CHAPTER V

MECHANISTIC STUDIES OF PARTICULATE SOIL DETERGENCY: II: HYDROPHILIC SOIL REMOVAL

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5.1 Abstract

In this work, the removal mechanism of kaolinite and ferric oxide (model hydrophilic particulate soils) from hydrophilic (cotton) and hydrophobic (polyester) fabrics was studied using three surfactant types: sodium dodecyl sulfate (SDS), octylphenol ethoxylate (OP(EO)10), and cetyl trimethyl ammonium bromide (CTAB). This work investigated the relations between zeta potential, surfactant adsorption, contact angle, solid/liquid spreading pressure, and dispersion stability in washing solutions as compared to detergency performance and antiredeposition as a function of surfactant concentration and pH level. The SDS showed the best detergency for both particulate soils, followed by OP(EO)10, with CTAB being the least effective surfactant. For SDS, the electrostatic repulsion between fabric and soil was found to be the dominant force for hydrophilic particulate soil removal. For the nonionic surfactant OP(EO)10, electrostatics are also important and steric effects aid particulate soil detergency. Electrostatic forces and solid/liquid interfacial tension reduction aids CTAB detergency. These same detergency mechanisms have previously been found for the case of hydrophobic soil removal from fabrics. Dispersion stability did not prove to be a dominant mechanism governing particulate soil detergency. From the SEM photos of soiled fabric, ferric oxide attaches to the fabric surface with no entrapment between fabric yarns; moreover, ferric oxide tends to form larger aggregates on cotton compared to polyester fabric. The adhesion of larger particles is hypothesized to be weaker than the smaller ones. Therefore ferric oxide can be more easily removed from cotton fabric than polyester. The SEM photos for kaolinite show little visual difference in particle agglomeration on polyester compared to cotton. Removal of kaolinite from cotton was found to be higher than from polyester, but there is less difference than for ferric oxide.

Keywords: Detergency, Particulate soil, Ferric oxide, Kaolinite

5.2 Introduction

Different types of solid particles or dirt are found to be present on fabrics. Solid particles known as particulate soil can be composed of inorganic oxides (such as ferric oxide), siliceous minerals (such as clay) and carbonaceous materials (such as ashes, soot and carbon black) [1]. The composition of particulate soil in naturally soiled fabric was reported by Sanders et al. [2]. The adhesion of particulates to fabric surfaces can be by either chemical or physical bonds, depending on the nature of both particulates and fabric surfaces. Hydrophobic particulates (non-polar) attach to the fabric surface through van der Waals forces whose magnitude and contact area are dependent on particle size. Hydrophilic (polar) particulate soils can associate with the fabric surface via different types of bonds: van der Waals forces, hydrogen bonding, or bridging by positively charged polyvalent ions [3]. Hydrogen bonding occurs when the hydrogen atoms on the particulate soil surface bond to the electronegative atom such as oxygen or nitrogen on the fabric surface or vice versa. Hydrogen bonding is stronger than the van der Waals force but not as strong as a covalent bond. Positively charged polyvalent ions such as Ca^{2+}, Mg^{2+} or Fe^{2+} may form a bridge between the negatively charged soil and the negatively charged fabric surface.

The heterogeneous nature of particulates and the highly attractive surface interactions between particulates and fabrics along with the interaction between surfactant, fabric, soil, and agitation speed can affect the detergency process [1, 4-7]. If the particle size is larger than 5 μm, it can be removed solely by water [8]. But smaller solid particles are more difficult to remove and tend to redeposit easily onto the fabric surface [9]. Moreover, solid particles having a particle size below 0.2 μm are unremovable by water alone and are little affected by mechanical agitation; nevertheless it can be removed with the aid of surfactants [10]. Surfactant adsorption on both fabrics and particulates enhances wetting of these surfaces, which is considered as the first step in the detergency process. However, the mechanism of particulate soil detergency is not dominated by the wettability of fibers and particulates. Besides, spreading pressure is usually not sufficient to overcome the adhesion force between solid particle and fabric [1, 2, 11]. Inducement of the electrostatic repulsion between the fabric surface and attached solid particles by ionic surfactants [12-16], solid/bath interfacial tension reduction, and steric repulsion forces all induced by surfactant adsorption, are major mechanisms of enhancement of particulate soil removal by surfactants [17]. Additionally, the dispersion stability of detached solid particles in washing solutions can affects redeposition and thus particulate soil detergency. From DLVO theory, the two main forces (attractive van der Waals and repulsive electrostatic forces) are involved in the electrostatic stabilization of colloidal dispersions. If the attractive force overcomes the repulsive force, the particles tend to aggregate, but when repulsive forces dominate, the colloid dispersion is stable [18, 19].

In this work, the removal mechanisms of hydrophilic particulate soils (kaolinite and ferric oxide) from either cotton (hydrophilic substrate) or polyester (hydrophobic substrate) were studied. Ferric oxide is an inorganic compound that occurs naturally as the mineral hematite which is the main source of iron for the steel industry. It is a reddish-brown to black powder. Ferric oxide forms a number of hydrates with variable structures and compositions. A common form is iron rust, produced by the combined action of moisture, carbon dioxide, and oxygen in the air with metallic iron. Reich and Vold [20] found that the controlling factor in preventing deposition of carbon black or ferric oxide on a fabric surface was the reduction of agglomerate particle size. The agglomeration of small particles is an irreversible process. But for larger particles, agglomeration and dispersion occur simultaneously. Schott and Kazella [21] concluded that the discoloration of fabrics in laundry detergency by colloidal dispersion occurred in the rinse step rather than wash step. Yoshikawa [22] found that particles of Fe_2O_3 adhered to fabrics were detached much more effectively with aqueous solutions of anionic surfactants, especially sodium oleate, than a nonionic surfactant (polyoxyethylene olein ether (C17P10)). It was concluded that the shift in the point of zero charge of the Fe_2O_3 particles to a lower pH by the adsorption of anionic surfactant promoted the detachment of the particles from the fabric surface and prevented the re-adhesion of detached particles onto the fabric. The statistical analysis of washing efficiency of solid particulate soil (ferric oxide) was studied by Ishikawa et al. [23].

Kaolinite is an aluminosilicate material, mostly found on fabrics due to the presence in the wide variety of products that use kaolinite as a raw material, such as ceramics, medicine, coated paper, food additive, and toothpaste. Kaolinite is white, soft, and mainly composed of fine-grained plate-like particles. Kaolinite is composed of a two-layer sheet of silica tetrahedral and aluminum hydroxide octahedral which held together by hydrogen bonds and van der Waals interactions [24]. The basal planes are negatively charged and independent of pH, while the edge charge created by the dissociation of silanol and aluminol groups changes from positive at a low pH to negative at a higher pH [25-27]. Powe [28] suggested that the presence of clay particles on washed fabric contributed to the unremovable portion of soil material. Tuzson and Short [29] studied the similarity between the agglomeration–dispersion process and the deposition–removal process of clay particles during washing. They found that the same types of forces are responsible for the agglomeration-dispersion process as for the deposition-removal process. Moreover, the agglomeration properties can be related to the soil characteristics. For example, the interaction of anionic detergents (sodium decyl sulfonate and sodium dodecyl sulfate) with montmorillonite clays was discussed by Schott [30], who concluded that the sorption of anionic detergents onto the montmorillonite clays occurred in two steps. First, alkyl sulfonate and sulfate anions were bound through the counterions of the montmorillonite clays followed by the sorption of sodium alkyl sulfonate and sulfate by association between their hydrocarbon tail and those of previously sorbed detergent anions through van der Waals forces.

In part I of this series [31], the removal of a model hydrophobic particulate soil (carbon black) from cotton and polyester was studied using the same anionic, nonionic, and cationic surfactants as in this work. In part III of this series, the use of anionic surfactant, methyl ester sulfonate (MES) for removal of hydrophilic and hydrophobic particulate soils will be examined.

5.3 Experimental Procedures

5.3.1 Materials

Kaolinite (purum) and ferric oxide (purity of more than 99%) were purchased from Sigma-Aldrich. The particle sizes of both kaolinite and ferric oxide were determined by a particle size analyser (Malvern/Mastersizer, X Ver. 2.18). Kaolinite was found to have a median particle size of 14.4 μm with the size distribution in the range of about 0.1– 20 μm, whereas the ferric oxide has a median particle size of 2.31 μm with the size distribution in the range of 0.5 – 3 μm. The specific surface areas of kaolinite and ferric oxide are shown in Table 5.1 as determined by a BET surface area analyser with nitrogen adsorption. All surfactants and fabrics used were described in part I of this series [31].

5.3.2 Experimental

All experiments were performed with similar procedures to those described in part I of this series [31] except that in the measurement of adsorption, the soil/liquid ratios were 100 g/L for kaolinite and 12.5 g/L for ferric oxide.

5.3.2.1 Dispersion Stability Measurements

The dispersion stability of the two studied particulates in the presence and absence of any studied surfactant was investigated using a UV-VIS spectrophotometer (Shimadzu, UV-1800). The light wavelength was found to not significantly affect the light absorbance for the two particulates and surfactants. Thus, in this present study, the wavelength was fixed at 500 nm (visible light region) [32, 33]. The series of dispersed particle systems were prepared at a particulate concentration of 0.2 %w/v in the presence and absence of studied surfactants with the pH range of 5-11. The solution pH was adjusted by adding either a 1 M NaOH or 1 M HCl solution. After being well mixed, the prepared solution was transferred to a cuvette of the spectrophotometer and the particulate-free solution for each system was transferred to the other cuvette as a blank. Then the absorbance (at the position of ¾ from the top or ¼ of the way from the bottom of the cuvette) was measured as a function of time at room temperature. A high absorbance indicates high dispersion stability, whereas a low absorbance indicates low dispersion stability or a high degree of coagulation.

5.3.2.2 Soiling Procedure

The fabrics were pre-washed using distilled water and were then cut into 5 cm × 5 cm swatches in the warp and weft directions. A 0.2 g/L ferric oxide liquid dispersion was prepared by ultrasonic treatment for 30 min while a 5 g/L kaolinite one was dispersed by using a Terg-O-Tometer (Copley Scientific, DIS 8000) for 30 min with an agitation speed of 120 rpm. Twenty pieces of the prewashed fabric were added to either prepared ferric oxide or kaolinite solution. Soiling time for both systems was 20 min in the Terg-O-Tometer at a constant temperature of 30°C with an agitation speed of 120 rpm. After that, the soiled fabric swatches were dried at room temperature for 1 day.

5.3.2.3 Quantitative Analysis of Kaolinite and Ferric Oxide Removal Using Digestion

The pre and post washed swatches were digested with concentrated hydrofluoric acid for the kaolinite or concentrated nitric acid for the ferric oxide. After the digestion step, the obtained filtrates were diluted with deionized water. The concentrations of silicon (Si) for the kaolinite or iron (Fe) for the ferric oxide were analyzed by using atomic absorption spectroscopy (Varian, SpectrAA300) at a wavelength of 251.6 nm for Si and 248.3 nm for Fe. The differences in the amounts of the studied particulates on pre and post washed swatches were used to calculate the detergency performance and redeposition. The detergency efficiency was calculated from the set of three washed swatches as replicates and the results were reported as a mean value with the standard deviation; i.e., the square root of the variance.

5.4 Results and Discussion

5.4.1 Surfactant Adsorption Results

Surfactant adsorption is a primary step for the mechanisms of particulate soil detergency. These induce interfacial tension reduction, adjustment of the electrical potential at the surfaces considered as the precondition of soil detachment, and the enhancement of dispersion stability of detached particulates [34, 35]. The surfactant adsorption isotherms are generally expressed based on the surface area of a dry substrate. Table 5.1 shows the specific surface areas of all studied particulates and substrates, which were measured on a dry basis. In wet form, the cotton surface area may alter due to swelling [36]. In Part I of this series [31], the surfactant adsorption isotherms on polyester and cotton as well as carbon black, a model hydrophobic particulate, were discussed and the conclusions of the previous work are incorporated into this section.

Table 5.1 Properties of studied particulates and substrates

Particulates/Substrates	**Point of zero charge (PZC)**	**Dry BET surface area (m^2/g)**
Ferric oxide	6.4	14.0
Kaolinite	2.5	10.6
Cotton	2.9	4.33
Polyester	2.4	2.50

The adsorption isotherms of all three surfactants (SDS, OP(EO)10, and CTAB) on the two model hydrophilic particulates (kaolinite and ferric oxide) and on the two studied fabrics (cotton and polyester) at different pH levels were detailed elsewhere [37] (see Appendix A). The surfactant adsorption reaches a plateau at concentrations above the CMC [5]. In general, the detergency application is practiced at a surfactant concentration above the CMC. Thus, in this study, the plateau adsorption levels on all studied surfaces are shown in Table 5.2.

In order to estimate the fractional monolayer coverage of each surfactant, the area per head group of surfactant molecules from air/water Gibbs close-packed monolayers was used [SDS: 5.7 nm^2/molecule; OP(EO)10: 7.4 nm^2/molecule; CTAB: 6.9 nm^2/molecule] [38]. The point-of-zero charge or PZC values of the kaolinite, ferric oxide, cotton, and polyester are shown in Table 5.1. The PZC of the ferric oxide is much higher than those of the others (6.4 vs. less than 3). Therefore, all surfaces are negatively charged over the studied pH range (5 to 11) except the ferric oxide at pH 5. The surfaces are more negatively charged as pH increases (see zeta potentials reported in Tables 5.3 and 5.4 for surfactant-free solution). Even when there is a net negative charge on each substrate, the anionic surfactant (SDS) shows substantial adsorption on each surface approaching bilayer coverage (fractional monolayer coverage = 1.77, Table 5.5) on cotton at pH 5. This can be attributed to the hydrophobic interactions between the surfactant hydrophobe and the surface and to the heterogeneity of the surface (some positively charged sites despite a net negative charge). The high adsorption (fractional monolayer coverage = 0.76) of CTAB on ferric oxide at pH 5 (below the PZC) also indicates these hydrophobic interactions and surface heterogeneity (Table 5.5).

For SDS, the order of adsorption for the kaolinite is cotton > kaolinite > polyester and for the ferric oxide is cotton > ferric oxide > 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 5.3 and 5.4). But there are no good correlation when comparing kaolinite and ferric oxide. With increasing solution pH, anionic surfactant adsorption decreases while cationic surfactant increases (Tables 5.2); consistent with the more negatively charged surface and the repulsion of like-charged anionic surfactants as well as the attraction of positively charged cationic surfactant.

Table 5.2 Maximum adsorption (Γ_{max}) of each surfactant on studied substrates

Maximum adsorption or Γ_{max} on studied substrates (µmole/m^2) / Substrate	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
Ferric Oxide	2.64	2.06	1.96	1.73	0.70	0.78	0.89	0.91	1.93	2.10	2.86	3.89
Kaolinite	2.63	2.25	1.80	1.39	1.53	1.24	1.24	1.21	4.74	4.87	5.24	5.64
Polyester	0.89	0.75	0.67	0.56	0.26	0.21	0.11	0.06	2.33	2.55	2.81	3.00
Cotton	5.54	4.10	3.03	1.86	0.51	0.43	0.41	0.39	4.40	5.42	6.09	6.00

Table 5.3 Detergency, redeposition, zeta potential and contact angle of surfactant-free solutions for polyester fabric

Polyester	Surfactant-free			
	pH 5	pH 7	pH 9	pH 11
Detergency of ferric oxide (%)	10.3±1.2	11.4±1.7	11.5±2.7	14.8±1.2
Detergency of kaolinite (%)	13.4±0.5	18.4±2.3	24.8±1.3	31.1±1.6
Redeposition of ferric oxide (%)	4.36	3.94	3.47	3.34
Redeposition of kaolinite (%)	1.29	1.22	1.20	1.21
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 ferric oxide (mv)	33.6±0.8	-30.3±0.2	-55.4±0.4	-69.5±0.6
Zeta potential or ζ of kaolinite (mV)	-42.9±0.5	-44.3±0.3	-50.0±0.5	-54.1±0.7
Summation of ζ of ferric oxide (mV)	-16.4	-94.6	-124	-140
Summation of ζ of kaolinite (mV)	-92.9	-109	-118	-124
Contact angle or θ on polyester (deg)	73.6	73.6	73.6	73.6

Table 5.4 Detergency, redeposition and zeta potential of surfactant-free solutions for cotton fabric

Cotton	Surfactant-free			
	pH 5	pH 7	pH 9	pH 11
Detergency of ferric oxide (%)	12.6±0.2	12.9±2.5	13.7±1.9	15.5±0.9
Detergency of kaolinite (%)	14.7±1.8	19.3±1.3	26.3±0.7	33.0±0.9
Redeposition of ferric oxide (%)	4.89	4.80	4.76	3.54
Redeposition of kaolinite (%)	1.30	1.45	1.12	1.02
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 ferric oxide (mv)	33.6±0.8	-30.3±0.2	-55.4±0.4	-69.5±0.6
Zeta potential or ζ of kaolinite (mV)	-42.9±0.5	-44.3±0.3	-50.0±0.5	-54.1±0.7
Summation of ζ of ferric oxide (mV)	19.9	-50.6	-78.7	-94.1
Summation of ζ of kaolinite (mV)	-56.6	-64.6	-73.4	-78.7

Table 5.5 Detergency, redeposition, 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 of ferric oxide (%)	49.5±0.7	51.8±0.8	56.8±1.8	61.1±1.6	42.3±2.4	42.7±1.8	44.5±1.9	51.5±1.0	25.9±0.6	26.5±2.4	28.7±2.2	29.4±1.5
Detergency of kaolinite (%)	58.3±2.2	63.4±1.6	70.4±2.0	74.4±1.7	40.2±1.9	41.0±0.6	43.1±1.7	45.1±1.0	29.2±1.8	32.7±2.2	38.7±0.8	42.7±2.4
Redeposition of ferric oxide (%)	1.19	1.01	0.98	0.54	0.75	0.73	0.74	0.51	2.58	2.64	2.56	2.52
Redeposition of kaolinite (%)	0.76	0.77	0.61	0.47	0.64	0.58	0.56	0.37	3.46	3.17	2.52	2.30
Fraction of monolayer adsorption (cotton)	1.77	1.31	0.97	0.60	0.23	0.19	0.18	0.17	1.74	2.14	2.41	2.37
Fraction of monolayer adsorption (ferric oxide)	0.84	0.66	0.63	0.55	0.31	0.35	0.40	0.41	0.76	0.83	1.13	1.54
Fraction of monolayer adsorption (kaolinite)	0.84	0.72	0.58	0.54	0.68	0.55	0.55	0.54	1.87	1.92	2.07	2.23
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 ferric oxide (mV)	-58.7±0.5	-62.3±0.7	-74.0±0.4	-82.0±0.3	-21.8±0.8	-29.4±0.6	-32.2±0.3	-35.3±0.8	96.0±0.3	87.7±0.8	78.5±0.4	75.9±1.3
Zeta potential or ζ of kaolinite (mV)	-75.1	-83.9	-92.6	-99.8	-16.5	-20.6	-25.8	-32.3	98.9	103	107	108
Summation of ζ for ferric oxide (mV)	-124	-132	-148	-161	-41.2	-54.8	-60.8	-65.4	111	108	102	107
Summation of ζ for kaolinite (mV)	-140	-154	-167	-178	-35.9	-46.0	-54.4	-62.4	114	124	130	139

Table 5.6 Detergency, redeposition, fraction of monolayer adsorption, zeta potential, surface tension, contact angle and surface pressure at solid/liquid interface 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 of ferric oxide (%)	44.2±1.8	46.7±0.6	52.7±0.8	56.7±2.6	34.6±1.9	38.2±0.8	42.5±1.2	48.6±0.4	17.4±2.0	17.5±2.2	25.4±0.8	26.7±0.8
Detergency of kaolinite (%)	52.6±1.5	56.0±1.8	62.7±2.5	69.1±0.9	26.4±0.3	30.3±2.5	38.7±0.6	42.1±0.2	16.5±0.8	22.3±1.4	31.4±1.6	36.9±0.7
Redeposition of ferric oxide (%)	1.34	1.35	1.48	0.99	1.47	0.82	0.63	0.67	3.23	2.13	2.44	2.14
Redeposition of kaolinite (%)	0.81	0.75	0.73	0.61	0.77	0.49	0.51	0.41	4.56	3.90	3.75	3.51
Fraction of monolayer adsorption (polyester)	0.29	0.24	0.22	0.18	0.12	0.10	0.05	0.03	0.92	1.01	1.11	1.19
Fraction of monolayer adsorption (ferric oxide)	0.84	0.66	0.63	0.55	0.31	0.35	0.40	0.41	0.76	0.83	1.13	1.54
Fraction of monolayer adsorption (kaolinite)	0.84	0.72	0.58	0.54	0.68	0.55	0.55	0.54	1.87	1.92	2.07	2.23
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 ferric oxide (mV)	-58.7±0.5	-62.3±0.7	-74.0±0.4	-82.0±1.2	-21.8±0.3	-29.4±0.4	-32.2±0.4	-35.3±0.5	96.0±0.7	87.7±0.9	78.5±0.4	75.9±0.2
Zeta potential or ζ of kaolinite (mV)	-75.1±0.5	-83.9±1.3	-92.6±0.7	-99.8±0.6	-37.6±1.4	-40.4±0.3	-46.4±0.8	-56.2±0.5	98.9±0.6	103±1.2	107±0.4	108±0.8
Summation of ζ of ferric oxide (mV)	-144	-152	-181	-197	-48.2	-64.8	-66.8	-75.4	121	114	112	121
Summation of ζ of kaolinite (mV)	-160	-174	-200	-214	-64.0	-75.8	-81.0	-96.3	124	130	140	153
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
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
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

Three pieces of evidence are used to conclude that tail-down monolayer adsorption or bilayer adsorption of a given surfactant is occurring: fractional monolayer coverage, effect of pH (for ionic surfactants), and whether the adsorption isotherm shapes indicate cooperativity or not in aggregate formation. If the surface becomes saturated, it is not obvious if a surfactant bilayer or admicelle (head-down and head-out) or a tail-down monolayer or hemimicelle would form unless greater than monolayer adsorption is observed, in which case bilayer aggregate formation is deduced. If 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, it means that the hydrophobic interactions between surfactant tails in the aggregated hemimicelle are no more favorable that than 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. Isotherm slopes greater than unity are consistent with bilayer formation; sometimes a clear critical admicelle concentration or CAC [39-41] is observed where these bilayered surface aggregates begin to form and the slope of the adsorption isotherm shows a sharp increase above the CAC. Due to head-group interaction with the surface, adsorption exhibits a substantial pH effect for bilayer adsorption while only a modest effect is seen for tail-down or monolayer adsorption [42]. From Part I, it was concluded that all three surfactants adsorb as a monolayer on hydrophobic fabric polyester, as a bilayer on hydrophilic fabric cotton, a monolayer for SDS on carbon black soil, and a bilayer for OP(EO)10 and CTAB on carbon black.

Maximum SDS adsorption on both kaolinite and ferric oxide is slightly less than a monolayer at pH 5 and the plateau adsorption is substantially pH dependent (Table 5.5), although not as much as on cotton. The adsorption isotherm slope is between 1 and 2 on ferric oxide and about 1 on kaolinite (data not shown). Both soils are completely wet like cotton, so are clearly hydrophilic. From this evidence, we conclude that bilayer formation with SDS is occurring on ferric oxide and probably occurring on kaolinite. The maximum fractional coverage is less than unity for OP(EO)10 on both kaolinite and ferric oxide (Table 5.5). Adsorption isotherms show slopes greater than unity for both soils; in fact, there is a clear discontinuity in slope corresponding to a CAC on ferric oxide. For the nonionic surfactant, pH effects don't illuminate aggregate structure. We conclude that bilayer admicelles are forming on both kaolinite and ferric oxide for OP(EO)10 as on the cotton. Polyethoxylate head groups can hydrogen bond with surfaces so there appears to be an attractive interaction between the EO groups and the surfaces. Decreasing pH causes a modest increase in OP(EO)10 adsorption on kaolinite, cotton, and polyester, but a modest decrease for ferric oxide.

From Tables 5.5 and 5.6, the adsorption of cationic surfactant CTAB is greater than either SDS or OP(EO)10 on both kaolinite and ferric oxide for all pH levels except ferric oxide at pH 5 (below its PZC) where the adsorption of SDS and CTAB is approximately the same. This indicates that non-electrostatic effects are very influential on their adsorption. The CTAB has 16 carbons but SDS has 12 carbons so hydrophobic interactions of the tail group are probably responsible. The maximum adsorption of CTAB on kaolinite is greater than monolayer coverage at all pH levels and for ferric oxide at higher pH levels. Substantial pH effects on CTAB adsorption are observed on both kaolinite and ferric oxide. The slope of the adsorption isotherm is more than unity in the case of kaolinite [32] and about unity for ferric oxide. So, bilayer adsorption of CTAB is occurring on both kaolinite and ferric oxide.

Table 5.7 summarizes the surface aggregate form for all fabrics and soils. Since either hemimicelles or admicelles have head-out configuration to the solution, from a practical viewpoint, the most important consequence of aggregate type is whether pH effect on adsorption will be substantial (admicelle) or modest (hemimicelle).

Table 5.7 Adsorbed surfactant aggregate structure at pH 11

	SDS	**OP(EO)10**	**CTAB**
Polyester	monolayer	monolayer	monolayer
Cotton	bilayer	bilayer	bilayer
Carbon black	monolayer	bilayer	bilayer
Ferric oxide	bilayer	bilayer	bilayer
Kaolinite	bilayer	bilayer	bilayer

5.4.2 Zeta Potentials and Point of Zero Charge Results

5.4.2.1 Surfactant-Free Solutions

The zeta potential (ζ) of a solid particle in solution is the electrical potential at the shear plane close to the Stern layer between the particle and the liquid as deduced from the electrophoretic mobility [43]. The zeta potential can be directly related to the colloid stability in electrostatically stabilized systems [44, 45]. Zeta potentials above an absolute value of 40 mV indicate a high charge density at the surface leading to high dispersion stability due to repulsion between particles in suspension [39, 46]. Usually, the hydronium cation and the hydroxyl anion are potentially determining ions; at low pH the particle has a positive charge and at high pH has a negative charge. The pH at which the surface exhibits a neutral net electrical charge on the particle or no net average charge on a group of particles (zero zeta potential) is interpreted as the point of zero charge (PZC) [5,47].

From Table 5.1, the PZC of the ferric oxide, kaolinite, cotton and polyester are 6.4, 2.5, 2.9 and 2.4 respectively which are in good agreement with previous studies [31, 48-54]. The zeta potential (ζ) at pH 11 is -70.0 mV for polyester, -24.6 mV for cotton, -69.5 mV for ferric oxide, and -54.1 mV for kaolinite (Tables 5.3 and 4). The ferric oxide zeta potential is more dependent on pH than the other substrates or carbon black [31, 55].

5.4.2.2 Zeta Potential in Surfactant Solution

Tables 5.5 and 5.6 show the zeta potentials for all studied surfactants/substrates at pH 5, 7, 9, and 11 at high enough surfactant concentrations where both surfactant adsorption and zeta potential (ζ) plateau.

The SDS causes ζ of all substrates to become even more negative as pH increases from 5 to 11 (Table 5.5 and 5.6), a similar trend as that in the absence of surfactant (Table 5.3 and 5.4). On ferric oxide at pH 5 (below its PZC), SDS causes charge reversal from positive to negative compared to the surfactant-free system and the ζ changes by between 92.3 mV at pH 5 and 12.5 mV at pH 11 compared to the surfactant-free system. For kaolinite, the ζ changes by between 32.2 mV and 45.7 mV compared to the surfactant-free solution. In the presence of SDS, the kaolinite surface is more negatively charged than ferric oxide for all pH values. But there is no clear correlation between ζ and the SDS adsorption on ferric oxide and kaolinite. 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 causes the surface to become more negatively charged, ζ changing by between 34.9 mV and 54.0 mV compared to the surfactant-free system [31].

The OP(EO)10 causes all substrates to be negatively charged and the ζ becomes even more negative for cotton at all pH levels and for ferric oxide at pH 5, but less negative for polyester and kaolinite at all pH levels, and for ferric oxide at pH 7 to 11. The effect of OP(EO)10 on ζ, as with SDS, is not correlated to the surfactant adsorption level. The effect of OP(EO)10 can be substantial, changing ζ by as much as 30.0 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 is probably due to the bound water–more bound water with EO groups will shift the shear plane [31].

The CTAB causes charge reversal for all substrates (substrates become positively charged) except for ferric oxide at pH 5 (originally positively charged), which has higher positive values of ζ. Increasing pH increases the negative charge on the surface available for CTAB adsorption. In the presence of CTAB, the surfaces of polyester, cotton and kaolinite become even more positively charged with increasing pH, in contrast to ferric oxide, which becomes less positive. Because of the PZC of ferric oxide is 6.4, at pH 5 the ferric oxide surface is positively charged and the adsorption of CTAB at that pH increases the positive charge on the surface. As with SDS and OP(EO)10, the change in ζ due to CTAB doesn't correlate with CTAB adsorption. This lack of correlation is because only plateau conditions are considered here; at lower adsorption levels below the CMC, a correlation would be expected.

"Summation of ζ" in Tables 5.3-5.6 is the sum of ζ for either ferric oxide or kaolinite and either polyester or cotton in order to quantify the electrostatic repulsion between the soil (ferric oxide or kaolinite) and fabric in a single parameter.

5.4.3 Dispersion Stability

The dispersion stability of detached soil particles in washing solutions is expected to relate to redeposition of particulate soil [56]. While dispersion stability measured here is in unmixed systems as is normal for this measurement [41, 50, 55], in real application, the mechanical force applied during the washing process will also aid the suspension of soil particles. In this work, the dispersion stability of studied particles, with and without surfactants, as a function of time is shown in Figure 5.1a and 5.1b via light absorbance (at pH =11); high light absorbance means high particle density and higher dispersion stability. The effect of solution pH on the dispersion stability of ferric oxide and kaolinite at settling times of 1 h. and 10 h., respectively and at plateau concentrations are shown in Figure 5.1c and 5.1d. The improvement of dispersion stability in the presence of surfactants as compared to surfactant-free solutions was observed for both studied particulate soils. From experimental results, it is clearly seen that the dispersion stability of the kaolinite is much better than the ferric oxide either in the presence or absence of surfactants. One possible reason is that the kaolinite has a large portion of small particles compared to ferric oxide. Even though the large particles of kaolinite quickly settle; the very small particles form a stable dispersion for a long period of time compared to ferric oxide. For kaolinite, higher dispersion stability is observed as pH increases for all systems. For ferric oxide, a similar trend was observed except for CTAB. The highest dispersion stability of ferric oxide in CTAB occurred at pH 5, which has the highest positive zeta potential, and its zeta potential slightly decreases with increasing pH as well as the dispersion stability, which slightly changes with pH levels.

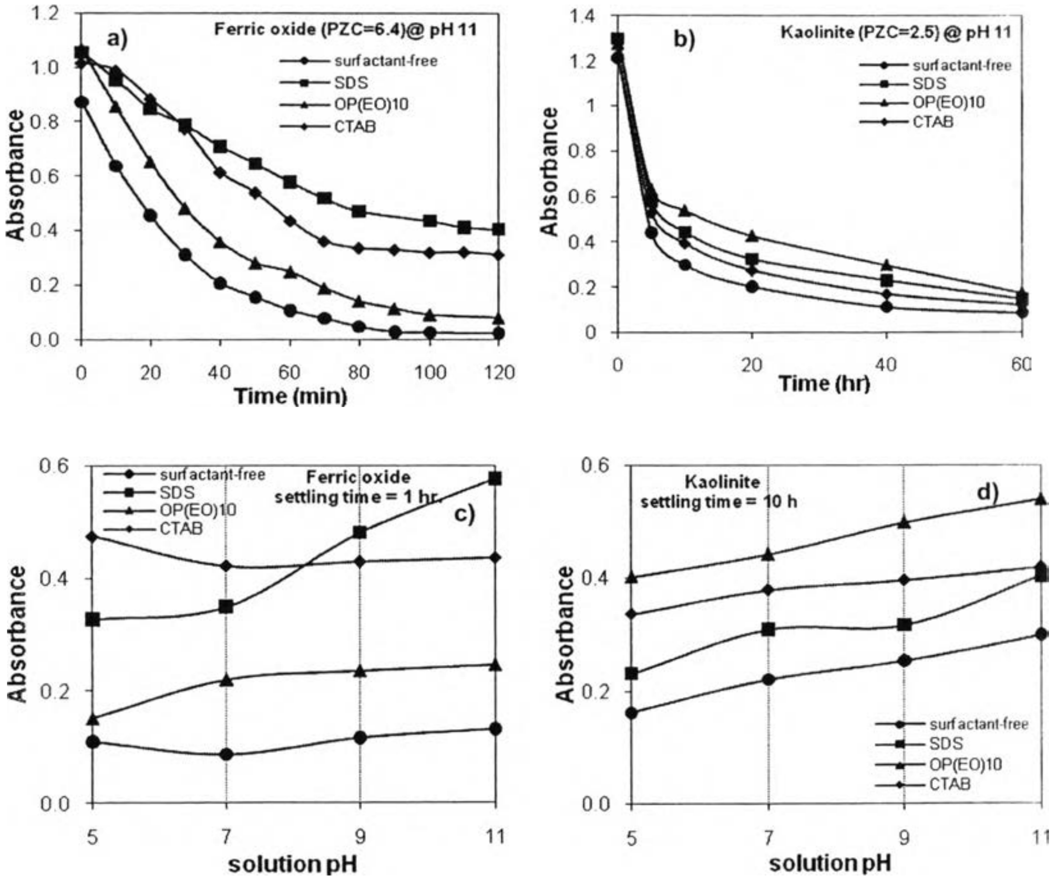


Figure 5.1 Dispersion stability; Effect of time (a) Ferric oxide, (b) Kaolinite, Effect of solution pH (c) Ferric oxide, (d) Kaolinite.

5.4.4 Contact Angle and Solid/Liquid Surface Pressures of Surfactant Solutions

Measurement of the contact angle of the aqueous solution onto the substrates has two basic purposes. First, the wash solution needs to contact the 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 [5, 11,57]. Second, contact angle is necessary to calculate solid/solution surface pressures. The solution/substrate contact angle for polyester is shown in Tables 5.3

and 5.6. Spontaneous wetting/soaking up of solution occurred on cotton, kaolinite, and ferric oxide (contact angle $\leqslant 0$), so θ was not measureable.

From Table 5.6, at a high pH, the order of wetting efficiency (lowest θ) on polyester is CTAB > OP(EO)10 > SDS. At a low pH, it is CTAB ≅ OP(EO)10 > SDS. Yet, the order of detergency performance is SDS > OP(EO)10 > CTAB, indicating that wetting is not an important factor affecting detergency in these systems – from visual observations, the polyester is wet well enough for the surface to always be in contact with the surfactant solution or even water only.

Surface pressure (sometimes called spreading pressure) at the solid/liquid interface (π_{SL}) is the difference between interfacial tension (IFT) at the solid/liquid interface for the solvent (γ_{SL}^{o}) and surfactant solution (γ_{SL}) [58] calculated from the contact angle and the air/solution surface tension as detailed in Part I [31]. 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 only be measured on polyester in this work, the surface pressure for it is shown in Table 5.6. The surface pressures on both fabrics and soils are important and in Part I, we added these together for carbon black soil and polyester fabric to get a parameter, which included IFT, effects for both surfaces. This sum of surface pressures did mirror the surface pressure on the polyester in that work, so we will consider the surface pressure on the polyester as representative of IFT effects on detergency of the system here. Although surface pressures on kaolinite and ferric oxide could not be measured, this assumption seems like a reasonable way to indicate the importance of IFT reduction on the surfaces due to surfactant adsorption.

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

For all systems, detergency increases with increasing surfactant concentrations until it reaches a plateau at a certain initial surfactant concentration; those data are detailed elsewhere [37]. Plateau concentrations for physical parameters like adsorption, zeta potential, and contact angle are lower than these for detergency because those parameters are plotted against final concentration, which is lower than initial concentration. So, by choosing the plateau concentration region based on detergency, all other parameters also plateau. It is these plateau parameters, which will be discussed through the rest of this paper.

Tables 5.3 and 5.6 show detergency, redeposition, and relevant physical properties for ferric oxide and kaolinite removal from polyester fabric while results in Tables 5.4 and 5.5 are for cotton. Surfactant–free systems are shown in Tables 5.3 and 5.4 as well as wash systems with SDS, OP(EO)10, and CTAB in Tables 5.5 and 5.6. Surfactant adsorption (as fractional monolayer coverage), zeta potential (ζ), contact angle θ (for polyester), and surface pressure π (for polyester) are given for both fabrics (cotton and polyester) and soils (ferric oxide and kaolinite). 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. The two exceptions to this are for the surfactant-free systems with ferric oxide at pH 5 for polyester (Table 5.3) and cotton (Table 5.4). As discussed earlier, the surface pressure could not be measured on cotton, ferric oxide and kaolinite surfaces. So, we will consider the surface pressure on the polyester as representative of IFT effects on detergency of the system here.

5.4.5.1 Polyester

In the absence of surfactant (see Table 5.3), detergency of both ferric oxide and kaolinite increases, redeposition decreases, and the absolute value of the summation of ζ increases with increasing pH. The detergency of ferric oxide goes from 10.3 to 14.8% while kaolinite goes from 13.4 to 31.1%. Both reach the maximum at the highest pH studied of 11, which suggests electrostatic repulsion as a main cause of detergency without surfactant as in the case of hydrophobic soil. In comparison between two types of soils, the kaolinite shows higher detergency than the ferric oxide at all pH levels. This is possibly due to the better dispersion stability of kaolinite and the difference in size and shape of the two soils. Ferric oxide has smaller size and is more uniform in both size and shape than kaolinite, which has an irregular hexagonal shape with a layered underlying structure. The kaolinite particle size is more heterogeneous, varying from about 0.1 to 20 μm [59, 60]. Smaller particle size has a higher adhesion force to the fabric surface, which can lead to greater difficultly in removal [61] and lead to easier redeposition. The difference between the size of ferric oxide and kaolinite are clearly seen in SEM photos (see Figure 5.2), which will be discussed in more detail in a later section.

In the presence of SDS (see Table 5.6), detergency increases, redeposition decreases, the sum of zeta potentials becomes even more negative, and the polyester surface pressure decreases with increasing pH for both ferric oxide and kaolinite. The sum of zeta potentials is up to 57 mV and 90 mV more negative for ferric oxide and kaolinite, respectively compared to that without surfactant (Table 5.3). Higher detergency for kaolinite compared to ferric oxide could be due to aforementioned differences in particle sizes, greater electrostatic repulsion as indicated by the zeta potential results, or the better dispersion stability of kaolinite or some combination of these three factors.

For OP(EO)10 (see Table 5.6), detergency increases, redeposition decreases, the sum of zeta potentials becomes more negative, and the polyester surface pressure slightly increases with increasing pH. Between pH 5 and 11, for ferric oxide, detergency increases from 34.6% to 48.6% and for kaolinite, detergency changes from 26.4% to 42.1%; analogous changes in the sum of zeta potentials are -48.2 mV to -75.4 mV for ferric oxide and -64.0 mV to -96.3 mV for kaolinite. In this case, no correlation was observed between detergency and sum of zeta potentials for ferric oxide compared to kaolinite. Detergency of ferric oxide and kaolinite in the presence of OP(EO)10 is less than SDS for all pH levels. This is because of the soil/fabric electrostatic repulsion and the IFT reduction for OP(EO)10 is less than those for SDS. Moreover, the presence of OP(EO)10 causes soil/fabric electrostatic repulsion to decrease compared to surfactant-free solutions at all pH levels (see Table 5.3). However, the presence of nonionic surfactant can induce much higher detergency in the case of ferric oxide (48.6% vs. 14.8% at pH 11) but not much improvement for kaolinite (42.1% vs. 31.1% at pH 11). If the electrostatic repulsion was an important parameter in soil removal, detergency would not increase. The presence of the nonionic surfactant reduces the sum of zeta potentials from -140 mV to -75.4 mV for ferric oxide and -124 mV to -96.3 mV for kaolinite (Tables 5.3 and 5.6, respectively), indicating a lessening of electrostatic repulsion forces. In the case of IFT reduction, the sum of surface pressure is much more for OP(EO)10 at pH 11 compared to SDS, yet SDS detergency is higher than OP(EO)10. Hence, neither electrostatic repulsion nor IFT reduction is the single dominant mechanism for detergency enhancement by the nonionic surfactant. As the part I of this series for carbon black soil, steric repulsion between soil and fabric is hypothesized as a mechanism aiding detergency with OP(EO)10 for ferric oxide and kaolinite removal also in addition to electrostatic repulsion.

The conclusion regarding SDS 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, detergency increases as electrostatic repulsion increases while surfactant adsorption decreases with increasing pH which means electrostatic repulsion is the most important cause of detergency increase due to the surfactant, with steric effects a contribution.

For CTAB (Table 5.6), detergency for kaolinite increases, sum of zeta potentials increases, and polyester surface pressures increases with increasing pH, but no good correlation between detergency of ferric oxide and the sum of zeta potentials is observed, unlike SDS and OP(EO)10 systems. The fluctuation of the sum of zeta potentials for CTAB is possibly due to the high PZC of ferric oxide compared to kaolinite resulting in a high positive charge on ferric oxide at pH 5. In all cases, detergency is less with CTAB than with either SDS or OP(EO)10. The high surface pressures for CTAB imply that IFT reduction as well as electrostatic repulsion contributes to CTAB detergency. Adsorption of CTAB onto all surfaces is not only greater than that of SDS or OP(EO)10, but is not as reversible (less desorption occurs). This is because the adsorption of CTAB onto negatively charged surfaces occurred via electrostatic interaction between the positively charged head groups of CTAB and negative charges on the fabric surface, which is a stronger interaction than that of SDS and OP(EO)10 with the fabric surface. This phenomenon leads to poor rinseability as shown in Table 5.8, which shows the residual adsorbed surfactant after the second rinse. This residual surfactant is probably responsible for the high redeposition levels during detergency for CTAB compared to SDS and OP(EO)10.

Table 5.8 Amount of surfactant adsorbed on fabric after the second rinse

Ferric oxide	**SDS (g surfactant/g fabric)**	**OP(EO)10 (g surfactant/ g fabric)**	**CTAB (g surfactant / g fabric)**
Cotton	0.13	0.11	0.22
Polyester	0.13	0.12	0.21
Kaolinite			
Cotton	0.03	0.05	0.24
Polyester	0.03	0.04	0.18

5.4.5.2 Cotton

The relative importance of electrostatic forces compared to IFT reduction in detergency on cotton could not be quantified since solid/liquid surface pressures couldn't be calculated due to our inability to measure contact angles on cotton. However, from Tables 5.4 and 5.5, detergency trends for cotton were analogous to those for polyester.

Detergency increases with increasing pH and the absolute value of the sum of zeta potentials for all studied surfactants, also has the similar order as polyester: SDS > OP(EO)10 > CTAB. Electrostatic forces are the dominant mechanism responsible for SDS and OP(EO)10 detergency on both cotton and polyester. However, the sum of zeta potentials does not explain the differences in detergency of cotton compared to polyester: the absolute value of sum of zeta potentials for cotton is less than those of polyester but the detergency of cotton is higher than polyester for both soils. The effect of fiber morphology from SEM photos will be described in a later section. Additionally on cotton, steric repulsion is hypothesized to be important for OP(EO)10; IFT reduction is probably important for CTAB; and low antiredeposition performance (Table 5.5) as well as low rinseability (Table 5.8) of CTAB on cotton contributes to lower detergency of cationic surfactant.

Redeposition is always lower at high 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 [62], although steric effects are a secondary mechanism of dispersed soil stabilization for the nonionic surfactant [63]. For all systems, redeposition is low compared to residual soil after washing (100% - detergency (%)). Except for the case of CTAB with kaolinite on both fabrics, the redeposition in the presence of CTAB is higher than that of the surfactant-free system. It is possibly due to some of the large kaolinite particles not only being easier to remove but also easier to redeposit onto the positively charge fabric. The highest level of redeposition/residual soil found for kaolinite on polyester in the presence of CTAB is equal to 0.06 and on cotton is 0.05. For SDS and OP(EO)10, the redeposition/residual soil varies from 0.006 to 0.02 which is relatively small. Thus, redeposition is not observed to be a very important factor relative to detergency trends.

5.4.6 Comparison between Quantitative and Qualitative Analysis for Ferric Oxide

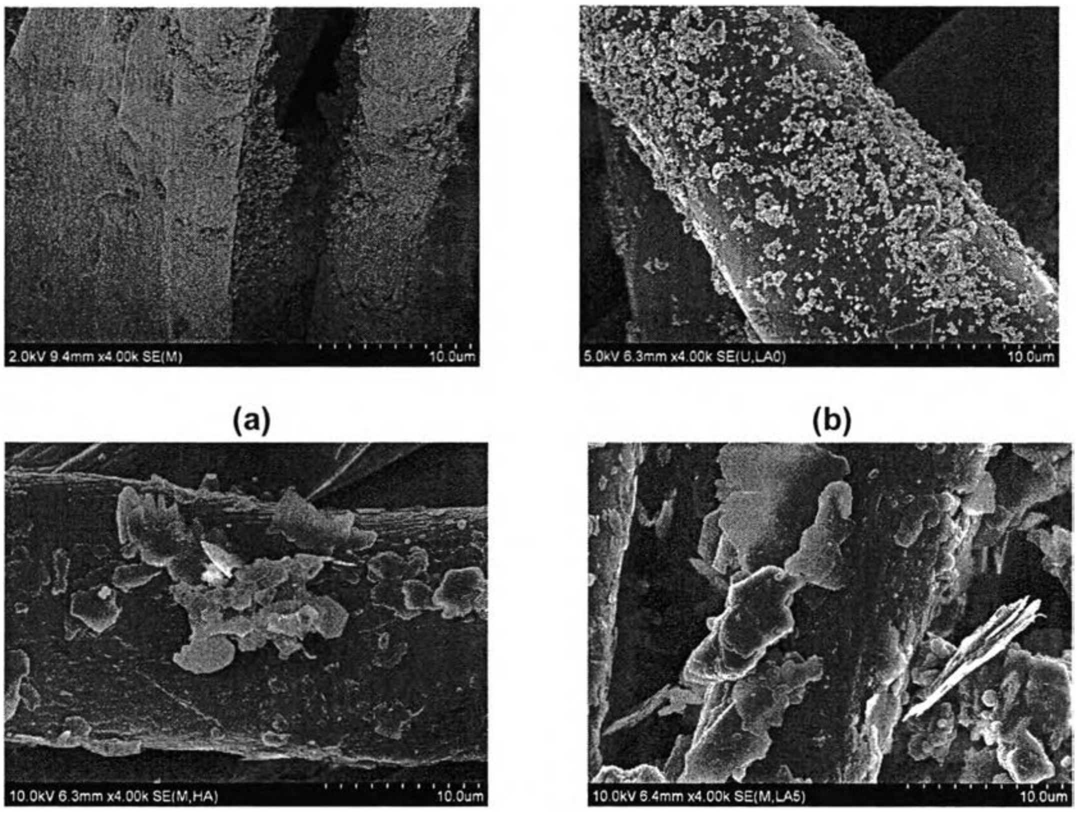
Ferric oxide has a red color, so detergency is easily analyzed by the widely used refraction method [20-24]. Kaolinite has a white color, so refraction is not effective to measure residual soil. Detergency of both kaolinite and ferric oxide can be obtained by analysis of digested fabric after cleaning by atomic concentration measurement using AAS. Table 5.9 shows the correlation between the two methods of analysis for ferric oxide. Excellent agreement is observed with agreement within 5%, justifying the use of AAS for quantifying detergency for kaolinite systems.

Table 5.9 Detergency (%) for ferric oxide analyzed by AAS and refraction method at plateau concentration and pH 11 for all studied surfactants

Analysis method	Surfactant-free		SDS		OP(EO)10		CTAB	
	Cotton	Polyester	Cotton	Polyester	Cotton	Polyester	Cotton	Polyester
Refraction method	15.5±0.9	14.8±1.2	61.1±1.6	54.3±2.6	51.5±1.0	48.6±0.4	29.4±1.5	26.7±0.8
AAS	16.7±1.2	13.2±0.7	57.4±0.9	52.9±0.8	55.7±0.8	50.1±1.2	27.0±0.4	24.2±0.7

5.4.7 Fiber Surface Morphology of Soiled Fabrics

Figure 5.2 shows SEM photos of soiled cotton and polyester fabrics with ferric oxide and kaolinite. Obviously, both soils just stick onto the fabric surfaces and the particles do not penetrate or become entrapped in the spaces between the fabric yarns. This is similar to observations of carbon black soil from Part I [31]. Ferric oxide (Fig. 5.2a and 5.2b) tends to form more extended aggregate on cotton fabric while smaller particles stick on the polyester surface. The adhesion force of small particles is stronger than for larger ones [40]. Thus, ferric oxide can be more easily removed from cotton than polyester fabric, which is consistent with detergency results. For kaolinite, the SEM photos (Fig. 5.2c and 5.2d) show little visual difference in particle agglomeration between cotton and polyester. Better detergency is observed for cotton than for polyester.



(a) (b)

(c) (d)

Figure 5.2 SEM Photos of Soiled Fabrics (a) Ferric Oxide/Cotton, (b) Ferric Oxide/Polyester, (c) Kaolinite/Cotton, (d) Kaolinite/Polyester.

5.5 Summary of Detergency Mechanisms

Electrostatic repulsion between fabric and soil particles is shown to be the primary mechanism responsible for detergency for anionic, nonionic, and cationic surfactants studied. Anionic surfactants adsorb onto the negatively charged fabrics and soils, yielding high negative electrical potentials and the best detergency [1, 4-6, 12-17, 22, 31]. 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 and antiredeposition. In addition to electrostatic forces, IFT reduction due to surfactant adsorption aids cationic surfactant detergency. Hydrophilic soils tend to form larger aggregates on cotton rather than polyester. This helps explain higher removal of kaolinite and ferric oxide from cotton and vice versa for hydrophobic soil (carbon black) [31]. The presence of surfactants can provide better stability of suspensions as compared to surfactant-free solutions. However, it was not a dominant mechanism governing particulate soil detergency.

5.6 Acknowledgements

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