

SURFACTANTS & DETERGENTS TECHNICAL

Liquid Detergents from Cationic, Anionic and Nonionic Surfactants. Adsorption, Detergency and Antistatic Properties

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The adsorption of a mixture of cationic (c) and anionic (a) surfactants on cellulose fibers is highly dependent on the molar ratio a/c with a maximum at a/c = 0.9. When a/c is > 1.1 the adsorption is negligible. The presence of nonionic surfactants in the solution impairs the adsorption of the ionic species; this effect is stronger for nonionic surfactants with long alkyl and polyglycol ether chains. The detergency—measured on WFK cotton cloth—is highest when a/c > 1 and decreases sharply when a/c goes below 0.8. The antistatic effect for a formulated liquid detergent based on these principles was compared to one commercial liquid detergent with softening and antistatic properties and one commercial detergent powder, and the test detergent was shown to be a better antistatic agent on polyester, polyacrylonitrile and polyamide. The detergency was about the same for the two liquid detergents.

The cleaning and softening/antistatic treatment of textiles is usually done as two different operations and with two different products. Many suggestions, however, have been made for a simultaneous process, and the addition of minor amounts of cationic surfactants to anionic detergent formulations in order to achieve this is well known (2-5). In these cases the anionic surfactant is dominating and the molar ratio of anionic to cationic surfactant (a/c) in the examples given is in the range 4-50, i.e., well over 1.0.

On the other hand, cationic textile softeners containing minor amounts of alkyl polyglycol ether sulphates have been on the market for many years. In this case the anionic surfactant will enhance the adsorption of the cationic product. The a/c is of the order 0.2 for these products.

This work comprises a study of the adsorption of cationic surfactant on cotton fibers in the presence of anionic surfactant and vice versa. The effect of various nonionic surfactants and other normal ingredients of detergents on this adsorption was also studied. Based on these findings a liquid detergent was formulated and its cleaning effect and antistatic properties compared to some commercial products. The work was undertaken in order to contribute to the understanding of the various factors influencing the result of laundering in mixtures of cationic, anionic and nonionic surfactants.

EXPERIMENTAL PROCEDURES

The adsorption studies were performed with ionic surfactants labelled with radioactive isotopes with the following structures:

Sodium alkylether sulphate, (Abbreviation: C18(EO)₂S^xO₄.) C₁₈H₃₇OC₂H₄OC₂H₄OSO₃ where part of the sulphur was S³⁵. This compound was synthesized by sulphating a chloroform solution of ethoxylated stearyl-alcohol with labelled chlorosulphonic acid followed by neutralization.

N,N - didecyl-2-oxipropyl,N,N - dimethylammonium chloride, (C₁₀H₂₁OCH₂CH(OH)CH₂)₂N⁺(CH₃)₂CL⁻ where part of the methyl groups are labelled with C¹⁴. Abbreviation: di-C10-K*. The compound was prepared by reacting the decylchloro glyceryl ether C₁₀H₂₅OCH₂CH(OH)CH₂Cl with a labelled dimethylamine under alkaline conditions. All other surfactants used were of technical grade. The fiber used for the adsorption studies was a combed Egyptian cotton purified according to (1).

For each adsorption test 100 mg cotton and 8 ml solution were placed in a 10-ml test tube with screw-cap and kept rocking gently in a thermostated water-bath, normally for one hr. The solution was then sucked off with a pipette and the fiber rinsed 5 times with distilled water, dried at 100°C and then placed in a desiccator. Five subsamples of 10 mg each were taken from each fiber sample and the activity measured in a liquid scintillation spectrometer (Nuclear Chicago Unilux III). The detergency testing was made partly in a Terg-O-Tometer and partly in a tumbler-type machine (MIELE W 761) at 40°C and a water hardness of 90 ppm CaCO₃.

The surface conductivity was measured in a Rotschild Static Voltmeter by charging 100 volts and measuring the time for the potential to drop to half this value.

Before measurement the test pieces were conditioned for 48 hr at 25°C and constant humidity.

RESULTS

The adsorption of cationic and anionic surfactant on cotton fibers from a solution containing a constant amount of the former and increasing amounts of the latter surfactant is shown in Figure 1 and the results analyzed in Figure 2-4. In Figure 2 it is clearly seen that the ratio of anionic to cationic surfactant (a/c) on the fiber is close to 1.0 in equilibrium with an a/c in the solution of 0.3 but will then decrease with increasing a/c. This peculiar behavior is more clearly demonstrated in Figure 3 where it can be seen that the minimum value of a/c for the absorbed surfactants (0.4) is in equilibrium with the maximum value of a/c in solution (2.4).

Figure 4 shows that a maximum amount of cationic plus anionic surfactant will be adsorbed when the initial a/c is between 0.7 and 0.9.

Figure 5 shows that some of the normal ingredients in a built detergent formulation, sodium

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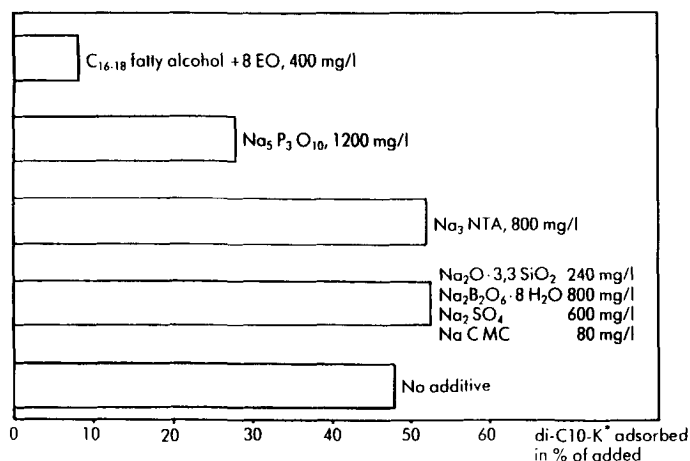


FIG. 5. Effect of detergent ingredients on the adsorption. a/c, 0.81; T, 60°C; t, 60 min; pH, 10.0.

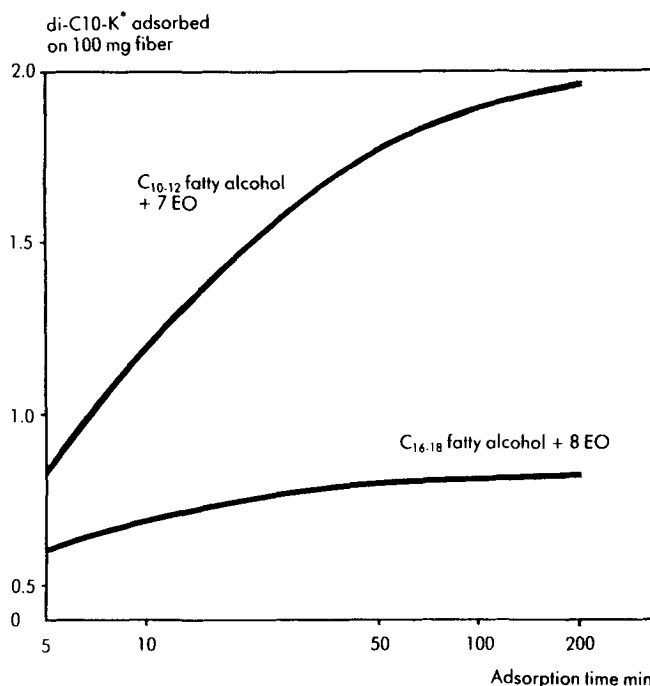


FIG. 7. Influence of nonionic surfactants on the adsorption rate of di-C10-K*. a/c, 0.81; T, 60°C; pH, 10.0; nonionic surfactant, 200 mg/l; builder salts, 2900 mg/l.

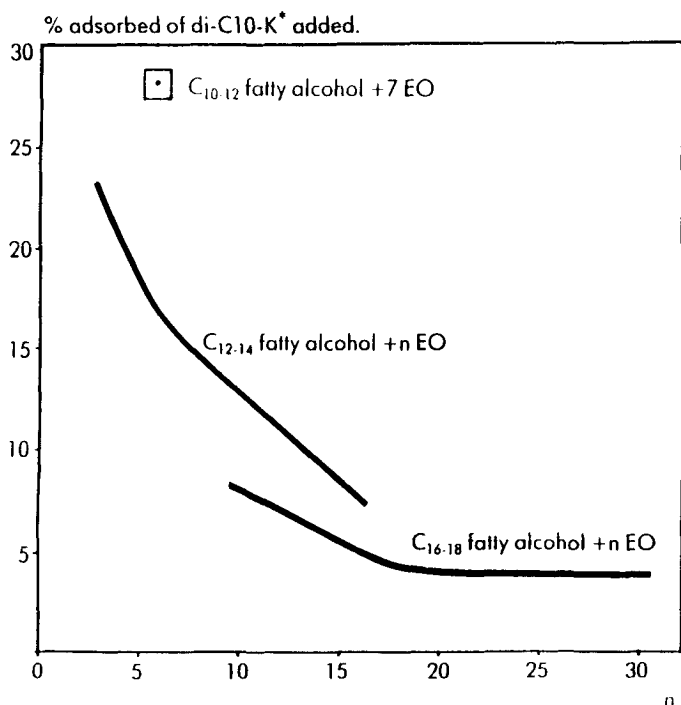


FIG. 6. Effect on adsorption by 200 mg/l of nonionic surfactants. a/c, 0.80; T, 60°C; t, 120 min; pH, 10.0; initial concentration of di-C10-K*, 2.20 mmol/l.

ionic surfactant, C18(EO)₂SO₄, 1.6%; nonyl phenol + 8 EO, 80%; propylene glycol and water, ad 100%. The detergency compared with a commercial liquid detergent (Fig. 10) with adequate results.

The antistatic properties on three synthetic fabrics have been tested for this formulation in comparison with the commercial liquid detergent mentioned previously and also a commercial powder detergent (Fig. 11).

DISCUSSION

An enhanced detergency for sodium dodecylsulphate

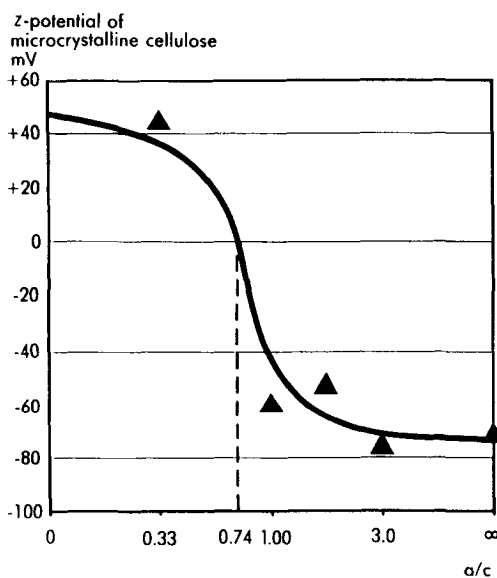


FIG. 8. z-Potential of microcrystalline cellulose as a function of a/c in the detergent solution. di-C10-K + C18(EO)₂SO₄, 0.25 mmol/l; C₁₀₋₁₂ fatty alcohol + 7 EO, 400 mg/l; t, 25°C; pH, 10.0.

on wool at 40°C through addition of dodecylpyridinium chloride has been found for a/c in the range 24–9 (6). At a/c in the range 16–9 the detergency results were fluctuating, which is explained by the low solubility of the surfactant mixtures.

The positive effect is explained by an interpenetration of the cationic surfactant in the adsorbed anionic monolayer and thereby decreasing the repulsion between the anionic groups and creating a more condensed layer.

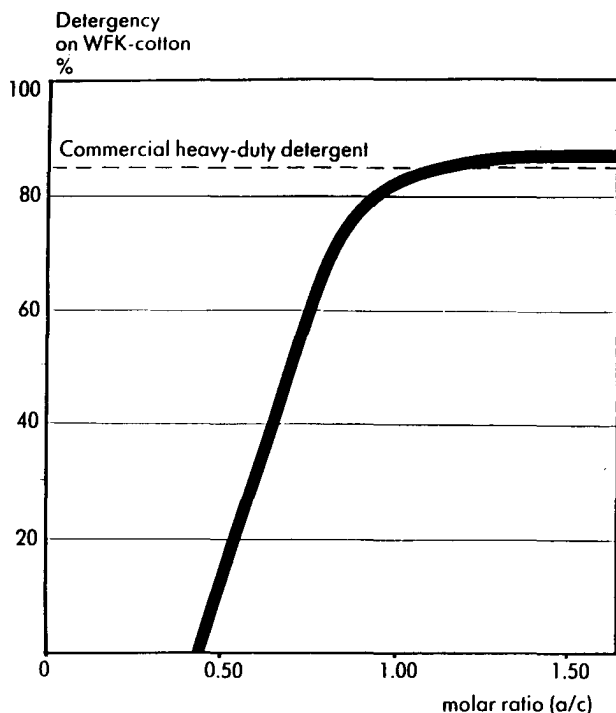


FIG. 9. Detergency of nonionic/anionic/cationic surfactant mixtures for various values of a/c. Initial concentration of di-C10-K: 0.17-sc0-0.51 mmol/l; D:o of C18(EO)₂SO₄: 0.34 mmol/l; D:o of C₁₆₋₁₈ fatty alcohol + 8 EO: 400 mg/l; builder salts, 3300 mg/l; T, 85°C; t, 15 min; Terg-O-Tometer; water, 21 ppm CaCO₃.

Similar effects have been shown for the reverse situation, i.e., minor amounts of anionic surfactants added to cationic (7).

The maximum total adsorption on cotton fibers according to the present work is 34 $\mu\text{mol/g}$ (Fig. 4) and occurs when the a/c in the added solution is 0.88. a/c on the fiber is then 0.44, and this is in equilibrium with a solution having a/c 2.4 (Fig. 3).

If the hydrocarbon chains of the surfactant molecules are assumed to be close-packed and each occupies 0.205 nm² forming an adsorbed double layer, then 34 $\mu\text{mol/g}$ will mean that 3.5 m²/g cotton fiber are covered. As the area on cotton fiber available for adsorption is highly dependent on the assumed minimum pore diameter necessary for the passage of the adsorbate in question, this value of 3.5 m²/g may be interpreted from (11) so that this min. diameter is approximately 10 nm.

The difference between the a/c for the adsorbed surfactants, e.g. 0.44 at the maximum adsorption, and the a/c in the solution, 2.40, in equilibrium with that can be explained by the preferential adsorption of cationic surfactant on the anionic sites on the cellulose, e.g., carboxylate groups.

This will lead to a slightly positive charge on the surface and negatively charged micelles and thus favor further adsorption.

The negative influence on the adsorption by various nonionic surfactant may best be explained by the use of the Critical Packing Parameter (CPP) concept by Israelachvili (8) and successfully applied on the cleaning of hard surfaces by Lindman et al. (9). According to the CPP concept it is understandable that nonionic surfactants with longer polyglycol ether chains will

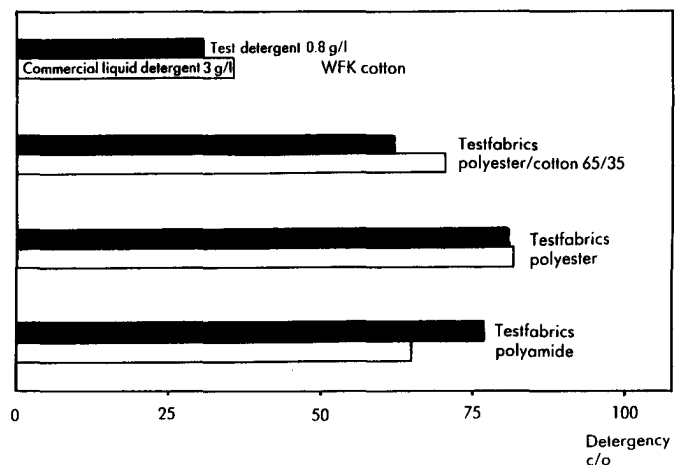


FIG. 10. Detergency of test detergent and commercial liquid detergent. Tumbler-type machine. T, 40°C; water, 90 ppm CaCO₃.

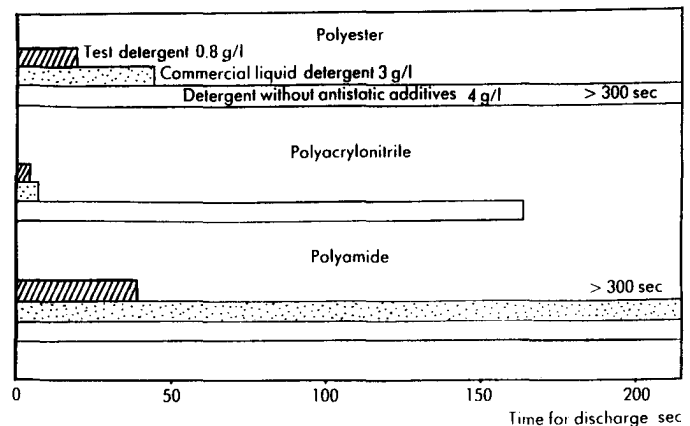


FIG. 11. Antistatic effects at 30% relative humidity of test detergent and two commercial detergents. Wash temperature, 40°C; water, 90 ppm CaCO₃.

have a stronger negative influence on the adsorption in spite of being less surface active. It will thus be assumed that the nonionic surfactant will be a part of the mixed adsorbed double layer and by its large hydrophilic group cause a less dense packing of this layer.

The profound positive effect of the cationic-anionic surfactant adsorption on the surface conductivity (antistatic effect) of synthetic fibers may be understood by the admicelle theory of Harwell et al. (10) assuming that the adsorption—either as mono- or bilayer—will take place as discrete patches and that these patches will constitute the conducting elements on the surface. An increased adsorption will then at some level abruptly increase the probability of contact between these patches.

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