⚸Effects of Adsorption on Detergency Phenomena: II

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ABSTRACT

Knowledge of adsorption of active agents onto different interfaces is fundamental to their technical application in the washing and cleaning process. Particularly important is their influence on interactions in multicomponent systems. By the formation of mixed adsorption layers consisting of at least 2 surfactants, an enhancement of adsorption is attained as compared with the adsorption isotherms of individual components. Parallel to this, the washing effect also increases. Water-soluble complexing agents are adsorbed specifically onto polar surfaces, particularly onto such surfaces that contain calcium ions. Their affinity to such surfaces is significantly greater than those of surfactants which are mainly adsorbed onto hydrophobic interfaces. Due to the complex composition of soil, both components complement each other. In addition to their ion exchange capacity for bivalent ions, zeolites have a certain ability to adsorb molecularly dispersed soil components as well as colloidal particles. Hence, they have a special effect as antiredeposition agents. Polymeric antiredeposition agents act by formation of adsorption layers on pigments and fibers. Only such compounds that cannot be displaced completely from interfaces by competing adsorption with surfactants show positive antiredeposition effects.

INTRODUCTION

Part I of this paper described the general importance of adsorption to soil removal as well as several basic results depending on the constitution of individual surfactants. In multicomponent systems, the effects may be substantially changed. Hence, mutual effects of active components are crucial.

ADSORPTION AND DETERGENCY OF SURFACTANTS IN MIXTURES

Because changes of interfacial chemical properties with regard to soil removal in washing and cleaning are positive with increasing adsorption, enhancement of adsorption must be attained by various physicochemical measures. A procedure frequently applied in practice is the optimization of products by directed application of mixtures of different agents that leads to an enhancement of nonspecific adsorption effects via the formation of adsorption layers of surfactants of different constitution. This is particularly pronounced in mixtures of anionic and nonionic surfactants. Depending on the concentration and on the ratio of both types of surfactants in the solution, mixed layers form in which each species is represented in different amounts (1,2).

With anionic surfactants, an incorporation of nonionic surfactants in the layer brings about a shielding effect of the negatively charged hydrophilic groups which causes an enhanced adsorption, already with substantially lower total concentrations than in the case of anionic surfactants, being the only kind of surfactants in the solution.

Figure 1 depicts this behavior for the water/air interface of a mixture consisting of very little nonionic surfactant and much anionic surfactant. The large shift of the surface tension vs concentration curve of the surfactant mixture by a factor of more than 10 with respect to the curve of the pure anionic surfactant shows the potential possibilities resulting from formation of mixed surfactant layers at interfaces.

Part I of this publication emphasized adsorption at solid/liquid interfaces. Using surfactant mixtures, it will be established that the general statements on the importance of ad-
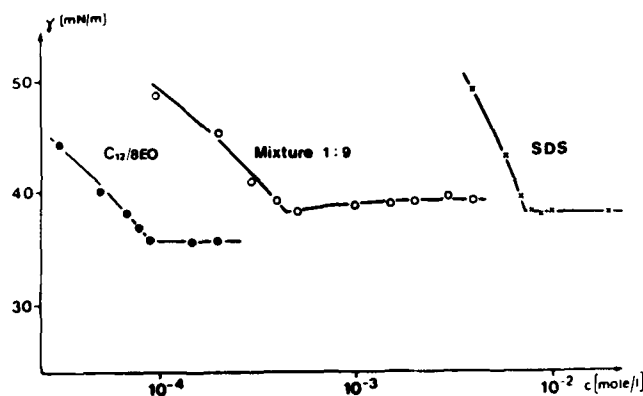

FIG. 1. Surface tension of surfactant mixtures in comparison to their components. Experimental conditions — temperature: 25 C; $C_{12}/8$ EO: dodecyloctaglycol-ether; SDS: sodiumdodecyl-sulfate.
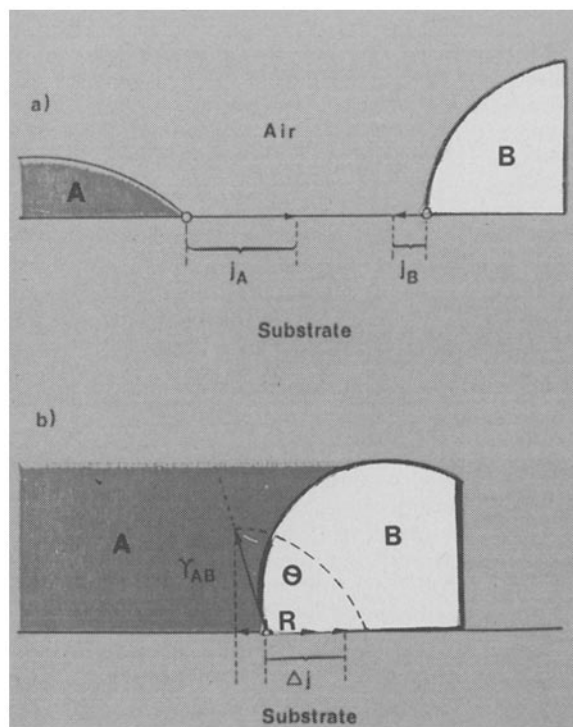

FIG. 2. Two liquids: (A) surfactant solution and (B) oily soil on a solid substrate (a) separated from each other, (b) in contact with each other.

sorption remain valid at gas/liquid and liquid/liquid interfaces, too. In this context, the strong decrease in interfacial tension between oily soil and detergent solution, which is a result of surfactant adsorption, is particularly important to the removal of oily soil.

Figure 2 schematically represents the removal of oily soil by the roll-up mechanism. The wetting tension, j, is active along the boundary of the 3 phases liquid/gas/solid. It is de-

fined according to Equation I:

$$j = \gamma_S - \gamma_{SL} = \gamma_L \cos \theta, \qquad \text{[1]}$$

where γ_S = interfacial tension solid/air; γ_{SL} = interfacial tension solid/liquid; γ_L = interfacial tension liquid/air; j = wetting tension; and θ = contact angle. γ_{SL} and γ_L are reduced by adsorption of surfactants. The decrease of γ_{SL} implies an increase of j, according to Equation I. When 2 drops of different liquids, e.g., detergent solution A and oily soil B, are put close together on a solid surface S, then the respective wetting tensions j_A and j_B are active in the basis surface. When both liquids come into contact and form a joint interface, the difference of the wetting tensions, Δj, defined as roll-up tension, is active at the contact boundary. In addition, there is a fraction of the interfacial tension γ_{AB} acting on the basis surface with opposite sign, il., $\gamma_{AB} \cdot \cos \theta_B$, where θ_B is the contact angle in the oily phase B.

As defined by Equation II, the tension R is the resulting force acting in a direction that causes the oil drop to be constricted:

$$R = \Delta j + \gamma_{AB} \cdot \cos \theta_B. \qquad \text{[II]}$$

By adsorption of surfactants from phase A, Δj is increased and γ_{AB} is reduced. As $\cos \theta_B$ is negative in the case of an obtuse contact angle, both factors result in an increase of the tension R according to Equation II and, hence, in an enhanced roll-up of the oil drop.

The reduction of the water/oil interfacial tension is, similar to surface tension, particularly strong in mixtures of ionic and nonionic surfactants. Figure 3 illustrates the dynamic interfacial tension of the system water/olive oil in dependence on the mixing ratio of the rather disadvantageous anionic surfactant sodium dodecylsulfate (SDS) with nonylphenol octaglycol ether (NP8) at constant overall concentration. The interfacial tensions of the pure surfactant solutions are so high that they are no longer detectable with the measuring method applied (spinning drop method), whereas addition of small amounts of the nonionic surfactant to the anionic surfactant have such significant effects that the interfacial tension is reduced to as low as 1,5 mN/m. The minimum of the interfacial tension is attained with a ratio of nonionic surfactant to anionic surfactant of ca. 1:4.

As known from adsorption experiments with several pigments, adsorption of anionic surfactants is enhanced by addition of nonionic compounds by the shielding effect, especially below the critical micellar concentration and in the range of low surfactant concentrations (1). Hence, increased adsorption from mixtures of anionic and nonionic surfactants, as represented by the model in Figure 3, with a concentration ratio of 1:4, should enhance the overall washing effect in the range of low surfactant concentrations. The results shown in Figure 4 confirm this conception. The fundamental effect is independent of the type of fiber and is basically observed with all soilings containing hydrophobic pigments and oils. In practical development of detergents, this knowledge is used in such a way that, in product formulations, mixtures of surfactants are applied as a rule in very definite ratios as they are most suitable for the purpose. Optimal conditions of adsorption onto interfaces are prerequisite here.

COUNTERION EFFECTS

Another means of enhancing adsorption, especially of anionic surfactants, results from counterion effects exerted by ordinary inorganic electrolytes. In such systems, the electric double layer is strongly compressed at all interfaces which leads to an enhanced attraction of, especially, ani-
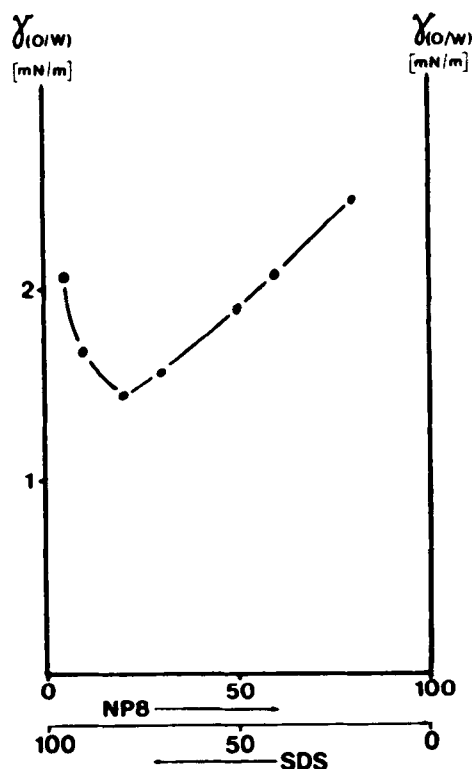

FIG. 3. Influence of the ratio of surfactants on the interfacial tension of water/olive oil at $1 \cdot 10^{-3}$ (mol/L). Experimental conditions — water hardness: 8 °d; temperature: 30 C; pH value: 7; time: 5 min; NP 8: nonylphenoloctaglycolether; SDS: sodiumdodecylsulfate.
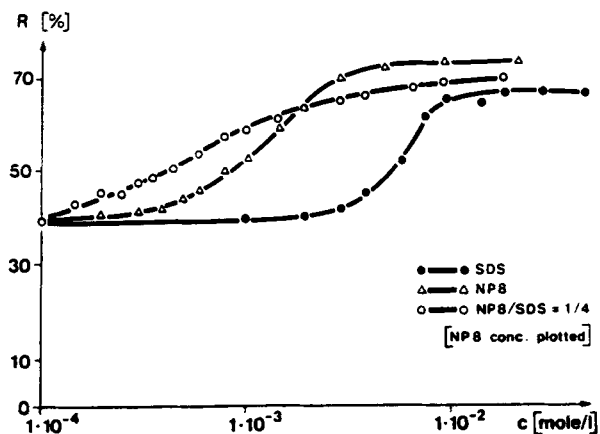

FIG. 4. Detergency of nonylphenoloctaglycol-ether (NP 8) and sodiumdodecylsulfate (SDS) on cotton. Experimental conditions — water: deionized; washing temperature: 30 ± 2 C; textile/solution ratio: 1:12; fabric: finished cotton.

onic surfactants. According to Schulze-Hardy's rule, these effects increase with increasing valency of the counterion. The positive counterion effect of sodium ions is overlapped by the strong reduction of surfactant solubility, especially in presence of calcium ions. Additionally, the electric double layer is strongly compressed with calcium ions in such a way that the electric repulsion between pigments and fibers is impaired.

Magnesium ions indeed reduce the solubility of conven-

tional surfactants. This reduction is substantially smaller than caused by calcium ions. Corresponding with this and in accordance to the Schulze-Hardy rule, the compression of the electric double layer with magnesium ions is stronger than with sodium ions. However, the disadvantageous properties of calcium ions do not exist here. Among ions frequently occurring in nature, magnesium ions hence take a special mid-position (3). Figure 5 shows that bivalent magnesium ions can reduce the surface tension of anionic surfactants more than monovalent cations, e.g., sodium ions.

As in alkaline, aqueous media, nearly all solid and liquid interfaces are negatively charged, mutual repulsion between the interfaces and the equally negatively charged hydrophilic groups of the anionic surfactants occurs. So far, a potential barrier is to be surmounted at which the hydrophobic interactions between the hydrophobic molecular parts and the interfaces become stronger than the sum of the electrostatic repulsion forces and the attractive forces with the solvent molecules. The compression of the electric double layer and, hence, the reduction of the mutual repulsion of the equally charged partners as well as the mass action law based reduction of solubility and dissociation of the anionic surfactants should result in an enhanced washing effect. Figure 6 shows how significant these effects are for the washing and cleaning process. It represents the removal of soil by sodium tetradecylsulfate, a surfactant that is comparatively less suitable for washing, increasing electrolyte concentration. It is understood that addition of small amounts of electrolyte strongly improves washing performance. Analogous to the trend of the effect of counterions on the electric double layer, the washing performance will change more weakly in higher counterion concentration ranges. With respect to the kind of counterion, Figure 6 shows that the effects increase with increasing valency. Hence, magnesium chloride indeed has a stronger positive influence on the washing effect than sodium chloride. Calcium ions in smallest concentrations basically have the same property; however, this is reversed with slightly increased, but still small, concentrations.

Because of the disadvantageous influence of calcium ions, complexing agents, mainly sodium triphosphate (STP), are used in laundry detergents. Sodium triphosphate unselectively complexes calcium and magnesium so that the stronger counterion effect of magnesium is substituted by the weaker influence of sodium. In conventional laundry detergents, only the counterion effect of sodium ions from sodium sulfate, sodium perborate or STP, e.g., can be active. However, when systems in which STP is substituted by zeolite A are considered, attention must be given to the fact that a higher selectivity exists toward calcium than toward magnesium ions. In the same way, ion exchange kinetics, especially at lower temperatures, is slower for magnesium ions because penetration into the cavities is impeded by the larger hydrate shell surrounding the ion. Thus, calcium is almost completely eliminated from the system by zeolite A, whereas a certain remaining amount of magnesium is still kept in solution under practical conditions. Hence, in using zeolite A in laundry detergents and cleaning agents, the positive counterion effects of magnesium can be used. These do not appear when phosphate is used due to the higher complex formation constant of STP.

Model experiments testing the washing effect of the linear alkyl benzene sulfonate (LAS), produced in large-scale, and zeolite A confirm that the existence of magnesium ions in the presence of zeolite A, indeed, has a positive effect on the washing process (3). The effect of magnesium counterions on alkyl benzene sulfonate is analogous to that on sodium n-tetradecylsulfate. It is notable that the positive effect of magnesium counterions is maintained upon addi-
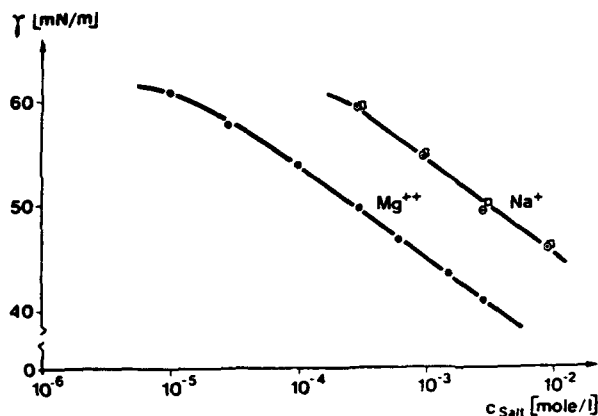

FIG. 5. Influence of sodium and magnesium salts on the surface tension of SDS. Experimental conditions — surfactant concentration: 1 o 10^{-3} mol/L; □ - □, NaCl; ⊕- ⊛, Na$_5$P$_3$O$_{10}$; ● - ● MgCl$_2$.
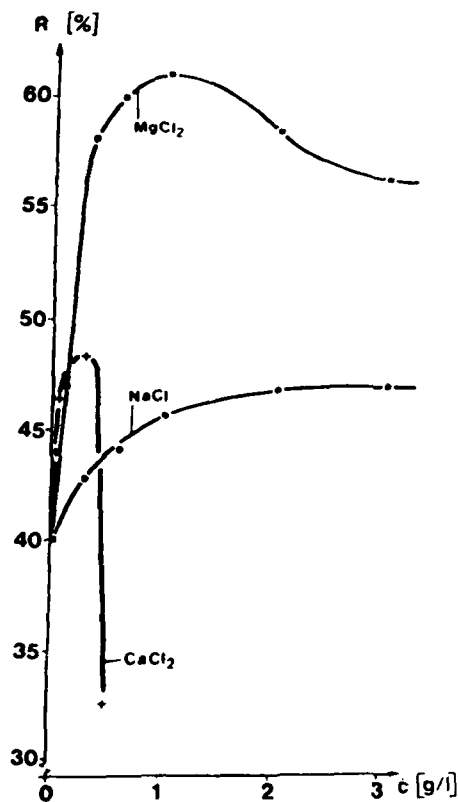

FIG. 6. Counterion effects on detergency of sodium-n-tetradecylsulfate on polyester/cotton. Experimental conditions — surfactant concentration: 5· 10^{-3} mol/L; temperature: 60 C.

tion of practically relevant sodium ion concentrations. Under the actual test conditions, the maximum effect of the magnesium ion lies at 25°d magnesium hardness, and addition of sodium chloride weakens the effect. With particularly high sodium chloride concentrations, this effect may even disappear. This was observed in an experiment with the system LAS/zeolite A/magnesium hardness upon addition of 0,08 mol/L of sodium chloride. For laundry detergents, the counterion concentration varies very strongly and depends on the special detergent composition. The assumed value of 0.04 mol/L of sodium counterions in Figure 7 sup-

posedly represents an average possible value with a relatively high substitution of sodium triphosphate in a laundry detergent. The pronounced maximum of the curve is, as in all complex processes, very strongly dependent on the special surfactant constitution, the textile fiber, the kind of soiling and the entire composition of the laundry detergent. For more poorly soluble surfactants, it will be shifted to lower magnesium ion concentrations. As a general principle, however, we must base our considerations on the fact that, if a proportion of the magnesium ions existing in nature (amounting to ca. 5-6 d in extreme, very rare cases) remains in the system, these ions have a positive effect on the overall result.

ADSORPTION ONTO ZEOLITES

Upon application of water-insoluble ion exchangers of the zeolite type in laundry detergents, additional adsorption effects that cannot be observed in conventional detergents are important. As a competing substrate for the adsorption of molecularly dispersed soluble substances and colloidal particles, zeolites are able to substantially contribute to the wash result, even in the range of antiredeposition.

In alkaline, aqueous media, zeolites are strongly negatively charged so that no undesired adsorption of important surfactant components and complexing agents onto the surface occurs. By the spray-drying process, however, the surface is made very slightly hydrophobic by laundry detergent ingredients. Hence, a certain adsorption affinity exists for higher molecular negatively charged particles. Figure 8 illustrates this behavior by a comparison of the adsorption of the dyestuff benzopurpurine onto pure zeolite A and onto zeolite A extracted from a finished laundry detergent. It is recognized that no adsorption exists onto pure zeolite whereas zeolite slightly modified by the spray-drying process has gained a certain adsorption affinity. As a consequence of this weak adsorption affinity, a significant improvement of the antiredeposition effect of a detergent after repeated wash cycles is observed. Table I shows this effect clearly. The zeolite-based laundry detergent tends to show a higher antiredeposition effect than a conventional one, the enhancement between the products produced by simply mixing the single ingredients and a spray-dried commercial product being clearly distinguishable. Obviously, this effect decreases with increasing detergent concentration.

Under particularly extreme conditions, under which very many graying soil particles may get into the system, zeolite-based laundry detergents may offer special advantages. By adsorption and heterocoagulation with such particles, deposition onto fabrics is strongly reduced and the reflectance values increase significantly (4). Table II shows the results of washing machine tests in which the detergency effect of phosphate-based detergents is compared to that of zeolite-containing model detergents for various kinds of white fabrics in presence and absence of particularly intensively black coloring components. The effects are very significant and show that the importance of the competition between zeolites and textile substrates for the adsorption of graying soil components is very pronounced.

SPECIFIC ADSORPTION

As depicted by Figure 5, STP enhances adsorption of anionic surfactants onto interfaces by unspecific counterion effects. However, this unspecific counterion effect can also be produced with other added electrolytes. More substantial for complexing agents, though, is specific adsorption onto some polar soil pigments that can play a part in the washing process (5,6).
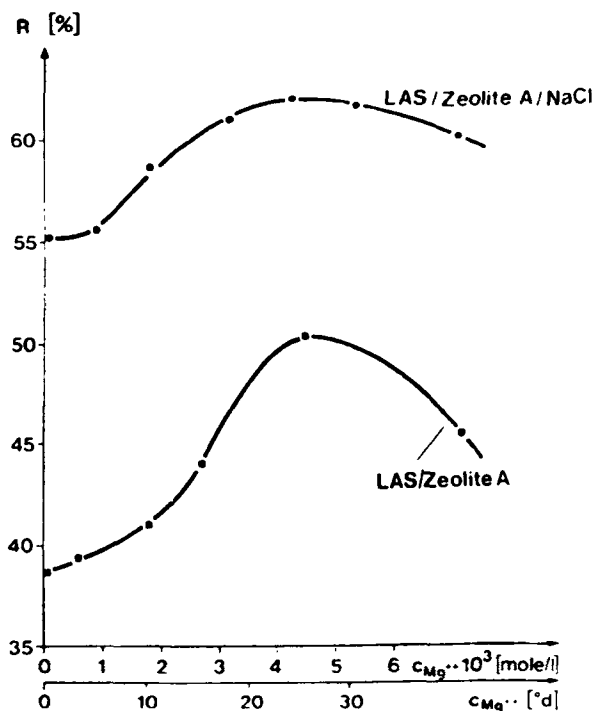
FIG. 7. Effect of Mg^{++}-ion on detergency of LAS/Zeolite A mixtures on polyester/cotton at 60 C. Experimental conditions — alkylbenzene-sulfonate (LAS). 1 g/L; Zeolite A: 2 g/L; NaCl: 0.4 mol/L; temperature: 60 C.
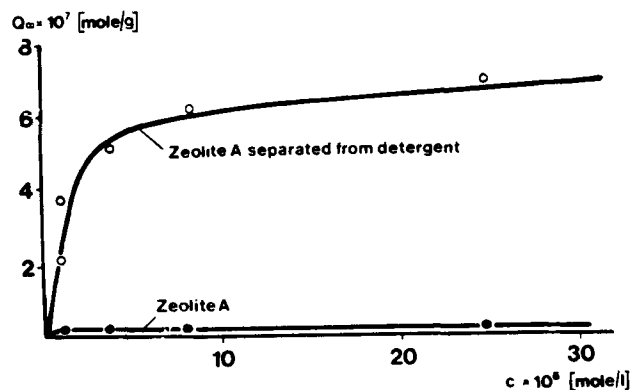

FIG. 8. Adsorption of benzopurpurine on Zeolite A. Experimental conditions — temperature: 23 C.

TABLE I

Redeposition Test in Zeolite-A-Containing Detergent Solutions after Three Cycles of Laundering

Detergent	Reflectance (%) polyester cotton laundered with:		Reflectance (%) finished cotton laundered with:	
	5 g/L	7.5 g/L	5 g/L	7.5 g/L
Spray-dried detergent with Zeolite A	48	63	70	73
Zeolite-A-containing detergent (components simply mixed)	45	61	64	71
Detergent without Zeolite A	40	59	60	70

Initial value for both fabrics: 84% remission.

TABLE II

Comparison of Detergency of Phosphate and Zeolite-A-Containing European-Type Heavy-Duty Detergents on Various White Wovens in the Absence and Presence of Black-Coloring Particles

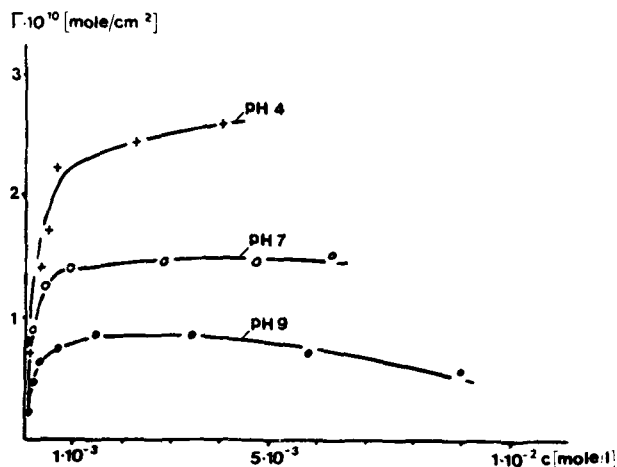| Model detergent	Nonfinished cotton:		Finished cotton:		Polyester/cotton:	
	Without black (all fabrics)	With black (all fabrics)	Without black (all fabrics)	With black (all fabrics)	Without black (all fabrics)	With black (all fabrics)
With Phosphate alone	83	67	74	66	70	49
With Zeolite A/ phosphate mixture	82	75	73	66	74	57

Detergency: % whiteness.
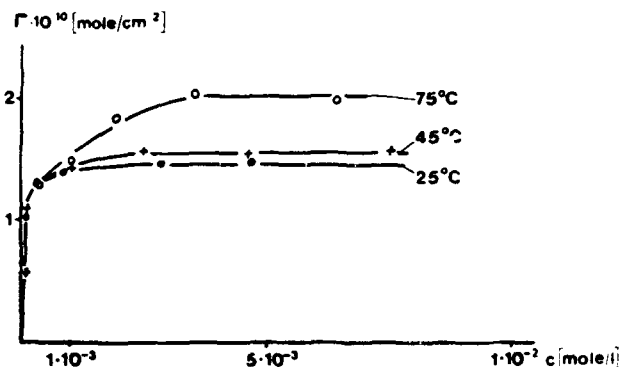

FIG. 9. Adsorption isotherm of STP on Al₂O₃ at 23 C.

FIG. 10. Adsorption isotherm of STP on Al₂O₃ at pH 7.

Figures 9 and 10 show adsorption isotherms of sodium tripolyphosphate onto aluminium oxide. As variable parameters, we have pH value and temperature, respectively. A strong, pronounced influence of the pH value can be observed here as the affinity of the anion to the surface increases significantly with decreasing pH. This effect can be read both from the adsorption densities in the range of saturation and from the degree of steepness of the initial part of the isotherms. Although adsorption, as a rule, has a negative temperature coefficient, Figure 9 illustrates that adsorption increases with rising temperatures in the system investigated. Calorimetric measurements indicate that the adsorption process of the polyanions is controlled by an increase of entropy. Without further profound examination of the special and different mechanisms of adsorption of complexing agents onto various polar surfaces, we may deduce from the investigations that the always-specific interactions of higher adsorption energy are concerned. The sign of the adsorption changes in Figures 9 and 10 also indicates that chemisorption is concerned. The high specificity even causes a displacement of surfactants from such surfaces due to their smaller adsorption energy (7).

Figure 11 shows that the adsorption of a poor sequestrant, such as sodium citrate, is smaller than that of a good one, such as sodium triphosphate (STP) (curves 1a and 2a), and that, as a consequence, the displacement of anionic surfactant from the surface by the poorer sequestrant is less pronounced (curves 1b and 2b). The weaker adsorption
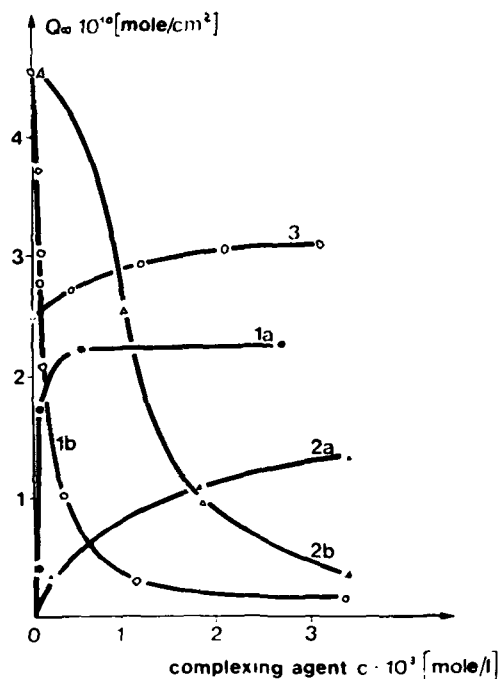

FIG. 11. Competitive adsorption Q∞ of STP and sodium citrate with anionic surfactants onto carbon black and γ-Al-oxide at pH=7 and 70 C. Initial surfactant concentration 1.5 × 10⁻² mol/L. Curve 1a: STP at γ-Al₂O₃; curve 2a: citrate at γ-Al₂O₃; curves 1b and 2b: n-decylbenzene sulfonate in presence of STP and citrate, respectively, at γ-Al₂O₃; curve 3: n-dodecylsulfate in presence of STP at carbon black.

of sodium citrate is also matched by a poorer washing efficiency of this sequestrant compared to sodium triphosphate. While sequestrants impede the adsorption of anionic surfactants onto γ-Al-oxide, they enhance such adsorption onto carbon black or synthetic fibers. This effect is solely due to the electrolyte character of STP.

The adsorption of complexing agents is strongly enhanced by the presence of multivalent cations in the adsorbate, especially by calcium salts. In soil on fibers, as well, salts of multivalent cations can almost always be found. As a rule, inorganic salts, e.g., calcium carbonate, are found. However, soil components frequently have chemical bonds with the fiber via cation bridges. These can form bridges via carboxylic groups that always exist in cotton by oxidation and via reactive centers of metal oxides or from soaps originating from sebum. The salt-like bonds are weakened by complexing agents, and the cation is dissolved by complex formation and desorption. Hence, no or only little adsorption of complexing agents is observed in the equilibrium frequently, although significant adsorption exists before equilibrium is attained. Dissolving of soil components by complexing agents results in break-up and facilitated removal of soil.

The stabilization of suspensions of kaolin can be used as an example for the consequences of the different adsorp-
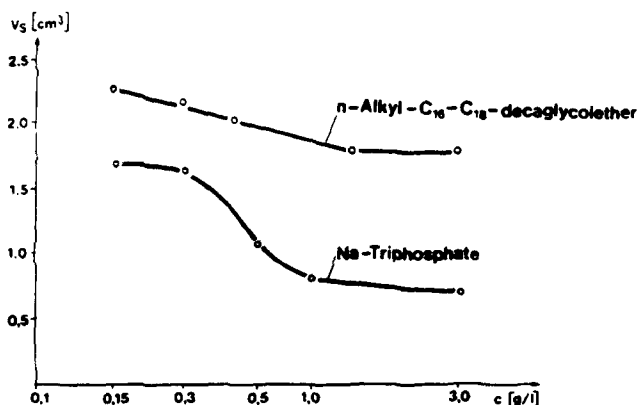
tion types, and thus the effect, of surfactants and complexing agents onto calcium-containing clay minerals. Figure 12 represents the sediment volume of kaolin vs concentration of STP and surfactants. Besides a soil removing effect for pigments, adsorption of surfactants and complexing agents results, as mentioned before, in dispersion and stabilization of pigments, and the possibility of a repeated deposit of removed pigments onto the substrate in the course of the washing process is reduced. The sediment volume can be considered a characteristic quantity for the dispersion power. When less effective dispersion agents are used that are insufficiently strongly adsorbed and are not able to build up a steric protection layer around the molecule or do not sufficiently increase the negative charge, coagulation processes are unsatisfactorily hindered and hence voluminous sediments form. Well-dispersed pigments deposit as close packings with small volumes. The less specific adsorbing n-alkyl decaglycol ether shows significantly higher sediment volumes than the strongly specific adsorbing STP. As mainly mixed soils consisting of the most different hydrophobic and polar components are to be removed from the fiber surface during washing, complexing agents and surfactants thus complete each other in an ideal way in their effect at interfaces.

Analogous to the explanations just given complexing agents show pronounced specific interactions with textile fibers, as well. Figure 13 shows the different effect of complexing agents and surfactants on detergency for a series of various textile fibers. For unfinished cotton, the anionic surfactant selected, alkylbenzene sulfonate, has nearly no effect, whereas STP already shows a considerable washing effect. For finished cotton, too, the effect of STP is higher than that of the sole surfactant. This fact changes when more hydrophobic fibers are used. For polyester/cotton blend and pure polyester, a significant effect by STP can still be observed. This effect can be attained by the surfactant, as well. At the same time, the overall washing effect decreases. For the very hydrophobic polyolefin fibers, the washing effect of the surfactant is substantially more pronounced than that of the complexing agent. These examples show how surfactants and complexing agents complete each other, not only for mixed soils, but also for different textile fibers. Particularly notable are the great enhancements of the effect of mixtures in comparison to the effect of the individual types of compounds.

FIG. 12. Sediment volume of kaolin in water solutions. Experimental conditions — kaolin: 0.5 g; volume: 10 cm³; water hardness: 16 °d.
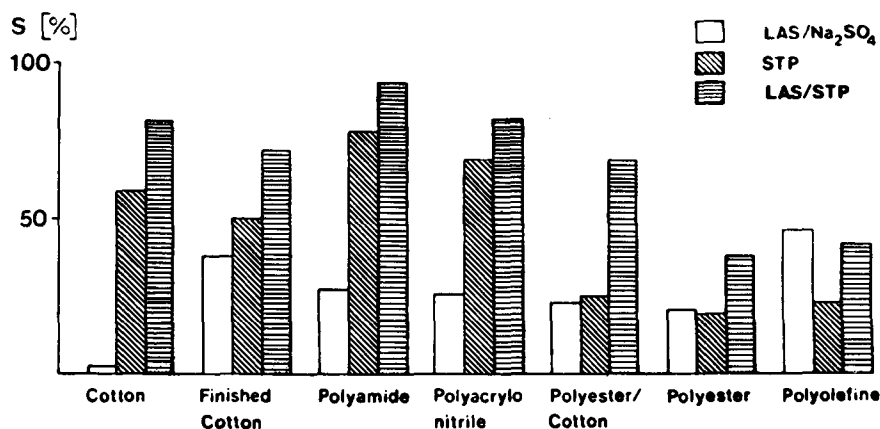

FIG. 13. Effect of the textile fibers on soil removal. Experimental conditions — alkylbenzene-sulfonate (LAS): 1 g/L; sodium triphosphate (STP): 2 g/L; sodium sulfate: 2 g/L; water hardness: 16 °d; ratio Ca:Mg: 4:1; temperature: 90 C for cotton and finished cotton, 60 C for synthetic fibers.
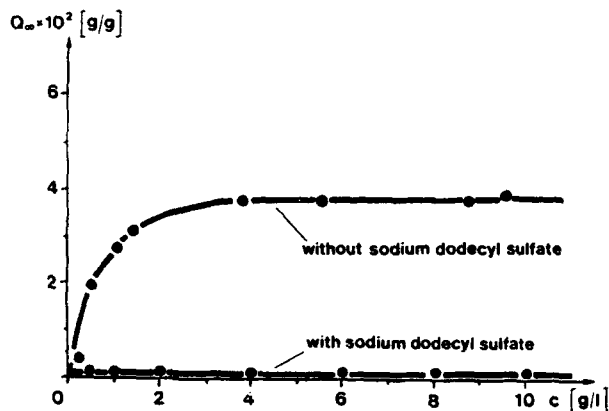
(S&D 84)

$Q_\infty \cdot 10^2 \; [g/g]$

FIG. 14. Adsorption of gelatin on powdered glass. Experimental conditions — temperature: 25 C.

FIG. 15. Influence of SDS on gelatin layer thickness, S, measured ellipsometrically. Experimental conditions — pH: 8.5; gelatin concentration: 0.5 g/L.

MACROMOLECULES IN LAUNDRY DETERGENTS

Besides low-molecular compounds, both soil and detergents contain natural or synthetic macromolecules. Two ways of consideration seem to be appropriate here. Natural proteins from blood, egg and proteinaceous food can be adsorbed onto textile fibers and have to desorb in the course of the washing process. Laundry detergents frequently contain polymeric antiredeposition agents that can prevent a redeposition of removed graying pigments by their adsorption and formation of steric protection layers onto substrate and pigments. Desorption of natural proteins and adsorption of antiredeposition agents in one event are opposite processes that particularly require a careful selection of antiredeposition inhibiting polymers.

In binary systems, macromolecules are effectively adsorbed onto solid surfaces irreversibly. The reason for the effective irreversibility of the process is the formation of many contact sites between macromolecule and substrate. From a statistical viewpoint, sufficient contact sites always ensure formation of bonds between molecule and substrate independent of the effective bonding strength of a contact site. It has to be considered that mostly weak hydrophobic interactions are concerned here. In multicomponent systems that contain surfactants in addition to macromolecules, competing adsorption at the surface of the substrate may occur. Thereby, surfactants successively break up the single contact sites of the macromolecule and displace it from the interface. This mechanism is, as a rule, observed with nonionic surfactants. Anionic surfactants frequently can form adsorption complexes of polymer and surfactant.

As a consequence, the conformation of the macromolecules is changed, which results in a change of the attraction to the interface.

Figure 14 depicts the adsorption of gelatin onto glass with and without addition of sodium dodecylsulfate. The figure illustrates that the adsorption isotherms strongly differ from each other. Adsorption of macromolecules is reduced by the addition of surfactants and virtually decreases to zero. Figure 15 shows the ellipsometrically determined thickness of a layer of gelatin vs the concentration of subsequently added sodium dodecylsulfate. The result shows that previously adsorbed gelatin may desorb and be displaced from the surface by surfactants subsequently added.

This process of competing adsorption of surfactants and macromolecules, which is particularly important with regard to soil removal, as well as the formation of complexes consisting of macromolecules and surfactants considerably impedes the opposite process of the adsorption of antiredeposition agents. The adsorption of antiredeposition agents, as a rule, occurs selectively and is dependent both on the chemical constitution of the substrate and on that of the polymer. For instance, the antiredeposition effect of carboxymethylcellulose is limited on hydrophilic fibers such as cotton. Cellulose ethers, e.g., hydroxypropylcellulose, show a good effect, mainly on hydrophobic fibers such as polyester. To ensure sufficient antiredeposition of fiber blends, combinations of 2 or even several antiredeposition agents are used frequently. In this connection, the absolutely adsorbed amount of substance has no controlling effect, but rather has the hydrophilation effect due to ad-

TABLE III

Comparison of Increments of Wetting Tension on Polyester with Increments of Reflectance for a European-Type Heavy-Duty Detergent (DI) and a Special Low-Temperature Detergent (DII) on Polyester[a]

D I (g/L)	D II (g/L)	Na-carboxymethylcellulose	Methylhydroxypropylcellulose	Hydroxyethylcellulose	D I Δj (mN/m)	D II Δj (mN/m)	D I $\Delta R(\%)$	D II $\Delta R(\%)$
		Antiredeposition agent — (%) addition to detergent:			Increments of wetting tension		Increments of reflectance	
7.4	4.5	0	0	0	0	-1	—	—
0	0	0.5	0	0	1	1	—	—
7.4	4.5	0.5	0	0	2	0	3	-1
0	0	0	0.5	0	22	22	—	—
7.4	4.5	0	0.5	0	14	14	17	16
0	0	0	0	0.5	22	21	—	—
7.4	4.5	0	0	0.5	3	2	5	0

[a] Δj = wetting tension for an advancing contact angle; R = reflectance; Δ = difference of wetting tensions against pure water after rinsing for treated and nontreated polyester; ΔR = difference of reflectance measured after three cycles of laundering in a standardized redeposition test on polyester fibers with and without polymer.
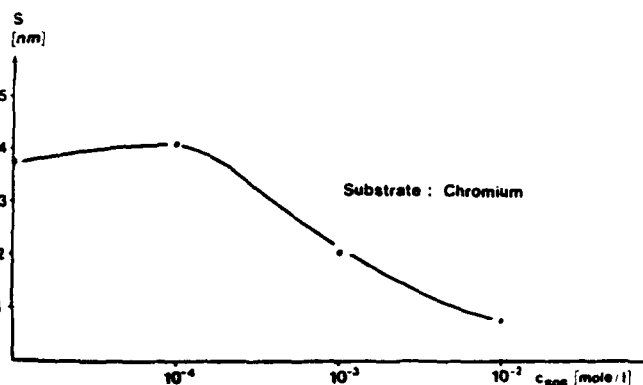
sorption, i.e., the change of the state of the surface compared to the basic state of the noncovered fiber surface. The latter state can be characterized by the increments of the wetting tension of the surface with respect to pure water (see Eq. I).

Table III shows that carboxymethylcellulose which has been applied in detergents as an antiredeposition agent for cotton for a long time does not effect any changes on polyester. Hydroxypropylcellulose, however, makes the surface of polyester very strongly hydrophilic. Particularly notable is that the effects, though slightly reduced, are maintained in both model detergents. A significant increase of the antiredeposition effect is observed from the increments of the reflectance values only under this condition. Hydroxyethylcellulose may be considered a representative substance for many polymers that certainly adsorb well from aqueous solutions and that cause significant hydrophilation in pure

water, but that can yet lose their effect almost completely in laundry detergent solutions because of competing adsorption with surfactants.

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