Influence of Calcium Concentration in the Washing Liquor on Detergency Performance of Linear Alkylbenzene Sulfonate

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The effect of the concentration of linear alkylbenzene sulfonate (LAS) on soil removal efficiency at various water hardnesses was studied. The present investigation indicates that: (i) For each LAS concentration, a calcium ion concentration interval exists, defined by $0.78 < (\mathrm{Log(LAS)}/\mathrm{Log(Ca)}) < 0.85$, where the detergency reaches a maximum; (ii) 24 h after having been prepared, the solutions present either clear solutions (water appearance), milky solutions (without precipitate in the bottom of the bottle), or clear solutions with precipitate in the bottom of the bottle. The milky solutions correspond to the defined interval. The solutions where the relationship LAS/Ca is defined are located, surprisingly in a precise zone of the LAS-calcium solubility diagram. The study has been carried out with and without ionic strength buffering, and the addition of electrolyte moves the maximum detergency performance interval to higher calcium concentrations.

KEY WORDS: Alkylbenzene, calcium concentration, detergency, ionic strength, LAS.

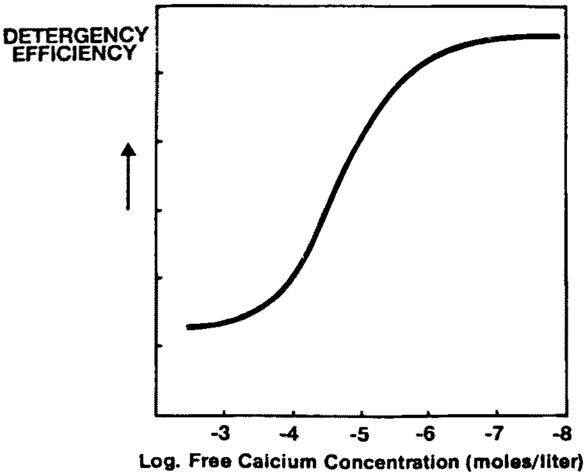

FIG. 1. Detergency efficiency as a function of free calcium concentration.

The technical literature (1,2) indicates that linear alkylbenzene sulfonate (LAS) detergency increases when water hardness decreases, with the maximum value at 10^{-6} molar calcium concentration (Fig. 1, Ref. 3). Other publications refer to the beneficial effect caused by Ca^{++} ions because they indirectly reduce the surface tension of water (4–6).

A number of researchers (7–8) have investigated the effect of water hardness on the solubilizing activity of anionic surfactants and have found maximum values at certain hardnesses. It was suggested that solubilization behavior in hard water is an important factor in understanding the fundamental behavior of anionic detergents in soil removal.

According to Arai (8,9), when the water hardness of a solution of an anionic detergent increases, it becomes turbid at some specific water hardness. A part of the Na-LAS in hard water is considered to be converted to water-insoluble Ca-LAS, which has a higher Krafft point than sodium salt. Accordingly, surfactant solutions can be obtained with various Ca-LAS to Na-LAS ratios with different hydro-lipophilic balances (HLB) or Krafft points.

On the other hand, as the water hardness in the solution of an anionic surfactant increases, the critical micelle concentration (CMC) changes and the micellar weight increases; therefore, the micellar weight of Na-LAS in hard water can be expected to show a maximum value at the same water hardness that gives the maximum solubilizing activity.

Other authors (10) refer to the higher charge and smaller ionic radius of calcium ions, which result in a stronger binding interaction to the micellar surface and, therefore, in less dissociation. This compression of the electric double layer decreases repulsion between the ionic head groups, allowing a closer packing in the surface layer and thus gives increased adsorption at surface, increased surface activity, decreased CMC and increased aggregation number.

However, according to Schwuger (11), calcium ions have many drawbacks when present in anionic solutions. They strongly reduce the surfactant solubility and they compress the electric double layer so strongly that the electric repulsion between soil particles and fibers is impaired.

Taking all this into account, we have conducted a study on this topic, but differed from those previously mentioned, not only in methodology (soil type and washing machine), but also in interpretation of the results.

EXPERIMENTAL PROCEDURES

Chemicals. The LAS used in the study was obtained in the laboratory by sulfonation of a commercial linear alkylbenzene (LAB) sample. The characteristics of both products are as follows: <phenyl-C10, 0.2 wt%; phenyl-C10, 8.6 wt%; phenyl-C11, 31.2 wt%; phenyl-C12, 30.9 wt%; phenyl-C13, 23.8 wt%; phenyl-C14, 1.8 wt%; branched alkylates, 3.1 wt%; tetralins, 0.2 wt%; docosahexaenoic acid, 0.2 wt%; and 2-phenyl alkanes, 17.4 wt%. The molecular weight was 242.8.

The sulfonic acid composition was active ingredient, 96.3 wt%; free oil (unsulfonated matter), 1.7 wt%; and free sulphuric acid, 1.5 wt%. The sulfonation reaction was carried out under the following conditions: SO_3/LAB molar ratio, 1.07; temperature, 45°C; and SO_3/N_2, 4.34 wt%.

The different water hardness concentrations were prepared from distilled water and reagent-grade $CaCl_2$ (Merck 2380, Darmstadt, Germany) after titration with ethylenediaminetetraacetic acid (EDTA).

Methods. Detergency performance was carried out according to ASTM-D-3050/75 method with the following equipment and materials.

Soiled fabrics were prepared by soiling EMPA-101 (cotton) and EMPA-104 (polyester and cotton) with carbon

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black and olive oil (10 × 10 cm swatches, EMPA, St. Gallen, Switzerland). The washing procedure in the Terg-o-Tometer (U.S. Testing Co., Hoboken, NJ) was conducted with six swatches of fabric per pot, which contained a liter of washing liquor formed by water of a given hardness and a predetermined detergent concentration.

The washing was done at 30°C during 20 min. The swatches were then rinsed for 10 min using distilled water. Finally the swatches were dried with hot air. The detergency performance was then determined by measuring the reflectance of the soiled fabrics on each swatch before and after washing, and the difference between both readings (ΔR) was used as the detergency performance (average of six readings in each case). The minimum significant difference between two readings with a confidence level of 95% was one reflectance unit.

The boundaries on the solubility diagram have been determined by visual observation of the turbidity of LAS-Ca solutions in 1-L glass bottles. These solutions were the same as those used for washing of soiled fabrics. The turbidity observation and the washing process were both conducted 24 h after preparation of solutions. It is our experience that by doing so, the diagram obtained does not significantly differ from the one where an He-Ne laser equipment is used.

This diagram is essentially a phase diagram drawn on a log-log plot. The precipitation boundary is the graphical representation of points at which the onset of precipitation is observed. The diagram is divided into areas where only monomers, or micelles, or both, exist. The different zones of the diagram are represented in Figure 2. A more detailed description is given in reference 10.

To cover a wide spectrum, the experimental work has been carried out at the following concentrations: LAS–0.3, 0.6, 1.2, 2 and 3 g/L; and Ca^{++}, from 0 to 300 ppm.

RESULTS AND DISCUSSION

Detergency on cotton (EMPA-101). The results obtained with EMPA-101 fabric at different LAS and Ca^{++} concentrations are represented in Figure 3. The following observations can be made from that figure.

Detergency performance (ΔR) increases with increasing Ca^{++} concentration up to a maximum, regardless of LAS concentration. Beyond that maximum, the detergency performance drops rapidly with increasing Ca^{++} concentration.

For each LAS concentration, a maximum in detergency performance is attained. The width and value of this maximum depends on the LAS concentration.

How does LAS concentration influence these two parameters? (i) As far as the value is concerned, we can say that detergency performance increases with LAS concentration up to a maximum, beyond which it remains constant. (ii) Concerning the width of the maximum (*i.e.*, calcium concentration interval for optimum detergency performance), we can conclude that the higher the LAS concentration, the wider the maximum.

However, more detailed observation of the Ca^{++} and LAS concentration values corresponding to the width limits of those maximums indicates that the following formula can be used to define the maximum:

$$0.78 \leqslant \log [\mathrm{LAS}]/\log [\mathrm{Ca}^{++}] \leqslant 0.85$$

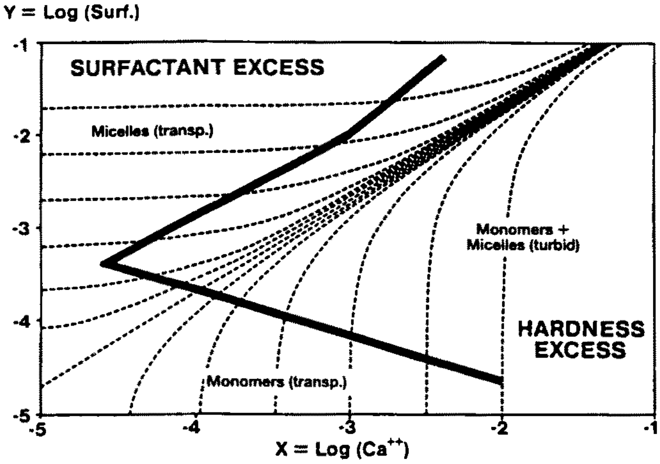

FIG. 2. Calcium precipitation boundary diagram LAS-Na^+, general diagram. LAS, linear alkylbenzene sulfonate.

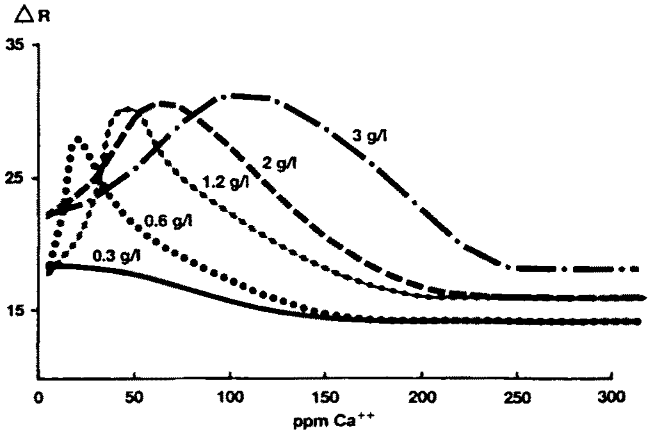

FIG. 3. Detergency of LAS *vs.* calcium (EMPA-101, 30°C). LAS concentrations: 0.3, 0.6, 1.2, 2 and 3 g/L. Abbreviations as in Figure 2.

These values depend on LAS molecular weight, as a different solubility diagram will be obtained for each type of LAS. Therefore, we can state that an optimum LAS/calcium concentration ratio interval exists where optimum detergency performance is attained.

All initial Ca^{++} and LAS concentrations used during the detergency study are depicted in Figure 4. It is interesting to note that all points within the optimum detergency zone have the following characteristics in common: (i) They belong to the diagram zone where there is an LAS excess over Ca^{++} (Fig. 4); (ii) More precisely, they belong to the zone limited by the LAS/Ca^{++} stoichiometric line and the micelles saturation line (Fig. 4). In addition, visual observation after 24 h of the solutions located within this zone will be characterized by turbidity (milky solutions) and the lack of a precipitated product in the bottom of the bottles.

The probable existence in this zone of a complex mixture of Ca^{++}/Na^+ micelle aggregates, together with $(LAS)_2$ Ca, in a suspended form, and LASNa, either dissolved or in solution in the monomeric form (10), all

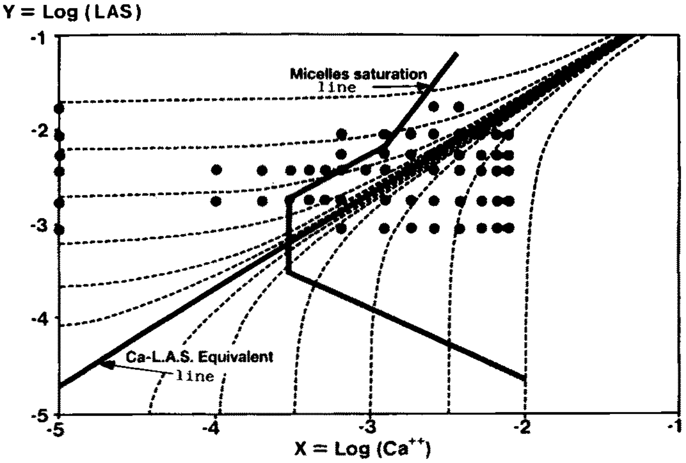

FIG. 4. Linear alkylbenzene sulfonate/calcium precipitation boundary diagram. The points are the concentration used.

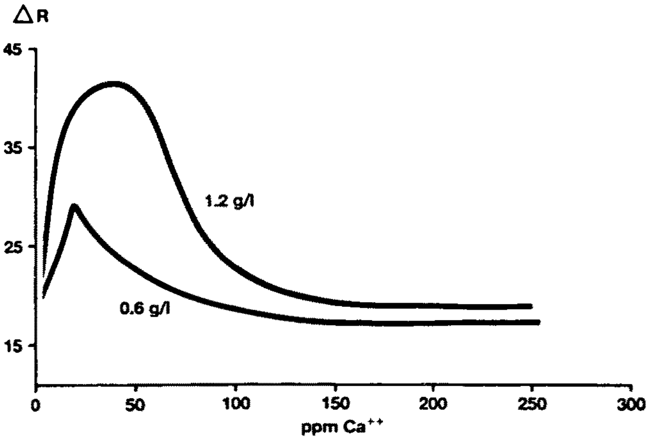

FIG. 5. Detergency of LAS *vs.* calcium (EMPA-104, 30°C). LAS concentrations: 0.6 and 1.2 g/L. Abbreviation as in Figure 2.

in an apparent thermodynamic equilibrium, may explain the results obtained. This is, in fact, the description of the solutions prior to the start of the washing process, which of course is dynamic. Nevertheless, we do believe that there must be some kind of strong relationship between the initial thermodynamic equilibrium and the subsequent kinetic detergency phenomenon.

Detergency on cotton-polyester (EMPA-104). The previously discussed detergency performance study was also extended to a cotton-polyester fabric (EMPA-104) to check the validity of the results with other types of textile. The data obtained are summarized in Figure 5, from which we can easily deduce that the conclusions obtained on cotton can be extended to cotton-polyester.

Effect of ionic strength buffering on detergency performance. Another means of enhancing adsorption, especially of anionic surfactants, results from counterion effects exerted by ordinary inorganic electrolytes. In such systems, the electric double layer is strongly compressed at all interfaces, which leads to an enhanced adsorption of anionic surfactant and a decrease of the equilibrium concentration needed to attain complete coverage of the interface. The relationship between solubility of free and associated calcium and LAS species found in detergent solution and ionic strength also needs to be taken into account.

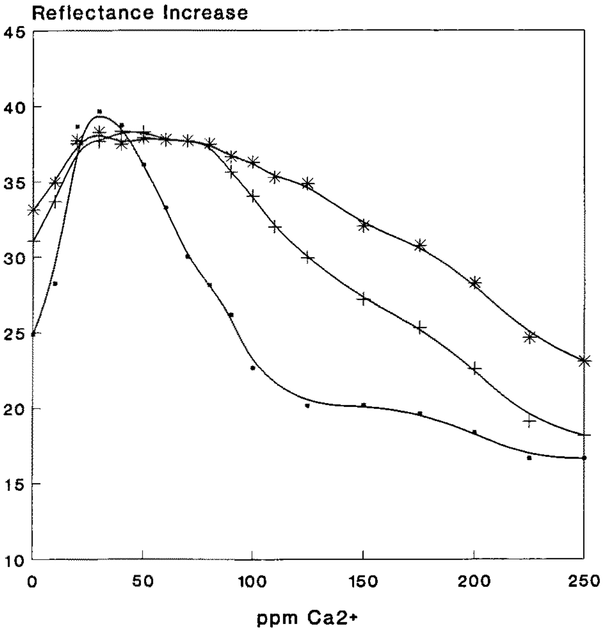

FIG. 6. Detergency of LAS/Na_2SO_4 *vs.* calcium (LAS 1.2 g/L, EMPA-104, 30°C). Abbreviations as in Figure 2. Squares, Og/L; crosses, 0.005 M; and asterisks, 0.01 M SO_4Na_2.

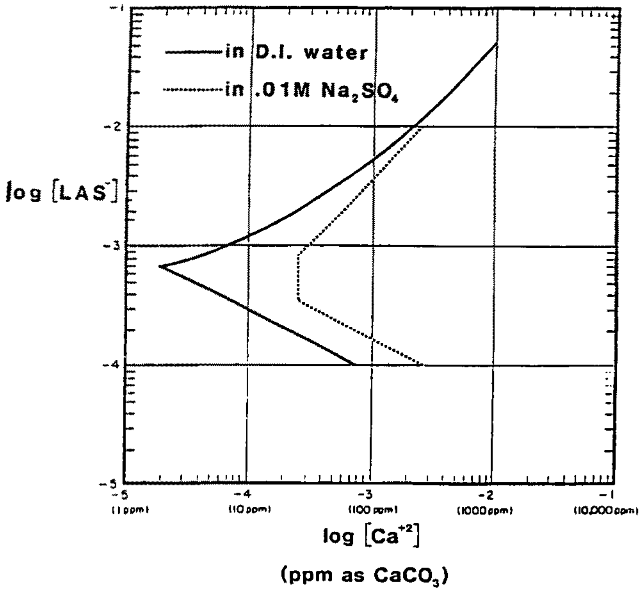

FIG. 7. $Ca(LAS)_2$ precipitation boundary diagrams for C_{12} ave. LAS. Abbreviation as in Figure 2.

To test these ideas, an experimental study was conducted with and without ionic strength buffering. In this study we have used three different sodium sulfate concentrations—0, 0.005 and 0.01 M. The detergency results are plotted on Figure 6. The two mentioned phenomena (*i.e.*, the electrolyte effect and the solubility effect) are clearly confirmed by the curves' trends. In the first calcium concentration range (below 40 ppm), the differences in performance by adding sodium sulfate can be attributed to the electrolyte effect. Beyond this concentration the differences in performance are mainly due to the solubility effect. In fact, if we look at the LAS-calcium solubility diagrams, with and without sodium sulfate, (Fig. 7), we see that LAS solubility is moved toward higher calcium concentrations when the electrolyte is added.

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