Hamaker constant. This weakens the adherence of the soil to the fabric which can lead to the dislodgement of particles.

Wetting of fabric or soil by the bath can affect detergency since imbibitions of the bath solution into the fabric weave is required for contact between the textile surface and the surfactant solution and to permit detachment/dispersing of particulate soil. The contact angle between bath and either fabric or particle (wettability) along with bath/air surface tension values can be used to calculate solid/bath spreading pressures which is closely related to solid/bath interfacial tensions (which can't be easily measured if at all). Cotton was used here as a model hydrophilic fabric, while polyester was used as a model hydrophobic fabric. The polyester fibers are smooth cylinders while the cotton has substantial fraying or small fibers sticking out from the large fibers, leading to the possibility of entrapment of soil particulates in this mass of small fibers. The importance of this particle filtering can be illuminated from scanning electron micrograph (SEM) images. The relationship between the particle size of carbon black and its adhesiveness to cotton was studied by Compton and Hart [21]. Later, Grindstaff et al. [12] reported that the carbon black could be more easily removed from the polyester fabric than from the cotton fabric because of the mechanical entrapment of the particles by the cotton fabric. The SEM images can show the configuration of particles on fabrics. Particulate soils are the agglomeration of small particles and most of these microparticles are not in direct contact with the fabrics at all. Hence, two actions may occur during washing process; removing the whole agglomerate by breaking the bond between the fabric and the contacting soil particles, or the particle agglomerate may be dispersed, causing removal of most of the soil with some particles still remaining on the fabric [13]. Besides the detachment of soil particles from fabric, the detached particles have a tendency to go back onto the substrate (redeposition). A more homodisperse distribution of particle sizes should reduce redeposition [13].

In this work, contact angles of bath with fabric and with soil were measured along with surfactant adsorption levels. For detergency process, it is necessary that a bath solution must spread and penetrate to the soil and the fabric surfaces, as determined by the wettability. The contact angle indicates the wettability of an applied surfactant solution on soil and fabric surfaces. This is relevant to the imbibitions of the bath solution into the fabric weave, which is considered as the first step in the detergency process. The zeta potential (electrical potential at particle surface) of the soil and fabric and air-water surface tensions were measured as well as SEM photos of fabric taken before and after washing. Detergency or soil removal and antiredeposition were measured. All these measurements were ultimately made for different surfactant concentrations and types (anionic, nonionic, or cationic), pH levels, fabric types, and soil types when soiling and washing conditions (mechanical action, time and temperature) were kept constant. As a result, the mechanical force applied during soiling affects the rate of soil removal and the concentration of surfactant required [22-24].

Here in Part I, a model hydrophobic soil with both hydrophobic and hydrophilic fabrics is discussed. In future papers in this series, the focus will be on hydrophilic soils. The study of the effect of surfactant charge, fabric hydrophilicity and fiber structure, and particle type is anticipated to yield even greater insight into detergency mechanisms. Ultimately, the question to be addressed is "how is the surfactant aiding particulate soil removal".

4.3 Experimental Procedures

4.3.1 Materials

Carbon black with a supplier provided specific surface area of 96 m^2/g and an average diameter of 0.24 μm was obtained from Cabot. Sodiumdodecyl sulfate (SDS), cetyltrimetylammoniumbromide (CTAB) and octylphenolethoxylate with an average of 10 ethylene oxides per molecule (OP(EO)10-tradename Triton X-100) with a purity of more than 99% were purchased from Sigma-Aldrich. The OP(EO)10 is heterogeneous with a distribution of number of ethylene oxides per molecule. Two types of fabrics, cotton and polyester, were purchased from Test Fabric Co. (Middlesex, NJ, USA).

4.3.2 Adsorption Isotherm Experiment

Adsorption experiments were carried out in order to find the amount of surfactant adsorbed on the solid surface and on fiber as a function of surfactant concentration. Adsorption experiments were performed using different concentrations of surfactants of SDS, OP(EO)10 and CTAB. Surfactant stock solutions were diluted with deionized water to obtain different surfactant concentrations and added to screw cap vials containing 0.25 g of carbon black, then pH was adjusted by adding a 1 M NaOH solution or 1 M HCl solution. The filled vials were allowed to equilibrate at 30°C in a shaker bath for 4 d. After equilibration, the supernatant was separated from the mixtures by centrifugation at 10,000 rpm for 30 min. The supernatant surfactant concentrations were then measured by using a total organic carbon analyzer (TOC) (Shimadzu, TOC 5000). For the adsorption isotherm experiment on fibers (cotton and polyester), a similar procedure was used but 1 g of fiber sample was used as the substrate.

4.3.3 Specific Surface Area Measurement

The carbon black was degassed at 150°C overnight; pure cotton and pure polyester cut into very small pieces weighting 1 g were degassed at 100°C overnight. Their specific surface area was determined by nitrogen adsorption BET measurement by a surface area analyzer (Quanta Chrome, Autosorb-1).

4.3.4 Zeta Potential Measurement

An amount of 1.5 mg of carbon black powder or 0.1 mg of fabric was added into a surfactant solution. The solution pH was adjusted at different values and the mixture was stirred for 24 h at 30°C. The solution was then transferred to an electrophoretic cell of a zeta meter (ZM3.0+) equipped with a microscope module. After applying a suitable voltage, the charged particles move towards to the electrode until attaining a steady state (the particles move with constant velocity). Their velocity was measured and referred as their electrophoretic mobility from which the zeta potential in millivolt units was calculated by using the Helmhotlz-Smoluchowski equation. For a given data set, at least 20 particles were monitored and the average zeta potential value was then obtained.

4.3.5 Fabric Pretreatment and Soiling Procedure

The test fabrics were washed with distilled water before use in order to remove the residues of mill-finishing agents. The pre-washing method followed ASTM standard guide D4265-98 [25]. The pre-washed fabrics were cut into 3 × 4 inches swatches in the warp and weft directions. An amount of 0.02 g of carbon black was added into 80 g of distilled water and mixed by using a magnetic stirrer before pouring on a test fabric specimen, which was placed in a plastic container and kept in a shaker bath for 1 h. After that, the soiled fabric swatch was dried at room temperature for 1 d.

4.3.6 Laundry Procedure

A Terg-O-Tometer was used in this study as a standard testing unit for detergency experiments. The testing system used 1000 mL of washing solution, 20 min washing, 3 min first rinse, and 2 min second rinse with de-ionized water. Temperatures of both washing solution and rinse water were held at 30°C. Three soiled swatches and one unsoiled swatch for antiredeposition testing were washed in each bucket for one cycle as replication. Experiments were conducted with washing solutions having different concentrations of SDS, CTAB, or OP(EO)10.

4.3.7 Detergency Performance Evaluation

The detergency performance was determined by the refraction method. The reflectance measurement was conducted using a colorimetric spectrophotometer (Hunter Lab, Color Flex). The color change of pre-washed and post-washed swatches was quantified by the lightness parameter (L*) which is reported in the range of 0 (completely black) to 100 (completely white) [26,27]. The colorimeter was calibrated against standard black and white plates before each actual measurement and measures were done at a minimum of 3 different positions for each sample. The detergency performance was quantified in terms of the percentage of detergency (%D) by using the following equation:

$$\%D = \text{Detergency}\ (\%) = [(A-B)/(C_0-B)]\times 100$$

where A is the average reflectance of the soiled swatches after washing, B is the average reflectance of the soiled swatches before washing and C0 is the average reflectance of the unsoiled swatches before washing [28-29].

4.3.8 Contact Angle Measurement

The contact angle measurement was carried out using the sessile drop technique by a contact angle measuring instrument (Krüss, DSA 10 Mk2). The carbon black powder or fabric was first compressed into a smooth sheet. The fabric samples which were cut in 0.5 cm × 0.5 cm pieces were put into a 22 mm diameter circular molding unit and then compressed at 140 kg/cm^2 and 270°C for 5 min by using a compression molding machine (LAB Tech, LP20) to obtain fused fabric samples. After that, the fused fabric surface was cleaned by deionized water and then dried at 80°C for 30 min in an oven. A 5 µL drop of the surfactant solution with different surfactant concentrations was then placed onto the fused fabric surface by using a micro-syringe and the contact angle was measured after 20 s. During the measurement, the sample chamber was kept at 30°C and saturated with water vapor to prevent drop evaporation.

4.3.9 Surface Tension Measurement

The measurement of surface tensions of solutions containing different surfactant concentrations of CTAB, SDS, and OP(EO)10 was conducted by using a bubble pressure tensiometer (Kruss, BP2). The rate of bubble generation was varied during measurement of the bubble pressure to ensure that this rate was low enough for attainment of equilibrium. The maximum value of the bubble pressure obtained from the plot of the bubble pressure vs. time was used to calculate the equilibrium surface tension.

4.3.10 Scanning Electron Microscope (SEM) Photos

The study of surface morphology of the fabric samples before and after washing at different studied conditions was investigated by using a scanning electron microscope, SEM (JEOL, 5200-2AE). The samples were coated by a thin film of platinum for 2 min prior to examination.

4.4 Results and Discussion

4.4.1 Surfactant Adsorption onto Fabrics and Carbon Black

Surfactant adsorption is one of the most important mechanisms that govern the particulate soil detergency since it can induce changes in the interfacial tension as well as electrokinetics properties of soil and fabric [30-36]. The surfactant adsorption isotherms are calculated from the difference between the initial concentration and the final concentration in the supernatant after the system reaches equilibrium and is based on the specific surface area of the dry substrate. The specific surface areas for the three substrates from BET measurements (in dry form) are shown in Table 4.1. In wet form, the cotton surface area might be altered due to swelling [36].

Table 4.1 Properties of studied substrates

Substrates	**Point of zero charge (PZC)**	**Dry BET surface area (m^2/g)**
Carbon black	2.30	96.0
Cotton	2.90	4.33
Polyester	2.40	2.50

The adsorption isotherms of all three surfactants (SDS, OP(EO)10, and CTAB) on all three substrates (carbon black, cotton, and polyester) at different pH levels are detailed elsewhere [37] (see appendix A). In all cases, the surfactant adsorption reached a plateau at concentrations above the CMC as is usual [3]. Since the detergency and antiredeposition are correlated to other physical properties above the CMC, in this paper, the plateau adsorption levels are shown in Tables 4.2 and 4.3 for all systems. In order to estimate the fractional monolayer coverage from these values, the area per head group of surfactant molecule from air/water Gibbs close-packed monolayers were used [SDS: 5.7 nm^2/molecule; OP(EO)10: 7.4 nm^2/molecule; CTAB: 6.9 nm^2/molecule] [38]. As discussed in the next section, the point of zero charge (PZC) of the carbon black, cotton, and polyester were between 2 and 3 (see Table 4.1). Therefore, the surfaces of all three substrates were negatively charged over the pH range studied here (5 to 11) and each surface was more negatively charged as pH increases (see zeta potentials reported in Tables 4.4 and 4.5) without surfactant. Despite the negative net charge on each substrate, the anionic surfactant SDS shows substantial adsorption on each surface approaching bilayer coverage (fractional monolayer coverage = 1.77) on cotton at pH 5. This can be attributed to hydrophobic interactions between the surfactant hydrophobe and the surface and to heterogeneity of the surface (some positively charged sites despite a net negative charge). For SDS, the order of adsorption was cotton > carbon black > polyester at all pH levels which corresponds to higher adsorption onto the least negatively charged substrate (lowest zeta potential) in the absence of surfactant (see Tables 4.4 and 4.5).

Table 4.2 Detergency, surface pressure at solid/liquid interface, contact angle, fraction of monolayer adsorption, and zeta potential at plateau concentration for polyester fabric

Polyester	SDS				OP(EO)10				CTAB			
	pH 5	pH 7	pH 9	pH 11	pH 5	pH 7	pH 9	pH 11	pH 5	pH 7	pH 9	pH 11
Detergency (%)	52.9±0.3	57.5±0.3	64.4±0.5	67.4±0.3	52.1±0.3	55.4±0.8	57.5±0.4	61.0±0.2	43.0±0.2	50.0±0.7	52.3±0.4	57.0±0.7
Redeposition (%)	4.95	3.72	2.41	1.45	3.67	3.40	2.07	1.24	6.82	4.46	2.62	1.88
Maximum adsorption or Γ_{max} on polyester (μmole/m^2)	0.89	0.75	0.67	0.56	0.27	0.21	0.11	0.06	2.33	2.55	2.81	3.00
Maximum adsorption or Γ_{max} on carbon black (μmole/m^2)	2.17	2.08	1.98	1.78	0.82	0.70	0.48	0.44	5.22	6.09	6.33	6.71
Fraction of monolayer adsorption (polyester)	0.29	0.24	0.21	0.18	0.12	0.09	0.05	0.03	0.92	1.01	1.11	1.19
Fraction of monolayer adsorption (carbon black)	0.72	0.69	0.65	0.59	0.36	0.31	0.21	0.20	2.06	2.40	2.50	2.65
Zeta potential or ζ of polyester (mV)	-84.9±0.3	-89.8±0.2	-107±0.2	-115±0.2	-26.4±0.4	-35.4±0.2	-34.6±0.4	-40.1±0.2	25.3±0.2	26.4±0.4	33.2±0.2	44.6±0.3
Zeta potential or ζ of carbon black (mV)	-33.2±0.5	-38.6±0.5	-40.0±0.3	-40.9±0.5	-16.5±0.3	-20.6±0.2	-25.8±0.5	-32.3±0.3	44.7±0.4	45.2±0.2	46.1±0.2	49.5±0.2
Summation of ζ (mV)	-118	-128	-147	-156	-42.9	-56.0	-60.3	-72.4	70.0	71.6	79.4	94.1
Contact angle or θ on polyester (deg)	46.6±0.3	47.5±0.2	48.1±0.4	50.2±0.4	23.1±0.3	23.3±0.2	24.0±0.4	25.6±0.6	26.1±0.3	25.5±0.3	20.3±0.2	11.4±0.4
Contact angle or θ on carbon black (deg)	45.0±0.4	45.2±0.5	45.4±0.4	45.0±0.5	22.3±0.3	22.9±0.5	23.7±0.3	24.7±0.3	19.3±0.2	16.8±0.1	14.7±0.3	12.1±0.6
Surface tension (mN/m)	47.5	46.9	43.0	31.8	30.5	30.6	30.6	31.3	37.8	37.8	37.8	37.8
Surface pressure or π_{SL} on carbon black (mN/m)	6.84	6.42	3.67	2.33	1.55	1.52	1.35	1.77	9.00	9.52	9.87	10.3
Surface pressure or π_{SL} on polyester (mN/m)	12.7	11.7	8.72	0.38	8.07	8.10	8.24	8.25	14.0	14.2	15.5	17.1
Summation of π_{SL} (mN/m)	19.5	18.1	12.4	2.71	9.62	9.62	9.59	10.02	23.0	23.7	25.4	27.4

* Surface tension of water at 30°C is 71.4 mN/m

Table 4.3 Detergency, surface pressure at solid/liquid interface, contact angle, fraction of monolayer adsorption, and zeta potential at plateau concentration for cotton fabric

Cotton	SDS				OP(EO)10				CTAB			
	pH 5	pH 7	pH 9	pH 11	pH 5	pH 7	pH 9	pH 11	pH 5	pH 7	pH 9	pH 11
Detergency (%)	49.2±0.8	52.5±1.2	61.3±0.3	63.3±0.7	40.2±0.4	41.0±0.8	43.1±0.5	45.1±1.3	26.4±0.4	28.4±1.3	32.5±0.5	35.3±0.9
Redeposition (%)	3.67	2.88	1.30	0.73	3.41	2.62	0.95	0.28	6.37	3.47	1.46	1.26
Maximum adsorption or Γ_{max} on cotton (µmole/m^2)	5.54	4.10	3.03	1.86	0.51	0.43	0.41	0.40	4.40	5.42	6.10	6.01
Maximum adsorption or Γ_{max} on carbon black (µmole/m^2)	2.17	2.08	1.98	1.78	0.82	0.70	0.48	0.44	5.22	6.08	6.33	6.71
Fraction of monolayer adsorption (Cotton)	1.77	1.31	0.97	0.59	0.23	0.19	0.18	0.17	1.74	2.14	2.41	2.37
Fraction of monolayer adsorption (Carbon Black)	0.72	0.69	0.66	0.59	0.36	0.31	0.21	0.20	2.06	2.40	2.50	2.65
Zeta potential or ζ of cotton (mV)	-64.9±0.3	-69.8±0.2	-74.2±0.2	-78.6±0.2	-19.4±0.2	-25.4±0.3	-28.6±0.2	-30.1±0.3	15.3±0.2	20.4±0.3	23.2±0.3	30.6±0.4
Zeta potential or ζ of carbon black (mV)	-33.2±0.3	-38.6±0.3	-40.0±0.2	-40.9±0.4	-16.5±-0.2	-20.6±0.2	-25.8±0.2	-32.3±0.2	44.7±0.3	45.2±0.3	46.1±0.3	49.5±0.4
Summation of ζ (mV)	-98.1	-108	-114	-120	-35.9	-46.0	-54.4	-62.4	60.0	65.6	69.4	80.1

Table 4.4 Detergency, zeta potential and contact angle of surfactant-free solutions for polyester fabric

Polyester	Surfactant-Free			
	pH 5	pH 7	pH 9	pH 11
Detergency (%)	5.42±0.9	9.84±1.2	13.2±0.8	16.1±0.6
Redeposition (%)	5.12	4.12	3.75	2.75
Zeta potential or ζ of polyester (mV)	-50.0±0.3	-64.3±0.3	-68.1±0.6	-70.0±0.4
Zeta potential or ζ of carbon black (mV)	-20.0±0.4	-36.4±0.4	-41.7±0.2	-44.6±0.2
Summation of ζ (mV)	-70.0	-101	-110	-115
Contact angle or θ on polyester (deg)	73.6±0.2	73.6±0.1	73.6±0.2	73.6±0.2
Contact angle or θ on carbon black (deg)	68.0±0.2	68.1±0.2	68.2±0.3	68.1±0.2

Table 4.5 Detergency, zeta potential and contact angle of surfactant-free solutions for cotton fabric

Cotton	Surfactant-Free			
	pH 5	pH 7	pH 9	pH 11
Detergency (%)	5.43±1.3	7.82±0.9	11.4±1.1	14.2±0.9
Redeposition (%)	4.09	3.76	2.91	2.45
Zeta potential or ζ of cotton (mV)	-13.7±0.3	-20.3±0.3	-23.3±0.1	-24.6±0.2
Zeta potential or ζ of carbon black (mV)	-20.0±0.2	-36.4±0.2	-41.7±0.3	-44.6±0.1
Summation of ζ (mV)	-33.7	-56.7	-65.0	-69.2

With increasing solution pH, anionic surfactant adsorption decreases while cationic surfactant increased (Tables 4.2 and 4.3), consistent with the more negatively charged surface and repulsion with like charged anionic surfactants and attraction for positively charged cationic surfactant. Since there are charged sites on the substrate in either case, if the surface becomes saturated it is not obvious whether a surfactant bilayer or admicelle (head-down and head-out) would form or a tail-down monolayer or hemimicelle. We have shown elsewhere [39] that SDS adsorbs tail-down on carbon black, consistent with less than monolayer coverage and modest pH effects on plateau adsorption in Table 4.3. These same trends with polyester imply tail-down adsorption for this hydrophobic fabric as well. The detailed adsorption isotherms [37] exhibit neutral or anti-cooperative behavior (slope of log [adsorption] vs. log [concentration] is equal to or less than unity) on these substrates. That means that the hydrophobic interactions between surfactant tails in the aggregated hemimicelle are no more favorable than those between the tail and the hydrophobic surface when the surfactant adsorbs in unaggregated form. Repulsion between charged surfactant head groups in the hemimicelle can make aggregation antagonistic.

For SDS adsorption on cotton, fractional monolayer coverage of as much as 1.77 is consistent with admicelle formation as are the high slopes of the adsorption isotherm (>1) [37]. The high slope indicates strong hydrophobic bonding in the admicelle and is commonly observed for surfactant adsorption on hydrophilic surfaces [40]. The plateau adsorption of the nonionic surfactant OP(EO)10 was less than the anionic SDS on all three substrates (Tables 4.2 and 4.3). Plateau adsorption levels were well below a complete monolayer for OP(EO)10 on all substrates, but that does not indicate whether adsorption is tail-down monolayer (hemimicelle) or a bilayer (admicelle), just that the CMC was reached prior to surface saturation. The adsorption isotherm slopes were less than or equal to unity for polyester, consistent with monolayer adsorption; on cotton, slope were much greater than unity indicating admicelle formation – both results were mechanistically similar to those with SDS. However, on carbon black, OP(EO)10 adsorption isotherm slopes were much greater than unity, implying bilayer adsorption. Polyethoxylate head groups can hydrogen bond with surfaces so there appears to be an attractive interaction between the EO groups and the carbon black surface. Surprisingly, decreasing pH caused a modest increase in adsorption on all three surfaces, which will be discussed further with zeta potential results.

From Tables 4.2 and 4.3, the adsorption of cationic surfactant CTAB was greater than either SDS or OP(EO)10 on all three surfaces. From Table 4.1 in the absence of surfactant, all three surfaces were net negatively charged at all pH levels studied (pH 5 to 11) since these pH levels are above the PZC. The order of CTAB plateau adsorption was carbon black > cotton > polyester. Maximum adsorption on carbon black and cotton exceeds bilayer coverage. This was probably due to higher adsorbed layer packing densities on the solid surface than at the air-water interface from which area per head group used to calculate fractional monolayer coverage was obtained, a phenomena observed for anionic surfactants. The cotton can also swell in water; increasing the surface area. Unlike SDS and OP(EO)10, the adsorption of CTAB increased with increasing pH on carbon black, cotton and polyester because the surface becomes more negatively charged with increasing pH as indicated by the zeta potentials with no surfactant in Tables 4.4 and 4.5. Detailed adsorption isotherms for CTAB [37] indicate cooperativity (slope > 1) for cotton and carbon black, but a slope of approximately 1 on polyester. This is consistent with bilayer adsorption on cotton and carbon black, but monolayer adsorption on polyester, also consistent with plateau adsorption densities in Tables 4.2 and 4.3.

4.4.2 Zeta Potentials and Point of Zero Charge of Carbon Black and of Fabrics

4.4.2.1 Surfactant-Free Solutions

The zeta potential of a solid particle in solution is the electrical potential at the shear plane between the particle and the liquid as deduced from the electrophoretic mobility. When the hydronium cation and the hydroxyl anion are potentially determining ions (as is usually the case); at a low pH the particle has a positive charge and at a high pH has a negative charge. The pH where there is net zero charge on the particle or no net average charge on a group of particles is called the point of zero charge (PZC) [3].

The PZC is determined from electrophoretic mobility measurements which are detailed elsewhere [37] (see Appendix B). From Table 4.1, the PZC of the carbon black, the cotton and the polyester are 2.30, 2.90 and 2.40, respectively which are in good agreement with previous studies [41-43]. The zeta potential (ζ) at pH 11 was -70.0 mV for polyester, -24.6 mV for cotton and -44.6 mV for carbon black (Tables 4.4 and 4.5). It seems surprising that the polyester fiber, which is generally known as a hydrophobic surface, has a higher magnitude of zeta potential than the cotton which is a hydrophilic fiber. It is probably due to the high density of ester functional group on the polyester surface. These functional groups are hydrolyzed into carboxyl and hydroxyl group which are electron donor groups [41], thus leading to a higher negative charge. Also, the cotton fibers have high hydration capacity, leading to the swelling of fibers. The interfibrillar swelling enlarges the specific surface area, and causes the shift of the shear plane into liquid phase so it will lower the absolute magnitude of the zeta potential [42]. The higher the zeta potential, the greater the repulsion between two particles [44].

4.4.2.2 Zeta Potential of Carbon Black and Fabrics in Surfactant Solutions

Tables 4.2 and 4.3 show the zeta potentials for all surfactant/substrates at pH 5, 7, 9, and 11 at high enough surfactant concentrations where both surfactant adsorption and zeta potential (ζ) plateau.

The SDS caused ζ to become even more negative with only two exceptions: carbon black at pH 9 and 11, where small decreases in the absolute magnitude of ζ were observed. The value of ζ becomes more negative with increasing pH in the presence of SDS, mirroring trends in ζ in the absence of surfactant for all three substrates. There was no clear correlation between the change in ζ due to the presence of SDS and SDS adsorption on the three substrates at different pH. This reflects the complex effect of surfactant adsorption level and configuration (e.g., bilayer vs. monolayer), effect of surfactant on potential determining ion interaction and counterion adsorption, among other effects. On both fabrics, the SDS caused the surface to become more negative, ζ changing by between 34.9 mV and 54.0 mV.

All three surfaces were negatively charged in the presence of OP(EO)10. The OP(EO)10 caused ζ to become more negative for cotton, but less negative for polyester and carbon black. The effect of OP(EO)10 on ζ, as with SDS, was not correlated to the surfactant adsorption level. The effect of OP(EO)10 can be substantial, changing ζ by as much as 30 mV at quite low adsorption levels. Based on charge effects only, the nonionic surfactant would not be expected to have a significant effect on the electrostatic charge. The substantial effect of OP(EO)10 on ζ was probably due to the water bound to EO groups which can shift the shear plane.

The CTAB causes charge reversal [45] (substrates or surfaces become positively charged) with increases in ζ as much as 114.6 mV due to the CTAB. As with SDS and OP(EO)10, the change in ζ due to CTAB does not correlate with CTAB adsorption. This lack of correlation is because only plateau conditions were considered here; at lower adsorption levels below the CMC, a correlation would be expected.

In order to have a single parameter which quantifies the electrostatic repulsion between the soil (carbon black) and fabric, in Tables 4.2-4.5; the "Summation of ζ" is the sum of ζ for carbon black and either polyester or cotton.

4.4.3 Contact Angle and Surface Pressures of Surfactant Solutions on Carbon Black and Fabrics

Measurement of the contact angle of the aqueous solution onto surfaces has two basic purposes. The washing solution needs to contact both soil and fabric to permit detachment and the contact angle indicates how well the solution wets the surface – a lower value of contact angle (θ) indicates better wetting [3]. Secondly, as discussed in the next section, contact angle is necessary to calculate solid/solution surface pressures. The solution/substrate contact angles for polyester and carbon black are shown in Tables 4.2 and 4.4. Spontaneous wetting/soaking up of solution occurred on cotton (contact angle ≤ 0), so θ was not measureable for that substrate.

At high pHs, the order of wetting efficiency (lowest θ) was CTAB > OP(EO)10 > SDS. At low pHs, it was CTAB ≅ OP(EO)10 > SDS. Polyester and carbon black showed similar contact angles. Higher pH yielded better wetting for CTAB, but had little effect on SDS or OP(EO)10.

Surface pressure (sometimes called spreading pressure) at the solid/liquid interface (π_{SL}) is the different between interfacial tensions at solid/liquid interface for the solvent (γ_{SL}^{o}) and surfactant solution (γ_{SL}). It can be calculated by subtracting Young's equation [46] for surfactant solution from that for the surfactant-free solution.

$$\pi_{SL} = \gamma_{SL}^{o} - \gamma_{SL} = [\gamma_{LV}\cos\theta] - [\gamma_{LV}\cos\theta]^{o}$$

where; π_{SL} = surface pressure at solid/liquid interface

γ_{SL} = interfacial tension at solid/liquid interface

γ_{LV} = interfacial tension at liquid/vapor interface

superscript "o" refers to surfactant-free solution

Even though reduction of solid/solution interfacial tension (IFT) of soil and fabric due to surfactant adsorption is considered as a key factor in particulate soil detergency [1-3], there is no feasible way to measure IFT on a solid surface to test this hypothesis. However, the surface pressure at the solid/solution interface can be calculated from the measurable parameters contact angle and air/solution surface tension. The surface pressure is the difference in IFT between the surfactant-free solution (in our case, just water) and the surfactant solution, which indicates the effect of surfactant on IFT. Higher surface pressure means lower IFT. Since contact angle could not be measured on cotton, the value of π_{SL} is only tabulated for polyester in Table 4.2. These results will be discussed in a later section.

4.4.4 Correlation among Surface Pressure at Solid/Liquid Interface, Maximum Adsorption, and Zeta Potential with Detergency at Plateau Concentration

Figure 4.1 shows detergency as a function of surfactant concentration for all six surfactant/fabric pairs. Detergency increases with surfactant concentration until it reaches a plateau at a certain initial surfactant concentration. One would expect this concentration to be the CMC if it was the final surfactant concentration, but this was not measured and was lower than initial concentration due to loss mechanisms like adsorption. Plateau concentrations for physical parameters like adsorption, zeta potential, and contact angle were lower than these for detergency due to this factor (those parameters are plotted against final concentration). So, by choosing the plateau concentration region based on detergency, all other parameters are in the plateau region also. It is these plateau parameters which will be discussed through the rest of this paper.

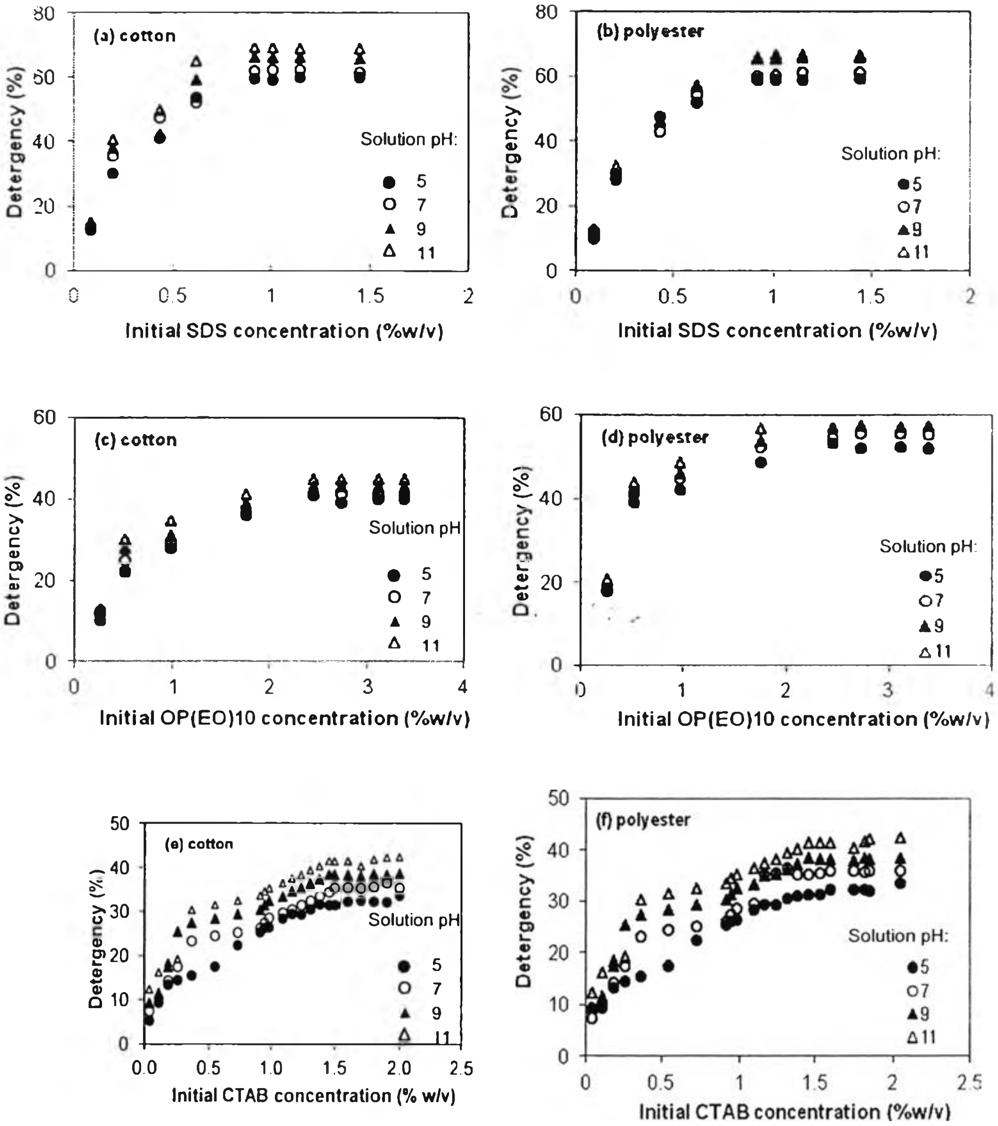


Figure 4.1 Detergency performance of surfactants on cotton and polyester fabric (a) SDS/cotton, (b) SDS/polyester, (c) OP(EO)10/cotton, (d) OP(EO)10/polyester, (e) CTAB/cotton, (f) CTAB/polyester.

Tables 4.2 and 4.4 show detergency, redeposition, and relevant physical properties for carbon black removal from polyester fabric while in Tables 4.3 and 4.5 for cotton fabric. Surfactant–free systems are shown (Tables 4.4 and 4.5) as well as plateau values for wash systems with SDS, OP(EO)10, and CTAB in Tables 4.2 and 4.3. Surfactant adsorption or Γ_{max} (both on a substrate area basis and as fractional monolayer coverage), zeta potential (ζ), contact angle (θ) (for polyester), and surface pressure (π) (for polyester) are given for both fabric and carbon black. In order to quantify the importance of electrostatic repulsion between fabric and soil, the sum of the values of ζ for the two are tabulated as "Summation of ζ". Since the charge on fabric and soil is always the same (positive for CTAB systems, negative for all other systems), the absolute value of this sum of ζ is indicative of electrostatic repulsive forces aiding soil detachment and antiredeposition. Similarly, the sum of surface pressures of polyester and soil indicates the total IFT reduction produced by the presence of surfactants on the new surfaces created when soil detaches from fabric [3]. This sum of π_{SL} cannot be calculated for cotton since the contact angle could not be measured on this fabric.

Even in the absence of surfactant, the highest contact angle on polyester is 73.6° and on carbon black is 68.2°, as shown in Table 4.4. All soil and fabric surfaces were completely wet by the solution in all experiments by visual observation. Therefore, improved wettability is not an important factor in surfactant-augmented detergency in these systems.

4.4.4.1 Polyester

From Table 4.4, it can be seen that both detergency and the absolute value of the sum of zeta potentials increased, and redeposition decreased with increasing pH in the absence of surfactant. The detergency was at a maximum (16.1%) at pH 11, which suggests electrostatic repulsion as the main cause of detergency without surfactant.

From Table 4.2, for SDS, it is obvious that detergency increased, redeposition decreased, the sum of zeta potentials became more negative, and the sum of surface pressure decreased with increasing pH. The somewhat surprising decrease in surface pressure with increasing pH was due to a plateau surface tension decrease with pH, rather than a change in the contact angle. The sum of zeta potential was at least 40.9 mV more negative than with no surfactant (Table 4.4). From Table 4.2 for OP(EO)10, detergency increased, redeposition decreased, the sum of the zeta potentials became more negative, and the sum of the surface pressures increased slightly with increasing pH. Between pH 5 and 11, for SDS, detergency increased from 52.9 to 67.5% while for OP(EO)10, detergency changed from 52.1% to 61.0%; analogous changes in sum of zeta potentials were −118 mV to −156 mV and −42.9 mV to −72.4 mV, respectively. At pH 5, detergency was almost the same for SDS and OP(EO)10, yet soil/fabric electrostatic repulsion and IFT reduction were less for OP(EO)10. At all pH levels, soil/fabric electrostatic repulsion was less for OP(EO)10 than with no surfactant, yet the presence of the nonionic surfactant induced much higher detergency (e.g., 61.0% vs. 16.2% at pH 11). If IFT reduction was an important contribution to soil removal, detergency would not increase so much with pH for SDS since the sum of surface pressures decreased dramatically with increasing pH. Also, at pH 11, the sum of surface pressures was much more for OP(EO)10 compared to SDS, yet SDS provided higher detergency than OP(EO)10.

The conclusion regarding SDS and OP(EO)10 is that soil/fabric electrostatic repulsion is the dominant mechanism responsible for soil removal with IFT reduction due to surfactant adsorption of relatively little importance. For OP(EO)10, there must be an additional mechanism aiding detergency which we hypothesize is due to steric repulsion between soil and fabric due to nonionic surfactant adsorption with the bulky poly(ethylene oxide) groups of the surfactant as well as the water bound to these EO groups. This hypothesis is supported by lower redeposition levels for OP(EO)10 compared to SDS. For OP(EO)10, since detergency increases as electrostatic repulsion increases while surfactant adsorption decreases with increasing pH, electrostatics are a more important contribution to detergency than steric effects.

From Table 4.2 for CTAB, detergency increased, sum of zeta potentials increased, and sum of surface pressures increased (due to increasing surfactant adsorption) with increasing pH. For CTAB, detergency is less than that with either SDS or OP(EO)10 at all pH levels. At pH 5, the sum of zeta potentials was the same for CTAB and no-surfactant systems. The high surface pressures for

CTAB imply that IFT reduction as well as electrostatic repulsion contributes to CTAB detergency. Adsorption of cationic CTAB onto the negatively charged polyester and carbon black was not only greater than those of SDS or OP(EO)10, but was not as reversible (less desorption occurs) [12]. This led to poor rinseability as seen in Table 4.6 which shows residual adsorbed surfactants after the second rinse. Residual CTAB adsorption on the polyester was at least double that of SDS or OP(EO)10. This residual surfactant was probably responsible for the high redeposition levels during detergency for CTAB compared to SDS and OP(EO)10, as seen in Table 4.2. The hydrophobic soil can reattach to the fabric by immersion in the hydrophobic surfactant groups in the adsorbed layer or bridging of soil and fabric can occur through the adsorbed surfactant layers.

Table 4.6 Amount of surfactant adsorbed on fabric after the second rinse

	SDS (g surfactant/g fabric)	OP(EO)10 (g surfactant/ g fabric)	CTAB (g surfactant / g fabric)
Cotton	0.11	0.10	0.21
Polyester	0.09	0.07	0.18

4.4.4.2. Cotton

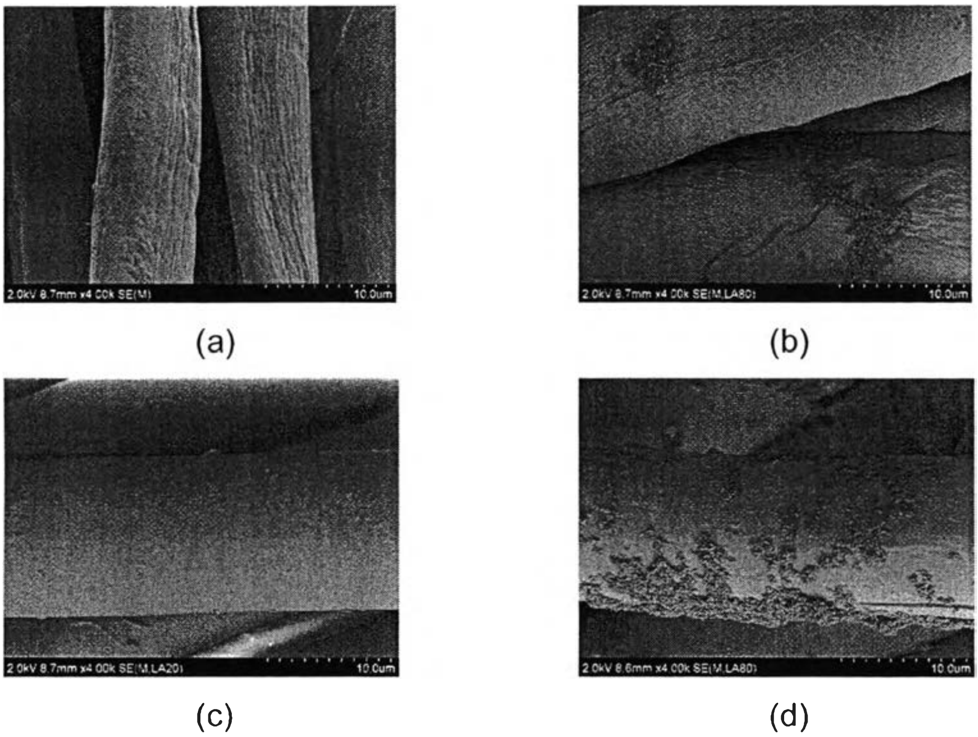
The relative importance of electrostatic forces compared to IFT reduction in detergency on cotton could not be quantified since solid/liquid surface pressures could not be calculated. However, from Tables 4.3 and 4.5, detergency trends for cotton were analogous to those for polyester. Detergency and the absolute value of the sum of zeta potentials were uniformly lower and redeposition was slightly less for cotton than polyester.

Detergency increased with increasing absolute value of sum of zeta potentials with variations in pH and comparing SDS and OP(EO)10. Detergency increased in the order SDS > OP(EO)10 > CTAB. Since electrostatic forces were the dominant mechanism responsible for detergency for all systems, the lower absolute value of the zeta potential on cotton compared to polyester was primarily responsible for the relative ease of soil removal. For example, zeta potentials of cotton vs. polyester at pH 11 were −24.6 mV versus −70.0 mV, −78.6 mV versus −115 mV, −30.1 mV versus −40.1, and 30.6 mV versus 44.6 mV for surfactant-free, SDS, OP(EO)10, and CTAB systems. Additionally on cotton, steric repulsion is hypothesized to be important for OP(EO)10; IFT reduction is probably important for CTAB; and low rinseability of CTAB on cotton (Table 4.6) contributed to the lower detergency of the cationic surfactant.

Redeposition is always lower at higher pH as detergency increases for all systems. This is consistent with electrostatic repulsion between fabric and soil being a primary antiredeposition mechanism as well as that causing soil detachment [13], although steric effects are a secondary mechanism of dispersed soil stabilization for nonionic surfactants [47] Redeposition was low compared to residual soil after washing (100% - detergency (%)), the highest level being for CTAB on polyester (redeposition/residual soil = 0.12) or on cotton (0.09). So redeposition is not a very important factor explaining detergency trends.

4.4.5 Fiber Surface Morphology of the Cotton Fiber and Polyester Fiber

Scanning electron microscope (SEM) images were obtained to study the surface morphology of fibers before and after soiling in order to clarify the attachment of carbon black on both fabrics. Figure 4.2 shows SEM photos of pure cotton and pure polyester fabrics before and after soiling. The cotton surface (Fig. 4.2a) is observed to be rougher than the polyester surface (Fig. 4.2c). From Figure 4.2d, the carbon black forms more extended aggregates of particles on polyester compared to cotton (Fig. 4.2b). The rougher cotton surface may contribute to lower detergency compared to polyester [12]. It was hypothesized that some microfibrils on cotton might entrap the particles but this was not observed in the SEM photos.



(a) (b)

(c) (d)

Figure 4.2 SEM micrograph of test fiber (x 4,000)
a) cotton fiber before soiling b) cotton fiber after soiling with carbon black
c) polyester fiber before soiling d) polyester fiber after soiling with carbon black

4.4.6 Summary of Detergency Mechanisms

Electrostatic repulsion between fabric and soil particles showed itself to be the primary mechanism responsible for detergency for the anionic, nonionic, and cationic surfactants studied. Anionic surfactants adsorb onto the negatively charged fabrics and carbon black soil, yielding high negative electrical potentials and the best detergency. Nonionic surfactants cause the surface of fabric and soil to be negatively charged, but also steric repulsion appears to aid detergency in this case. Cationic surfactants have the lowest detergency due to poor rinseability. In addition to electrostatic forces, IFT reduction due to surfactant adsorption aids cationic surfactant detergency. Detergency is higher for polyester than cotton which is attributed to the higher electrical potentials as well as a smoother surface of the fiber.

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