The Influence of Sodium Tripolyphosphate and Zeolites on Detergency of Linear Alkylbenzene Sulfonate in the Presence of Mg⁺⁺

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The influence of sodium tripolyphosphate (STPP) and zeolites on the detergency performance of linear alkylbenzene sulfonate (LAS) has been evaluated at different water magnesium ion levels. This study demonstrates that LAS/STPP gives better results in the presence of calcium than in the presence of magnesium, whereas the LAS/zeolite mixture gives better results in the presence of magnesium than in the presence of calcium.

KEY WORDS: Alkylbenzene, detergency, LAS, magnesium concentration, STPP, sulfonate, zeolites.

In previous reports (1–3), linear alkylbenzene sulfonate (LAS) and LAS/builder detergency performance have been studied in the presence of calcium and magnesium ions. Some authors (4) have pointed out different behavior between sodium tripolyphosphate (STPP) and zeolites, depending on the dissolved ions (calcium or magnesium).

The present investigation, where LAS/STPP and LAS/zeolites mixtures are evaluated in the presence of magnesium, completes the research about interactions between LAS/builders and water hardness ions.

MATERIALS AND METHODS

Products. Different water hardness levels were prepared by dissolving reagent-grade $MgCl_2$ (Merck 2380; Merck, Darmstadt, Germany) in distilled water and ethylenediaminetetraacetic acid (EDTA) for titration. The characteristics of STPP (Rio Rodano S.A., Huelva, Spain) were purity, 95%; pyrophosphate (Na), 1.5%; metaphosphate (Na), 0.5%; sulfate (Na), 2.0%; P_2O_5 (dry basis), 56.5%; and other, 1.0%. Zeolites used were commercial products (Degussa AG, Frankfurt, Germany).

LAS was obtained in the laboratory by SO₃ sulfonation of a commercial linear alkylbenzene (LAB) sample [Petrelab 550; Petresa, San Roque (Cadiz), Spain] with the following distribution: < 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%. The molecular weight was 242.8. The sulfonation conditions were SO₃/LAB, 1.07 molar; SO₃/N₂, 4.34 wt%; temperature, 45 °C. The resulting sulfonic acid contained: active ingredient, 96.3 wt%; free oil, 1.7 wt%; free sulfuric acid, 1.5 wt%.

Detergency measurements. The detergency performance was determined according to ASTM D-3050/87 (5) with the following equipment and materials. Soiled fabrics were EMPA-101 (cotton) (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 per pot containing 1 L of washing solution prepared with given surfactant and water hardness concentrations. The washing process temperature was 30° C with a 20-min wash time. After washing, the swatches were rinsed with distilled water for 10 min and dried in an air stream. The agitator speed of the Terg-o-Tometer was 150 rpm.

The detergency performance was determined by measuring the reflectance of the soiled fabrics before and after washing. The increase in reflectance was expressed as the average of six different swatches used in each pot. One unit of reflectance difference between two determinations was significant at a 95% confidence level.

Surfactant/builder concentrations used were as follows: LAS = 1.2, 2 and 3 g/L; STPP/zeolite = 0.25, 0.5 and 1.0 g/L; Mg²⁺ concentration from 0 to 250 ppm.

RESULTS AND DISCUSSION

Detergency of LAS/STPP. Figures 1 through 4 show some of the experimental results. For the sake of comparison, the results in the presence of calcium have been included as well. Figure 1 can be used as a baseline; it shows performance of surfactant without any builder so that the contribution of the builder to detergency is reflected.



FIG. 1. Linear alkylbenzene sulfonate (LAS) detergency vs. calcium and magnesium ion (30°C, EMPA-101, St. Gallen, Switzerland). LAS 1.2 g/L.

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FIG. 2. LAS/sodium tripolyphosphate (STPP) detergency vs. magnesium and calcium (30° C, EMPA-101). LAS 1.2 g/L, STPP 0.25 g/L. Abbreviation and source as in Figure 1.



FIG. 3. LAS/STPP detergency vs. magnesium and calcium (30°C, EMPA-101). LAS 2 g/L, STPP 0.5 g/L. Abbreviations and source as in Figure 2.



REFLECTANCE INCREASE

FIG. 4. LAS/STPP detergency vs. magnesium and calcium (30°C, EMPA-101). LAS 1.2 g/L, STPP 1 g/L. Abbreviations and source as in Figure 2.

REFLECTANCE INCREASE

 $\begin{array}{c} 40 \\ - - Mg^{2+} \\ 35 \\ 30 \\ 25 \\ 20 \\ 0 \\ 50 \\ 100 \\ 150 \\ 200 \\ 250 \\ 250 \\ 200 \\ 250 \\ 250 \\ 200 \\ 250 \\$

FIG. 5. LAS/zeolite detergency vs. magnesium and calcium (30°C, EMPA-101). LAS 1.2 g/L, zeolite 0.5 g/L. Abbreviation and source as in Figure 1.

HARDNESS



FIG. 6. LAS/zeolite detergency vs. magnesium and calcium (30° C, EMPA-101). LAS 2 g/L, zeolite 0.5 g/L. Abbreviation and source as in Figure 1.



FIG. 7. LAS/zeolite detergency vs. magnesium and calcium (30° C, EMPA-101). LAS 1.2 g/L, zeolite 1 g/L. Abbreviation and source as in Figure 1.



FIG. 8. LAS/builders detergency vs. magnesium (30°C, EMPA-101). LAS 1.2 g/L. Abbreviation and source as in Figure 1.

Although LAS/STPP behavior is identical in the presence of calcium and magnesium on a qualitative basis, quantitatively, detergency performance in the presence of calcium is better than in the presence of magnesium.

This behavior can be explained because STPP complexes calcium and magnesium nonselectively (4). As was demonstrated and explained in a previous paper (3), Mg^{2+} ions have more positive counterion effects than Ca^{2+} , so that the removal of the former by STPP has a more dramatic influence on detergency performance.

Detergency LAS/zeolites. Figures 5, 6 and 7 show more of the experimental results. A minimum and a maximum are reached independent of the counterion used. However, in this particular case, better results are obtained in the presence of magnesium ions than for calcium ions. The results can be explained. When zeolite is used, a higher selectivity exists toward calcium than toward magnesium ions. Thus, calcium is probably eliminated from the washing liquor, whereas the beneficial effects of a certain amount of magnesium kept in solution still remain. This hypothesis is confirmed in Figure 8, where zeolites are compared to STPP for a given LAS concentration as a function of magnesium concentration. The theory launched earlier (2) to explain the shape of the curves, i.e., the existence of a minimum and a maximum, can be completed by the arguments presented in Figure 9.

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FIG. 9. Shape of the detergency curve vs. water hardness. Abbreviation as in Figure 1.

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