Organic Acids as Builders in Linear Alkylbenzene Sulfonate Detergent Formulations

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Abstract

Sodium salts of citric, glycolic, diglycolic and three sugar acids, directly derived from D-glucose, were evaluated as builders in a formulation for a linear alkylbenzene sulfonate detergent. Only sodium citrate and diglycolate were at least 60% as effective as sodium tripolyphosphate in building action in hard water. Detergency appeared to be related to calcium sequestration by the salts at pH 10.

Introduction

In a previous investigation (1) we evaluated several carboxylated starch derivatives as replacement builders for sodium tripolyphosphate (STPP) in a standard formulation for a linear alkylbenzene sulfonate (LAS) detergent. We have extended our studies to determine the building efficiency of several acids, derived directly from D-glucose, which are known to have metal ion sequestering properties in 2–4% alkali (2). These are D-gluconic, D-glucoheptonic and D-glucaric (3) acids. Citric, glycolic and diglycolic acids were also evaluated for their building effect in hard water. Besides STPP, both nitrilotriacetic (NTA) and polyitaconic acids (4,5) are known to have good building action with LAS detergents and were used to confirm the adequacy of the detergency test procedure. The sodium salts of the acids were incorporated in the detergent formulations on a 50% weight basis.

Experimental Procedures

Materials

STPP, NTA, sodium citrate, sodium D-glucoheptonate, sodium D-gluconate, glycolic and diglycolic acids were commercial products. Polyitaconic acid ("Polycon B") was obtained from Pfizer, Inc., Brooklyn, New York. Potassium acid D-glucarate was prepared by nitric acid oxidation of D-glucose (3).

Standard detergent was Conoco SA-697, a 97% active linear tridecyl-benzene sulfonic acid produced by Continental Oil Company, New York. FDS standard soiled cotton was purchased from Foster D. Snell, Inc., subsidiary of Booz-Allen Applied Research, Inc., Florham Park, New Jersey.

Detergency

The basic detergent formulation contained 15% Conoco SA-697 (neutralized with sodium hydroxide), 50% STPP, 24% sodium sulfate, 10% sodium metasilicate and 1% carboxymethyl cellulose. In the experimental formulations, the 50% STPP was replaced by 50% organic acid salts. Detergency was measured as the average increase in reflectance, ΔR, after washing six swatches of standard soiled cotton in a Terg-O-Tometer for 20 min at 60 C and 105 cycles/min. Relative detergency was calculated from the ratio of ΔR for the experimental formulation and ΔR for the STPP standard formulation.

[1] No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE I

Detergent Building Efficiency[a] in Hard Water

Compound[b]	Hardness: 150 ppm, ΔR	150 ppm, $\frac{\Delta R}{\Delta R, STPP^d} \times 100$	Hardness: 300 ppm, ΔR	300 ppm, $\frac{\Delta R}{\Delta R, STPP} \times 100$
STPP	27.2[e]	100	17.5[e]	100
NTA	25.3	93	24.3	139
Polyitaconate	22.1	80	25.0	148
Citrate	17	63	10.6	61
D-Gluconate	5.6	21	4.6	26
D-Glucoheptonate	5.6	21	4.3	25
D-Glucarate[f]	5.5	21	5.6	31
Glycolate	6.7	25	9.6	55
Diglycolate	17.2	63	12.5	72

[a] Total detergent concentration 0.15% (0.023% active detergent, 0.075% builder; exclusive of sodium sulfate, sodium metasilicate and carboxymethyl cellulose).
[b] Sodium salt was 50 wt % of total detergent solids.
[c] The least significant differences in ΔR at 95% probability are comparable to those reported previously (1).
[d] Abbreviations: STPP, sodium tripolyphosphate; NTA, nitrilotriacetic acid (trisodium salt).
[e] Reflectance with STPP as 100%.
[f] Potassium sodium D-glucarate.

Calcium Sequestering Capacity

Chelation of calcium ions by the various compounds investigated as builders was determined at pH 10 and 25 C (±1°) as follows: 1.0 g of the sodium salt of the builder was dissolved in 50 ml of distilled water in a 150 ml beaker by magnetic stirring and adjusted to pH 10 with sodium hydroxide solution. Then 3 ml of 2% sodium oxalate solution was added, and the solution titrated with 1% calcium acetate solution to slight turbidity. Each milliliter of 1% calcium acetate is equivalent to 6.32 mg of $CaCO_3$ sequestered.

Results and Discussion

Table I shows the building efficiency of the various compounds investigated as additives in an LAS detergent formulation in water having 150 ppm or 300 ppm of hardness.

Building efficiency was poor with the sodium salts of D-gluconic, D-glucoheptonic, D-glucaric and glycolic acids. Although the sugar acids are good sequestrants for calcium ions in 2–4% sodium hy-

TABLE II

Calcium Sequestering Capacity at pH 10 and 25 C

Compound[a]	mg $CaCO_3$/g of compound
STPP[b]	341
NTA	321
Polyitaconate	461
Citrate	94
Glycolate	19
Diglycolate	206
D-Gluconate	8
D-Glucoheptonate	6
D-Glucarate[c]	26

[a] Sodium salts.
[b] Abbreviations: see Table I.
[c] Potassium sodium D-glucarate.

droxide solutions (2), they do not have much chelating effect at pH 10 and 25 C (Table II). Sodium citrate and sodium diglycolate performed somewhat better in building action and calcium sequestration at pH 10 but were only 61% and 72% as effective, respectively, as builders compared to STPP in 300 ppm of hard water. The high building efficiency of both NTA and polyitaconate are also shown in Table I for comparison with the other sodium salts and to confirm the adequacy of the detergency test method. These salts appear to be much better builders at the higher hardness level. The good calcium sequestering properties of STPP, NTA and polyitaconate (Table II) reflect the importance of calcium chelation at pH 10 for good building action.

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