Effects of Adsorption on Detergency Phenomena: I

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ABSTRACT

Knowledge of the adsorption of surface-active substances onto different interfaces is of basic importance for its technical application in washing and cleaning processes. Important parameters are adsorption kinetics and adsorption equilibria. The criteria of adsorption kinetics and adsorption equilibrium change in opposite directions with increasing length of the hydrophobic group. Equilibrium adsorption increases exponentially, whereas the diffusion coefficient decreases linearly with increasing number of CH_2 groups in the *n*-alkyl part of nonbranched surfactants. Branching of the hydrophobic group has the same effect as shortening the chain length. The wetting effect changes in the same direction as the diffusion coefficient, whereas the washing effect changes similarly to equilibrium adsorption. The generally positive temperature effect on soil removal may be reversed in the opposite direction for nonionic surfactants at temperatures above the cloud point. Separation of phases brings about a decrease of adsorption and washing performance.

INTRODUCTION

Washing and cleaning in aqueous media are complex processes in which numerous mechanical, physicochemical and chemical effects concur. Basically, it should be distinguished between the primary step of removal of poorly water-soluble deposits, i.e., soil, from soiled surfaces by an aqueous solution of water-active substances and the secondary stabilization of the dispersed particles in the wash bath. Redeposition of soil that is removed from the fiber must be prevented.

The following effects exert a substantial influence on the washing process: composition of the detergent; kind of soil; properties of the substrate; mechanics of laundering; time; and temperature.

Most parameters cannot be changed or can only be changed in a limited range so that, generally, only the composition of the laundry detergent can be influenced.

When the time and technology parameters of washing or cleaning are considered constant, the effect depends on the special interactions between the surface of the substrate, the soil and the components of the detergent. Here, not only the mutual interactions of these partners are to be considered but, particularly with soil, also those of the various components of the soil between each other. The great multiplicity of the chemically different partners that play a part in the washing and cleaning process indicates how complex the whole process must be.

When washing and cleaning are considered as separations without changes in matter, then, in the primary step of soil removal, only surfactants and complexing agents are directly effective and, in an indirect way, water-insoluble ion exchangers and ordinary inorganic electrolytes, too. In preventing secondary redeposition of removed soil components onto the fibers, antiredeposition agents are additionally important.

Physical separation of soil from textiles is based on the nonspecific adsorption of surfactants onto different interfaces involved in the process and on the specific adsorption of complexing agents onto definite polar soil particles. The mechanism of calcium ion exchange that results in detachment of calcium ions from soil and fibers, as well as in break-up of the soil, and the compression of the electric double layer at interfaces by ordinary inorganic electrolytes effect jointly the dissolving of oily and particulate soil from textile substrates and hard surfaces. Table I summarizes those interface properties that are changed by adsorption of detergent ingredients onto different interfaces involved in the washing process. Thus, adsorption of detergent ingredients induces changes in the interfacial properties and may be considered a precondition for the detachment of soil. The importance of the individual changes of properties depends on the system and is different. Generally, it may be postulated that the changes in properties are positively influenced in the sense of the washing process with increasing equilibrium adsorption and adsorption kinetics.

EVIDENCE OF THE IMPORTANCE OF SURFACTANT ADSORPTION TO THE WASHING PROCESS

An analysis of the importance of adsorption to soil removal is conducted by comparing sodium *n*-alkylsulfates with sodium fatty acid methylester α-sulfonates. Investigations with several synthetic and native textile fibers show that sodium fatty acid methylester α-sulfonates in comparison with sodium *n*-alkylsulfates with equal chain length of their hydrophobic part give slightly less advantageous wash results. For both homologous series, however, soil removal increases with increasing chain length in the hydrophobic part. This is illustrated in Figure 1 with the detergency on polyamide of the trademark Perlon® as an example (1).

For several different classes of homologous compounds, it was shown that the amount of substance adsorbed onto hydrophobic substrates in the state of equilibrium increases with increasing molecular weight of the adsorbent. This means that, according to general physicochemical laws, the adsorption forces for surfactants will increase with increasing length of the hydrophobic part, and that a rise in the equilibrium adsorption is to be expected. Because of an increase of the hydrophobicity of the hydrophobic part there is an enhancement of the interaction between the adsorbent and the surfactants. The logarithm of the adsorbed amount Q_∞ in mol g^{-1} in the state of equilibrium is a linear function of n, the number of carbon atoms in the hydrophobic part. This has been shown several times (2).

$$Q_\infty = \exp(\alpha n + \beta), \qquad [I]$$

where α and β are characteristic constants.

Using graphite as a model of hydrophobic carbon-based particulate soil, the validity of Equation I is confirmed. However, it appears particularly remarkable that both classes of substance are arranged in one curve (Fig. 2). This result indicates that the stronger hydrophilic character of

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TABLE I

Interfacial Properties Which Are Changed by the Absorption of Ingredients of the Detergent Formula

Interface—water/air	Interface—liquid/liquid	Interface—solid/liquid	Multiple-phase systems
Surface tension	Interfacial tension	Disjoining pressure	Wetting
Foam formation	Emulsification	Suspension stability	Rolling up
Film elasticity	Electrical charge	Electrical charge	—
Film viscosity	Mass transfer	—	—

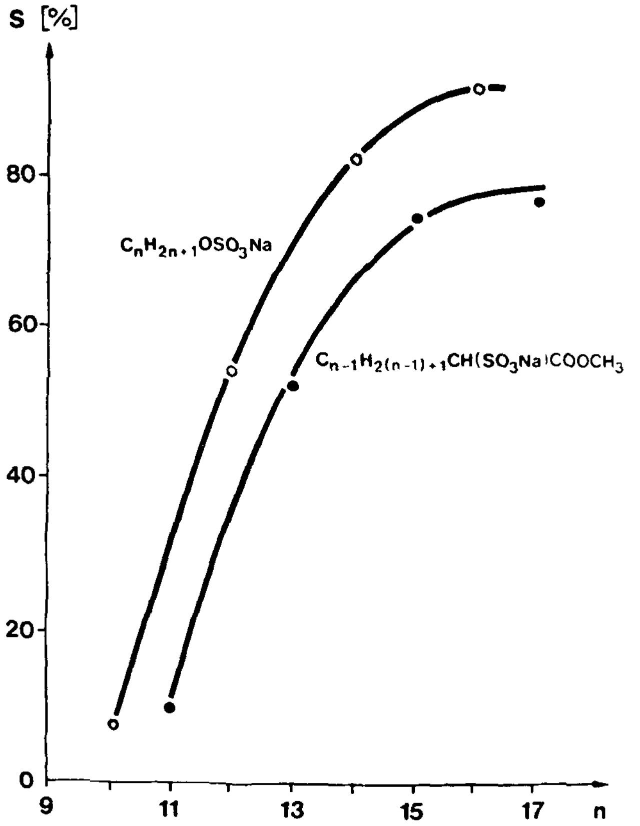


FIG. 1. Effect of chain length on soil removal for Perlon®. Experimental conditions—surfactant concentration: 2 · 10^{-3} (mol/L); temperature: 45 C; washing-time: 15 min; rinsing-time: 4 X 30 sec; textile/solution ratio: 1:30; water hardness: 0 °d; apparatus: Launder-o-meter. Soiling of test fibers was carried out from CCl_4 with 0.49% of sebum (2), 0.2% kaolin, 0.04% Fe_3O_4 and 0.02% carbon black with a particle diameter of 250 Å and a BET-surface of 111 m^2/g. Soil removal S is defined by:

$$S = \frac{(1g\ R_n - 1g\ R_s)\ 100}{1g\ R_o - 1g\ R_s}\ (\%)$$, where R_s = reflectance of solid fiber; R_o = reflectance of clean fiber; and R_n = reflectance of washed fiber.

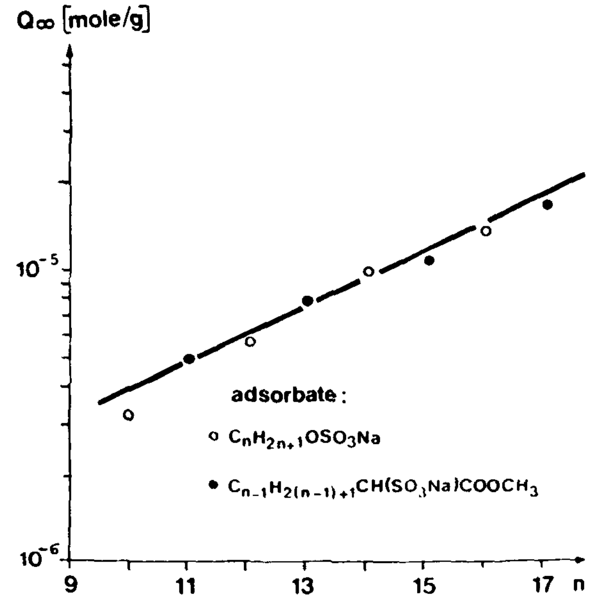


FIG. 2. Equilibrium adsorption of ionic surfactants on graphite. Experimental conditions—surfactant concentrations: 1 · 10^{-4} mol/L; graphite: 0.1 g; volume: 25 mL; temperature: 36.5 C.

the hydrophilic group of sulfo fatty methylesters and the contribution of the methyl group compensate one another in their interactions with the hydrophobic surface so that no significant difference in adsorption between either homologous series exists in this respect.

Because adsorption onto carbon-containing hydrophobic soils is equal for both classes of surfactants, differences in soil removal capability of the textile fibers cannot be explained by this property. Therefore, it must be assumed that adsorption onto another component of the soil or of the textile fiber causes these differences. The composition of the artificial soil used in these investigations comprised mainly sebum, carbon black, kaolin and iron oxide. In this respect, a different behavior of adsorption onto kaolin could be expected, especially as this soil pigment as an aluminium silicate shows, in contrast to the hydrophobic pigments carbon black and graphite, a different surface structure.

Kaolins differ from each other, depending on their geological deposit and especially with regard to the presence of bivalent ions. Figure 3 depicts the comparison of a natural kaolin with the Na^+ and Ca^{++} ions treated form. The graph shows the sediment volume of 0.5 g kaolin in 10 mL of distilled water. The Na^+ form is wholly hydrophilic, sediments in single particles and thus form dense sediments, whereas the Ca^{++} form is substantially less hydrophilic, tends to heterocoagulate and thus forms voluminous sediments. Natural kaolins mostly take a mid-position.

In comparison to sodium *n*-alkylsulfates, a decrease in adsorption of sodium α-sulfo fatty acid methylesters onto kaolin is observed. The dependence of the adsorption on the number of carbon atoms in the hydrophobic part (see Fig. 4) is in accordance with the same laws as for adsorption onto graphite; however, it is substantially stronger.

This can be deduced from the higher values of the change in free energy of adsorption per carbon atom in the hydrophobic part, by which the influence of the

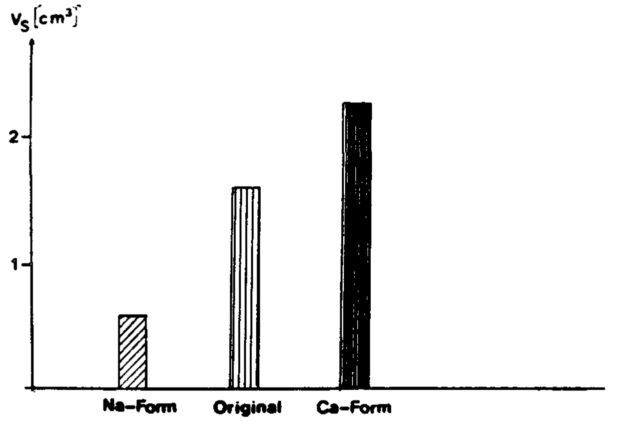


FIG. 3. Sediment volume of different kaolins in water. Experimental conditions–kaolin: 0.5 g; volume of water: 10.0 cm³; temperature: 25 C.

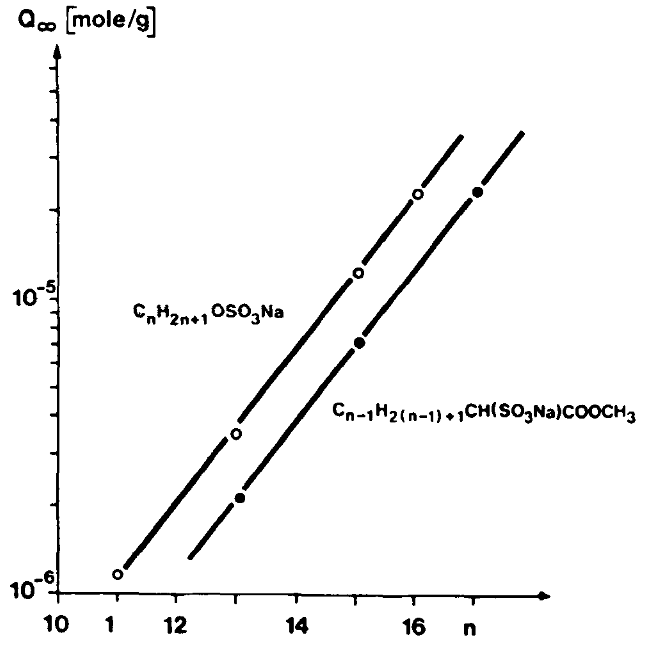


FIG. 4. Equilibrium adsorption of ionic surfactants on kaolin. Experimental conditions–temperature: 40 C; surfactant concentration: $5 \cdot 10^{-4}$ mol/L; kaolin: 0.2 g; volume: 45 mL.

different properties of the pigments manifests itself. The adsorption curves are shifted parallel to each other so that equal values of ΔE_A exist for both surfactant classes. The lower adsorption of sodium α-sulfo fatty methylesters onto kaolin is in line with their lower detergency.

A deduction is made about the importance of adsorption onto kaolin by washing experiments with soilings that were prepared with and without kaolin. Sodium *n*-pentadecylsulfate and sodium α-sulfo palmitic acid methylester, 2 comparable compounds with regard to the hydrophobic parts, show equal detergency toward soilings without kaolin (3). When kaolin is a component of the soiling, the reflectances of the textiles after washings with the ester are substantially lower than those for the sulfate (Table II). Although kaolin itself doesn't affect the reflectance very strongly, it obviously has a strong influence on the removal of the other pigments of the soil. This indicates that removal of the individual pigments from the fiber does not occur as an isolated phenomenon, but in large conglomerates consisting of carbon black, kaolin and iron oxide. This result shows that the hypothesis concerning the importance of adsorption to the washing process can be maintained.

In addition, it appears that, when 2 compounds with similar structure (e.g., 2 anionic surfactants or 2 nonionic surfactants) are compared, approximately equal wash results can be expected if these surfactants are about equally well adsorbed onto individual pigments contained in the soil and onto the textile fiber. Differences in the adsorption onto one single component of the soil or onto the textile fiber will have such an effect on the wash result that the compound which is less adsorbed will give the smaller soil removal. Of course, this statement is not valid for substances that remove soil pigments by different mechanisms, such as nonionic and anionic surfactants. (Nonionic surfactants do not influence the electrical charge whereas anionic surfactants will significantly increase the negative ζ-potential.) When the hydrophobic groups are equal, results of washing and adsorption depend on the nature of the hydrophilic group and decrease with increasing hydrophilicity. For oily soil, adsorption at the liquid/liquid interface, as well as solubilization, emulsification and formation of mixed phases have to be considered additionally.

IMPORTANCE OF EQUILIBRIUM ADSORPTION AND ADSORPTION KINETICS

In contrast to equilibrium adsorption, the basic equations of adsorption kinetics show, for free and pore diffusion, a decrease in the diffusion coefficient with increasing molecular diameter and weight. With respect to surface diffusion, mass transport is strongly dependent on surface coverage, too. Moreover, it makes a difference whether diffusion occurs in the first or in farther adsorption layers.

Thus, the overall process is not completely clear. However, we can expect a decrease in adsorption kinetics with increasing molecular volume. This requires an experimental examination of the dependence of the diffusion coefficient on the chain length. Figure 5 shows the change of the mean apparent diffusion coefficient $\bar{D}$ as a function of n, the number of carbon atoms in the hydrophobic part for the adsorption onto a highly porous activated carbon (4). For both sodium *n*-alkylsulfates and for *n*-fatty acids, the relationship is linear:

$$\bar{D} = -\Psi . n + \bar{D}_0$$

$$\text{with } \Psi = \frac{\bar{D}_i - \bar{D}_j}{i - j} , \qquad [II]$$

where $\bar{D}_0$ is the average apparent diffusion coefficient of the first member of the homologous series.

It is particularly notable that the chain length has an opposite effect on the 2 quantities that are most important for the adsorption process: the equilibrium adsorption increases with increasing chain length, whereas the diffusion coefficient decreases.

With the aid of Equations I and II, the kinetic Equation III can be analyzed.

$$Q_t = Q_\infty \left[1 - \exp \left(- \frac{\pi^2 \bar{D}}{r^2} t \right) \right]^{0.5} , \qquad [III]$$

where Q_t = amount adsorbed at the time t; t = time; and r = radius of the particles.

The validity of Equation III has been proven several times for spherical particles with the assumption that diffusion within the particles is rate-determining and the con-

TABLE II

Comparison of Adsorption Q_∞ and Soil Removal S of Sodium Pentadecylsulfate (1) and Sodium-α-sulfopalmitic Acid Methylester (2)

Substrate	Q_∞ in 10^{-6} mol/g (1)	Q_∞ in 10^{-6} mol/g (2)	S (%) Soil with Kaolin (1)	S (%) Soil with Kaolin (2)	S (%) Soil without Kaolin (1)	S (%) Soil without Kaolin (2)
Polyacrylonitrile (Dralon)	0.28	0.23	76	50	64	64
Polyamide (Perlon)	1.245	1.23	90	66	78	76
Wool	1.245	1.245	91.5	74	–	–
Graphite	11.5	11.6	–	–	–	–
Kaolin	12.5	7.0	–	–	–	–

centration of the adsorbent is kept constant in the wash bath. Thus, we obtain Equation IV:

$$Q_t = \exp(\alpha n + \beta) \cdot \left\{ 1\text{-}\exp - \frac{\pi^2}{r^2} (-\Psi_n + \bar{D}_o)\, t \right\}^{0.5}, \qquad [\mathrm{IV}]$$

where $\alpha > 0$, $\Psi > 0$, $(\Psi_n - \bar{D}_o) \leqslant 0$ and n is an integer number. The range of n-values for which the increase in Q_t with increasing n is monotonic for all positive values of t is of special interest. The solution gives the following range:

$$0 \leqslant n \leqslant \frac{\bar{D}_o}{\Psi} - \frac{1}{2\alpha}. \qquad [\mathrm{V}]$$

Equation V is a necessary condition to obtain a monotonic increase in Q_t at a fixed ratio of constants. Evaluation of the coefficients α, Ψ and $\bar{D}_o$ for the investigated homologous series has revealed upper limits of n = 7 for n-carbon acids and n ≈ 14 for sodium *n*-alkylsulfates. Experimental values of the diffusion coefficients for sodium *n*-pentadecylsulfate and sodium *n*-hexadecylsulfate slightly deviate from the linear relationship, as Figure 5 shows. The agreement between the theoretical limit (Eq. V) and the experimental result shows the applicability ranges of the individual equations.

Differences between surfactants effecting rapid wetting and surfactants having good washing properties are thus caused by the structure of the hydrophobic part (5). Branching of the hydrophobic part is a particularly good example to illustrate this. Surfactants with heavily branched hydrophobic parts very often have good wetting and poor washing properties, whereas comparable surfactants with linear hydrophobic groups show good washing and poor wetting properties. This behavior is illustrated by a series of stereoisometrically branched hexadecylsulfates (6,7). Figure 6 depicts their equivalent conductivity as a function of concentration. The critical micellar concentration (cmc) is characterized by the deflection point of the $\lambda/\sqrt{c}$ curve. It increases with decreasing number of carbon atoms in the main chain. Besides inferences with regard to surfactant association, the slope of the curves also gives evidence of the fact that the mobility of the molecules increases with increasing chain branching. The increase in cmc with a decrease of the length of the main chain is effected by the same rules as for nonbranched alkylsulfates, according to Stauff's rule (8,9):

$$\log c_M = -an + b, \qquad [\mathrm{VI}]$$

where c_M is the cmc and a and b are constants.

The change is, however, substantially smaller than that for nonbranched alkylsulfates. This means that a transfer of a CH_2 group from the main chain into a chain branch

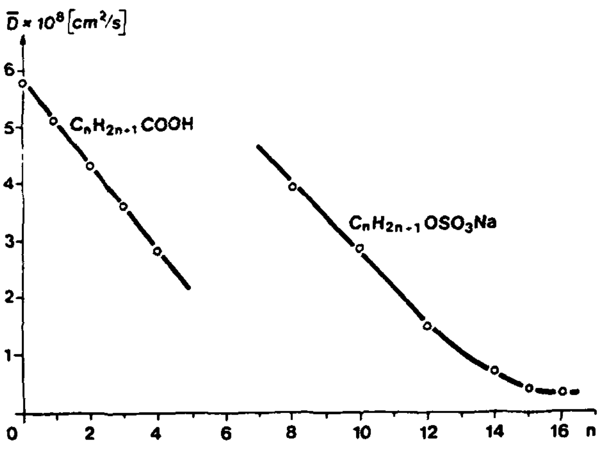


FIG. 5. Diffusion coefficient as a function of chain length. Experimental conditions—adsorbent: activated carbon; amount of adsorbent: 0.050 g; adsorbates: $C_nH_{2n+1}COOH$; $C_nH_{2n+1}OSO_3Na$; concentration (constant): $5 \cdot 10^{-4}$ mol/L; average particle radius: 0.084 cm; temperature: 25 C.

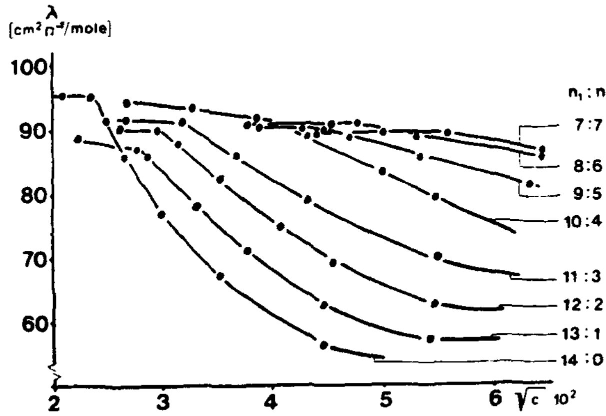
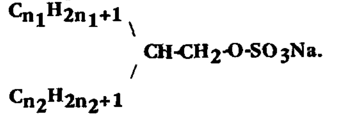


FIG. 6. Conductivity of stereoisomeric hexadecyl-sulfates. Experimental conditions—temperature: 40 C; general formula:



$$\begin{array}{l} C_{n_1}H_{2n_1+1} \\ \quad\quad\quad\quad \backslash \\ \quad\quad\quad\quad\quad CH\text{-}CH_2\text{-}O\text{-}SO_3Na. \\ \quad\quad\quad\quad / \\ C_{n_2}H_{2n_2+1} \end{array}$$

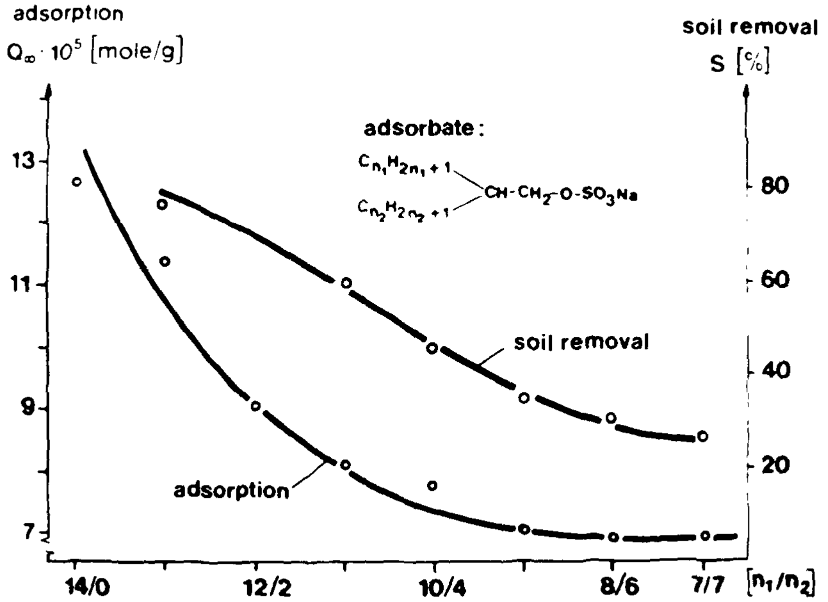


FIG. 7. Adsorption and soil removal of stereoisomeric sodium hexadecyl-sulfates. Experimental conditions—woven: cotton nonfinished; temperature: 90 C; water hardness: 16 °d; textile/solution ratio: 1:12.5; surfactant concentration: $2.91 \cdot 10^{-3}$ mol/L; adsorbent: activated carbon. Definition of soil removal and soil composition are given in Fig. 1.

changes the free energy of association by the same value. The change of the increment of the free energy for the transition from solution into the micellar state has a value of 154 cal mol^{-1} per CH_2 group. Thus, this change is substantially smaller than that for a prolongation of the main chain of sodium *n*-alkylsulfates, which amounts to 396 cal mol^{-1} per CH_2 group. Hence, it follows that, with constant molecular weight, branching of the hydrophobic part causes a decrease in hydrophobicity of the molecule.

Analogous to the formation of micelles, equilibrium adsorption onto carbon strongly decreases with increased branching of the hydrophobic group. We can expect similar results for washing experiments. Figure 7 compares results of experiments concerning equilibrium adsorption and soil removal. The curve of the decrease of washing performance indeed follows a course similar to that of equilibrium adsorption. So far, only sparingly branched compounds should be used in processes for which equilibrium adsorption plays a predominant part. With increased or reduced washing time, the same principle results, but different absolute soil removal values have been obtained.

In contrast to the absolute value of the adsorption equilibrium for branched compounds, this equilibrium is attained faster than for those that are nonbranched. Figure 8 shows that the mean apparent diffusion coefficient for the overall process increases linearly when branching increases. This is in analogy to the results of conductivity measurements (Fig. 6) revealing that the mobility of the micelles continuously grows with increased branching. The results clearly indicate that the postulated good wetting properties of surfactants with heavily branched hydrophobic groups is caused by an enhanced rate of adsorption and an increased mobility of molecules and micelles compared to nonbranched compounds. Hence, processes in which kinetics prevail are advantageously affected by branching of the hydrophobic part. This rule is not limited to the systems investigated, as can be inferred from the wetting experiments with cotton shown in Table III.

EFFECT OF TEMPERATURE

Besides the change in equilibrium adsorption and diffusion coefficient of surfactants in dependence on constitution, the change in these quantities as a function of temperature is particularly important. The Brownian molecular motion, the diffusion coefficient, the viscosity of fats and the solubility of salts, as well as a further series of quantities important to the washing process, change so that the removal of deposits from textile fibers is accelerated and facilitated. In contrast to this well known experience and in spite of increasing adsorption rate, equilibrium adsorption for anionic surfactants decreases with increasing temperature, according to general physical rules. With regard to the opposite signs of both effects, it is notable that the general positive temperature effect counterbalances and superimposes the small decrease in adsorption. In systems containing anionic surfactants, an increase in the washing performance is always obtained with increasing temperature and constant surfactant concentration.

Basically different is the temperature effect on the adsorption of nonionic polyglycol ethers. For this type of surfactant, solubility decreases and adsorption increases with increasing temperature due to dehydration of the hydrophilic group (10). The affinity to water as the solvent is decreased and, hence, a separation into 2 phases occurs at a definite temperature, the cloud point, which is characteristic for each surfactant. Above the cloud point, formation of one phase rich in surfactants and one poor in surfactants causes very disadvantageous conditions for surfactant adsorption. Hence it decreases significantly. As a consequence, soil removal and dispersion of the soil in the wash bath decreases for nonionic systems at temperatures above the cloud point.

Table IV lists results of model washing experiments with various nonionic surfactants from large-scale production, the cloud points of which are close to 40 C. Soil removal is most effective in the vicinity of the cloud point, where

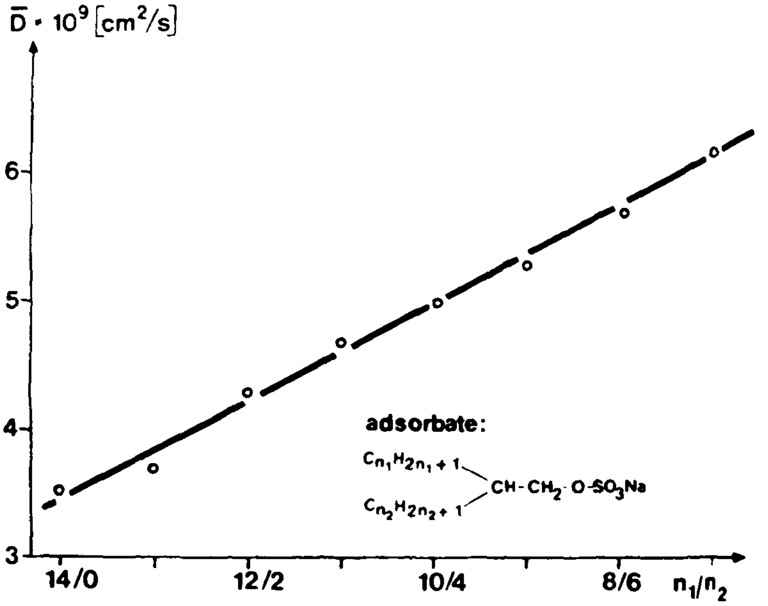


FIG. 8. Diffusion coefficient of sodium hexadecyl-sulfates. Experimental conditions—adsorbent: activated carbon; amount of adsorbent: 0.050 g; average particle radius: 0.084 cm; temperature: 25 C; concentration (constant): 1 · 10^{-4} mol/L.

TABLE III

Immersion Wetting Test DIN 53 901 (German Standards) with Sodium Hexadecylsulfates[a]

n_1/n_2	Wetting time (s)
13/1	42
12/2	35
11/3	35
10/4	29
9/5	29
8/6	27
7/7	25

[a] $(C_{n_1}H_{2n_1+1})(C_{n_2}H_{2n_2+1})CHCH_2OSO_3Na$; $n_1 + n_2 = 14$.

TABLE IV

Influence of Temperature on the Detergency of Technical Nonionic Surfactants on Nonfinished Cotton Surfactant Concentration (1 · 10^{-3} mol/L)

Surfactant	Cloud point (C)	Soil removal S (%) at: 40 C	90 C
Sec. C_{15}-alcohol-7EO	39	43	0
Vic. C_{16}-diol-7EO	42	56	35
Vic. C_{14}-diol-7EO	44	40	20
Nonylphenol-8EO	31	43	0
Nonylphenol-9EO	47	51	40
Dodecylphenol-10EO	38	61	18

adsorption conditions for every substance are optimal. The significant decrease at high temperatures shows, however, the importance of exact harmony between the physical properties of surfactants in connection with their constitution and the conditions of application.

Analogous results are obtained for the dispersion ability. Figure 9 depicts the turbidity of a suspension of carbon black with increasing surfactant concentration at a temperature close to the cloud point and at one far above it. It is notable that the fine dispersion of carbon black at 28 C remains stable and does not deposit any more above a definite surfactant concentration (after a storage time of 3

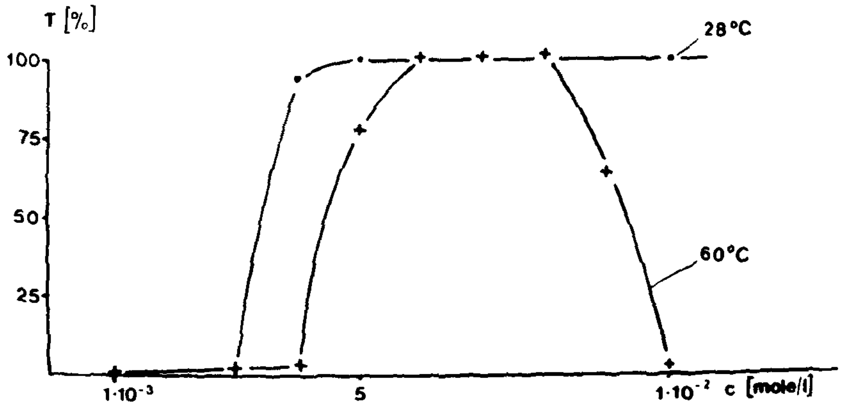


FIG. 9. Turbidity of carbon black dispersion in nonylphenoloctaglycolether solution, depending on surfactant concentration. Experimental conditions–carbon black: 1 g; volume: 50 mL; and cuvette: 10 mm. Turbidity measurements have been done 72 hr after dispersing the pigments for 5 min by ultrasonic treatment and keeping the samples at the indicated constant temperature. Turbidity is indicated in terms of transmittance, T (%).

days). The concentration limit of the stabilization of the suspension at 60 C is shifted toward higher values. It is particularly notable that the stability of the suspension prepared at 60 C strongly decreases at higher surfactant concentrations so that complete separation is reached at a concentration of 10^{-2} mol/L after the same storage time. This concentration dependence is influenced by the concentration dependence of the cloud point at very low surfactant concentrations. Similar behavior cannot be observed even at high temperatures when using surfactants with higher cloud points. In this respect, for nonionic surfactants under certain conditions, the generally positive temperature effect may be reversed.

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