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M. Tagawa[a]
[a] Department of Clothing Science, Nara Women's University, Kita-uoya-nishi-machi, Nara-shi, Japan

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REMOVAL OF PARTICLES FROM SUBSTRATES BY ELECTRO-OSMOTIC FLOW

M. Tagawa
Department of Clothing Science,
Nara Women's University
Kita-uoya-nishi-machi, Nara-shi, 630 Japan

Introduction

The detergent process or detergency is defined as the removal of soil, or matter out of place, from a substrate immersed in a medium through the application of a mechanical force in the presence of a detergent which lowers the adhesion of the soil to the substrate[1]. Regarding the mechanical force in the detergent process for porous solids such as fabrics, detergency is considered to be governed by flow behavior of the washing medium inside the porous solids. For example, the fabric can be considered as a system of capillaries; the space between fibers is a capillary and the fiber surface is the capillary wall. In the washing process, soil particles adhering to the fiber surface can be detached by the tangential flow of washing liquid in the capillaries.

The flow of liquid in ordinary mechanical washing is a hydrodynamic flow of the Poiseuille scheme which gives a parabolic velocity profile. Therefore, small soil particles adhering to the surfaces are difficult to remove for lack of effective hydrodynamic force. In contrast to the Poiseuille flow, the electro-osmotic flow which takes place in the electrical double layer on

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the surface gives rise to a velocity profile of piston flow, and hence is expected to produce a drastic detaching force on soil particles.

In this paper, the author will show the effectiveness of electro-osmotic flow on the removal of soil particles and its usefulness in analyzing the process of particle removal by a well-defined tangential flow near surfaces.

Theoretical background

If a solid or water-immiscible liquid is placed in contact with water containing an electrolyte, an excess of ions of one type will generally be present on the surface of the non-aqueous phase and an equivalent amount of ions of opposite charge will be distributed in the aqueous phase near the interface[2]. The distribution of excess charges on the surface and in the solution constitute an electrical double layer. Counterions are attracted to the surface charges by Coulombic forces and at the same time they tend to move toward the bulk solution because of their thermal motion. Thus, the equilibrium distribution of counterions is established. On the other hand, co-ions are excluded from the surface as a result of electrostatic interaction and they tend to diffuse because of their thermal motion. Thus, the diffuse double layer is formed due to the excess of counterions and depletion of co-ions (Gouy-Chapman model)[3].

The electric potential in the diffuse double layer, ψ, is expressed by the Poisson-Boltzmann equation of the Gouy-Chapman theory on diffuse double layer. When the Debye-Huckel approximation holds for a flat double layer, ψ is given by[4]

$$\psi = \psi_0 \exp(-\kappa x) \qquad (1)$$

where ψ_0 is the surface potential, x the distance from the surface and κ the Debye reciprocal length parameter, which is given by

$$\kappa^2 = \frac{8\pi n e^2 z^2}{\varepsilon k T} \qquad (2)$$

where n is the number concentration of ions in the bulk solution, e the elementary charge, z the valence of the ion, ε the dielectric constant of the medium, k the Boltzmann constant and T the absolute temperature. The distance $1/\kappa$ at which $\psi = \psi_0/e$ ($e = 2.718\cdots$) is called the thickness of the diffuse layer. As can be seen in equation (2), the thickness of the diffuse layer, $1/\kappa$, depends on the concentration and valence of the ion. For aqueous solutions containing a 1 - 1 electrolyte of 1×10^{-3} mol/dm^3 at 25°C, $1/\kappa$ is about 100 Å.

If an external electric field is applied to the diffuse double layer, the ions in the double layer will move as the result of an applied potential gradient, and hence, water will flow. This phenomenon is called electro-osmosis. If water flow is caused by an external force tangential to the interface, an electric field will be generated. This is called streaming potential. These phenomena, including electrophoresis and sedimentation potential, are generally called electrokinetic phenomena.

As mentioned above, electrokinetic phenomena are caused by the flow of charge and liquid in an electrical double layer relative to the surface. In the slipping plane the electric potential (which in bulk solution is taken as zero) is called the zeta potential. Although the slipping plane is considered to be located somewhere in the liquid, the zeta potentials are usually used as approximation of surface potentials whose direct measurements are impossible.

According to the fundamental equation of hydrodynamics, the stationary flow velocity u at level r from the axis of a capillary is given by[5)]

$$u = \frac{P}{4\eta L}(R^2 - r^2) - \frac{\varepsilon X}{4\pi\eta}(\zeta - \psi) \qquad (3)$$

where η is the liquid viscosity, P the hydrostatic pressure, L the capillary length, R the capillary radius, ε the dielectric constant of the liquid phase, X the electric field parallel to the axis, and ζ the Stern potential of the capillary wall, which can be approximated by the zeta potential obtained experimentally.

For X = 0, equation (3) gives the parabolic velocity profile of the Poiseuille flow (see Fig. 1 A):

$$u = \frac{P}{4\eta L}(R^2 - r^2). \tag{4}$$

In the case of electro-osmotic flow, where P = 0, we obtain

$$u = -\frac{\varepsilon X}{4\pi\eta}(\zeta - \psi). \tag{5}$$

Since the electric potential ψ reduces to almost zero at the distance from the wall of double layer thickness $1/\kappa$, $\psi \simeq 0$ for $r = R - 1/\kappa$, the flow velocity is constant in almost all levels in the capillary cross section:

$$u_s = -\frac{\varepsilon X}{4\pi\eta}\zeta \tag{6}$$

where u_s is the electro-osmotic velocity. Equation (6) gives the velocity profile of piston flow (see Fig. 1 B).

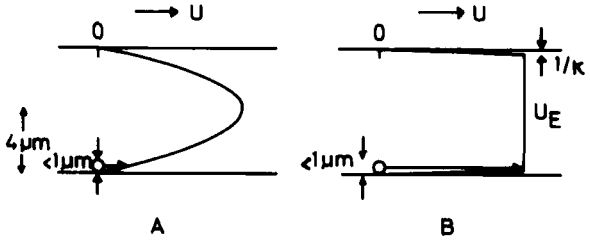


FIGURE 1
Flow velocity profile. A, Poiseuille flow; B, electro-osmotic flow (From reference 5).

In ordinary mechanical washing, Poiseuille flow of the wash liquid takes place in the capillaries of porous solids such as textile fabrics. Hence, the hydrodynamic force acting on small particles attached to the wall is negligible, even when the bulk flow velocity is high. Thus, such tiny particles are difficult to remove by this mechanical action. In fact, soil particles of 0.1 μm in direct contact with fibers are practically impossible to remove by ordinary washing techniques[6].

Let us consider for example a particle of diameter 1 μm attached to the capillary wall. The average radius of capillaries in cotton fabrics is about 4 μm[7], and the electro-osmotic velocity is practically constant at a distance 30 Å from the wall ($1/\kappa$ = 30 Å) when the wash liquid contains a 1×10^{-2} mol/dm^3 univalent electrolyte, as shown in Fig. 1. Since the distance $1/\kappa$ is small compared with the particle radius, the particle is acted on by the hydrodynamic force due to electro-osmosis and hence can be removed from the wall.

Experimental trials in particle removal by electro-osmosis

The cell for removal experiments ($10 \times 5 \times 4$ cm^3), as schematically shown in Fig. 2, was made of polyvinylchloride resin. The standard soiled cloth (5×5 cm^2), C, was prepared by immersing a standard white cotton cloth in a soiling bath containing carbon black by the method of Japan Oil Chemists' Society. This inserted between two separating plates, S and S', with windows of diameter 2.5 cm, W and W', and placed vertically in the middle of the cell. The cell was filled with an aqueous surfactant solution and dipped in a thermostat. When an electric field was applied perpendicularly to the cloth by using electrodes, E and E', electro-osmotic flow was generated in the cloth.

First, the effect of applied voltage on detergency was examined. The detergency which was detected by reflectance

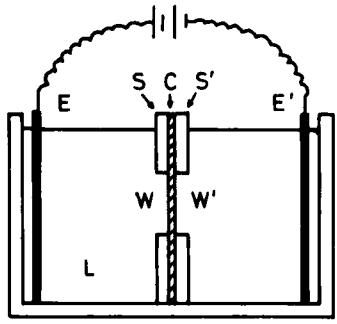


FIGURE 2
Apparatus of electro-osmotic washing. E, E', electrodes; S, S', separating plates; W, W', windows; C, standard soiled cloth; L, wash liquid (From reference 5).

increased with increasing applied voltage up to 50 volts (d.c.). The effects of temperature, time, surfactant concentration and type of current were investigated[5]. For example, the effects of time and surfactant (sodium dodecyl benzene sulfonate, DBS) concentration on detergency are shown in Fig. 3. It will be noticed that the detergency at the center of the cloth, which corresponds to the portion facing the bath liquid at the windows of the separators, is lower than that at the periphery for longer wash time and for higher DBS concentration. This is due to the deposition from the bath as will be shown later. The curve with inverted triangles in Fig. 3 shows the results in the absence of applied voltage; the standard soiled cloth was simply dipped in the bath, showing no washing effect. Thus, particle removal by electro-osmotic flow is effective.

In order to show that the low detergency at the center is due to the deposition from the bath, two standard white cotton cloths were placed on both sides of the soiled cloth between the separators in the cell with a porcelain diaphragm around the anode to impede carbon particles detached from the carbon anode. Soiling took place in the center and the degree of soiling was higher for the cloth on the side facing the anode. This means

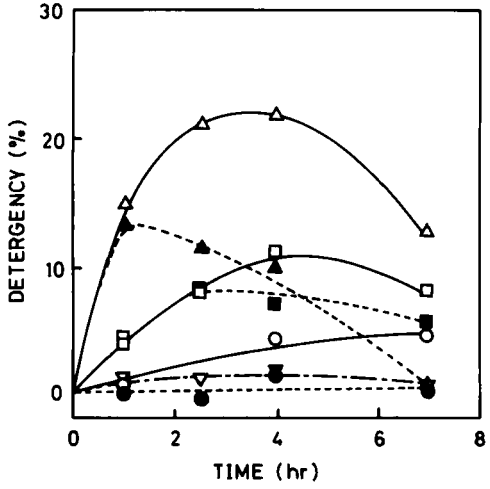


FIGURE 3
The change in detergency with time. Applied voltage, 50 V (dc); DBS concentration: ○,●, 3×10^{-4} ; □,■, 3×10^{-3}; △,▲, 3×10^{-2} mol/dm^3 (open symbols are for the peripheral part of the cloth and closed ones for the center part of the cloth). Control: ▽, 0 V, (DBS concentration, 3×10^{-3} mol/dm^3).

that the decrease in detergency in the center of the standard soiled cloth is also due to the soiling of that part through the window of the separator facing the anode during electro-osmosis. Atomic absorption analysis of the bath liquid after electro-osmosis identified zinc, copper, iron and magnesium in fairly high amounts[5]. It is supposed from the above results that metal ions are dissolved by the anode reaction from the impure carbon electrode and migrate toward the cathode in the cell, during which time the ions are precipitated as hydroxides on the cotton fibers by an increase in pH value. The blue staining of the center part, which was observed by using copper electrodes, also supports this consideration.

Several ways of preventing soiling due to materials produced at the anode were tested[5]: addition of tripolyphosphate or ethylenediaminetetraacetate to the bath, use of cation exchange

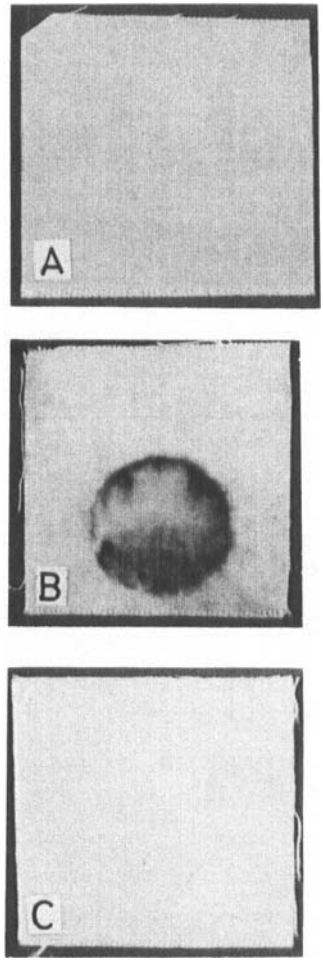


FIGURE 4
Photographs of cotton cloths. A, soiled by clay; B, washed using carbon electrodes; C, washed using titanium electrodes. Applied voltage, 50 V (dc); DBS concentration, 3×10^{-2} mol/dm^3.

resin or a cellulose film as a diaphragm, and geometrical improvement of separators. The highest detergency was obtained by using the cellulose film inserted between the soiled cloth and the separator (with 25 holes of diameter 2 mm) on the anode side. The

detergency (40%) thus obtained was higher than that (30%) obtained by a launderometer.

Since contamination due to the anode was detected even under the condition for the highest detergency, the problem was successfully solved by applying alternating current using titanium electrodes[8]: a soiled cloth was held between two perforated plastic plates and dipped in the wash bath, and electro-osmotic flow took place when an electric field was applied perpendicularly to the cloth using titanium electrodes, changing the polarity every 15 seconds (see Fig. 4).

Removal of particulate soil from textile fabrics by electro-osmosis

The effect of electro-osmotic flow on particle removal was investigated in the absence of contamination due to anode reaction by applying alternating current by titanium electrodes described above[8,9]. Particles of iron (III) oxide (modal diameter, d_m=0.06 μm), carbon black (d_m=0.3 μm), polystyrene latex (d_m=0.6 μm) and clay (Kanto loam) were used. The relation between electro-osmotic velocity and detergency detected by the reflectance of green light (wavelength:530 nm) is given in Fig. 5. Here, the electro-osmotic velocity, u_s, is calculated from equation (6) using the electrokinetic potentials, ζ, of soiled cloths obtained by the streaming potential measurements. The detergency increases with increasing u_s for all kinds of particles. Since, as shown in equation (6), u_s depends on ζ and the electric field applied, X, the change in ζ caused by addition of ionic surfactants relates not only to the change in electrostatic interaction between the particle and the fiber but also to the change in hydrodynamic force. The results in Fig. 5, except those in closed circles, include the changes in ζ and X. The results shown by closed circles, obtained with constant ζ and changing X, show directly the effect of hydrodynamic force due to electro-osmosis on particle removal.

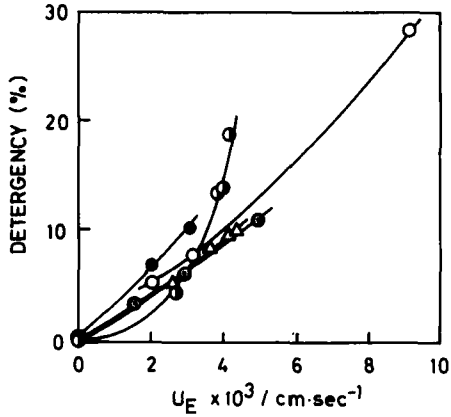
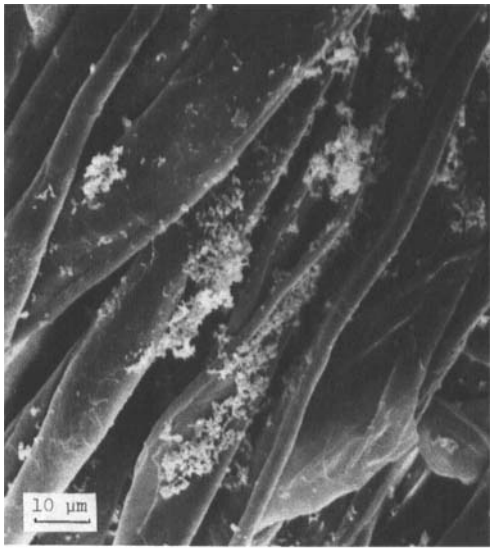


FIGURE 5
The effect of electro-osmotic velocity on detergency in the presence of anionic surfactant (DBS or SDS). ○, clay; ◎, carbon black; △, polystyrene latex; ◑, ●, colloidal iron (III) oxide.

Scanning electron micrographs of standard soiled and washed cloths are shown in Fig. 6. Comparison with the soiled cloth (A) shows effective removal of soil particles in both the cloth washed by a launderometer (B) and that washed by electro-osmosis (C). Besides, it will be noticed that the removal from fiber surfaces inside the fabric is much more complete in the case of electro-osmotic washing than that of mechanical washing by the launderometer. In addition, it was found by scanning electron micrographs in low magnification that the disturbance of fiber arrangement, i. e., the mechanical damage, is practically absent in the case of electro-osmotic washing[5].

Removal of particles from a quartz plate by electro-osmotic flow

The upper plate wall of a quartz cell shown in Fig. 7 was used as a substrate. The cell was filled with an aqueous dispersion of particles, then turned over, and allowed to stand on



A

B

FIGURE 6
Scanning electron micrographs of cotton cloths. A, standard soiled cloth; B, washed by the launderometer; C, washed by electro-osmosis (From reference 5). (Continued)

C

Figure 6 Continued.

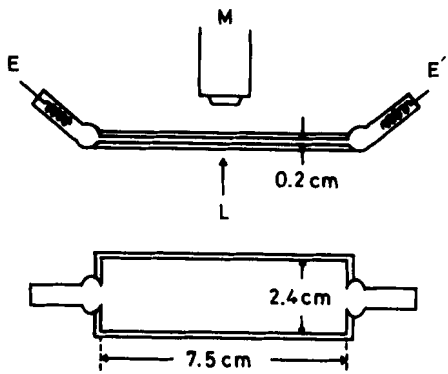


FIGURE 7
Quartz cell. E, E', platinum electrodes; M, microscope; L, light source (From reference 10).

the stage of a light microscope for 2 hours to make particles deposit on the inner wall of the upper plate of the cell. The number of particles deposited was counted through micrographs. After the cell was returned to its original position, the number of particles remaining in the same visual field was counted again. The particle adhesion efficiency was determined by these particle numbers.

Nylon particles (nylon 12 sphere, d_m=5 μm) and iron (III) oxide particles (d_m=0.3 μm) used have isoelectric points of 5 and 7 respectively, as shown by ζ versus pH curves in Fig. 8. After determination of adhesion efficiency, the particle removal experiments were carried out; in the case of iron (III) oxide, after the particles had adhered to the quartz plate from an aqueous dispersion of pH 4, the dispersed medium was drained away, and a washing liquid was immediately introduced into the cell. The cell was then allowed to stand for 1 hour. Nylon particles adhered from aqueous dispersions of various pH and removal experiments were carried out without drainage of dispersed medium. The difference in these procedures is due to the difference in adhesion behavior of the particles[10-12].

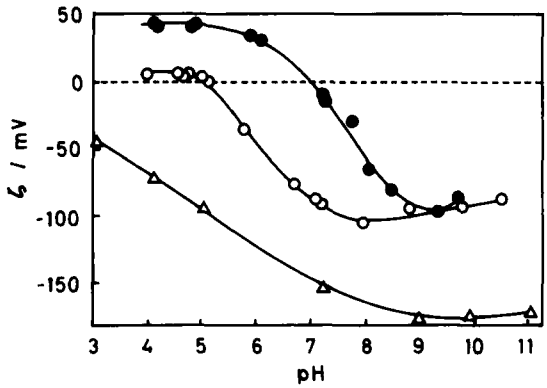


FIGURE 8
ζ-potentials of particles and quartz as a function of pH ([KCl]=1 × 10^{-4} mol/dm^3). ●, iron (III) oxide; ○, nylon; △, quartz.

When an electric field was applied parallel to the wall by using platinum electrodes, E and E' in Fig.7, the electro-osmotic flow was generated along the wall. The polarity of electrodes was changed every 5 minutes to prevent bubbling at the electrodes. The number of particles remaining on the wall at time t, n_t, was determined from photographs. The removal efficiency was expressed by $(n_0 - n_t)/n_0$, where n_0 is the number of particles at time t = 0.

The effect of pH on removal in the absence of surfactants is given in Fig. 9. Compared with nylon particles, iron (III) oxide particles are difficult to remove (they are practically impossible to remove in acidic solutions). In the presence of 1×10^{-3} mol/dm^3 SDS, the iron (III) oxide particles were removed at pH lower than isoelectric point without any applied electric field. The effect of electric field, X, on removal is shown in Fig.10. The removal efficiency increased with increasing electric field, and hence with increasing electro-osmotic velocity, for both kinds of particles. This shows that the hydrodynamic force due to electro-osmotic flow acts as a mechanical force in the systems.

It is interesting to compare the effect of flow types, electro-osmotic flow and ordinary water flow without electrokinetic

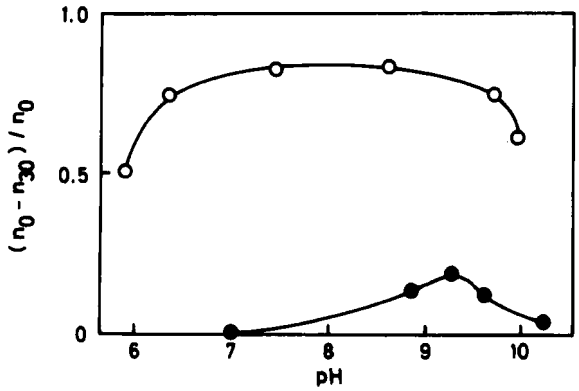


FIGURE 9
The effect of pH on particle removal. ○, nylon (X = 12.4 V/cm); ●, iron (III) oxide (X = 9.75 V/cm).

effect (Poiseuille flow). In order to estimate the hydrodynamic force the flow velocity profile in the quartz cell for electro-osmotic flow was determined by particle velocities at various levels in the cell, giving a parabola at the stationary state due to the reflux in the closed cell[12]. The flow velocity at the distance $1/\kappa$ (0.01 - 0.03 μm) is the electro-osmotic velocity u_s, and the velocity at the distance 0.3 μm (the same as the particle diameter of iron (III) oxide) is calculated to be $0.999\,u_s$, which almost equals u_s. Therefore, the flow velocity for particle removal by electro-osmosis can be considered as the constant flow velocity of u_s. Thus, the hydrodynamic force, the frictional drag (F_f), can be estimated by the Stokes equation:

$$F_f = 6\pi\eta a u_s \qquad (7)$$

under the condition of the sufficiently low Reynolds number (10^{-6} - 10^{-5}), where a is the particle radius. Using the same cell, the particle removal experiments were carried out by ordinary water flow due to the pressure difference and the hydrodynamic force was

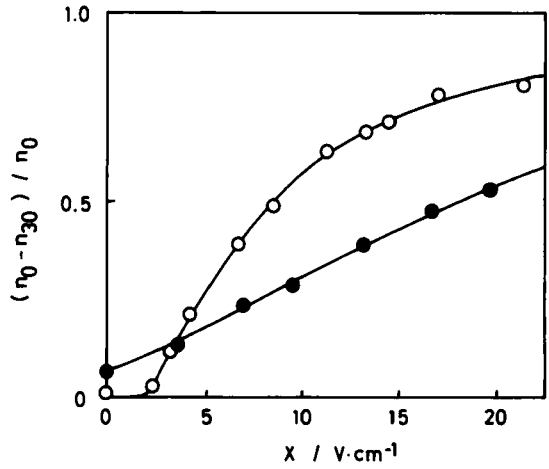


FIGURE 10
The effect of electric field on particle removal. ○, nylon (pH 9.86 ± 0.2); ●, iron (III) oxide (pH 4, [SDS] = 1×10^{-3} mol/dm^3).

estimated by the equation derived by Goldman et al. in shear flow[13];

$$F_f = 1.7 \times 6\pi\eta a u_c \qquad (8)$$

where u_c is the flow velocity at the level of particle center, which was calculated by the Poiseuille's low using the volume flow velocity obtained experimentally. The Reynolds number in this case was of the order of 10^{-3} - 10^{-2} (<< 1).

The effect of hydrodynamic force thus estimated on particle removal is shown in Fig. 11, in which the closed circles are for electro-osmotic flow and the open ones for ordinary flow. The removal efficiencies increase with increasing F_f and the both results are essentially the same in the relation of removal efficiency to hydrodynamic force, although the data for ordinary flow are scattered.

Next, let us compare the flow types from the viewpoint of volume flow velocity. The volume flow velocity for removal efficiency 0.5, $Q_{1/2}$, can be calculated by using the value of u_s

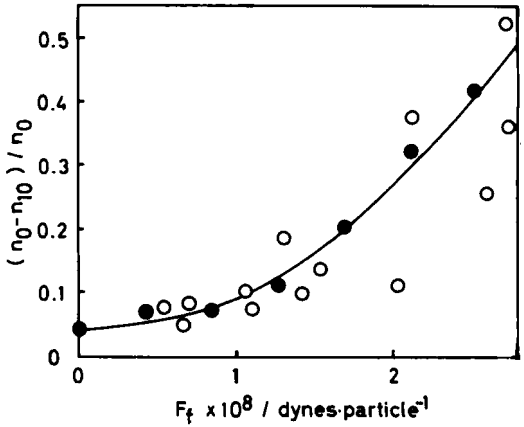


FIGURE 11
Relation between removal efficiency and hydrodynamic force ([SDS] = 1 × 10^{-3} mol/dm^3). ●, electro-osmotic flow (X = 0 - 19.5 V/cm); ○, ordinary flow (Q = 0 - 1.5 cm^3/sec) (From reference 12).

for removal efficiency 0.5 and the cross-sectional area of the cell, assuming that the cell is not closed[12]. The value of $Q_{1/2}$ for electro-osmotic flow thus estimated was 3.84×10^{-3} cm^3/sec and that for the ordinary flow experimentally obtained was 1.5 cm^3 /sec. The former is extremly small compared with the latter, showing the effectiveness of particle removal by electrokinetic effect of electro-osmosis.

Investigation of removal processes by electro-osmotic flow

Since the electro-osmotic flow is a well-defined flow near surfaces and can be controled by electric field, it is expected to be of use for the analysis of removal processes. In general, the rate constant depends on the magnitude of energy barrier and it will be affected by the mechanical force in a certain energy barrier. From this point of view, the change in particle residue with time was analyzed by the semilogarithmic plots, the first-order kinetics. It was found that the removal processes of iron (III) oxide and nylon particles were characterized by two different rate constants, those of rapid and slow processes[10, 12]. The rate constant of slow process, k_s, at a given concentration of surfactant increased with increasing electric field for iron (III) oxide particles[13]. This means that the electro-osmotic flow acts as a mechanical force to overcome the energy barrier in the removal process.

The relation between the rate constant and the surfactant concentration is shown in Fig. 12. The dependence of k_s on sodium dodecyl sulfate (SDS) concentration varied with the electro-osmotic velocity; at a given u_s, the rate constant increased with increasing SDS concentration and this trend was noticeable as the electro-osmotic velocity increased. This shows that the effect of

surfactant on particle removal is enhanced by mechanical force in the removal process. Since this result can not be explained by the change in electrokinetic potentials of the particle and the substrate due to the adsorption of surfactant[12], the increase in the separation distance between the particle and the substrate can be pointed out; the increase in the separation distance causes the decrease in energy barrier.

From the practical point of view, the effect of aging on particle removal was investigated using nylon particles[14]. After the particles were attached to the quartz plate, the dispersed medium was drained away and the plate was dried in air at 20°C for 18 hours. Then the cell was filled with wash liquid and an electric field applied in the presence of surfactant.

In this case, no particles were removed for the first 10 minutes or more; the wetting phenomena are observed in the first

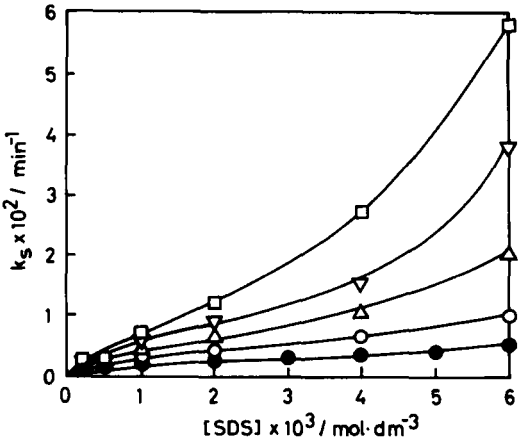


FIGURE 12
Relation between the rate constant of the slow removal process and SDS concentration for iron (III) oxide particles. Electro-osmotic velocity: ●, 0; ○, 1×10^{-3}; △, 2×10^{-3}; ▽, 3×10^{-3}, □, 4×10^{-3} cm/sec.

step. At the beginning, substrate and particles may be wetted by the surrounding liquid but no liquid can penetrate between the two in the contact zone. After the penetration of a thin liquid layer between substrate and particle, the separation distance may become at least as large as to allow the formation of layers of solvation or adsorption of surfactant and the electrical double layers. This process is accelerated by hydrodynamic force in the presence of surfactants.

Conclusion

The direct application of electrokinetic phenomena to detergency was tried for porous solids such as cotton cloths. When an electric field was applied perpendicularly to the cloth, electro-osmotic flow took place and the soil particles were removed from the fiber surfaces. In contrast to ordinary hydrodynamic flow of Poiseuille scheme which gave a parabolic velocity profile, the electro-osmotic flow gave rise to a velocity profile of piston flow, and hence produced a drastic detaching force on particles; washing by electro-osmotic flow was found to give a higher detergency without damage to cloths than mechanical washing by a launderometer. This method has a feature of removing soil particles on surfaces under cover and on irregular surfaces, where ordinary mechanical washing methods are ineffective.

Further investigation using model systems which consist of a quartz plate and nylon particles or iron (III) oxide particles confirmed the effectiveness of particle removal by electro-osmotic flow in comparison with the ordinary flow of water without electrokinetic effect. The analysis of removal processes by using the well-defined flow of electro-osmosis is useful in clarifying the mechanism of detergency in general, and will give information about the interaction between two bodies at close range.

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