Study of Detergency. I. Effect of the Concentration and the Kind of Detergent in Hard Water

HARUHIKO ARAI, Household Goods Research Laboratories, Kao Soap Co., Ltd., 2-Chome, Bunka, Sumida-ku, Tokyo, Japan

Abstract

The effect of concentration and kind of detergent, and nature of oil-on-oil removal efficiency in hard water was studied. Maximum oil removal efficiencies are shown at the same water hardness for a given oil. As the concentration of detergents increases, the water hardness at maximum oil removal efficiency increases and the sharpness of the oil removal peak is lessened. A linear relationship between concentration of detergent and water hardness at maximum oil removal efficiency was found. This relationship is dependent on the nature of the oily soil and kind of detergent.

Introduction

Although detergency using oily soil has been variously studied (1), the mechanism of removal is not clearly understood (2). It may be assumed, however, that the most important phenomenon involved is the solubilization or microemulsification by detergent of the oily soil, which is then suspended in the water away from the textile. This phenomenon, in short, makes a stable emulsion a condition for detergency.

The mechanism of emulsification has been studied by many (3,4). They have suggested that, in order best to make a stable emulsion, the hydrophile-lipophile balance (HLB) of detergent will be varied, depending on the nature of the oil.

If sodium dodecylbenzene sulfonate (NaDBS) is used in various water hardnesses, a part will be converted to calcium dodecylbenzene sulfonate (CaDBS), which is insoluble in water and more lipophilic than NaDBS. Accordingly, detergent solutions can be obtained of various CaDBS/NaDBS ratios (that is, the detergent solutions of various HBL values). Therefore, if a detergent such as NaDBS is used for washing in hard water, it may be expected that maximum detergency will be shown at the same water hardness for any given oil. Although there are many reports on the effects of hard water on detergency (5–11), these did not seem adequate to test the above idea. The present investigation was undertaken to obtain data on detergency at various water hardnesses, to test this idea.

Experimental

Materials

Sodium dodecylbenzene sulfonate (NaDBS, Neoplex 05: Kao Soap Co.) was purified by extraction with petroleum ether and repeated crystallization from water.

Sodium dodecyl sulfate (SDS, Emal O: Kao Soap Co.) was used without purification.

The hard water was prepared from distilled water, using calcium chloride (extra pure), and the calcium content determined by EDTA titration.

Cotton cloth (Sarashi-Kanakin: Kanebo Co.) was soiled with various amounts of oil. Three oily soils were used: beef tallow (acid value; 7.13, saponification value; 194.2, iodine value; 0.64, melting point; 57.3C: Kao Soap Co.), liquid paraffin (cp), and a mixture of beef tallow and liquid paraffin in 1:3 ratio. All were dissolved in carbon tetrachloride, and a constant weight of carbon black (C-carbon: Tamagawa Co.), suspended in the solution. Test swatches (5 cm × 10 cm) were cut from a roll of soiled cloth after removal of solvent by evaporation. The amount of oil adhering to the swatches was determined by the Soxhlet extraction.

Method

Washing was carried out in the Launder-o-Meter (Atlas Electric Devices Co.). Two test samples were placed in each jar with 60 ml of various hard water/detergent solutions, and 20 rubber balls were also included to provide agitation. Washing was carried out for 30 min at 30C.

Following washing, each swatch was rinsed once with 60 ml of distilled water using the Launder-o-Meter for 5 min, at the same conditions as for washing, and then air-dried.

Soil removal efficiency was measured by reflectance. The instrument used was the Color Machine (Color Machine Co.), and the soil removal efficiency (% SRE) was calculated according to the formula

$$\% \text{ SRE} = (Rw - Rs)/(Ro + Rs)$$

where Rw, Rs, and Ro are the reflectance of the laundered swatches, of the soiled swatches, and of the original unsoiled fabric, respectively. In these experiments, Ro was in the neighborhood of 87 and Rs in the neighborhood of 30.

The amount of Ca detergents (CaDBS or calcium dodecyl sulfonate) were determined as follows: Na detergents (NaDBS or SDS) converted to Ca detergents in various hardness of water were separated by filtration and were also calculated from measurement of Na detergents in the filtrate by the Epton method.

Results and Discussion

The Conversion to Ca Detergents in Hard Water

When a constant concentration (0.1 wt %) of Na detergents was used in various water hardnesses, a part was converted to water-insoluble Ca detergents, and these were separated by filtration. The results are shown in Table I.

In Table I, the conversion to Ca detergents is a little less than theoretical, but if one considers that a part of the Ca detergents would form a mixed micelle with Na detergents (8), or the slight solubility of Ca detergents, this conversion can be regarded as approximately theoretical.

TABLE I
The Amount of Conversion to Ca Detergents in Each Water Hardness/Na Detergent (0.1 wt %) Solutions*

Water hardness, ppm	NaDBS ($x10^{-2}$ wt %)		SDS ($x10^{-2}$ wt %)	
	1	2	1	2
22.3			1.2	1.4
44.5	2.6	3.3	2.0	2.6

* Where 1 is the experimental value, 2 is the theoretical value.

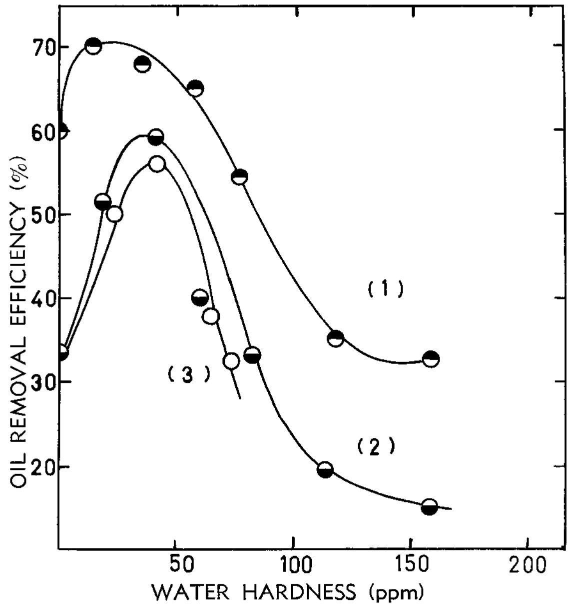

FIG. 1. The effect of kind of oil soils on the oil removal efficiency vs. water hardness.
The concentration of NaDBS is 0.1 wt %. The kind of oil is (1) beef tallow [amount of oil (g)/swatch: 0.023], (2) beef tallow-liquid paraffin mixture [amount of oil (g)/swatch: 0.017] and (3) liquid paraffin [amount of oil (g)/swatch: 0.046].

Effect of Oily Soils on Oil Removal

Oil removal efficiency vs. water hardness curves were determined for three oily soils and plotted in Figure 1. Beef tallow soil was most easily removed, followed by beef tallow-liquid paraffin mixture, and liquid paraffin. Beef tallow was most efficiently removed when the hardness of water was 20 ppm; for the mixture, 34 ppm; and for liquid paraffin, 41 ppm. The polar beef tallow showed greatest oil removal efficiency, while nonpolar liquid paraffin showed least oil removal efficiency. However, the relationship between the water hardness at maximum oil removal efficiency for each soil and oily soil polarity was parallel. That is, a proportional relationship is apparent between the polarity of the oil (log dielectric constant) and the hydrophile-lipophile balance (HLB) of the detergent (12): the mixture of the detergents of this ratio would be the most effective HLB of detergents for each oil soil at maximum detergency.

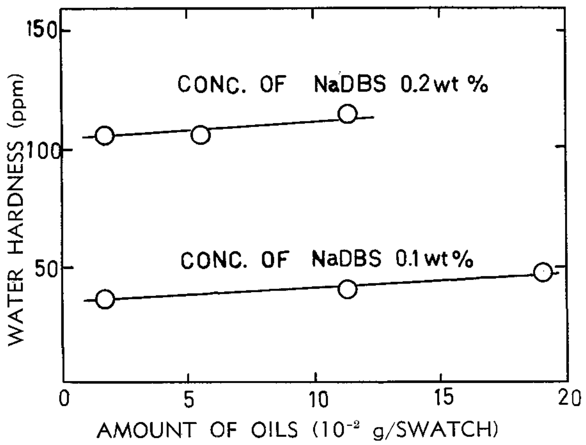

FIG. 2. The correlation between the amount of oil (beef tallow-liquid paraffin mixture) soil vs. the water hardness at maximum oil removal efficiency.

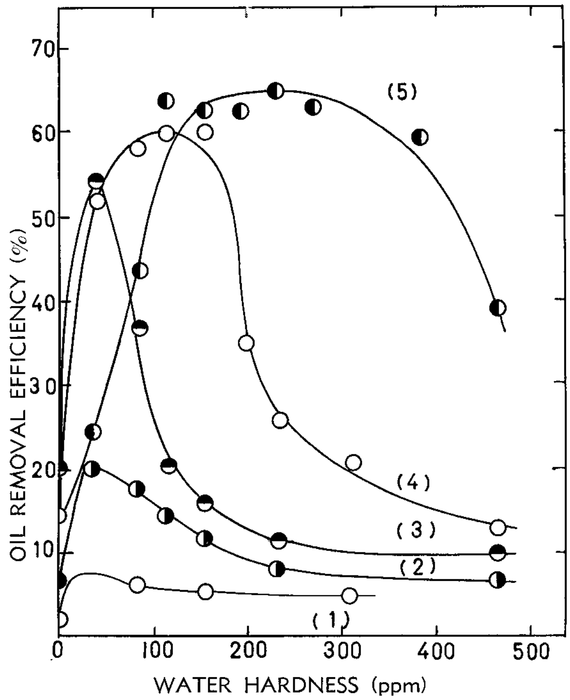

FIG. 3. The effect of the concentration of NaDBS on the oil removal efficiency vs. water hardness.
The concentration of NaDBS (wt %) is 0.04 (1), 0.06 (2), 0.1 (3), 0.2 (4), and 0.4 (5). Amount of oil (beef tallow-liquid paraffin mixture) soil (g)/swatch is 0.055.

Effect of Amount of Oily Soil

As the water hardness had such a remarkable effect on oil removal efficiency in each system, it was expected that the different amounts of oily soil would not markedly change the hardness of water at maximum oil removal efficiency. The relationship between the water hardness at maximum oil removal efficiency and the amount of oily soil is shown in Figure 2. This relationship did not greatly change for the different amounts of oily soil used.

Effect of Detergent Concentration on Oil Removal

It was expected that as the concentration of detergents was increased, that the hardness of water at

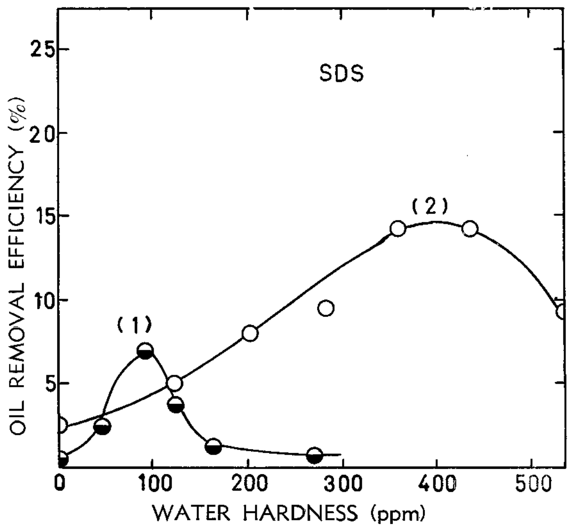

FIG. 4. The effect of the concentration of SDS on the oil removal efficiency vs. water hardness.
The concentration of SDS (wt %) is 0.1 (1) and 0.4 (2). Amount of oil (beef tallow-liquid paraffin mixture) soil (g)/swatch is 0.055.

maximum oil removal efficiency would be increased so that the ratio of CaDBS/NaDBS at the maximum oil removal efficiency would remain constant. This effect was measured, and the data obtained are plotted in Figure 3. The same results were obtained with a different amount of oily soil (amount of oil soil (g)/swatch is 0.017). As the concentration of NaDBS and water hardness was increased, oil removal efficiency increased, and the sharpness of the oil removal peak was lessened. This result may be regarded as explaining the data of Tahibana (13) which showed a maximum oil removal efficiency at the same concentration of SDS.

Effect of Kind of Detergent on Oil Removal Efficiency

Oil removal efficiency curves were also determined with SDS. The results are plotted in Figure 4. The maximum oil removal efficiency of SDS was lower and was shown at higher water hardness than NaDBS. This would be explained by the difference in affinity between the detergents and oil or the hydrophilicity of the detergents.

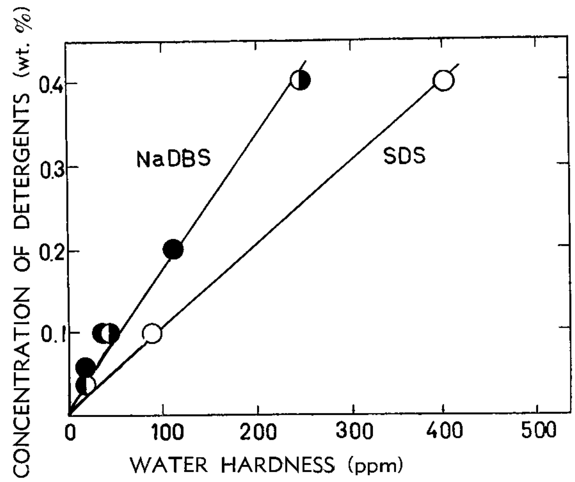

FIG. 5. The relationship between water hardness vs. concentration of detergents at maximum oil (beef tallow-liquid paraffin mixture) removal efficiency.
In the case of NaDBS, the amount of oil soil (g)/swatch is 0.055 (◑) and 0.017 (◐).

The Relationship Between the Detergent Concentration and Water Hardness

From the above results, the concentration of NaDBS and SDS vs. hardness of water at maximum oil removal efficiency were plotted in Figure 5. It is clear from Figure 5 that the relationship between detergent concentration and water hardness at maximum oil removal efficiency is linear, and, the molar ratio of CaDBS/NaDBS is 0.21: in the case of SDS, it is 0.28. At this ratio, the optimum hydrophile-lipophile detergent balance for a given washing is shown. From the results of Figures 1 and 5, this ratio is also shown to be dependent on the nature of the oily soil and kind of detergent.

The relationship between the solubilizing power of some kinds of NaDBS in hard water were measured by Kimura et al. (8), and others (14). They found that the ratio of CaDBS/NaDBS at maximum solubilizing power with Orange-OT was about 0.4–0.5 molar ratio. From our data, the CaDBS/NaDBS ratio at maximum solubilizing power was a little larger than that determined by detergency values.

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