SURFACTANTS & DETERGENTS

Liquid Laundry Detergents Based on Soap and α-Sulfo Methyl Esters[1]

Joseph C. Drozd* and **Dilip D. Desai**
Stepan Company, Northfield, IL 60093

It is well known that soap is one of the most effective cleaning agents in soft water. However, soap is equally notorious for some of its deficiencies, especially formation of soap scum due to the precipitation of calcium and magnesium soaps in hard water, low solubility in water, poor cleaning in cold water, greying of fabrics and dulling of hard surfaces such as ceramic tiles. Attributes of soap that should not be overlooked, especially in today's environment, include an abundant and natural raw material supply (vegetable oils and fats) and excellent human and environmental safety profiles that are superior to most synthetic surfactants.

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It has been suggested that many of these problems with soap could be overcome by combining it with synthetic surfactants, particularly those that are good lime soap dispersants (1–4). α-Sulfo methyl esters (ASMEs) are among the best lime soap dispersants known. It has been shown that powdered laundry detergents containing tallow soap can be formulated with the aid of α-sulfo methyl tallowate and silicate builders to give performance equal to commercial household detergents built with phosphate (4).

Until recently, soap has not been present along with synthetic surfactants in any major laundry detergent in the U.S. Now at least one major laundry liquid contains some coconut soap. Liquid laundry detergents have become very important and now hold approximately 40% of the laundry detergent market in the U.S. If the difficulties of incorporation and performance of soaps in liquid detergents could be overcome, gains stand to be made in lower cost, improved human and environmental safety and possibly even performance.

In 1988 liquid α-sulfo methyl esters derived from lauric oil became commercially available from the Stepan Company (Northfield, IL) under the ALPHA-STEP trademark. The properties and performance of these α-sulfo methyl laurate (ASML) surfactants in detergent products have been well discussed (5). Among the most significant properties of ASML in the context of being used with soap are that ASML cleans well in hard water, is an excellent solubilizer for other surfactants and is a good lime soap dispersant. The complimentary properties of soap include: cleans well in soft water; low water solubility; and insoluble soaps precipitated in hard water. The properties of ASML seem to be exactly those needed to make the use of soap practical in heavy duty liquids.

The purpose of our work was to determine the feasibility of using a combination of soap and lauric oil derived α-sulfo methyl ester as a new alternative in the manufacture of heavy duty liquids.

Compatibility of soap and ASME. It is indeed possible to formulate liquid products containing high concentrations of soap using ASME as a co-surfactant (Fig. 1). The soap used was Ivory Snow® manufactured by the Procter and Gamble Company (80:20 tallow/coconut soap; Cincinnati, OH) and the ASME was ALPHA-STEP™ ML-40 (40% sodium α-sulfo methyl laurate) manufactured by the Stepan Company. Up to 20% soap could be formulated into clear fluid mixtures using from 40 to 60% ALPHA-STEP ML-40 and small amounts of ethylene glycol and/or tetrasodium EDTA. Clear liquids containing 5% soap and only ML-40 could be formulated without any additives. ALPHA-STEP ML-40 has an average carbon chain length of 12. Virtually identical results were obtained with another ASME, ASMC, with an average carbon chain length of 13.6. The detergency obtained with ASMC was somewhat better than that obtained with ALPHA-STEP ML-40, and therefore all of the following comments and results refer to ASMC. ASMC is not yet a commercially available product.

Detergency of soap and ASME. The detergency of soap and ASMC is good. Figure 2 shows the detergency of various combinations in moderately hard water (140 ppm hardness as $CaCO_3$, Chicago tap water). At a total concentration of 0.8 g/L, good detergency (ΔR greater than 30) was obtained using up to about 40% soap, with the remainder being ASMC. These were standard Terg-O-Tometer (U.S. Testing Co., Inc., Hobokan, NJ) tests. In these tests ΔR is the sum of the differences in average reflectance measurements of washed and unwashed soiled test fabric swatches: $\Delta R = \Sigma(R\ \text{final} - R\ \text{initial})$. "Standard" soiled swatches used were obtained from Scientific Services (Oakland, NJ) and Testfabrics, Inc. (Middlesex, NJ).

In this same test the detergency of six brand name laundry liquids ranged from $\Delta R = 30$ to 41 when used according to manufacturers' instructions of 1/2 cup per load. This equates to 2 g/L in the "Terg" test or, since the products were at least 30 to 40% solids, 0.6 to 0.8 g solids/liter.

The significance of the compatibility and detergency results is a little clearer when we combine the two types of data (Fig. 3). Again, the area under the curve gives combinations of soap and ASMC that result in clear liquids. The detergency values given along the 40% solids line are those that would result from using combinations of soap and ASMC at a total of

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*To whom correspondence should be addressed.

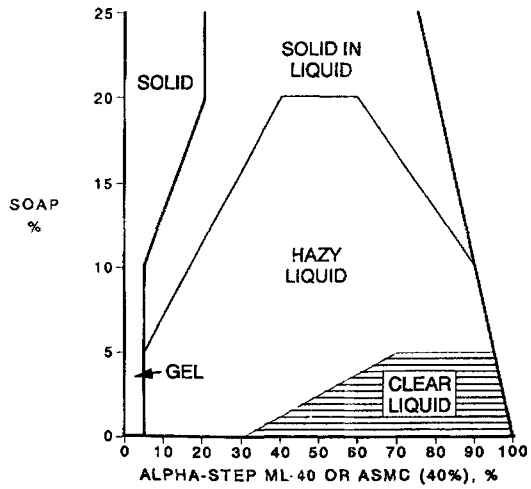

FIG. 1. Appearance of mixtures of soap and α-sulfo methyl esters in water at room temperatures.

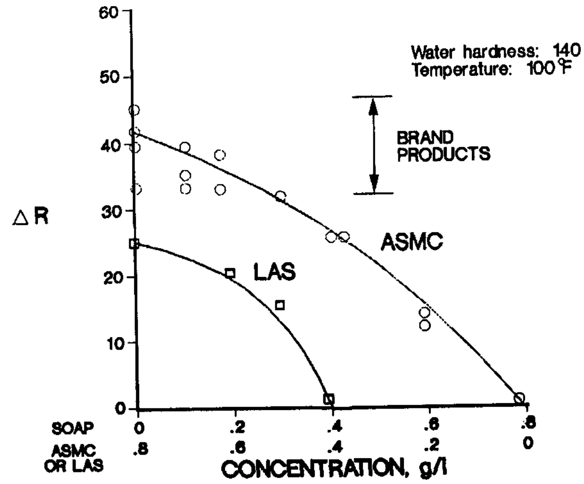

FIG. 2. Detergency of soap and ASMC or LAS in moderately hard water.

40% solids using up to 20% soap at 1/2 cup per wash load. These compositions are liquid and the detergency is at least as good as the brand products. Since soap is less expensive than most surfactants it is desirable to use as much as possible in the formulation.

How does LAS compare? It is of obvious interest to know how the most commonly used surfactant, LAS (sodium dodecylbenzene sulfonate) would compare to ASMC in these tests. First of all, it is known that LAS is more sensitive to water hardness than ASMC, and also that it is not a particularly good lime soap dispersant. The ability of LAS to combine with soap to give slightly hazy to clear solutions is much less than ASMC (Fig. 4). The most soap that can be solubilized with LAS is 10%, as compared to 20% for ASMC. The detergency of 35% solids LAS/soap blends that were liquid was low (ΔR = 20–25), and nowhere near that obtained with ASMC (Figs. 2 and 5).

Effect of water hardness. Over the range of soft water to 300 ppm hardness, acceptable detergency can be obtained with soap and ASMC (Fig. 6 and 7). ASMC alone does not appear to be particularly sensitive to water hardness in this range; soap, of course, is.

In soft water the detergency of soap/ASMC blends increases with increasing amounts of soap. ASMC does contribute to cleaning here, but, on an equal weight basis, it can be seen that soap is more effective. The detergency of brand products is better in soft water and the differences between them has increased. In hard water the detergency of the blends decreases with increasing amount of soap. At 300 ppm hardness, more than twice the stoichiometric amount of calcium and magnesium ions needed to completely complex with the soap is present. Soap does not appear to contribute to the detergency under these conditions. What is significant here is that it appears that a product consisting of soap and ASMC can give good detergency across the board in soft to hard water and that concentrated liquids containing an appreciable amount of soap can be formulated.

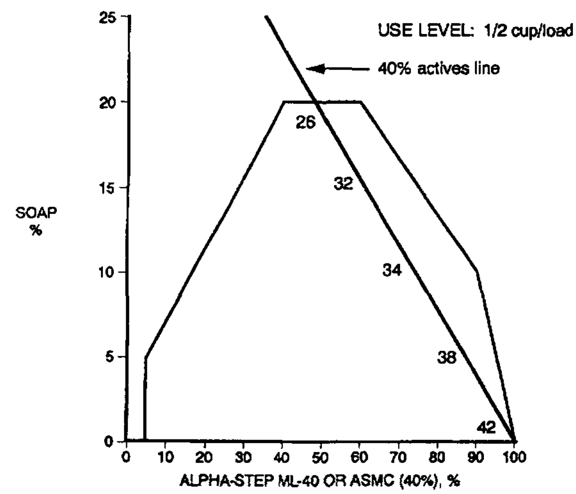

FIG. 3. Detergency of soap and ASMC mixtures at 40% active in moderately hard water.

HDL formulations. The following starting formulations for an HDL containing soap and ASME were prepared based on this work (Table 1). These formulations were compared to brand name products in soft, moderately hard and hard water (Fig. 8). The overall detergency of the blend containing 10% soap and 30% ASMC was good in soft and hard water. Although the blend containing more soap was better in soft water, it was poorer in hard water. This is as would be predicted from the earlier results.

The results in Figure 9 show the performance of both soap/ASMC formulations on four types of soiled fabric in moderately hard water as compared to the range in detergency observed for the brand products that were tested. The formulation containing 10% soap and 30% ASMC cleaned in the range of the brand

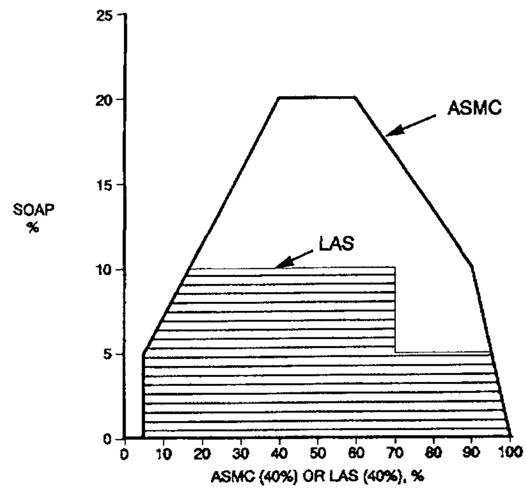

FIG. 4. Mixture of soap and ASMC or LAS resulting in liquids.

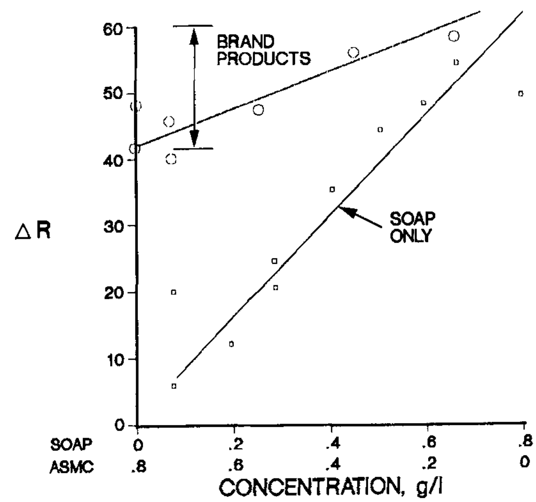

FIG. 6. Detergency of soap and ASMC mixtures in soft water.

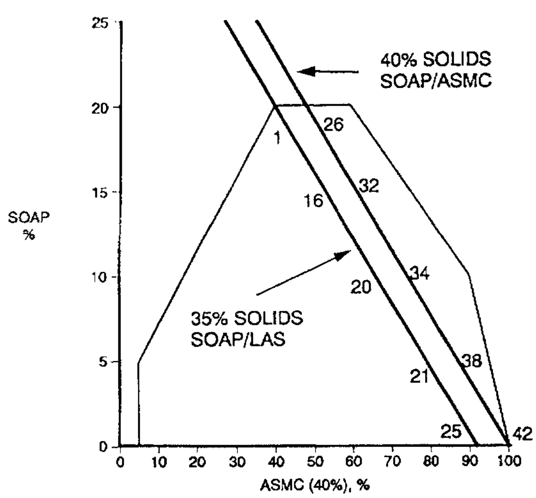

FIG. 5. Detergency of soap and ASMC mixtures at 40% active in moderately hard water.

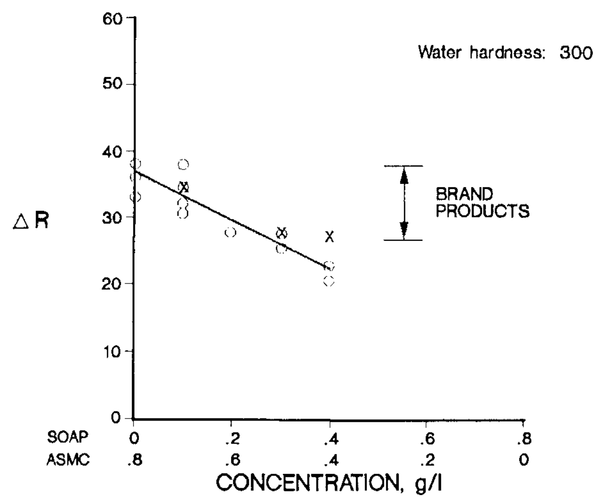

FIG. 7. Detergency of soap and ASMC mixtures in hard water.

products. The 20% soap-20% ASMC blend cleaned somewhat poorer in two cases.

Fabric softening. It is mentioned in the literature that tallow soap also imparts softness to fabric besides being a good detergent (1). It was therefore decided to evaluate the above 20% soap based liquid formula for softening against commercial liquid products, with and without fabric softener at 1/2 cup/load in a home laundry machine. Under identical conditions the soap/ASMC formula was found to impart more softness to cotton towels than either of the two commercial products. Therefore, it is possible that a soap based liquid formula would have this advantage over other liquid products based on conventional cationic/nonionic surfactants. On the other hand, softening implies that a residue has been left on the fibers. This may lead to "greying."

It has been shown that tallow/coco soap based liquid detergents can be formulated with the aid of naturally derived α-sulfo methyl ester surfactants. Furthermore, these detergents can be both economical and

TABLE 1

Soap/ASMC HDL Formulations

	1	2
Tallow/coco (80:20) soap	20.0	10.0
α-Sulfo methyl cocoate	20.0	30.0
Propylene glycol or ethyl alcohol	12.0	2.0
Na_4EDTA	1.0	1.0
Water	47.0	47.0
Total	100	100
Appearance	Clear, pourable liquid	
Solids, %	40	
Use level	1/2 cup per load	

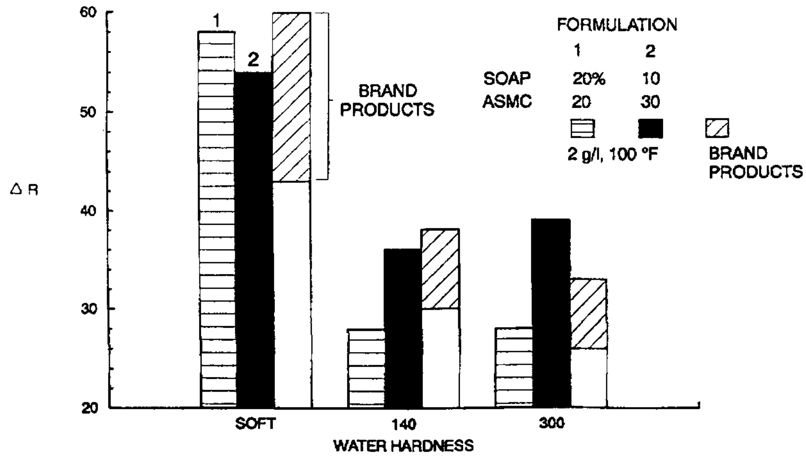

FIG. 8. Comparison of overall detergency of two soap/ASMC blends to brand products.

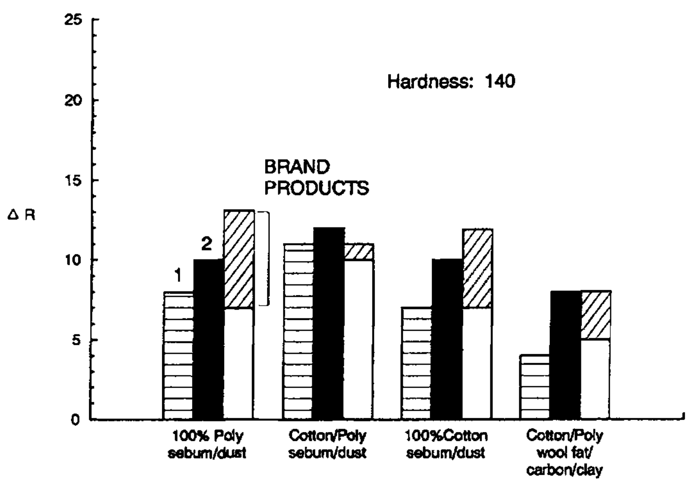

FIG. 9. Comparison of detergency of two soap/ASMC formulations to brand products on different fabric-soil types.

effective in performance at low and high levels of water hardness. Such a product may have other advantages over current products based on conventional surfactants such as environmental safety, biodegradability, mildness, and fabric softening properties.

This study still leaves some questions unanswered such as a possible greyness build-up upon repeated washing of fabrics with such a product since washing with soap alone shows this weakness. Though we presume that α-sulfo methyl esters, because of their lime soap dispersing ability, may help in eliminating this weakness, work has to be done in this area to confirm that. One has to keep in mind that this was primarily a laboratory scale study and a considerable amount of work has to be done with respect to detergency evaluation under home washing conditions, stain removal ability, enzyme stability, use of detergent builders and possible greyness build-up problems.

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