Detergency of Binary Mixtures of LAS/STPP and LAS/Zeolites: Influence of (Ca^{++}) on the Washing Liquor

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The influence of sodium tripolyphosphate (STPP) or zeolites on the detergency performance of linear alkylbenzene sulfonate (LAS) has been evaluated at different water hardness levels. This study demonstrates that STPP or zeolite behaves either as a sequestrant or through an important synergism with LAS, showing a minimum and a maximum in detergency performance, depending on the water hardness level. There is an optimum LAS/builder ratio for each individual water hardness level. This optimum has to be determined experimentally as it will not always necessarily coincide with the highest surfactant and/or builder concentrations.

KEY WORDS: Alkylbenzene, builder, calcium concentration, detergency, LAS, STPP, water hardness, zeolites.

Several authors (1–4) have already studied the influence of STPP (sodium tripolyphosphate) on the detergency performance of linear alkylbenzene sulfonate (LAS). There seems to be a general agreement that the basic function of STPP during the detergency process is to eliminate the Ca^{2+} ions in the washing liquor. STPP also performs other well-known roles, such as pH control and flocculation enhancement.

Other previous studies (5,6) have pointed out that optimum LAS detergency is reached within a certain water hardness interval. This could lead to the suspicion that the behavior of STPP and/or zeolites on such an interval is negative if all Ca ions are eliminated, because it has already been proved (5,6) that optimum detergency requires the presence of (Ca^{++}). It was therefore found useful to evaluate the effect of different concentrations of STPP/zeolites on the detergency performance of LAS.

MATERIALS AND METHODS

Products used. Different water hardness levels were prepared by dissolving $CaCl_2$ reagent grade (Merck 2380, Darmstadt, Germany) in distilled water and ethylenediaminetetraacetic acid (EDTA) for titration.

The STPP (Rio Rodano S. A., Huelva, Spain) characteristics were: purity, 95%; pyrophosphate (Na), 1.5%; metaphosphate (Na), 0.5%; sulfate (Na), 2.0%; P_2O_5 (dry basis), 56.6%; and other, 1.0%.

Zeolites used were commercial products (Degussa AG, Frankfurt, Germany).

Linear alkylbenzene sulphonate was obtained in the laboratory by SO_3 sulfonation of a commercial linear alkylbenzene (LAB) sample (Petrelab — 550, (Petresa, San Roque (Cadiz), Spain) with the following distribution: < phenyl C_{10}, 0.2 wt%; phenyl C_{10}, 8.6 wt%; phenyl C_{11}, 31.2 wt%; phenyl C_{12}, 30.9 wt%; phenyl C_{13}, 23.8 wt%; phenyl C_{14}, 1.8 wt%. The molecular weight was 242.8.

The sulfonation conditions were: SO_3/LAB, 1.07 molar; SO_3/N_2, 4.34 wt%; temperature, 45°C. The resulting sulfonic acid was: active ingredient, 96.3 wt%; free oil, 1.7 wt%; free sulphuric acid, 1.5 wt%.

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Detergency measurements. The detergency performance was determined according to ASTM D-3050/75 with the following equipment and materials: Soiled fabrics were prepared by soiling EMPA-101 cotton with carbon 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 6 swatches per pot containing 1 liter of washing solution prepared with given surfactant and water hardness concentrations. The process temperature was 30°C with total duration of 20 min. After washing, the swatches were rinsed with distilled water for 10 min and subsequently dried in an air stream. The detergency performance was then determined by measuring the reflectance of the soiled fabrics before and after washing. The increase in reflectance was expressed as the average of 6 different swatches used in each pot. One unit of reflectance difference between two determinations was considered significant for a 95% confidence level.

Surfactant/builder concentrations used were: LAS = 1.2, 2 and 3 g/L, and STPP/zeolite = 0.25, 0.5 and 1.0 g/L. The following concentrations are representative of the range commonly used in daily household washing practices. For a detergent concentration of 1.5 g/L and an STPP concentration in the formulation of 20%, the STPP concentration in the washing liquor will be 0.3 g/L. For a detergent concentration of 6 g/L and an STPP concentration in the formulation of 20%, the STPP concentration in the washing liquor will be 1.2 g/L.

RESULTS AND DISCUSSION

Deionized water. Figures 1 and 2 show the detergency performance of the three ingredients (LAS, STPP, zeolite) either individually or combined in the absence of calcium ions, indicating a clear improvement (synergism) when LAS is mixed either with STPP or with zeolites. The results reflect only one LAS concentration, but they are also valid for the whole range of concentrations used in the study. This behavior can be explained by taking into account the pH and ionic strength modifications caused by STPP or zeolite addition to the washing liquor.

Detergency in hard water. Figures 3 to 6 depict the results obtained with 1.2 and 2 g/L LAS concentrations through a wide water hardness concentration range.

In both cases, LAS/STPP and LAS/zeolite, detergency decreases with calcium concentration increase, reaching a minimum with two well-defined characteristics: the higher the STPP or zeolite concentration, the higher the value of the minimum; and the higher the STPP or zeolite concentration, the higher the Ca^{++} concentration (water hardness) corresponding to such minimum.

Thereafter, detergency increases with increasing water hardness, reaches a maximum, and then the performance decreases. This maximum, however, is reached at different water hardness levels, depending on the builder concentration; the higher the concentration of the builder, the higher the (Ca^{++}) for the maximum.

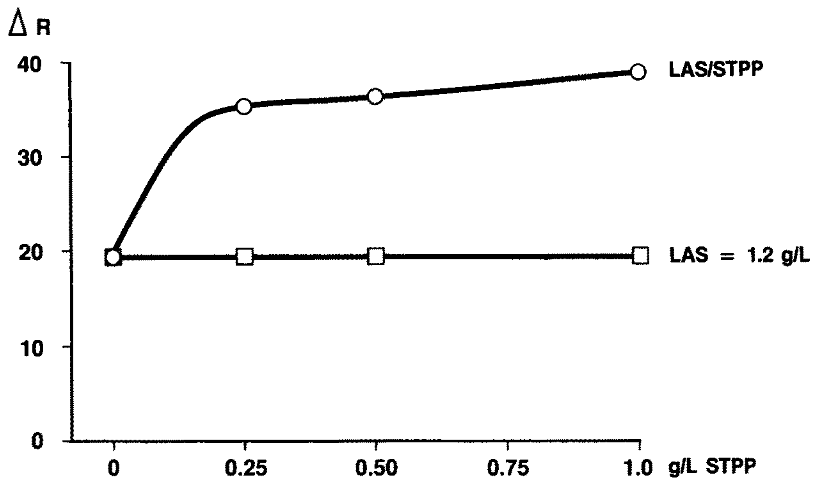

FIG. 1. LAS/STPP synergism. EMPA-101, T = 30°C, Ca^{++} = 0 ppm.

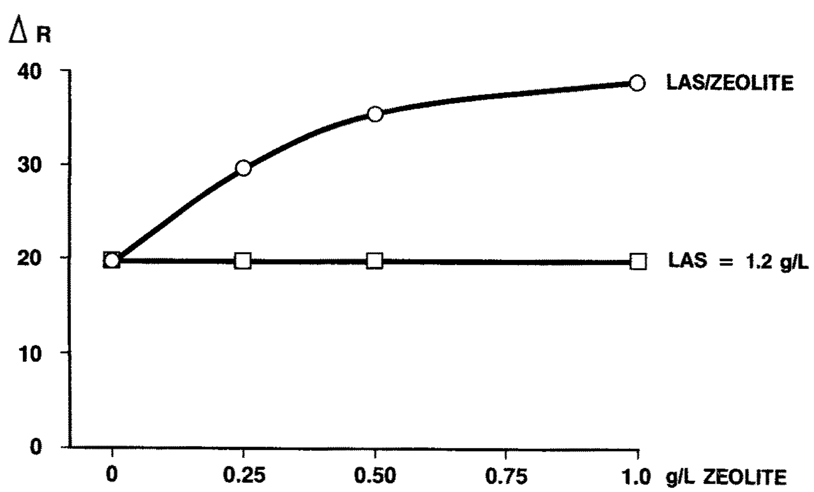

FIG. 2. LAS/zeolite synergism. EMPA-101, T = 30°C, Ca^{++} = 0 ppm.

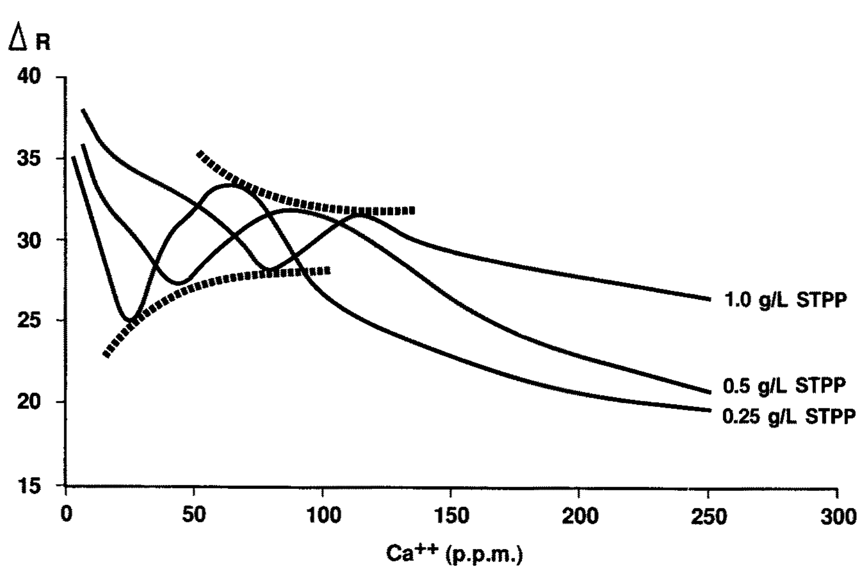

FIG. 3. LAS/STPP detergency *vs.* Ca^{++}. LAS = 1.2 g/L.

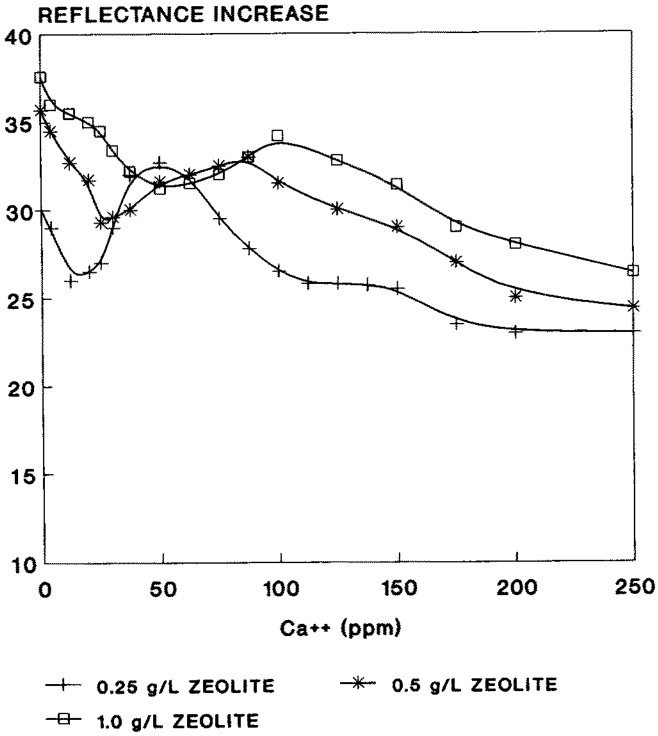

FIG. 4. LAS/zeolite detergency *vs.* Ca^{++}. LAS = 1.2 g/L.

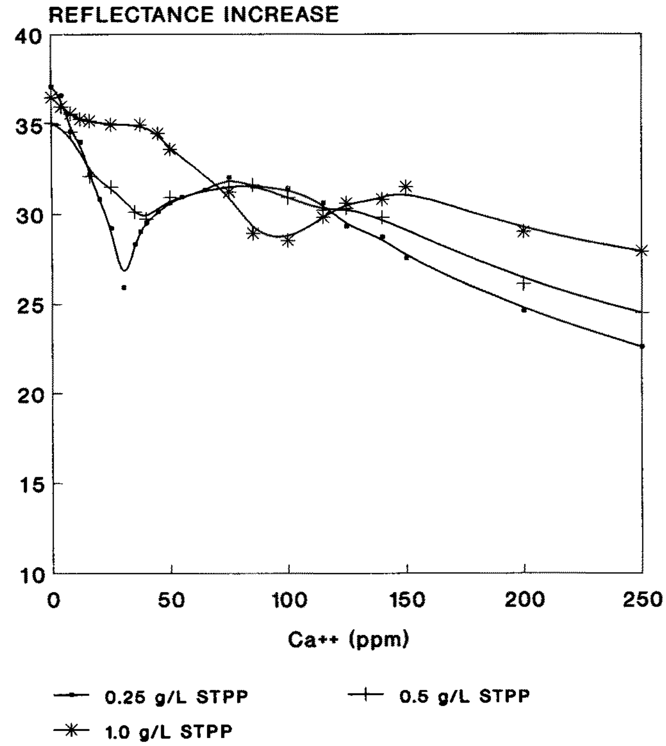

FIG. 6. LAS/zeolite detergency *vs.* Ca^{++}. LAS = 2.0 g/L.

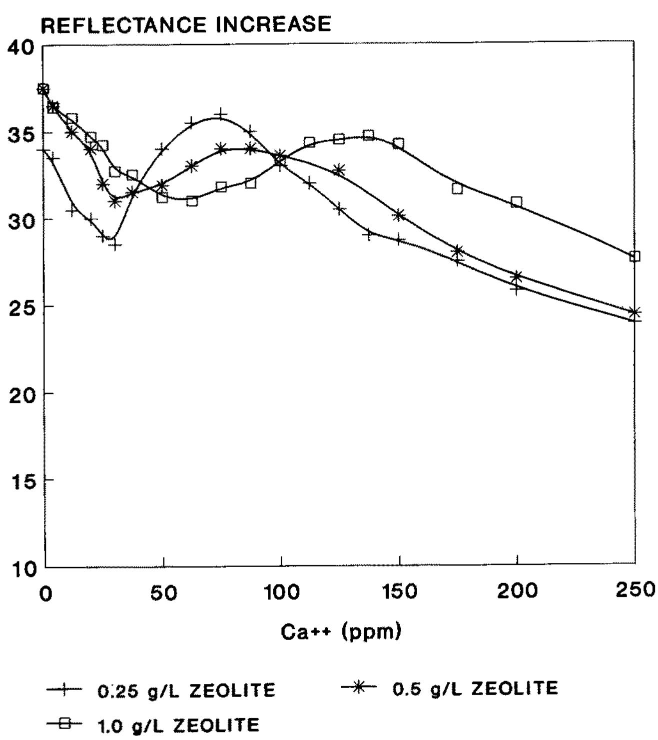

FIG. 5. LAS/STPP detergency *vs.* Ca^{++}. LAS = 2.0 g/L.

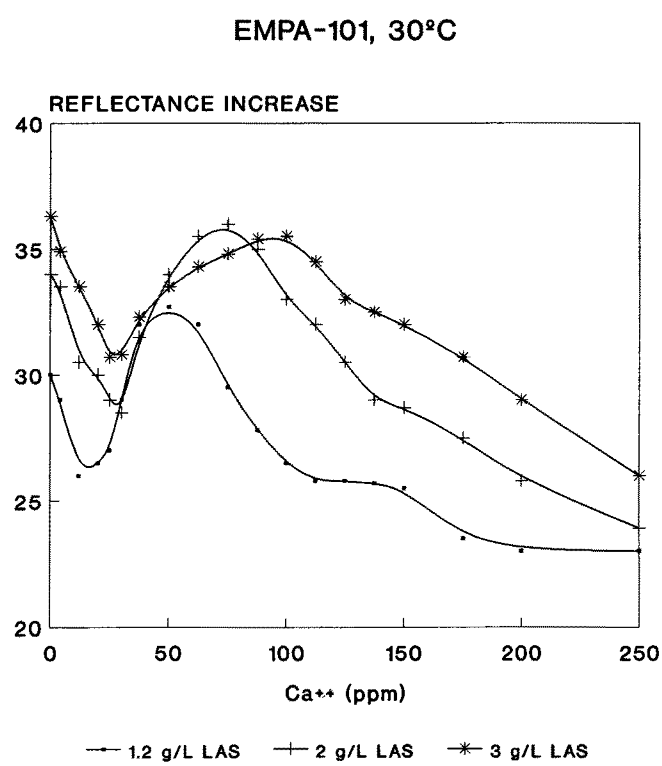

FIG. 7. LAS/zeolite detergency *vs.* Ca^{++}. Zeolite = 0.25 g/L, EMPA-101, T 30°C.

As indicated in Figure 3, an optimum LAS/builder ratio exists for each calcium concentration.

Figure 7 shows the reflectance increase obtained at different LAS concentrations for a given builder level (0.25 g/L). The figure represents the results obtained with zeolites, although the conclusion is also valid when STPP is used. The detergency performance passes through a minimum and then a maximum, depending on LAS concentration.

The shape of these curves can be partially explained on the assumption that the best detergency is shown when an amount of unsequestered calcium ion is present in the wash liquor. However, this argument does not explain the existence of a minimum.

In order to get an overall view of LAS/STPP mixture behavior in hard water, other possible reasons must be brought about. It could be the existence of two detergent mechanisms with different kinetics with regard to LAS' and STPP' individual behavior when calcium is present: one mechanism for pigment soil (carbon black) and another one for oily soil (olive oil) could explain this apparent phenomenon.

As a matter of fact, when the same study is carried out with only one type of soil on the same substrate, detergency decreases in a regular manner with increasing calcium ion concentration.

REFERENCES

1. Cooper, R.S., and A.D. Urfer, *J. Am. Oil Chem. Soc. 41*:337 (1964).
2. Vitale, P.T., J. Ross and A.M. Schwartz, *Soap 32:41* (1956).
3. Ross, J., P.T. Vitale and A.M. Schwartz, *J. Am. Oil Chem. Soc. 32*:200 (1955).
4. Arai, H., *Ibid. 43*:312 (1966).
5. Arai, H., *Ibid. 43*:315 (1966).
6. Cohen, L., A. Moreno and J.L. Berna, *XXI Jornadas del Comité Español de Detergencia Barcelona:* 207 (1990).

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