Zwitterionic Surfactants: Structure and Performance

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ABSTRACT

The performance and biodegradability of some zwitterionic surfactants have been compared with those of conventional anionic and nonionic surfactants. The zwitterionics are superior base materials for formulating laundry products with or without phosphates. In addition to having excellent performance properties, ammoniocarboxylates are highly biodegradable with respect to functional and ultimate degradation.

INTRODUCTION

Synthetic detergents find wide application in domestic and industrial outlets. In the domestic area, two end uses predominate, namely clothes washing and dishwashing, which account for some 60% of the total surfactant market. Of these two, the larger consumption of surfactants is by the laundry products, accounting for about 65% of all surfactants used in household applications.

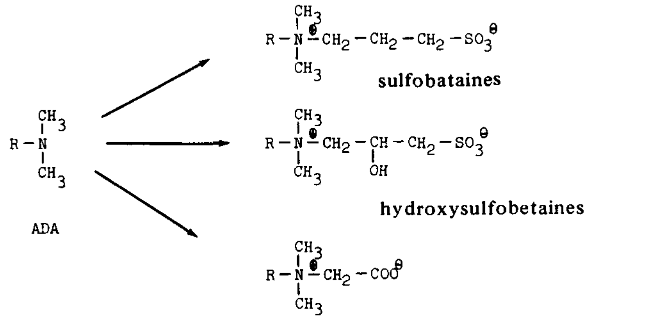
The active materials currently used in laundry products are anionics and nonionics, as such and in blends. The anionic workhorse, linear alkylbenzene sulfonate (LAS), exhibits good cotton detergency only when used with builders capable of reducing the calcium ion concentration of the wash liquor to below 10^{-6} g ions per liter (<0.1 ppm as $CaCO_3$) (1). Nonionics, especially primary alcohol ethoxylates (PAEO), however, are much more tolerant toward the presence of unsequestered calcium ions (2) and show even better detergency performance when used in combination with phosphates (3). An interesting class of compounds are the zwitterionics, which can be described as derivatives of quaternary ammonium compounds. Evidence from the literature indicates such surfactants to be good detergents in cold water (4) and to be relatively insensitive to the presence of calcium ions (5). Such materials are more expensive than LAS and PAEO and are, therefore, speciality rather than commodity surfactants. However, when considering the requirements of the next-generation surfactants (effective at low washing temperatures, efficient in the presence of free calcium ions, etc.), an increase in surfactant cost may be offset by a saving in formulation and energy costs.

This paper highlights the results of an investigation into the relationship between structure and performance of some zwitterionic surfactants.

EXPERIMENTAL PROCEDURES

Sructures Examined

The following zwitterionic surfactants may be readily prepared from long-chain N,N-dimethylalkylamines (ADA):



Evaluation Procedures

Fabric detergency: All detergency measurements were

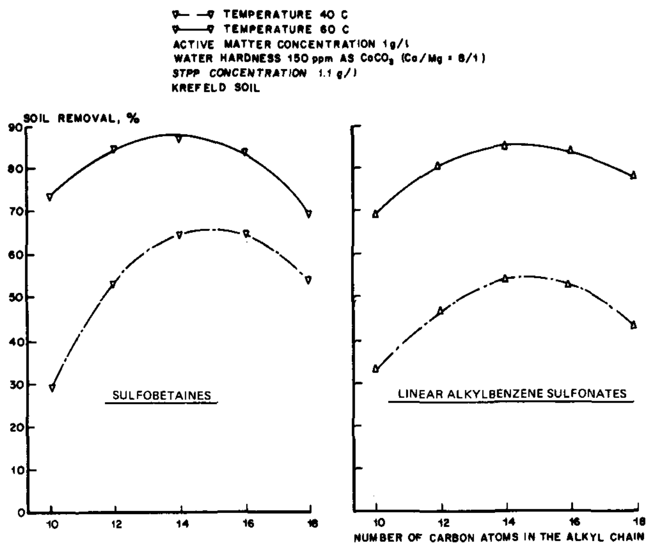


FIG. 1. Cotton detergency of sulfobetaines and linear alkylbenzene sulfonates.

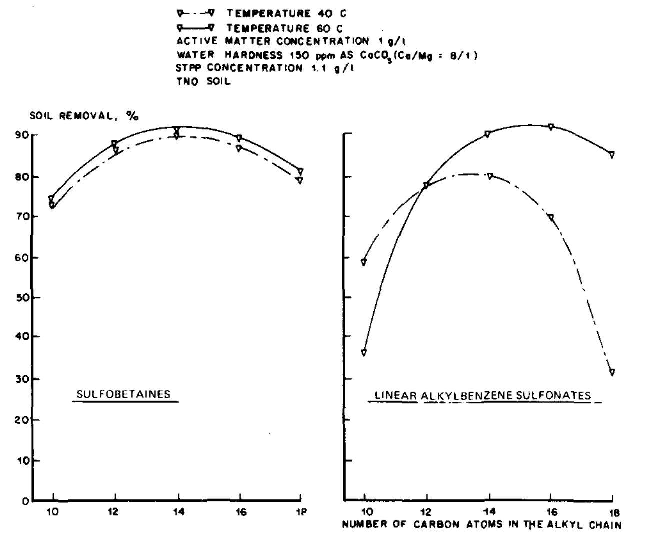


FIG. 2. Polyester/cotton detergency of sulfobetaines and linear alkylbenzene sulfonates.

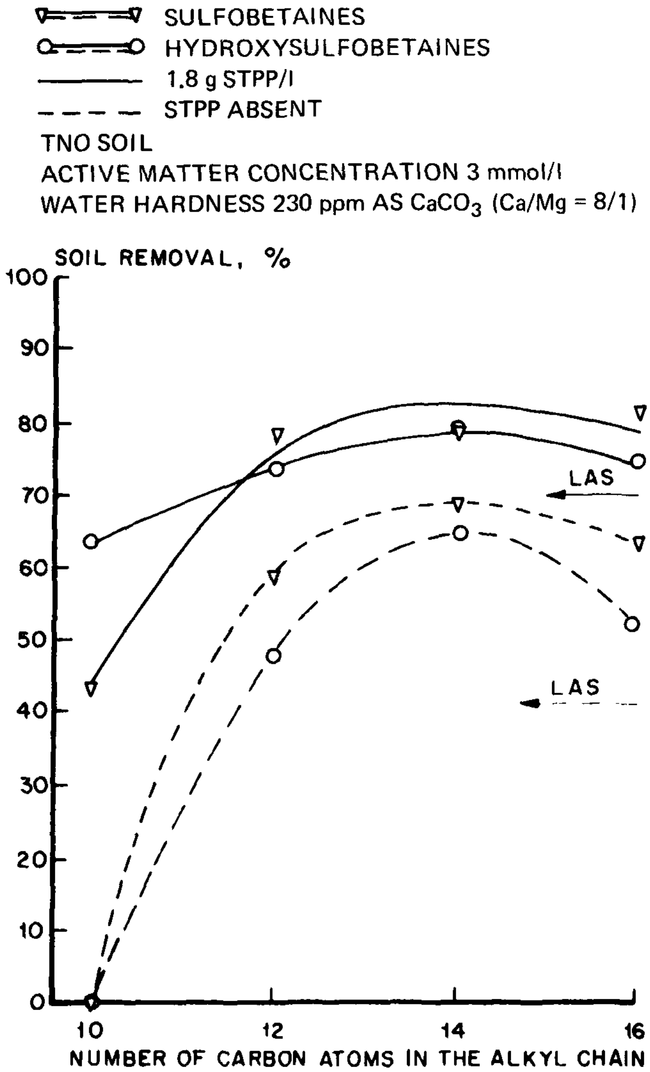


FIG. 3. Cotton detergency of sulfobetaines and hydroxysulfobetaines at 60 C.

made using the Terg-O-Tometer and artificially soiled test cloths. Cotton test cloth was obtained from Krefeld (Germany) and TNO (The Netherlands). The compositions of the soils applied to these cloths are as follows:

Krefeld

Kaolin	0.69	%w on fabric
Soot	0.068	
Black iron oxide	0.034	
Red iron oxide	0.017	
Sodium chloride	0.85	
Wool fat	3.30	

TNO

40% Peanut oil	applied as a paste
40% Finely ground quartz	
10% Tallow	
5% Petroleum jelly	
5% Red iron oxide	

Soil removal was calculated from reflectance measurements according to the formula:

$$\% \text{ soil removal} = \frac{R_w - R_s}{R_u - R_s} \times 100,$$

where R_s = reflectance of soiled fabric before washing; R_w = reflectance of soiled fabric after washing; R_u = reflectance of the unsoiled fabric.

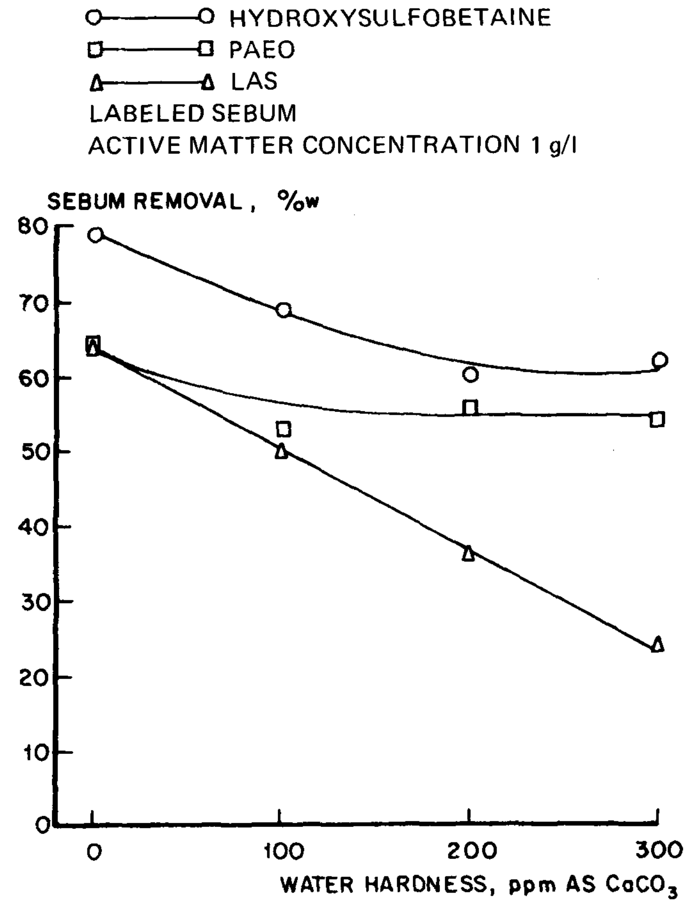


FIG. 4. Effect of water hardness on polyester/cotton detergency at 45 C.

Polyester/cotton detergency was determined using the Shell Radio Labeled Sebum Technique (6) and polyester/cotton from Test Fabrics Inc. (style 7406 or 7406/WRL, the latter type having a permanent press finish). The composition of the sebum applied is:

Component	%w	Label
Lubricating oil	25	^{3}H
Tristearin	10	^{3}H
Peanut oil	20	---
Stearic acid	15	^{14}C
Oleic acid	15	^{14}C
Octadecanol	8	^{14}C
Cholesterol	7	^{14}C

A sebum loading of 28 mg per swatch (10 x 10 cm) was applied. Sebum removal, in %w, was calculated by the method of Shebs and Gordon (7).

A few tests were also made using Krefeld and TNO soils applied to polyester/cotton finished with a propylene urea formaldehyde resin. Reflectance measurements were used to calculate the soil removal from these cloths.

Foaming properties: The ISO version (ISO/R696) of the Ross-Miles test (ASTM D 1173) was used.

All solutions used for the detergency/foaming investigation contained sodium silicate ($Na_2O \cdot 2SiO_2$) and sodium sulfate at concentrations of 0.24 and 0.6 g/l, respectively. Active matter, sodium tripolyphosphate (STPP), and water hardness were varied as given in the figures.

Biodegradability: Biodegradability was measured using the OECD screening and confirmatory tests (8), the Fischer bottle test (9,10), and the Sturm CO_2 test (11).

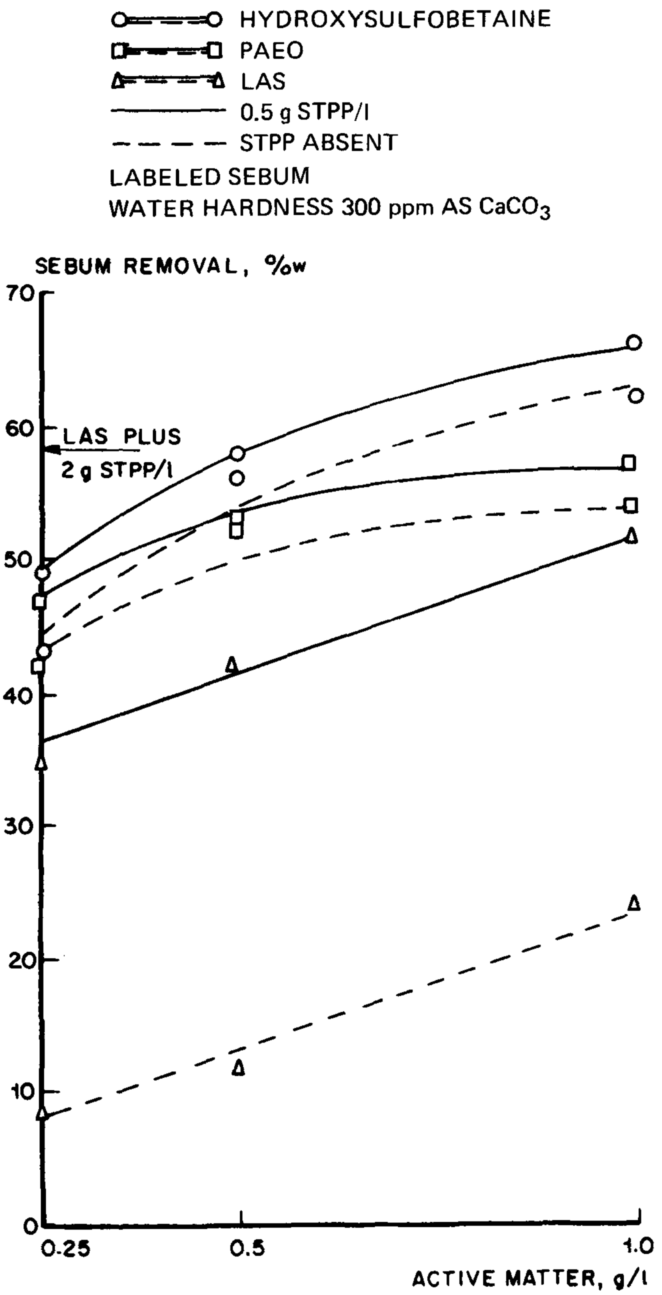
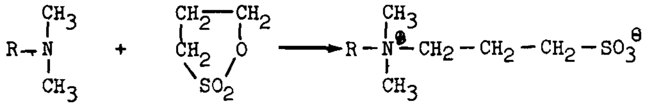


FIG. 5. Effect of active matter concentration on polyester/cotton detergency at 45 C.

SULFOBETAINES

These were prepared in quantitative yield from ADA and propane sultone according to the following scheme:



R = C_{10} to C_{18} primary alkyl

Fabric detergency measurements were carried out using artificially soiled Krefeld cotton and TNO polyester/cotton test cloths; data were obtained at temperatures of 40 and 60 C in water containing 0.55 g/l of STPP in excess of the stoichiometric requirement. As reference materials, monocarbon samples of LAS were used. The data are illustrated in Figures 1 and 2. The better performance of the sulfobetaines is clearly evident, especially for cleaning polyester/cotton. The optimum chain length for both surfactants is C_{14}.

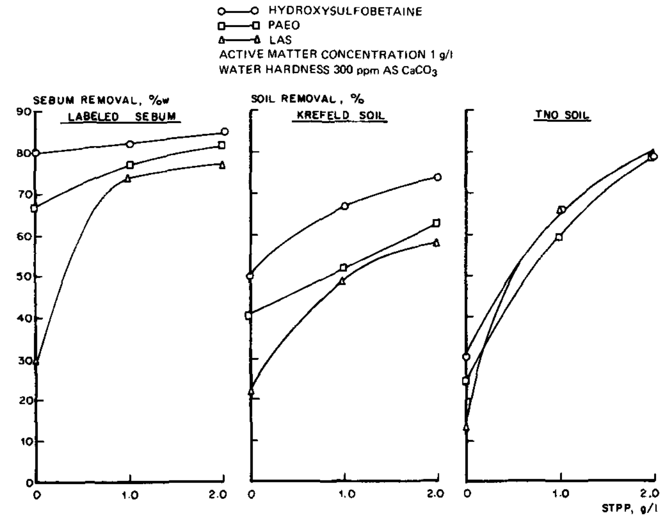
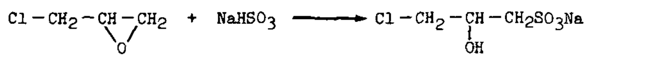


FIG. 6. Polyester/cotton detergency at 45 C with three types of artificial soil.

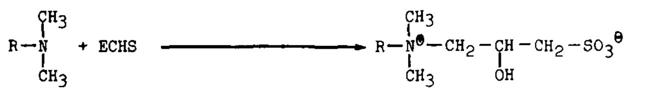
The hazardous nature of propane sultone (12) precludes the use of this route as a commercial method for the preparation of sulfobetaines.

HYDROXYSULFOBETAINES (HSB)

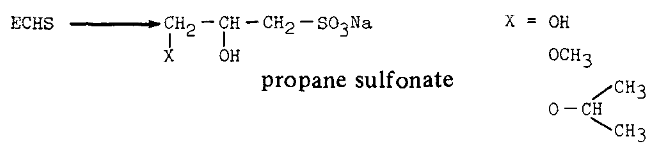
These materials may be conveniently prepared (13,14) by reacting ADA with the addition product of epichlorohydrin and sodium bisulfite (15).



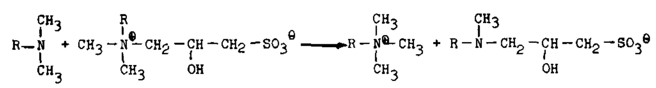
epichlorohydrin sulfonate (ECHS)



Depending on the process conditions, varying amounts of by-products are formed which may remain at least partly in the final product. In the coupling of the ADA and ECHS some solvolysis may occur:



Furthermore, the HSB formed may react further with ADA to yield long-chain cationic and anionic compounds:



Samples of HSB were prepared from C_{10}, C_{12}, C_{14}, and C_{16} ADA. The cotton detergency of the derived materials was measured using artificially soiled cotton cloth (ex TNO) and compared with that of sulfobetaines derived from the same ADA. Tests were carried out in hard water in the presence and absence of STPP. The data obtained are illustrated in Figure 3.

Good detergency results were obtained with both types of zwitterionic. Differences in performance were small and, in general, nonsignificant. The data show that the cotton detergency of both zwitterionics is less sensitive than that of LAS to the presence of unsequestered calcium ions. The zwitterionics are superior to LAS when phosphates are

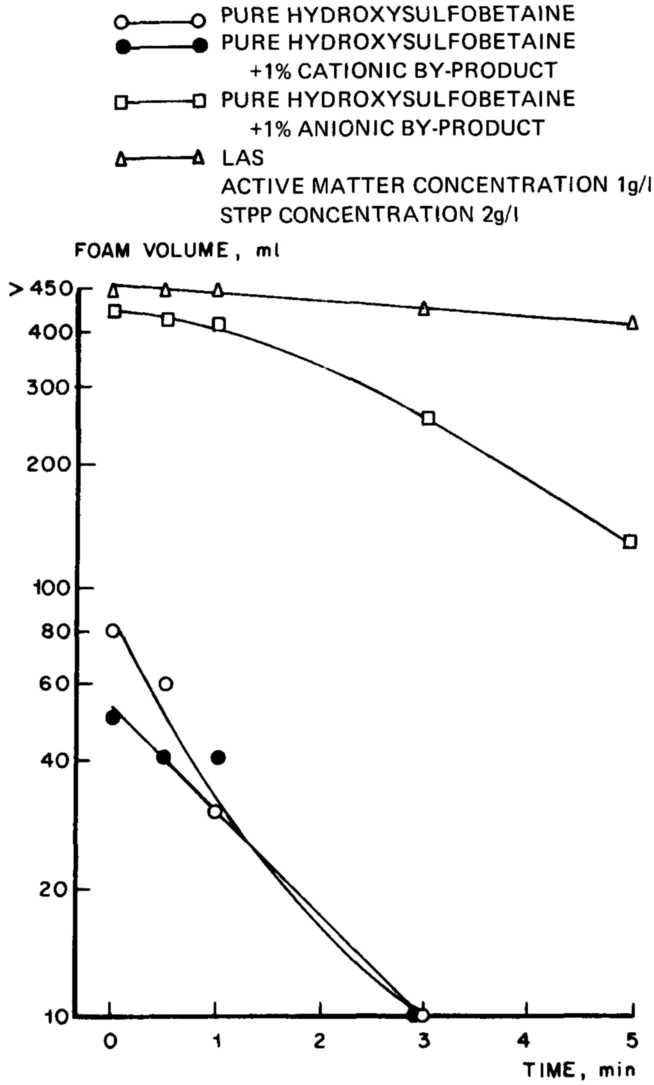


FIG. 7. Foaming properties at 60 C.

present; in hard water in the absence of STPP the zwitterionics show the same cotton detergency as LAS built with phosphate.

In view of the increasing importance of polyester/cotton, the investigation included measurements on this substrate. LAS and PAEO were used as reference materials. To enable true comparisons with the reference materials to be made, the HSB sample used contained the by-products at concentrations likely to be encountered in commercial production. For this work the labeled sebum was applied to the polyester/cotton. The effect of calcium ions on sebum soil removal by HSB, LAS, and PAEO is shown in Figure 4.

Of the surfactants examined, HSB is preferred. The zwitterionic is markedly superior to the anionic and marginally less sensitive to calcium ions than the nonionic.

As zwitterionic surfactants are likely to be more expensive than anionic and nonionic materials, cost/performance is of prime importance. Therefore, data were obtained for polyester/cotton detergency (labeled sebum) of HSB, LAS, and PAEO as a function of active matter and STPP concentration and are shown in Figure 5.

The performance level of LAS at 1 g/l in the presence of 2 g STPP/l is attained by 0.7 g HSB/l without phosphates, or by 0.5 g HSB/l plus 0.5 g STPP/l. In areas where phosphates are prohibited, HSB offers the possibility of formulating products without a loss in cleaning properties consequent upon a reduction in phosphate content. The anticipated higher cost of the zwitterionic compared with

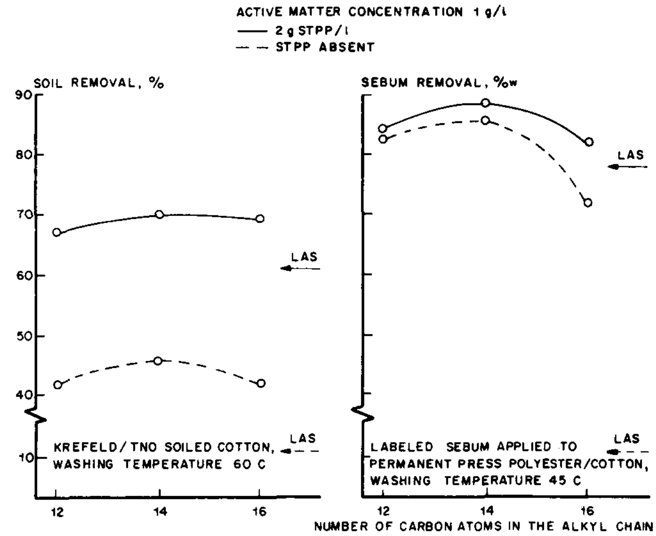


FIG. 8. Cotton and polyester/cotton detergency of betaines in hard water (300 ppm as $CaCO_3$).

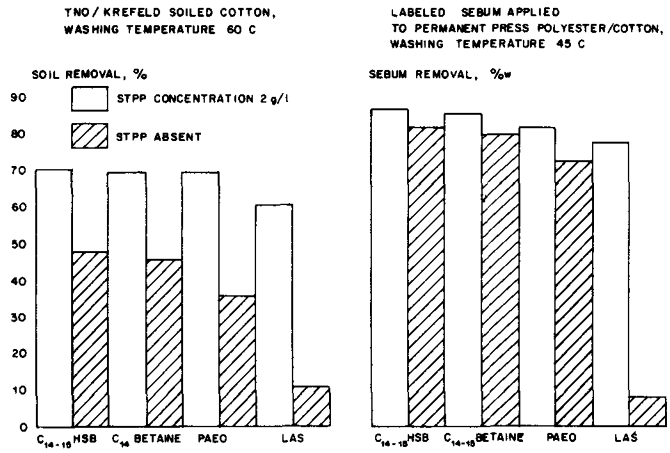


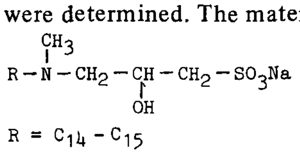
FIG. 9. Cotton and polyester/cotton detergency of surfactants in hard water (300 ppm as $CaCO_3$).

LAS may, therefore, be offset by the lower concentration of active material required, coupled with the saving in the phosphate component.

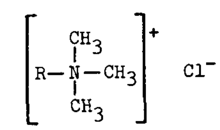
To exclude the possibility that the exceptionally good performance of HSB was dependent upon the artificially soiled test cloth chosen, the investigation included permanent press polyester/cotton soiled with TNO, and Krefeld soils and the labeled sebum. Data obtained are shown in Figure 6. Although differences are observed between the three types of artificial soil, the level of cleaning of the zwitterionic is at least as good as that of either the anionic or nonionic surfactants examined.

INFLUENCE OF BY-PRODUCTS ON THE PERFORMANCE OF HSB

As by-product formation is inevitable, it is highly desirable to know what effects such impurities will have on the detergency and foaming properties of the derived HSB. The long-chain anionic and cationic materials were synthesized, and their influence on the performance of pure HSB were determined. The materials synthesized were:



anionic by-product



cationic by-product

TABLE I

Biodegradation (in %) Measured According to the OECD Test Procedures[a]

Test procedure	Soft standard (Marlon A)	Hard standard ("DOBANE" PT sulfonate)	HSB
Screening	93.5	10	96
Confirmatory			94.8

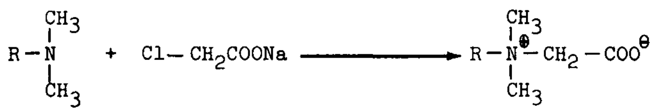
[a]Anionic degradation followed by methylene blue activity, biodegradation of HSB by a polarographic method (16).

It was found that the anionic component had little effect on the fabric detergency; the cationic, however, reduced soil removal and increased soil redeposition.

Foaming measurements showed that pure HSB can be classified as low-foaming compared with LAS. The anionic component acts as a powerful foam promoter, even at levels of 1% on HSB active matter. The cationic, on the other hand, acts as a foam depressor. Of the two effects, foam production and depression, the action of the anionic is much greater than that of the cationic. Quantified, ca. 5%w cationic is required to overcome the foam-promoting effect of 1%w anionic, all additions being based on HSB active material. These effects are illustrated in Figure 7. It was further found that all anionic surfactants act as foam promoters for HSB; nonionics have no effect on foam stability.

BETAINES

These were synthesized according to the following scheme:



R = C_{12} to C_{16} primary alkyl

Fabric detergency was measured in the presence and absence of STPP using artificially soiled cotton (Krefeld and TNO) and permanent press polyester/cotton (labeled sebum). The data obtained are shown in Figure 8.

The optimum chain length for both fabrics is C_{14}; the polyester/cotton detergency of C_{12} and C_{14} betaines in the absence of phosphates exceeds that of LAS built with STPP.

COMPARISON OF ZWITTERIONICS WITH OTHER GENERIC TYPES

The cotton (Krefeld and TNO soils) and polyester/cotton (labeled sebum) detergencies of zwitterionics derived from C_{14}-C_{15} ADA and of LAS and PAEO are shown in Figure 9. HSB and the betaine are at least equivalent to PAEO and are markedly superior to LAS, especially in phosphate-free formulations.

TABLE III

Biodegradation as Measured by the Sturm CO_2 Test and DOC[a] on Solution Remaining at the End of the CO_2 Test

Active material	CO_2 production, % of theoretical amount	Loss of DOC, % of initial value
C_{12} sulfobetaine	49	
C_{16} sulfobetaine	56	
C_{14-15} HSB	40	
C_{12} betaine	91	99
C_{14} betaine	84	98
C_{16} betaine	84	97
C_{14-15} betaine	81	93
LAS	63	

[a]DOC = dissolved organic carbon.

BIODEGRADABILITY

The introduction of a new base material for laundry products must not create environmental problems. Ideally, biodegradation should not only be functional (disappearance of original active species) but also ultimate in terms of carbon dioxide formation and mineralization. Current concern is primarily related to functional degradation, but products now at the R&D stage should also be examined in the context of complete mineralization.

Biodegradation tests undertaken during this investigation were those described by OECD, Fischer, and Sturm. Data obtained are given in Tables I-III.

The OECD test procedures and a polarographic (16) method for determination of active material show that the HSB molecule, and the surface activity for which it is responsible, disappear rapidly and completely. The behavior of sulfobetaines and HSB in tests based on oxygen consumption or CO_2 production is less straightforward. Degradation is only partial and appears to stop when about half the theoretical amount of oxygen has been consumed or half the theoretical amount of carbon dioxide produced. This implies that a rather stable intermediate is formed.

Betaines, on the other hand, show very high levels of carbon dioxide formation and loss of dissolved organic carbon, which indicate total biological breakdown without the formation of hard residues.

ACKNOWLEDGMENTS

The author thanks the management of Shell Research B.V. for permission to publish this paper and colleagues who assisted in this investigation.

TABLE II

Biodegradation Measured According to the Fischer Closed Bottle Test

Active material	Oxygen absorbed, % of theoretical amount[a]	Biodegradation as loss of polarographic activity, %
C_{12} sulfobetaine	25	90
C_{16} sulfobetaine	26	97
C_{14-15} HSB	40	100
C_{12} betaine	55	100
C_{14} betaine	58	
C_{16} betaine	45	
C_{14-15} betaine	52	
LAS	58	91
PAEO	69	

[a]According to Fischer (17), an oxygen uptake of about 40% represents a working minimum level of acceptability.

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