

# Linear Alkylbenzene Sulfonate Detergency Behavior in Water Containing Magnesium Ions

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**Detergency performance of linear alkylbenzene sulfonate (LAS) in water containing magnesium ions has been investigated. LAS showed the same behavior with magnesium as with calcium, on a qualitative basis. However, the detergency performance with magnesium is significantly higher than with calcium.**

**KEY WORDS:** Detergency, ionic strength, LAS, magnesium ion.

As all solid and liquid interfaces in an alkaline medium are negatively charged, a mutual repulsion takes place between the interfaces and the negatively charged hydrophilic groups of anionic surfactants. Hence, a potential barrier must be overcome when they approach each other closely. However, a close approach is possible when the hydrophobic interactions between the hydrophobic parts of the molecules and the interfaces are stronger than the repulsion forces and the attractive forces of the solvent (1). Addition of electrolytes causes a compression of the electric double-layer and, hence, reduces the mutual repulsion of similarly charged particles. As a result an enhanced adsorption of anionic surfactants and a decrease of the equilibrium concentration to attain complete coverage of the interface take place. For that reason, the presence of polyvalent cations, such as calcium and magnesium, in a surfactant solution causes an increase in the adsorption of anionic surfactants.

According to the Shultz-Hardy rule, the compression of the electric double-layer by magnesium ions is stronger than by sodium ions, without contributing the unfavorable effects of calcium ions. The advantages of  $Mg^{2+}$  ions over  $Ca^{2+}$  ions can be summarized by two points: (i)  $Mg^{2+}$  salts of common anionic surfactants are more soluble than the  $Ca^{2+}$  salts; (ii)  $Ca^{2+}$  ions compress the electric double-layer more strongly than  $Mg^{2+}$  ions, so that the electric repulsion between soil particles and fibers is negatively affected.

In a previous study (2), the detergency performance of linear alkylbenzene sulfonate (LAS) as a function of calcium ion concentration was investigated. To get an overall view of LAS behavior in hard water, the experimental work has been extended to magnesium ion, as well as to several calcium/magnesium mixtures. A study also has been completed in which ionic strength buffering of the washing liquor was evaluated.

## MATERIALS AND METHODS

**Chemicals.** 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: < phenyl-C10, 0.2 wt%; phenyl-C10, 10.1 wt%; phenyl-C11, 40.6 wt%; phenyl-C12, 28.1 wt%; phenyl-C13, 15.5 wt%; phenyl-C14, 1.0 wt%; branched alkylates, 4.5 wt%; tetralins, 0.1 wt%; 2-phenyl alkanes, 16.1 wt%. The average molecular weight was 239.3. The sulfonic acid composition was: active ingredient, 97.0 wt% free oil (unsulfonated matter), 1.5 wt%; free sulfuric acid, 1.5 wt%.

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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 with distilled water and  $CaCl_2$  reagent grade (Merck 2380, Darmstadt, Germany) after titration with ethylene diaminetetraacetic acid.

**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 black and olive oil ( $10 \times 10$  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, containing a liter of washing liquor formed by water of a given hardness and a predetermined detergent concentration. The washing was done at 30°C for 20 min. Once concluded, the swatches were rinsed for 10 min in 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 ( $\Delta R$ ) was used as the detergency performance (average of six readings in each case). The minimum significant difference between two readings was 1 reflectance unit with a confidence level of 95%.

The LAS-magnesium precipitation boundary was obtained by visual observation of the turbidity of LAS-magnesium solutions prepared in 1-L glass bottles. The turbidity observation and the washing process were both conducted 24 h after preparation of the solutions. These solutions were the same as those used for washing the soiled fabrics.

The precipitation boundary diagram is a graphical representation of points at which the onset of precipitation is observed. The diagram is divided into areas where monomers or micelles or both exist. A more detailed description is given elsewhere (3). The different zones of the diagram are represented in Figure 1.

To cover a wide spectrum, the experimental work has been carried out at the following concentrations: LAS at 1.2, 2 and 3 g/L, and  $Mg^{2+}$  from 0 to 250 ppm.

## RESULTS AND DISCUSSION

**Detergency vs. Magnesium.** The results obtained for different LAS and Mg concentrations are plotted on Figure 2. The curves have the same shape as those obtained with calcium (1). However, Figures 3 and 4 show that the LAS-Mg mixture gives a significantly higher performance than the corresponding LAS-Ca combination.

**Detergency vs. Ca/Mg mixtures.** This study has been carried out with 1.2 g/L of LAS and the following Ca/Mg blends, expressed on a w/w basis: Ca/Mg 1/6.6, 1/2, 2/1 and 6.6/1. The experimental data are plotted in Figures 5 and 6. From these data the main conclusion to be drawn is that the detergency performance increases as the level of

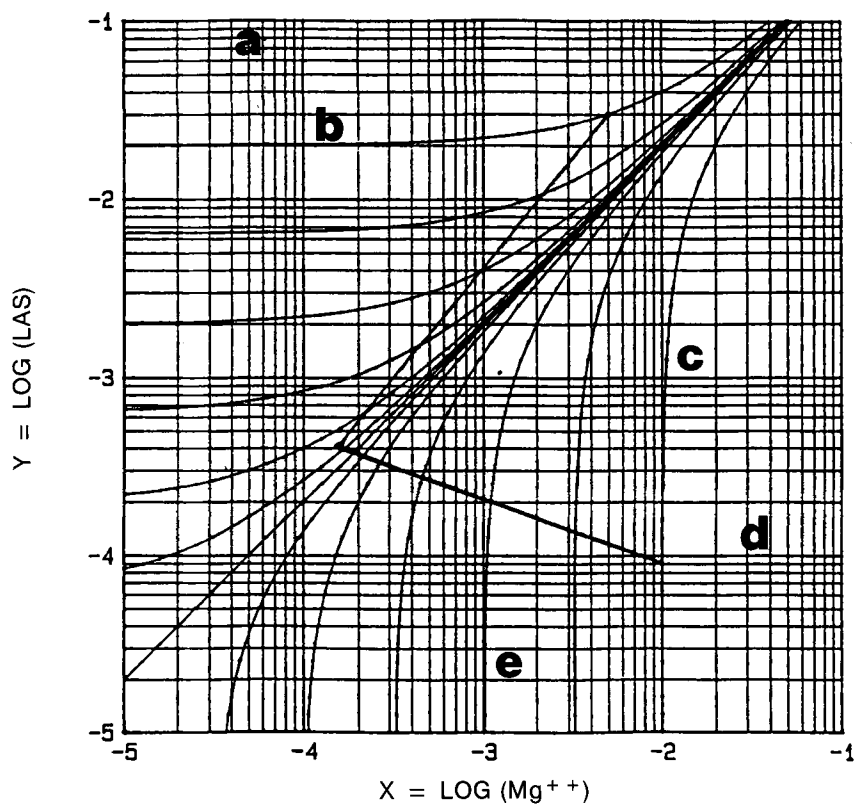


FIG. 1. Magnesium precipitation boundary diagram linear alkylbenzene sulfonate (LAS)-Na.

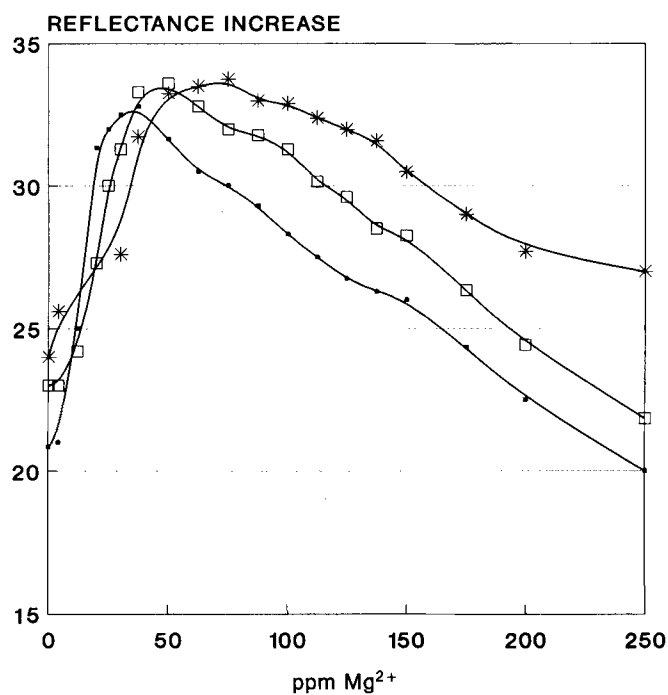


FIG. 2. Detergency of linear alkylbenzene sulfonate (LAS) vs. magnesium (EMPA-101, 30°C). —■—, LAS 1.2 g/L; —□—, LAS 2.0 g/L; —\*—, LAS 3.0 g/L.

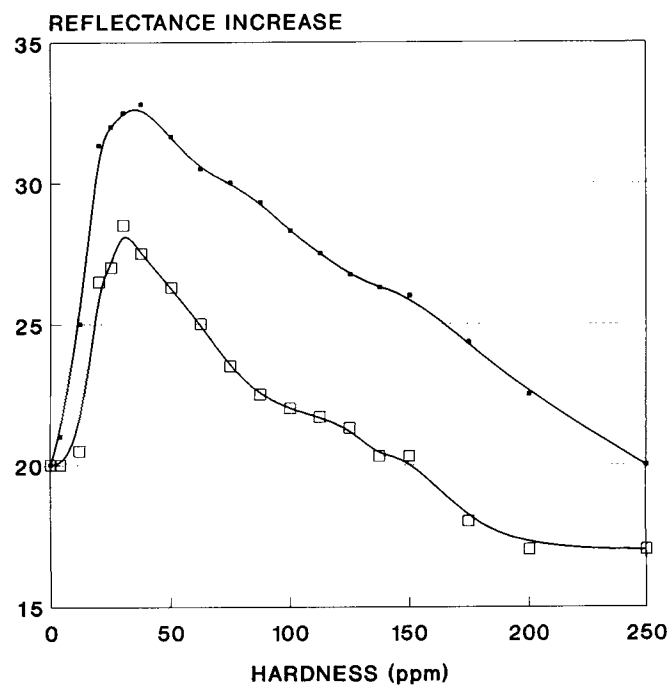


FIG. 3. Detergency of linear alkylbenzene sulfonate vs. calcium and magnesium (EMPA-101, 20°C). Linear alkylbenzene sulfonate concentration 1.2 g/L. —■—,  $Mg^{2+}$ ; —□—,  $Ca^{2+}$ .

## LAS DETERGENCY BEHAVIOR IN WATER

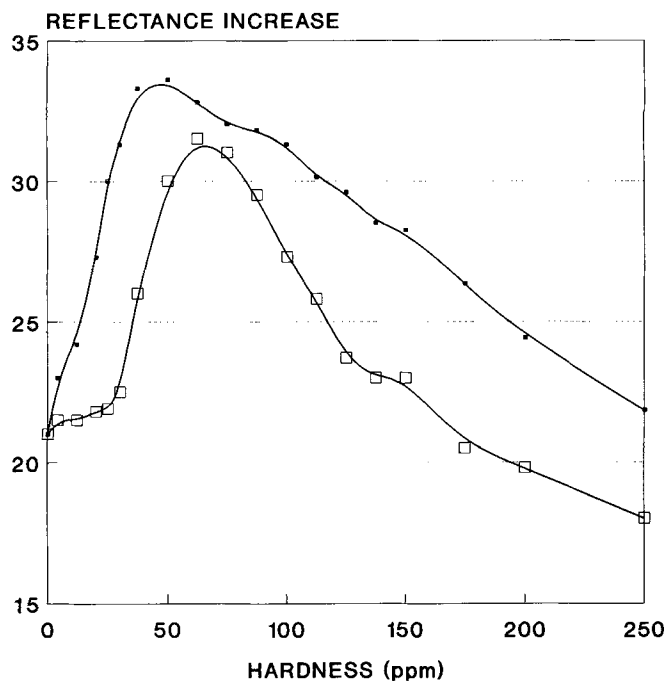


FIG. 4. Detergency of linear alkylbenzene sulfonate vs. calcium and magnesium (EMPA-101, 30°C). Linear alkylbenzene sulfonate concentration 2 g/L. —■—,  $Mg^{2+}$ ; —□—,  $Ca^{2+}$ .

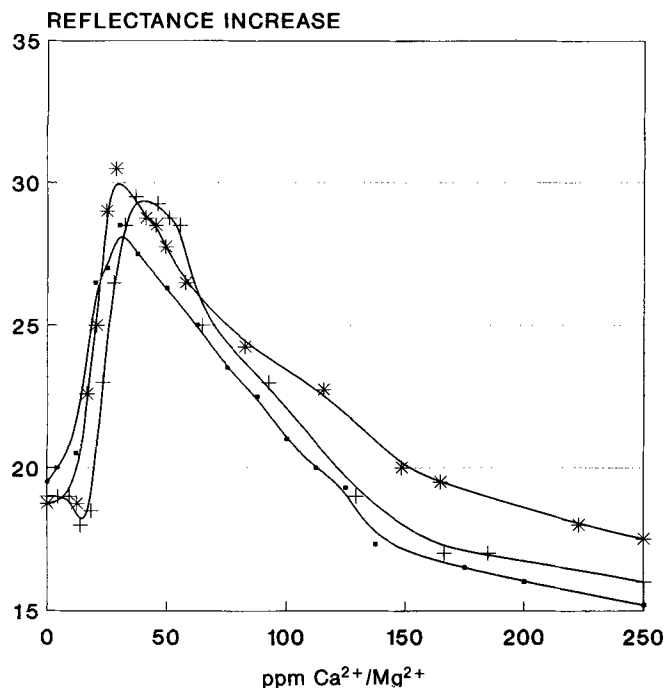


FIG. 6. Detergency of linear alkylbenzene sulfonate vs. calcium/magnesium mixtures (EMPA-101, 30°C). Linear alkylbenzene sulfonate concentration 1.2 g/L. —■—,  $Ca^{2+}$ ; —+—,  $Ca^{2+}/Mg^{2+}$  6.6:1; —\*—,  $Ca^{2+}/Mg^{2+}$  2:1.

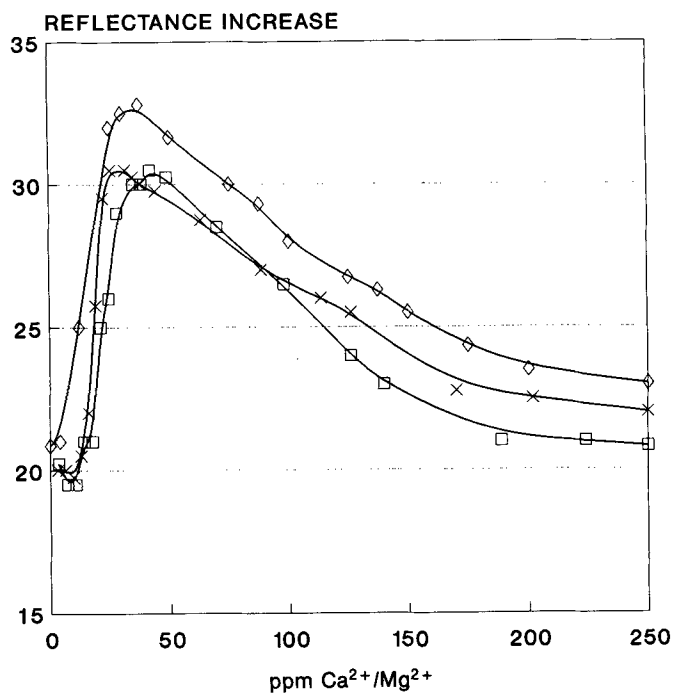


FIG. 5. Detergency of linear alkylbenzene sulfonate vs. calcium/magnesium mixtures (EMPA-101, 30°C). linear alkylbenzene sulfonate concentration 1.2 g/L. —□—,  $Ca^{2+}/Mg^{2+}$  1:2; —\*—,  $Ca^{2+}/Mg^{2+}$  1:66; —◆—,  $Mg^{2+}$ .

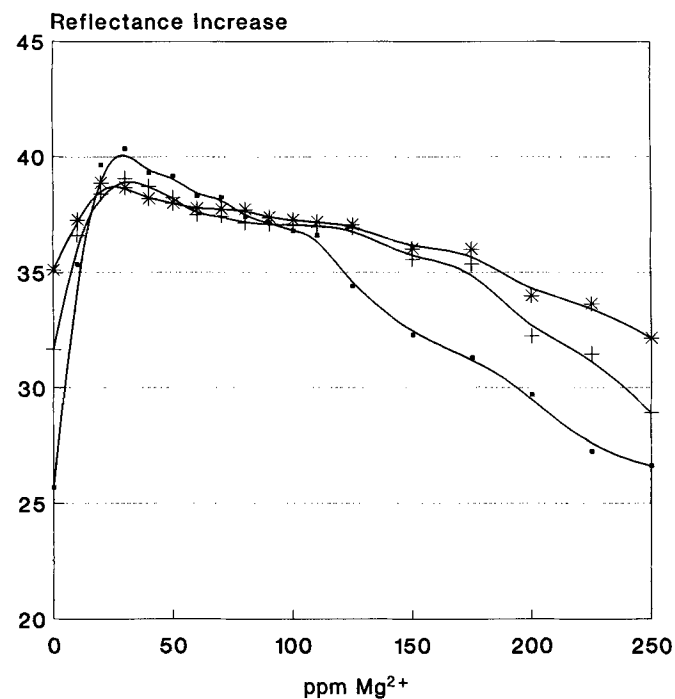


FIG. 7. Detergency of linear alkylbenzene sulfonate/ $Na_2SO_4$  vs. magnesium (linear alkylbenzene sulfonate 1.2 g/L, EMPA-104, 30°C). —■—, 0; —+—, 0.005 M; —\*—, 0.01 M  $Na_2SO_4$ .

magnesium increases in the mixture. Thus, the best behavior is obtained for Ca/Mg, 1/6.6. These results were expected and are in good agreement with the theory given in the introduction.

*Influence of ionic strength on detergency performance.* As explained in a previous study (2), two phenomena take place when an electrolyte is added to a surfactant solution: (i) the electrolyte effect, which is mainly related to an enhancement of surfactant adsorption at the interfaces; and (ii) the solubility effect, dealing with a modification of surfactant species' solubility due to ionic strength.

The experimental results plotted in Figure 7 show three different behaviors: (i) Below 20 ppm of magnesium ion, the contribution of the electrolyte effect to detergency improvement is clearly evident; (ii) from 20 to 100 ppm, surprisingly, no effect is observed by adding sodium sulfate, which can be explained because within this interval the interfaces are saturated by surfactant molecules, of that

no enhancement is allowed; and (iii) beyond 100 ppm, the differences in performance are essentially due to the solubility effect.

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#### REFERENCES

1. Cutler, G., and E. Kissa, *Detergency Theory and Technology*, Vol. 20, Marcel Dekker Inc., New York, 1987.
2. Cohen, L., A. Moreno, and J.L. Berna, *J. Am. Oil Chem. Soc.* 70:79 (1993).
3. Matheson, K.L., and M.F. Cox, *Ibid.* 62:1391 (1985).

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