Removal of Triglycerides from Hard Surfaces by Surfactants: An Ellipsometry Study

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The removal of triglycerides from hard surfaces by surfactants was studied by means of ellipsometry. Various surfactants were examined, and as the nonionic surfactants of the alkyl polyoxyethylene type proved to be most efficient, they were studied in particular detail. The influence of factors such as surfactant critical micelle concentration, the length of the polyoxyethylene chain in the nonionic surfactants, the pH, the temperature, and the agitation were investigated. The cleaning process involves many consecutive steps on the molecular level, and the measurements provide interesting information about the cleaning mechanism.

In general, the cleaning of hard surfaces, e.g. floor cleaning, is done by using products which normally consist of a mixture of active components dissolved in water. The most important components are surfactants, alkaline builders and organic solvents. This article will concentrate on the behavior of pure surfactant systems, leaving the synergistic effects of various components to a later study.

The surfactants can be divided into four main groups, depending on the character of the hydrophilic group, i.e. anionic, cationic, nonionic and zwitterionic surfactants. The anionic surfactants dominate, followed by the nonionics. The trend in detergency today is toward an increase in the proportion of nonionics in the total amount of surfactants used. This is expected to continue in the future (1).

There are many reasons to expect the present trend in hard surface cleaning to continue. Some of these are:

- The favorable cost gap for the anionics has decreased.
- When manufacturing products, the nonionics are very flexible in the sense that it is easy to alter the surfactant's hydrophilic-hydrophobic balance by changing the lengths of the two parts of the molecule.
- There is a general desire to lower the cleaning temperature; many anionic surfactants, though suitable for other reasons, cannot be used at low temperatures because of their high Krafft points.
- The nonionics are, in general, low foaming. The tendency to use more machines in various cleaning processes favors the nonionics because too much foam often disturbs the functioning of the machine.
- The nonionic surfactants have very low critical micelle concentrations (CMC), and because this property affects the amount of surfactant needed (see below), the use of nonionics allows lower surfactant concentration. Furthermore, the nonionic surfactants have some other interesting properties, such as the cloud point phenomenon.
- Many investigations have shown that nonionic surfactants have better dermatological properties than the most common anionic surfactants (2,3), and this is of special interest in professional cleaning.

For the above reasons, the main part of the present work deals with nonionic surfactants.

In two other articles (4,5) we have described a method for the study of cleaning of hard surfaces based upon ellipsometry. In the first article, some advantages of the method were pointed out, such as the sensitivity and the possibility of following the cleaning process continously. In the second one, the applicability of the method and the models used were discussed in greater detail. The same method has been used here to investigate the cleaning properties of some surfactants. The aim of the study is to get a better understanding of hard surface cleaning and in this way help manufacturers to formulate these types of products.

EXPERIMENTAL

The equipment and the procedures described previously (5) were used, with the exceptions mentioned below.

As models for dirt, the triglycerides trilaurin (TL), tripalmitin (TP) and triolein (TO) were used. These substances are nonpolar fats, insoluble in water. Before application onto the surface, they were dissolved in toluene. A drop of this solution was placed on the surface, and the surface was rotated five min at 4,000 rpm. Trilaurin and tripalmitin are solid at room temperature, and a layer prepared in this way crystallizes in the β-form (6) with melting points of 46 C and 66 C, respectively. The fat layer obtained in this way was rather evenly distributed, but not completely smooth, as could be seen by electron microscopy (5). Triolein is liquid at room temperature with a melting point of −5 C. All triglycerides (99% purity) were manufactured by Sigma Chemical Company, St. Louis, Missouri.

The surfaces used consisted of polyvinylchloride (PVC) and plasma-cleaned chromium coated glass. From water wettability tests it was apparent that the PVC surface was hydrophobic and the chromium surface hydrophilic. All measurements were carried out in doubly distilled water at 25 C with agitation, unless otherwise stated.

Nonionic surfactants used: Monodisperse polyoxyethylene alkyl ethers (CxEy), manufactured by Nikko Chemicals Co, Japan, and polydisperse polyoxyethylene nonylphenol ethers (NFEz), manufactured by Berol AB, Sweden.

Anionic surfactants used: Dodecyl benzene sulphonic acid (DBS), 98%, manufactured by Ventron GMBH, West Germany, neutralized by sodium hydroxide; sodium dodecyl sulphate (SDS), manufactured by BDH Chemicals Ltd, England, and fatty acids, manufactured by BDH Chemicals Ltd, England, neutralized by monoethanoleamine.

The measuring procedure. After deposition of the fat on the substrate, the amount was determined in water according to the mass formula given in Ref. 5. Then the surfactant under study was added to the cuvette and the ellipsometer angles were recorded continously and the amount of fat determined from them during at least 10 min. The removal was defined as $m(t) = \frac{m_s - m_t}{m_s}$ where m_s is the initial amount and m_t the amount after a certain time, usually four or 10 min, and expressed in percent.

CLEANING MECHANISMS

It is not possible to describe cleaning by one single mechanism. The cleaning process proceeds through many subsequent or alternative steps depending on the properties of the system.

A good basis for discussion is to divide the cleaning process into three steps, according to Schlussler (7):

(i) Transport of the cleaning agents to the soiled surface and subsequent adsorption to the surface.

(ii) Interaction between the cleaning agents and the dirt. This transforms the originally water-insoluble dirt to a form in which it is loosened from the surface. The removed dirt can then be dissolved, dispersed or solubilized in the water phase.

(iii) Transport of the products formed in (ii) from the surface to the aqueous phase.

Let us now consider the different steps in more detail.

The first step (i) consists of transport and adsorption. The transport could be divided into two steps, a fast movement in the aqueous phase to the surface and a slow diffusion in the pores of the surface to the final adsorption site. In our case, in contrast to textile detergency, the surfaces are relatively smooth and the pore diffusion is therefore of less importance. The equilibrium adsorption is obtained rather quickly and is reached in our case in about 30 seconds. Schwuger (8) has shown a connection between detergency and surfactant adsorption for anionic surfactants, while no such connection exists between detergency and surfactant diffusion. However, the connection between surfactant equilibrium adsorption and surfactant cleaning efficiency is not clear.

Due to interaction between dirt and surfactant (ii), aggregates will be formed which could be transported into the aqueous bulk phase. The conversion of the fatty soil to water soluble substances by chemical reaction, e.g. saponification of triglycerides in alkaline solution, will not be considered further in this study. The reason is that no removal has been detected in the absence of surfactants at the temperatures and pH values used in our experiments. This reaction is therefore unimportant under the conditions of normal household cleaning.

The following mechanisms are probably the most important in hard surface cleaning:

(a) Rolling up of liquid soil (9).

(b) Displacement of solid soil as a result of a lowering of the adhesion energy due to surfactant wetting (10).

(c) Formation of mixed phases between fatty polar soil and surfactants (11). As triglycerides are not known to form mesomorphic phases with aqueous surfactant solutions (12), this mechanism is probably of less importance here.

(d) Penetration of detergent solution into cracks and crevices in the soil film, with subsequent dislodging of particulate soil (12).

The transport of the formed aggregates to the bulk phase could take place in the following ways:

Emulsion: In mechanism (ii)a, the dirt is transformed to small drops; these could form an oil-in-water emulsion. The presence of forces which prevent coalescense is necessary. The surfactants adsorb to the interface, depress the interfacial tension and thus lower the tendency to decrease the total oil/water interface by coalescence. If the surfactants are ionic, a diffuse electrostatic double layer is formed on the droplets, which gives electrostatic repulsion between them. The coalescense also could be prevented sterically, e.g. by nonionic surfactants.

Suspension. Solid soil particles could, like droplets, be dispersed in water by surfactants. Electrostatic repulsion and steric stabilization are also important here. Particles formed by mechanisms (ii)b and (ii)d could be transported in this way.

Solubilization. Above the CMC and the Krafft point, the surfactants form micelles. In the interior of these, water insoluble substances could be dissolved. The aggregates formed in mechanism (ii)c could, upon dilution, be transferred to solubilized states. The (ii)d products probably could be solubilized also.

The question is which of the three steps, adsorption, soil-surfactant interaction and desorption, is rate-determining.

RESULTS AND DISCUSSION

Concentration dependence and the role of CMC. Figure 1 shows the removal of tripalmitin and triolein from PVC by a nonionic surfactant ($C_{12}E_7$). For tripalmitin, the removal starts below the CMC, rises near the CMC and reaches a plateau value. For the liquid fat triolein, the increase in removal continues at higher concentrations.

Figure 2 shows the results for the removal of tripalmitin by NFE_{10} and SDS from a chromium surface. The behavior is the same as in Figure 1, with an increase in efficiency near the CMC, but the removal from the chromium surface is more extensive. It is obvious that the onset of detergency occurs at a lower concentration for the nonionic surfactant compared to the anionic. As nonionic surfactants in general have lower CMC than anionic surfactants, the conclusion is that the nonionic surfactants are superior when low surfactant concentrations are desired.

Our findings may be compared to the results obtained by Harris (13,14), who investigated the removal of triolein from glass at 35 C and 58 C and the removal of tristearin at 75 C, in all cases by NFE_{10}. He found that the removal started at the CMC and

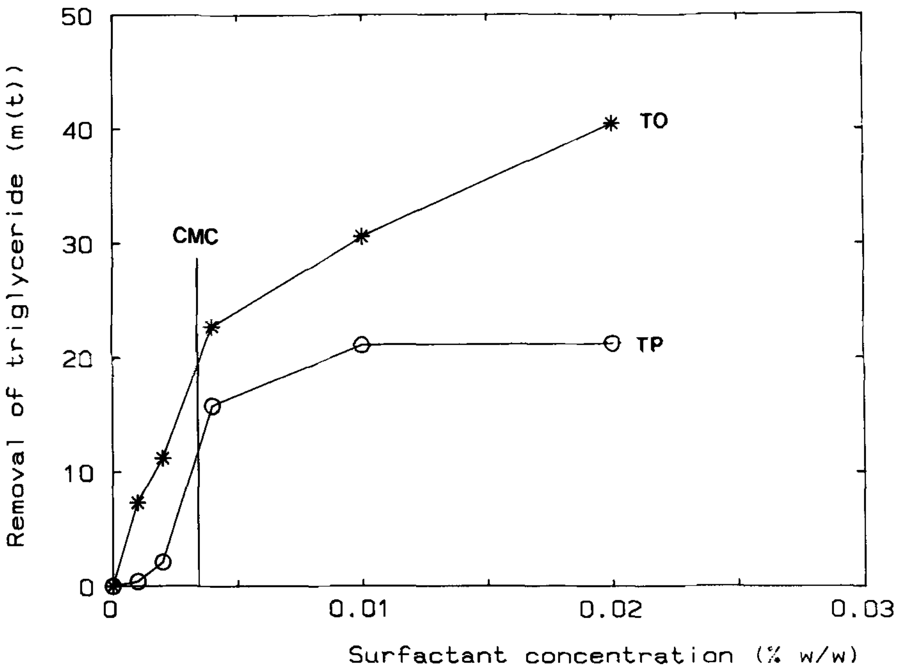

FIG. 1. The removal of tripalmitin (o) and triolein (*) in % from PVC by $C_{12}E_7$ at various concentrations (t = 4 min, agitation = 120 rpm).

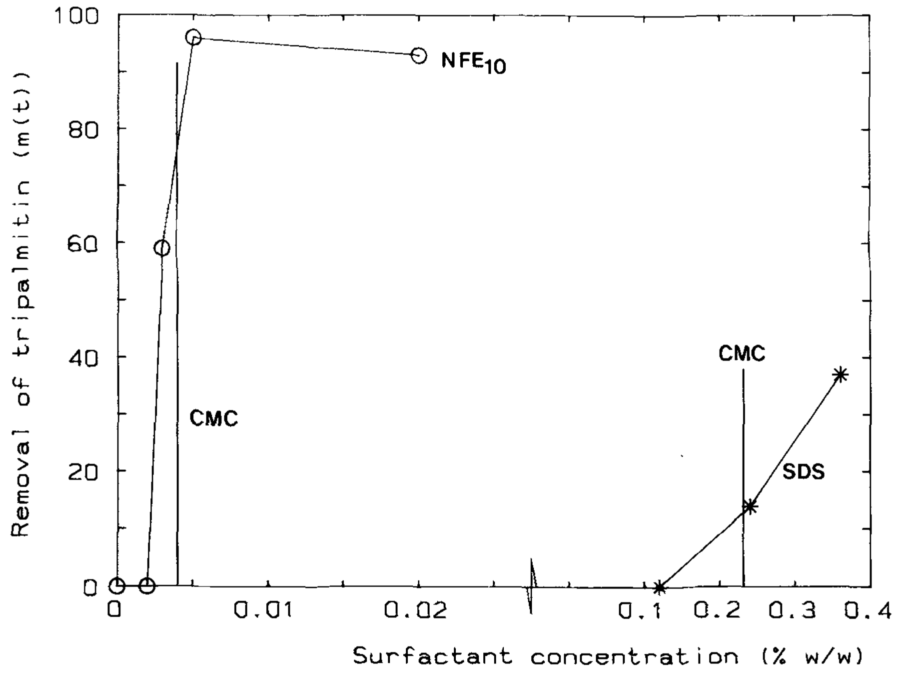

FIG. 2. The removal of tripalmitin from chromium in % by NFE_{10} (o) (t = 4 min, agitation = 325 rpm) and SDS (*) (t = 10 min, agitation = 120 rpm) at various concentrations.

reached a plateau value at much higher concentrations (>10 × CMC). The removal at the CMC was low.

Mankowich (15) studied the removal of triolein from steel at 82 C by different NFE's. The removal was low below the CMC, increased steeply near the CMC and reached the maximal value at about 10 × CMC.

The pattern found in these studies is no or little removal below the CMC, a steep increase in removal near the CMC and an attainment of a plateau

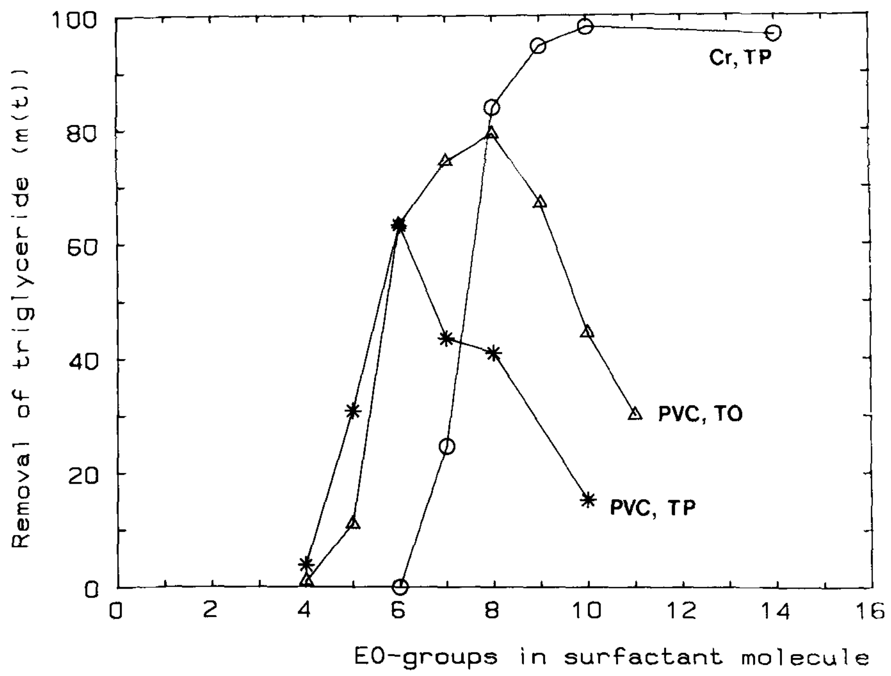

FIG. 3. The removal of tripalmitin and triolein in % by NFE$_z$ with varying length of the polyoxyethylene chain (t = 10 min). o, Chromium, TP, 0.01 % NFE$_z$, agitation = 120 rpm; *, PVC, TP, 0.05 % NFE$_z$, agitation = 325 rpm; Δ, PVC, TO, 0.05 % NFE$_z$, agitation = 325 rpm.

value above the CMC. In our experiments the degree of removal at the CMC is higher, and our results indicate neither that the cleaning starts at very low surfactant concentration nor that presence of micelles is necessary. It is interesting to note that many surfactant adsorption isotherms (16) resemble our cleaning curves. On hydrophobic surfaces surfactants adsorb and form aggregates below the CMC, and these aggregates probably play an important role in the cleaning process.

The length of the polyethyleneoxide chain. For a fixed hydrophobic part, e.g. nonylphenol, in a nonionic surfactant the length of the ethyleneoxide (EO) chain affects the properties of the molecule. The effect on fat removal of different EO chain lengths for both PVC and chromium in a nonylphenolpolyxyethylene surfactant is illustrated in Figure 3. The figure reveals there is an optimal EO chain length for attainment of maximum fat removal, at least for the PVC surface. Furthermore, the optimum in EO chain length is about eight for triolein and six for tripalmitin on PVC. For tripalmitin on chromium, the EO chain length has to be above nine. For EO chain length less than five, little or no cleaning effect is seen.

For more general conclusions, results from other investigations must also be included. In Table 1 some such results are summarized (14,17,18,19).

From the table it is clear that optimal number of EO groups depends very much on the properties of the system under study. One difficulty in the comparison is the varying ways to express the hydrophilic/hydrophobic balance of the molecule, and the published results are sometimes ambiguous. The table includes results from different surfaces, temperatures

TABLE 1.

Dirt Removal by Nonionic Surfactants With Varying EO Content.

Surface	Temp. °C	Dirt	Surfactant type	Number of EO groups in best surfactant	% EO (w/w) in best surfactant	Reference
Glass	75	Tristearin	$C_{12}E_z$	10	70	14
Steel	82	Oleic acid	NFE$_z$	30	86	17
Steel	82	Hydrocarbon	NFE$_z$	7	58	17
Painted masonite	room	Grease	$C_{10}E_z$	4	50	18
Ceramic	22	Fat mixture	NFE$_z$	9-10	66	19
Chromium	25	Tripalmitin	NFE$_z$	10	67	This work
PVC	25	Tripalmitin	NFE$_z$	6	55	This work
PVC	25	Triolein	NFE$_z$	8	62	This work

and dirt compositions and allows the following generalizations about the optimal EO content in the molecule:

(i) The more polar the dirt is, the longer should the EO chain of the surfactant be.

(ii) The more polar the surface is, the longer should the EO chain of the surfactant be.

(iii) The higher the temperature is, the longer should the EO chain of the surfactant be.

The existence of a maximum in removal for a certain EO chain length in a surfactant molecule could be understood as follows. Increasing the number of EO groups in the molecule to a large value means an increase of the favorable interaction with water and thus a decrease in the surface activity. As an example of this, Corkill et al. (20) have shown that adsorption of nonionic surfactants to hydrophobic surfaces is reduced with increasing EO content, and this should lower cleaning efficiency. A decrease in EO content increases the surface activity; this should be beneficial to cleaning. Cox (21) has shown that the penetration of a nonionic surfactant to stearin grease soil increases with decreasing EO content. At a certain point, however, the EO content is too low to make the surfactant water soluble, and this also lowers the cleaning efficiency.

Temperature. In Figure 4 the removal of fat versus temperature is shown. For the nonionic surfactant, the removal increases with increasing temperature for all three lipids, but for the anionic surfactant, a maximum is obtained at 35 C. The melting point of the β-form of trilaurin is 46 C, and this temperature is passed in the experiment, but the effect of passing the melting point is masked by the increasing efficiency of the nonionic surfactant.

It is a generally accepted rule that cleaning performance is improved at higher temperatures (7, 12, 22). However, as was shown above, this is not always true.

Considering the soil, there are several factors which promote cleaning at higher temperatures:

(i) For a solid soil the melting point could be passed, which makes it possible to remove the soil by rolling up.

(ii) For a liquid soil the viscosity decreases, which facilitates rolling up.

(iii) The diffusion rate of soil aggregates is generally increased.

(iv) The dielectric constant of water is decreased, which makes it a better solvent for fatty soil.

Considering the surfactants, the picture is more complicated and completely different for nonionic compared to anionic surfactants. Table 2 shows the effect of increasing temperature on the surfactant system (below the cloud point for the nonionics).

TABLE 2.

Effect on Various Properties of Increasing Temperature

	Effect on property		Expected effect on cleaning efficiency	
Property	Nonionic	Anionic	Nonionic	Anionic
Diffusion	+/- (23)	+	+/-	+
Adsorption	+ (20)	- (25)	+	-
CMC	- (24)	+/- (26)	+	+/-
Micellar size	+ (24)	- (24)	+	-

*+, increasing; -, decreasing, and xx, reference.

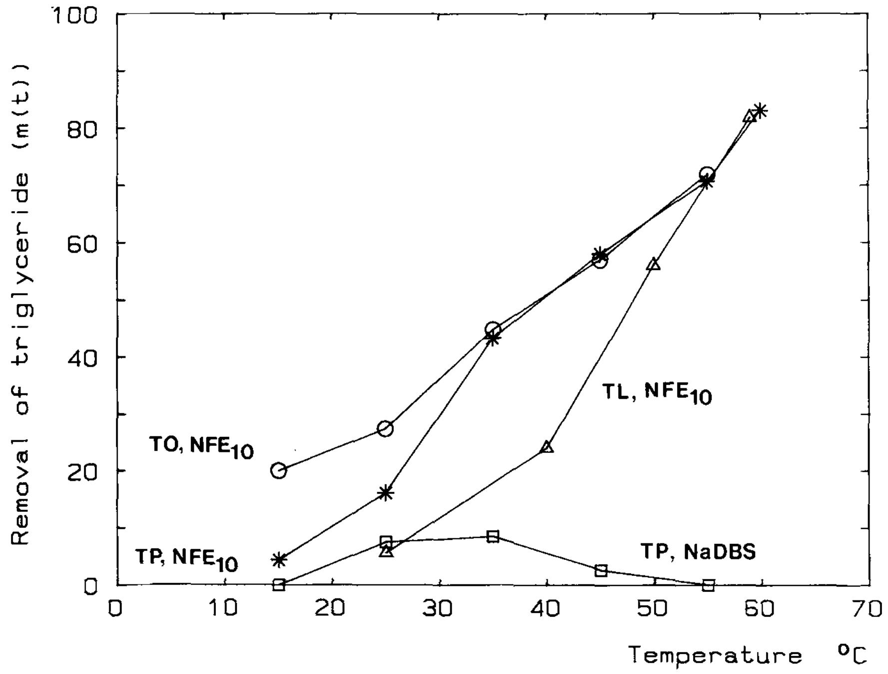

FIG. 4. The removal of tripalmitin, triolein and trilaurin in % from PVC at different temperatures (t = 4 min, agitation = 325 rpm). □, TP, 0.2% NaDBS; *, TP, 0.05% NFE$_{10}$; o, TO, 0.05% NFE$_{10}$; Δ, TL, 0.05% NFE$_{10}$; t, 0.25 min.

The table shows the striking differences between nonionic and anionic surfactants, due to the intricate interaction between polyoxyethylene and water (27).

For nonionic surfactants the conclusion from the table is that almost every change with increase in temperature favors soil removal. One exception is the case where the cloud point is so greatly exceeded that the solubility of the surfactant becomes critical.

For the anionic surfactant, it is more difficult to explain why there is a maximum at a certain temperature. In this particular case, the CMC increased with increasing temperature but did not exceed the concentration used. Obviously, two different mechanisms are rate-determining in different temperature intervals.

pH. Very little has been written about the influence of the pH value on cleaning efficiency in surfactant systems. We have, therefore, investigated some systems considering this aspect; the results are shown in Figure 5. The figure reveals there is a small increase of fat removal with increasing pH for the nonionic surfactant. The properties of nonionic surfactants are not primarily affected by the pH value of the water solution. The weak pH-dependence is also valid for the anionic surfactants which are salts of strong acids (sulphonates, sulphates).

On the other hand, the properties of surfactants which are salts of weak acids, for instance fatty acid salts, are strongly pH-dependent. In Figure 5, the removal of tripalmitin by monoethanolzamine laurate is shown and a large pH effect is apparent. The reason for this is to some extent analogous to the attainment of a maximum in detergency for nonionics with varying EO chain length. In water solutions of carboxylic acids, there is a pH-dependent equilibrium between the acid and salt form. These two forms will coexist in a broad pH interval, but the fraction of the acid will increase with decreasing pH value. The uncharged carboxylic acid molecules will screen the electrostatic repulsion between the carboxylic ions; this facilitates formation of micelles, adsorption and formation of surface aggregates and will, in turn, have a favorable effect on fat removal. On the other hand, carboxylic acids have a low water solubility, and at high fractions of the acid the surfactant will precipitate and its ability to transport dirt disappears. In commercial soaps for floor cleaning, we have found that the pH values are often too high.

The properties of the soil and the surface can also be affected by the pH value of the detergent solution.

Most soils are weakly negatively charged in water, due to adsorption of ions or dissociation of molecules at the surface. It is assumed that anionic and nonionic surfactants adsorb to the soil by orienting with the polar head outwards, and thereby facilitate interaction with water. Cationic surfactants adsorb by coulombic attraction with the polar headgroup toward the negative soil and the hydrophobic tail flat on the surface, and thereby maintain the hydrophobic character of the soil. The cationics alone are therefore not suitable as detergents and are seldom used for cleaning purposes.

If the soil contains hydrolyzable groups, the pH effect could be dramatic. Fatty acid soil forms water soluble carboxylate ions in contact with alkaline solutions, with the rate very much depending on temperature. There is also a possibility that triglycerides hydrolyze in strong alkaline solutions. To make sure that this reaction did not disturb our investiga-

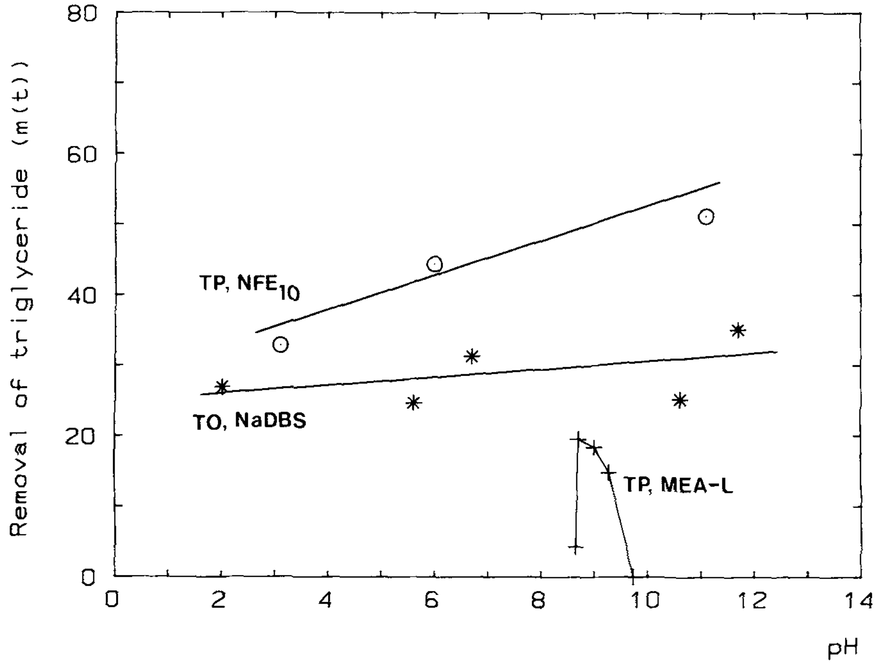

FIG. 5. The removal of tripalmitin and triolein in % at various pH (agitation = 325 rpm). + TP, 0.8% monoethanolamine laurate, t, 10 min; o, TP, 0.05% NFE$_{10}$, t, 4 min; *, TO, 0.2% NaDBS, t, 10 min, T, 35 C.

tions, the effect of pure NaOH solutions was examined, and no removal occurred. This is an contrast to the results obtained by Bourne and Jennings (28), who observed that tristearin was removed from steel by pure NaOH solutions.

For many polar surfaces, e.g. metals and metal oxides, the (H+)- and (OH−)-ions are potential-determining. These surfaces are positively charged at low pH and negatively charged at high pH. For example, a chromium oxide surface, used in our experiments, has an isoelectric point at pH 7 (29). The potential of the surface affects the adsorption of ionic surfactants. For instance, the adsorption of sodium dodecylbenzene sulphonate to these kinds of surfaces decreases with increasing pH and ceases at the isoelectric point (30). However, this effect is probably of less importance for us, because our surfaces are covered by triglycerides.

Liquid and solid soil. Liquid soil is generally easier to remove than solid soil. This is easily demonstrated if the temperature of the cleaning solution is raised above the melting point of the solid, which leads to a substantial increase in removal rate (12). However, increasing the temperature also affects other important properties as was discussed above. An attempt to avoid this difficulty is shown in Figure 6, where the transition from soild to liquid soil is studied by means of various mixtures of tripalmitin (solid) and triolein (liquid). The figure shows that the removal rate increases markedly when the soil is transformed into liquid form. The reason is that the removal now can proceed through a faster mechanism, rolling up. The concentration of the surfactant has been chosen so that the removal was not complete even for the liquid fat. Of the two liquid soils, the one with most triolein was easiest to remove.

Mechanical agitation. The removal process is of both a chemical and mechanical nature. The latter is outside the scope of the present investigation, but because agitation is needed to get homogenous surfactant solutions, its influence must be considered.

Studies of the influence of agitation in the surfactant solution show that agitation increases the removal rate (18, 31, 32, 33). Theoretically, increased mechanical energy input should be beneficial to the removal process in the earlier proposed steps (see Cleaning mechanisms) for the following reasons:

(i) Increases the surfactant transport and thereby the adsorption rate.

(ii-a) Speeds up the rolling up process.

(ii-b) Speeds up the displacement process.

(ii-c) No obvious influence.

(ii-d) No obvious influence.

(iii-a) Increases the transport rate of the emulsified droplets from the surface and stabilizes the emulsion.

(iii-b) Increases the transport rate of the suspended particles from the surface and stabilizes the suspension.

(iii-c) Increases the transport rate of solubilizing micelles from the surface.

Figure 7 shows the removal of tripalmitin from PVC and chromium and the removal of triolein from PVC by nonionic surfactants as a function of the speed of the magnetic stirrer in the cuvette.

It is interesting that the removal of tripalmitin from PVC is not at all affected, the removal of triolein

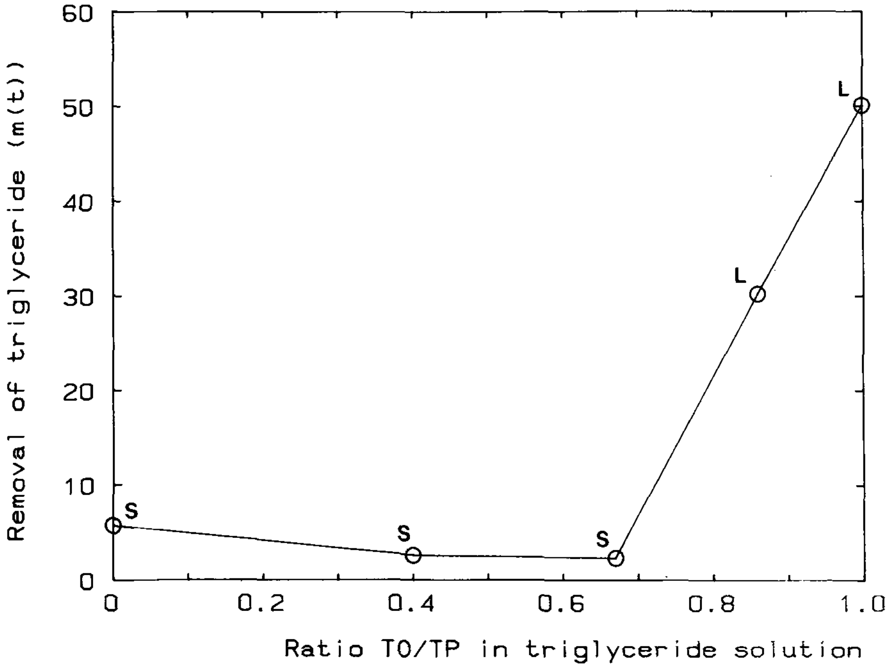

FIG. 6. The removal of a mixture of tripalmitin and triolein in % from PVC at different triglyceride ratios. The ratio is referred to the content in the toluene solution before drying. S means that the mixture is solid and L that the mixture is liquid after evaporation of toluene (0.02% $C_{12}E_5$; t, 4 min; agitation, 120 rpm).

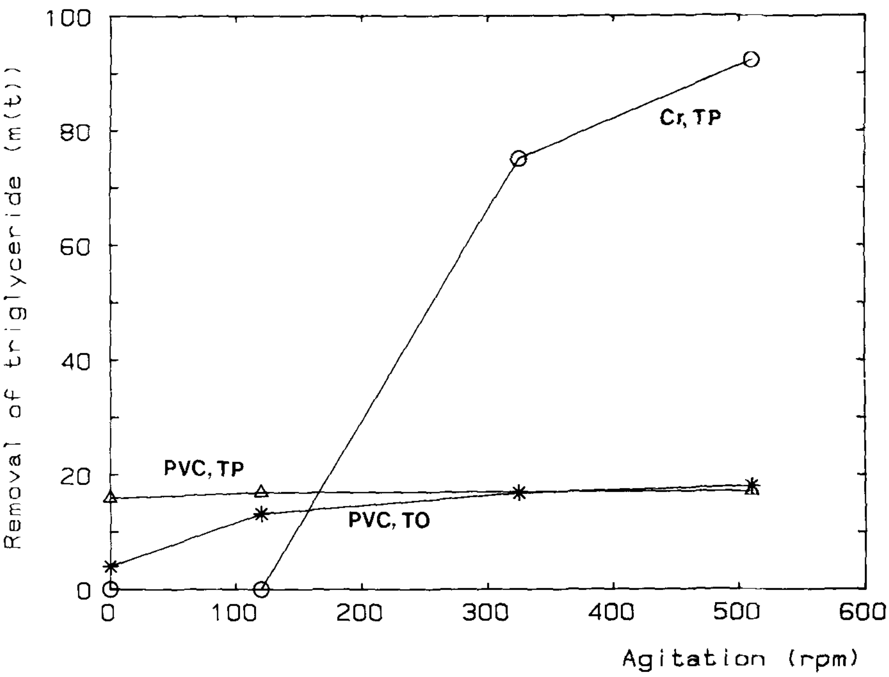

FIG. 7. The removal of tripalmitin and triolein in % at various agitation rates (t, 10 min). o, Chromium, TP, 0.02% $C_{12}E_8$; Δ, PVC, TP, 0.02% $C_{12}E_8$; *, PVC, TO, 0.05% NFE_{10}.

from PVC is somewhat affected and the removal of tripalmitin from chromium is highly dependent on the agitation rate. This indicates that different mechanisms are rate-determining in the three cases, and the data suggest the following interpretation:

TP-PVC: The removal follows the route i–ii-d–iii-b/iii-c (diffusion-penetration-suspending and/or solubilization), i.e. the solid fat is loosened in small fragments which are suspended or solubilized in the surfactant solution. The aggregate formation step is rate determining.

TO-PVC: The removal follows the route i–ii-a–iii-a/iii-c (diffusion-rolling up-emulsification and/or solubilization), i.e. the liquid fat is rolled up and emulsified and/or solubilized.

TP-Cr: The removal follows the route i–ii-b–iii-b (diffusion-displacement-suspending), i.e. the solid fat is displaced and suspended. The removal of tripalmitin from chromium should be very favorable energetically because it includes the breakdown of a hydrophobic/hydrophilic interface (fat/chromium) and the formation of a hydrophilic/hydrophilic interface (water/chromium). Therefore, the formation step probably is not rate determining, but the mass transport from the surface is. Near the surface an "unstirred layer" is formed, and when enhancing the agitation the thickness of this unstirred layer will decrease until the fat aggregates are reached and could be transported away. This explains the sudden increase in removal rate at a certain magnetic stirrer speed.

ACKNOWLEDGMENTS

Stimulating discussions with Thomas Arnebrandt and Tommy Nylander are gratefully acknowledged, as is the support from the Swedish Work Environment Fund. Björn Lindman and Håkan Wennerström gave us valuable criticism of the first manuscript.

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[Received October 22, 1986;
Accepted April 30, 1987]