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Multi-Functional Polyacrylate Polymers in Detergents[1]

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ABSTRACT

Alkali metal salts of polyacrylic acids are water-soluble, multi-functional polyelectrolytes which exhibit a variety of solution properties useful in laundry and dishwashing detergents. This paper describes a number of studies carried out to identify the multi-functionality of polyacrylates under simulated detergent use conditions. Solution properties of several commercially available polyacrylates, with average molecular weight ranging from about 2500 to 250,000, are presented. These include: adsorption onto model particulate soil materials and fabrics, particulate soil and lime-soap dispersancy, sequestration of calcium, magnesium and ferric ions, calcium carbonate precipitation inhibition, buffer action and detergency. Where appropriate, these solution properties are compared with those of commonly used non-polymeric detergent ingredients.

INTRODUCTION

Alkali metal salts of polyacrylic acids are water-soluble, multi-functional polyelectrolytes exhibiting a variety of solution properties useful in laundry and dishwash detergent compositions. These polyacrylates contain anywhere from 10 to upwards of 4000 repeating monomer units having the structural formula: $-CH_2\cdot CH(COO\ )-$. Historically, the use of sodium polyacrylates as thickeners and builders in synthetic detergents has been suggested (1) as early as in 1949. At about the same time, Edelson and Fuoss, (2,3) used sodium polyacrylates as model compounds in their basic studies illustrating the fundamental differences between such polyelectrolytes and simple electrolytes as sodium bromide. However, large scale commercial use of sodium polyacrylates in synthetic detergent compositions probably did not come into effect until almost two decades later, as is evident from recently published reviews (4,5) on patents literature. In spite of this growing industrial use of polyacrylates in both commercial and institutional cleaner products, the published literature on the diverse functional benefits they confirm upon the end-use performance of a compounded detergent product is, at best, scanty (6-9). This paper describes a number of experimental studies carried out to identify the multi-functional benefits of these specialty detergent additives under simulated detergent-use conditions, and the likely role played by polyacrylates in basic detergency mechanisms.

EXPERIMENTAL PROCEDURES

Materials

Polyacrylic acids used in this study were selected from the range of commercial (BF Goodrich Chemical) materials, whose analytical characteristics are shown in Table I. These were converted to their corresponding sodium salts by neutralization with sodium hydroxide to pH 10.5 and were used without further purification. Polyacrylate concentrations given in this report are on dry polymer basis. Details on other materials and reagents are given under appropriate experimental procedures described below.

Adsorption Isotherms

Complete details of the method will be published elsewhere

TABLE I

Analytical Characteristics of Polymeric Polyacrylates

Trade name	Molecular weight (by GPC)		Total solids (%)	pH 1% aqueous solution
	Weight-average (M_w)	Number-average (M_n)		
Good-rite® K-752	2,100	1,000	63	3.1
Good-rite® K-732	5,100	2,100	50	2.8
Good-rite® K-XP10	5,500	2,000	40	7.6
Good-rite® K-XP11	20,000	5,300	40	9.1
Good-rite® K-XP18	60,000	14,000	35	10.0
Good-rite® K-722	170,000	21,000	37	3.3
Good-rite® K-702	240,000	39,000	25	3.0

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[1] Presented at the 75th Annual AOCS Meeting, Dallas, 1984.

(10) and, hence, only a brief description will be given here. Polyacrylate adsorption isotherms were determined at 30 C using conventional solute-depletion-from-solution method. To facilitate analysis of very low levels of polyacrylate anions in solution, a spectrofluorophotometric method was used using specially synthesized 2-vinyl naphthalene (fluorescence) labeled polyacrylic acids having weight-average molecular weights around 2000, 5000 and 50,000. The adsorbents used in the study included kaolin clay, iron oxide and carbon black, chosen as model particulate laundry-soils and cotton fabric pieces. Known weights (m) of solid adsorbents were equilibrated with aqueous solutions containing different polyacrylate concentrations and added electrolyte (Na_2SO_4) strength of 0.10 weight-percent. The pH of these unbuffered solutions were adjusted initially to 10.5 using dilute sodium hydroxide solution. The initial polymer concentrations (C_i) ranged from 0 to 100 mgl^{-1} (or ppm). After shaking the adsorbent and solution mix for 20 hr in a temperature-controlled water bath, the solids were settled in a constant temperature (30 C) ultra-centrifuge. The clear supernatant solutions were analyzed for residual polyacrylate to give equilibrium solute concentrations (C_e). The quantity of polyacrylate adsorbed ($w/m = [C_i - C_e]/m$) is plotted against the corresponding equilibrium solute concentrations (C_e), to give the familiar w/m vs C_e adsorption isotherm plots.

Particulate-Soil Dispersancy

Optical microscopy and sedimentation were the two techniques used to illustrate the soil-aggregate dispersancy or peptization property of sodium polyacrylates under alkaline (pH: 10.5) conditions and at room temperature (25 C).

Optical microphotographs were recorded using Zeiss photomicroscope (magnification of ×165) of iron oxide particles dispersed in aqueous medium with and without 500 mgl^{-1} of sodium polyacrylate having M_w=5,100. The photographs were taken within 30 min after shaking the iron oxide with aqueous solutions.

The median particle sizes (μm) of model particulate-soil agglomerates were also measured in the absence of polyacrylate and in the presence of 100-500 mgl^{-1} polyacrylate of M_w=5,500 at pH: 10.5 and room temperature (25 C). Fisher Scientific Company's Andreasen-Sedimentation pipet (Catalog No. 14-232) was used for this purpose. The particle sizes were calculated from Stoke's law according to the falling velocity of the sedimenting particles given by the equation $r = \sqrt{9\ hn/2(D_1 - D_2)gt}$, where r is the radius of the particles (cm), n is the viscosity of the suspending medium in (poise), h is the hydrostatic pressure-head (cm) at the time of drawing the sample, D_1 is the specific gravity of the solid particle (g cm^{-3}), D_2 is the specific gravity of the suspending medium (g cm^{-3}), g is the gravitational constant (980.7 cm sec^{-2}) and t is the time from start of test (sec). Details of the experimental and the subsequent data analysis method are as supplied by Fisher Scientific Co.

Lime-Soap Dispersancy

The lime-soap dispersing powers of the polyacrylates were determined at room temperature (25 C) and using sodium oleate (Fisher Reagent) as the model soap. The experimental procedure described by Borghetty and Bergman (11) was used without any alterations, and the results are expressed as percent lime-soap dispersing power = (grams of dispersing agent to disperse lime-soap/grams of lime-soap) × 100. Similar tests also were carried out on other selected detergent ingredients.

The undispersed lime-soap agglomerates in the absence of sodium polyacrylate and the dispersed lime-soap particles in the presence of 150 mgl^{-1} of polyacrylate (M_w=20,000) also were photographed at a magnification of ×10,000 using a scanning electron microscope.

Precipitation-Inhibition

Calcium carbonate precipitation inhibiting ability of polyacrylate (M_w=2,100), when incorporated in a nil-phosphate sodium carbonate built laundry detergent, was assessed using the procedure described below. Several white cotton test pieces (Testfabrics, Inc., Middlesex, New Jersey, WFK-10A test cloths) were subjected to 10 standard wash-rinse-dry cycles in a Terg-O-Tometer (U.S. Testing Co. Inc., Hoboken, New Jersey). The detergent used was a commercial nil-phosphate sodium carbonate built laundry detergent powder (Amway Corporation, Ada, Michigan). The test conditions used were: detergent dosage: 0.1%; polyacrylate dosage: 0, 0.0025%, 0.0050% and 0.0100%; water hardness ($2Ca^{++}/1Mg^{++}$): 150 mgl^{-1} as $CaCO_3$; wash and rinse temperature: 49 C; agitation: 90 rpm; wash time: 10 min; rinse time: 2 × 5 min each, drying in an oven with forced air circulation for 30 min at 60 C. After 10 cycles, the test cloths were extracted with 0.1N hydrochloric acid and their calcium concentrations were determined through Standard EDTA titrations. The results were converted to give mg $CaCO_3$ deposit found per gm of washed cotton test fabric, using appropriate conversion factors.

Scanning electron micrographs of representative washed test pieces from the above Terg-O-Tometer test also were taken at a magnification of ×1000.

Sequestration

An electrometric method for the determination of builder-sequestration data discussed in this report already has been published from this laboratory (12). The method involves the measurement of free hardness ion concentration in equilibrium with varying amounts of builder (g/100 ml solution) under experimental conditions closely simulating practical use-conditions of detergents: starting hardness= 2.00×10^{-3}M $2Ca^{++}/1Mg^{++}$ hardness ions; additional electrolyte concentration: 0.1g Na_2SO_4 per 100 ml; builder concentration (100% dry basis): 0, 0.005, 0.010, 0.020, 0.030, 0.040, 0.060, 0.080, and 0.100 g/100 ml; pH: 10.5; temperature: 30 C. From the resulting plots of free hardness ion concentrations vs builder concentrations, the builder concentrations required to reduce the free hardness ion concentrations to between 10^{-4}M and 10^{-5}M are easily read off. At these low levels of free hardness ion concentrations, significant increase in detergency is known to occur (13).

Ferric ion sequestering ability of sodium polyacrylate is semi-quantitatively assessed by observing the prevention of ferric hydroxide precipitation at alkaline conditions (pH = 10.50).

Buffer Capacity

pH titration of 100 ml of 1.0% solution of sodium polyacrylate (M_w=170,000) and STPP were carried out using 2.82N hydrochloric acid at room temperature (25 C). The buffer capacity is calculated as dB/dpH, where B is the amount of acid added, at a few representative pH values. The procedure used is similar to that reported by Tokiwa and Imamura (14), who have reported extensively on the buffering ability of various detergent builder materials.

Detergency

Standard Terg-O-Tometer (U.S. Testing Co., Hoboken, New

Jersey) tests were carried out under the following test conditions:

Detergents	Percent in formulation A	B	C
Anionic surfactant (LAS)[a]	20	20	20
Alkaline sodium silicate (Na_2O:SiO_2=1:2.4)	20	20	20
Sodium sulfate	45	20	40
Sodium tripolyphosphate	5	30	5
Sodium polyacrylate (M_W=170,000)	0	0	5
Moisture	10	10	10

[a] Conoco-C560 straight chain dodecylbenzene sodium sulfonate, a commercial detergent active from Conoco Chemicals Inc., Houston, Texas.

Test cloths: Four 3" × 3" WFK-10C clay soil cotton test cloths (from Testfabrics Inc., Middlesex, New Jersey) per 1000 ml wash-solution. Water hardness ($2Ca^{++}/1Mg^{++}$): 2×10^{-3}M; pH=11.0; detergent dosage=0.2%; wash/rinse temperature: 50 C; 10-min wash plus two 5-min rinses. Agitation: 90 rpm; drying in an oven with forced air circulation for 30 min at 60 C. Reflectance measurements made using Photovolt Reflectometer, Model 670, Green filter.

Percent detergency values were calculated using the following equation reported by Lambert and Sanders (15): % detergency = $[(R_W-R_S)/(R_O-R_S)] \times 100$, where R_O represents the reflectance measured on clean, untreated cotton fabric, R_S on soiled cloth and R_W on washed cloth.

RESULTS AND DISCUSSION

Adsorption Isotherm

The adsorption isotherms for sodium polyacrylate (M_W= 50,000) on model particulate-soils are shown in Figure 1. The dashed line (curve 5) in this figure represents the data for sodium tripolyphosphate (STPP), at 30 C and pH 7.0, taken from the work of Lyons (16). The monolayer surface-coverage values read from the plateau portion of the adsorption isotherms for kaolin clay are 2.36 and 0.36 mg per g kaolin clay for sodium polyacrylate and sodium tripolyphosphate, respectively. The initial slopes of curves 2 and 5 indicate that these monolayer surface-coverage limits are reached at significantly lower equilibrium solute concentration in solution for sodium polyacrylate, as compared to STPP. The adsorption isotherms for the lower molecular weight (M_W=2000 and 5000) sodium polyacrylate, reported separately (10), also indicate that they are strongly adsorbed on model particulate-soils at very low equilibrium solute concentrations in solution.

Particulate Soil Dispersancy

Figure 2 illustrates the deagglomerating or peptization property of polyacrylate in the case of iron oxide used here as the model particulate soil. Similar work (not shown here) on other particulate soil materials and polyacrylates with M_W=2100 to 240,000, lead us to conclude that polyacrylates possess the ability to break down large-sized (50-100μm) soil agglomerates to sub-micrometer (<1μm) size dispersions at relatively low levels of use concentrations (for example, 20 mgl^{-1}).

Figure 3 illustrates the results from sedimentation-pipet tests on median particle sizes of typical laundry soil particulates, both in the presence and the absence of polyacrylates. The median sizes (40-120mμ) of the initially agglomerated particulate soils are seen to shift downward to much lower values (<10μm) in the presence of sodium polyacrylate.

Lime-Soap Dispersancy

Figure 4 shows lime-soap dispersions in the presence and

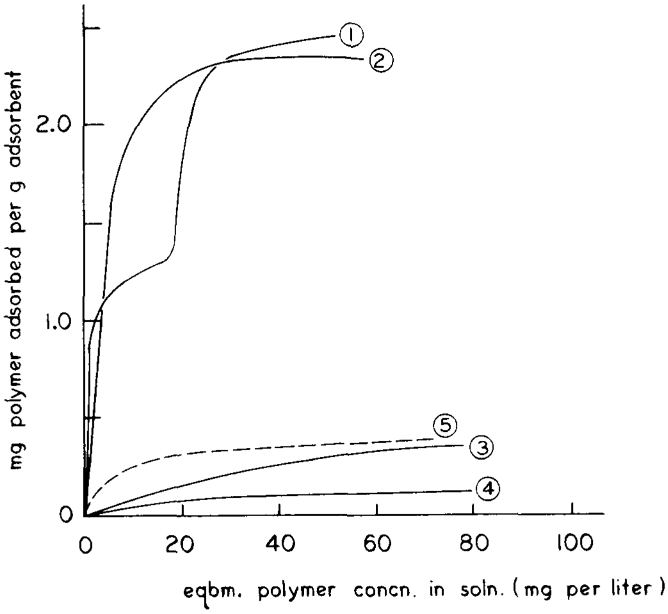

FIG. 1. Sodium polyacrylate adsorption isotherms. ① Fe_2O_3. ② kaolin. ③ carbon black. ④ cotton fabric. ⑤ STPP. (The adsorption isotherm for STPP on clay is taken from Ref. 16).

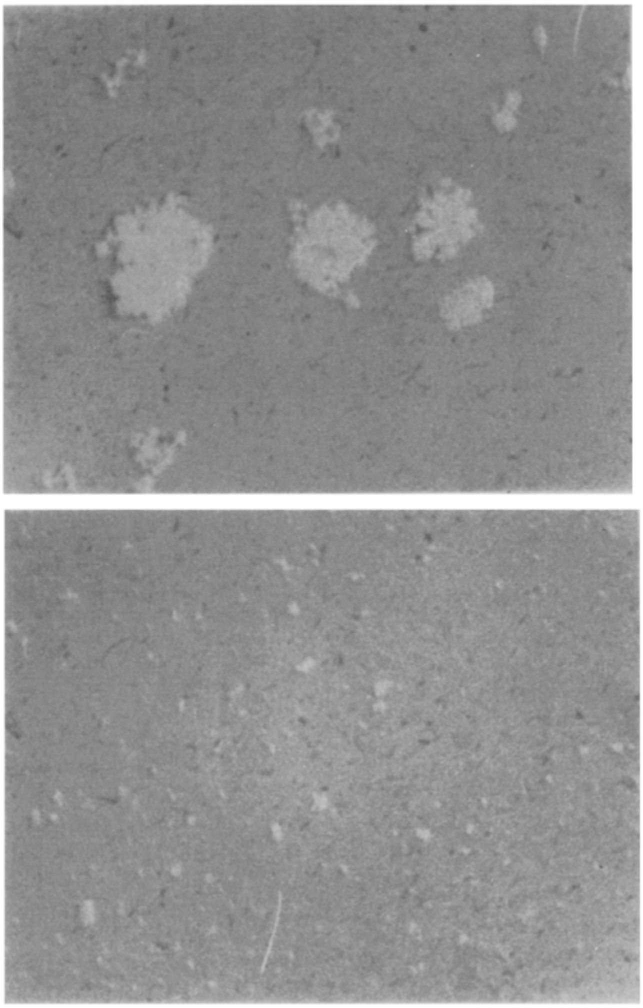

FIG. 2. Optical micrographs of undispersed and dispersed Fe_2O_3. Top photo: polyacrylate absent; bottom photo: polyacrylate present.

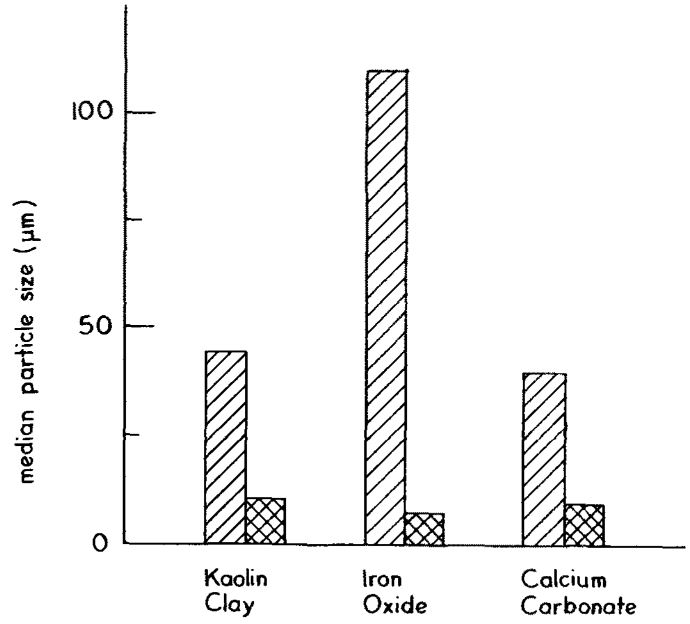

FIG. 3. Particulate soil dispersancy. ▨: polyacrylate absent; ▩: polyacrylate present.

TABLE II

Lime-Soap Dispersing Power of Sodium Polyacrylate

Ingredient	Percent lime-soap dispersing power
Na-polyacrylate (M_W=20,000)	17.5
Sodium tripolyphosphate	111.1
Sodium nitrilotriacetate	71.4
Sodium dodecyl benzene sulfonate (LAS)	33.3

the absence of a sodium polyacrylate (M_W=20,000). Table II lists lime-soap dispersing powers of sodium polyacrylate, as well as those of a few common detergent ingredients. The percent lime-soap dispersing power, as defined by Borghetty and Bergman (11), directly gives the weight percent of the dispersing agent to be included in sodium soap (or oleate) to achieve total dispersion of the lime-soap scum. In the Borghetty and Bergman test, the sodium oleate concentration works out to 0.083% and hardness ion concentration to 3.33×10^{-3}M (or 333 ppm as $CaCO_3$). The data given in Table II indicate that sodium polyacrylate is approximately twice as effective as LAS in dispersing lime-soap scum in very hard water (333 ppm $CaCO_3$) use situations. Agglomerated lime-soap scum, viewed as a soil, poses cleaning problems both in bar soap product-use situations (ring around the wash tub or basin) and in detergent laundry product-use situations (build-up of lime-soap formed in-situ on soiled fabric containing free fatty acids from human sweat sebum soils).

Figure 5 gives the scanning electron micrographs of the agglomerated lime-soap scum (50-100mµ) which are dispersed by sodium polyacrylate to sub-micron (1mµ and below) sized particles. These sub-micron sized milky-dispersions of lime-soap are less likely to settle in detergent product-use situations and are easily disposed of during the rinsing operations.

Precipitation-Inhibition

Figure 6 illustrates the ($CaCO_3$) anti-precipitation benefit obtained with varying concentrations of sodium polyacrylate (M_W=2,100) added to a nil-phosphate Na_2CO_3-built commercial detergent wash in a Terg-O-Tometer test. The absence of calcium carbonate incrustations on cotton test-fabric pieces washed several times with the carbonate-built detergent plus adequate levels of sodium polyacrylate is illustrated in the scanning electron micrographs shown in Figure 7.

Sequestration

The ability of polyacrylates with varying molecular weights

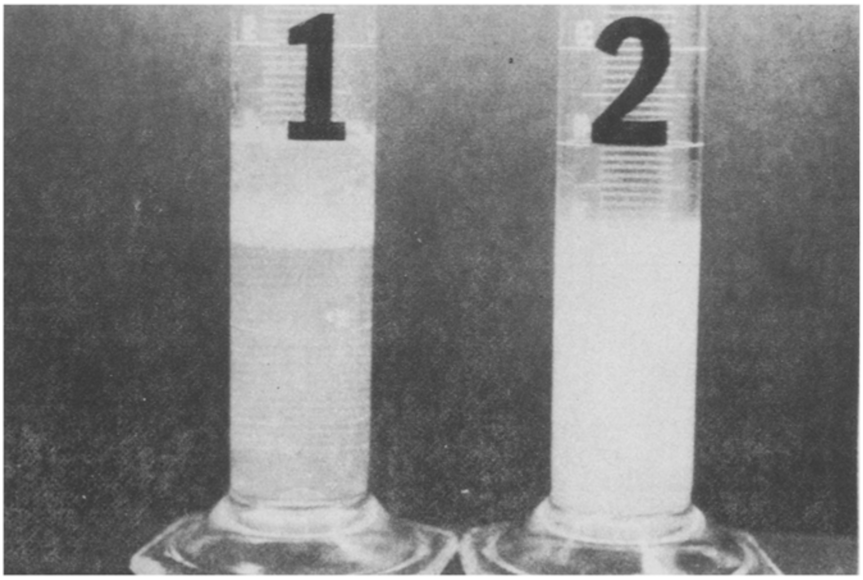

FIG. 4. Lime-soap dispersancy. 1. Polyacrylate absent; 2. Polyacrylate present.

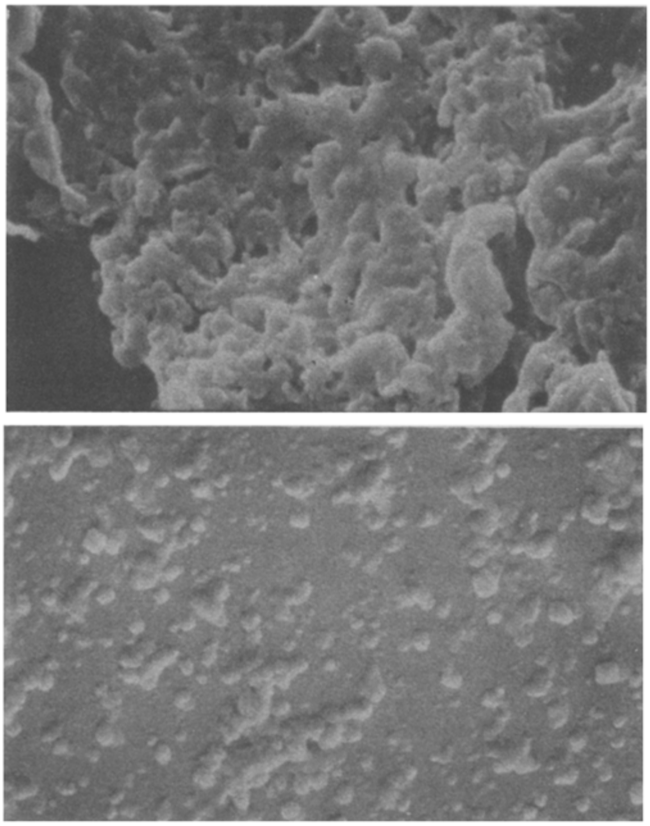

FIG. 5. SEM pictures of undispersed and dispersed lime-soap soil. Top photo: polyacrylate absent; bottom photo: polyacrylate present.

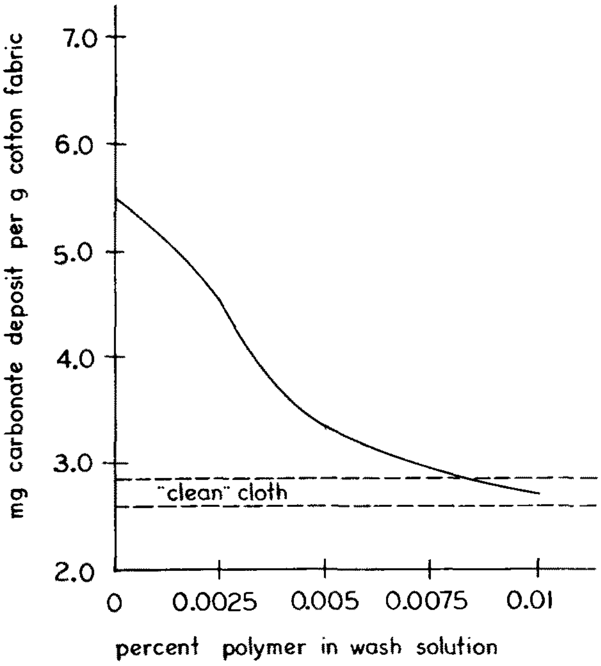

FIG. 6. Calcium carbonate precipitation-inhibition (analytical results).

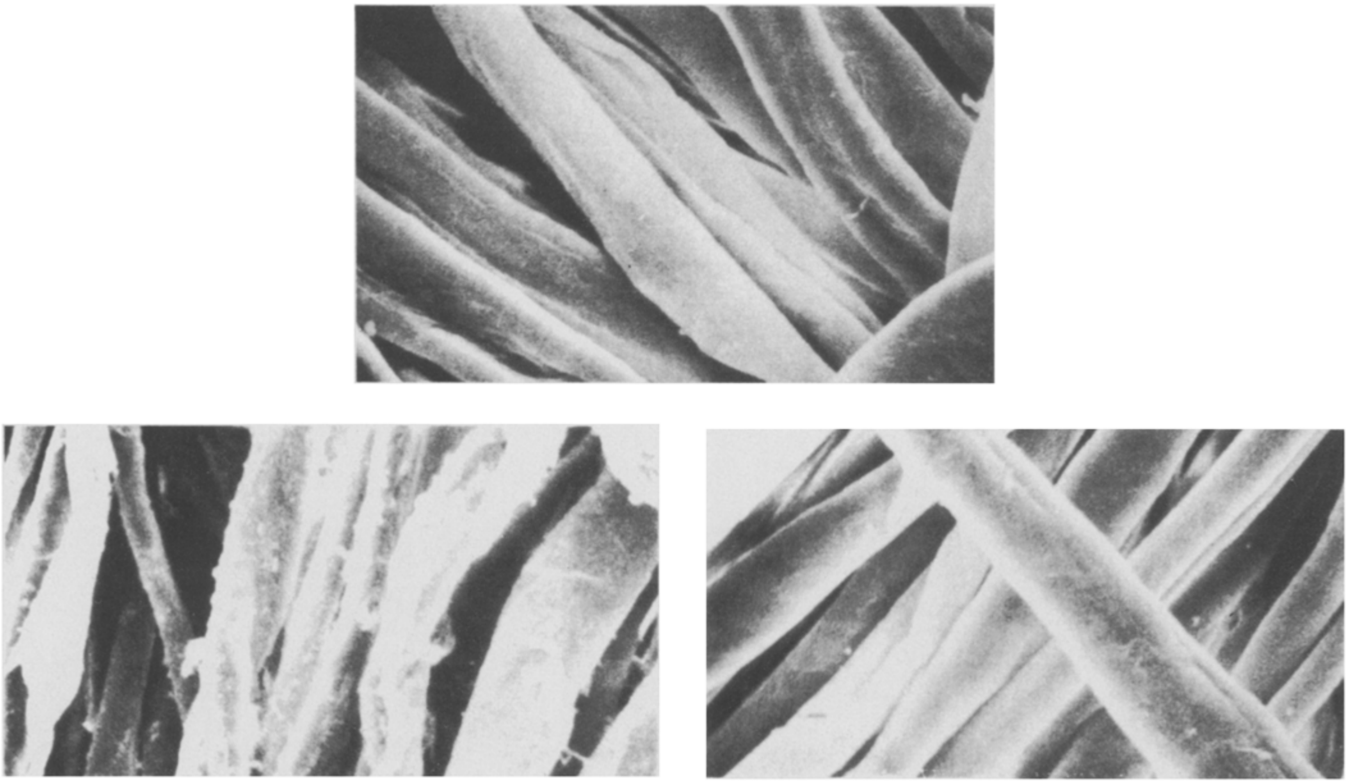

FIG. 7. Calcium carbonate precipitation-inhibition (SEM photograph). Top photo: clean cotton fabric; bottom left: polyacrylate absent; bottom right: polyacrylate present.

(M_W=2,100 to 240,000) in sequestering calcium-magnesium (2:1 mole ratio) water hardness ions under simulated detergent-use conditions already has been reported from this laboratory (12). Figures 8 and 9 given here are reproduced from our earlier work (Figs. 4 and 2 from reference 12, respectively), and these demonstrate that the free hardness ion lowering capacities of sodium polyacrylates are (a) significantly better than commonly used weak-builders like zeolite and sodium citrate at all use concentrations, and (b) equivalent to or better than strong-builders like sodium tripolyphosphate and nitrilotriacetic acid, depending on the use concentration of the detergent builder.

Table III records our preliminary experimental observations on sodium polyacrylate-Fe^{+3} systems under alkaline conditions (pH 10.5). These results indicate the ferric ion sequestering capability of sodium polyacrylate, which could offer particular benefit in preventing equipment-scaling in institutional laundry or dishwash systems.

Buffer Capacity

Figure 10 gives the pH titration curves obtained in the present work for sodium polyacrylate and STPP. The significantly greater acid (soil) resistance of sodium polyacrylate over STPP is apparent both from Figure 10 and from the calculated buffer capacities of these two builders at pH 9.5 (dB/dpH for Na-polyacrylate = 1.02 ml acid per 1 pH unit drop and for STPP = 0.16 ml).

Detergency

Figure 11 represents the percent detergency values obtained for Formulations A, B and C. The results suggest that, on equal weight basis, sodium polyacrylate is approximately five times more effective than STPP in boosting the detergency of anionic detergent formulations. In other words, other things being equal, 5% sodium polyacrylate compensates for the drop in detergency observed for 30-5=25% STPP in the formulation.

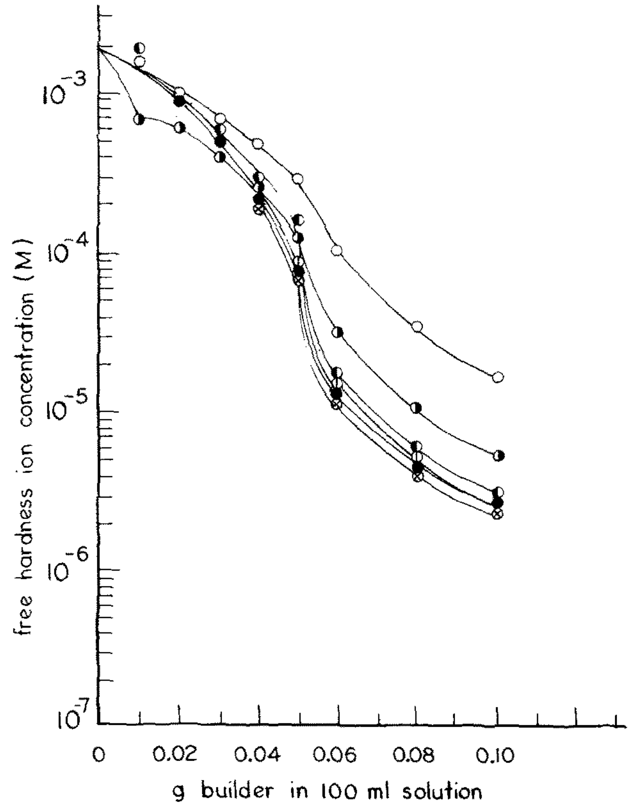

FIG. 8. Water hardness ion sequestration by sodium polyacrylates. ⊙: M_W=2,100; ◑: M_W=5,100; ◐: M_W=20,000; ●: M_W=60,000; ⊗: M_W=170,000; ⌀: M_W=240,000.

Overview of Polyacrylate Functions in Detergents

The detergency performance equivalence of a 20 LAS/20 Na-silicate/40 Na_2SO_4/5 STPP/5 Na-polyacrylate detergent formulation with that achievable by a 20 LAS/20 Na-silicate/20 Na_2SO_4/30 STPP formulation (Fig. 11) arises from the multi-functional benefit-roles of sodium polyacrylate in detergent-use situations. Some of these polyacrylate functions in detergents indicated by the present study are: (a) anionic surfactant protection in hard water via sequestration and buffer actions; (b) particulate soil removal, peptization, dispersion and anti-redeposition via the build-up of strong electrostatic repulsive forces between the soil particles and the surfaces to be cleaned, and (c) specialized wash benefit effects like prevention of lime-soap soil build-up on washed fabrics and other surfaces, prevention

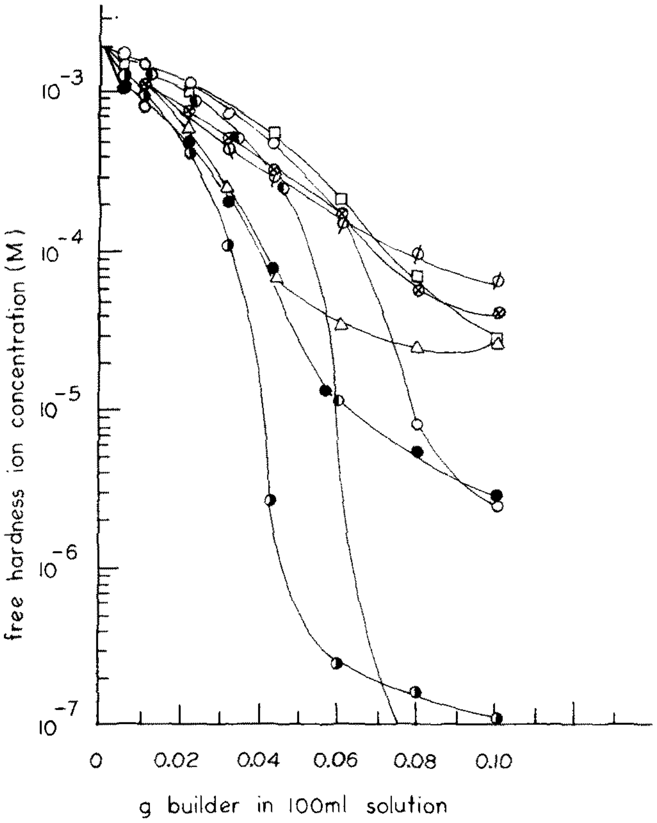

FIG. 9. Water hardness ion sequestration by various detergent builders. ●: sodium polyacrylate M_W=170,000; ○: STPP; ◑: NTA; ◐: EDTA; ⌀: sodium citrate; ⊗: CMOS; △: sodium carbonate; □: zeolite-A.

TABLE III

Fe^{+3} Sequestration

Experiment	Observation
Mix 5 ppm Fe^{+3} NaOH to pH 10.5	Flocculant red $Fe(OH)_3$ precipitate
Mix 5 ppm Fe^{+3} 100 ppm polyacrylate* NaOH to pH 10.5	Clear red solution
Add to #1 100 ppm polyacrylate pH to 10.5	Clear red solution

*M_W=5000 - 250,000.

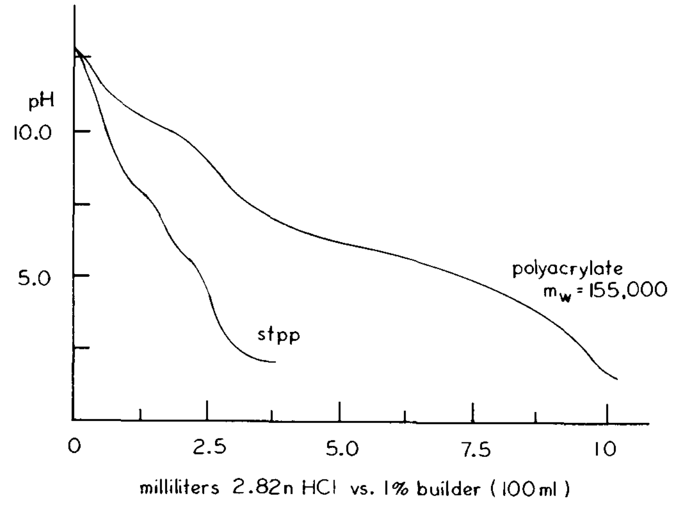

FIG. 10. pH titrative curves (buffer capacity).

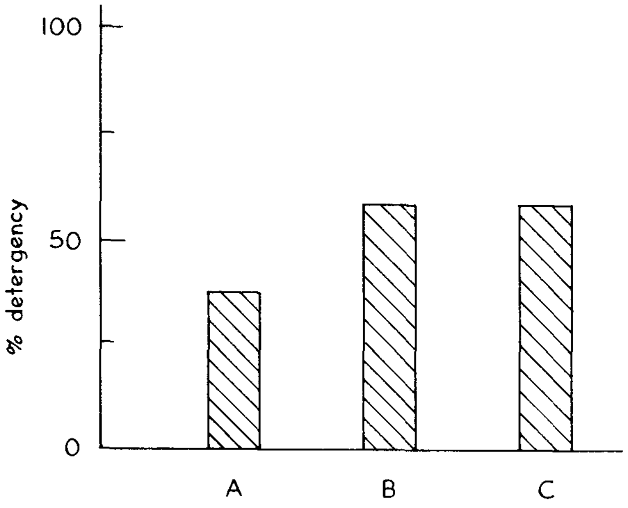

FIG. 11. Terg-O-Tometer detergency.

of insoluble calcium carbonate deposits on washed fabric and washing equipment surfaces, etc. Because of the extreme complexity of detergency mechanisms operating in practical detergent-use situations (17,18), it is not possible to relate quantitatively the diverse multi-functional benefits obtained through the use of sodium polyacrylates in detergents to any single detergency test result.

ACKNOWLEDGMENT

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