Surfactants
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♣ Water Hardness Control by Detergent Builders

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ABSTRACT

Commercial detergent additives to control water hardness are of three main types, sequestrant, precipitant or ion-exchange builders. These builders lower the free hardness ion (Ca^{+2}, Mg^{+2}) concentration in a wash system by different mechanisms. An electrometric experimental method was used to evaluate the relative water hardness control performances of different builder-types under conditions closely simulating those of detergent's end-use. Experimental data for the following builders are presented: EDTA, NTA, STPP, PAA, CMOS, Na-Citrate, Na_2CO_3 and type A zeolite. It is shown that the relative rankings of the various builders in water hardness control differ significantly with differences in use level concentration of the builder (0.005-0.100 gm per 100 ml). The application of the method to the selection of optimum molecular weight range of the newly emerging class of organic polymeric detergent builders like sodium polyacrylates (Na-PAA) (M_w=2000–220,000) also is discussed.

INTRODUCTION

Calcium and magnesium ions present in water used for laundering clothes are known to decrease (1,2) the detergency performance of an unbuilt detergent composition. There are at least two major mechanisms (3) through which this loss in detergency occurs: (1) removal of the active surfactant from the wash solution as its insoluble calcium or magnesium salt, and (2) increased levels of calcium-bound or calcium-bridged redeposited soils. Water hardness ion controlling agents (called detergent-builders) are com-

mon constituents in modern synthetic detergent composition because they boost detergents' effectiveness. Their key function is to reduce the free hardness ion concentration to values below 10^{-4} or 10^{-5} M. At these low levels of free hardness ion concentration, significant increase in detergency is known to occur (4). Examples of hardness ion controlling agents commonly used in the detergent industry are: (1) Sequestrant builders like Sodium tripolyphosphate (STPP), nitrilotriacetic acid (NTA), citric acid and, more recently, polyacrylic acid (PAA); (2) Precipitant builder like Sodium carbonate, and (3) Ion exchange builder like crystalline sodium aluminosilicate or Zeolite Type A.

The mechanisms by which the different types of detergent builders control water hardness in wash solutions are entirely different. Therefore, the experimental parameters and the experimental methods used in assessing their value in water hardness control differ widely. For sequestrant builders, their chelation values (the amount of calcium or magnesium ions bound per mole or per unit weight of a sequestrant) and stability constants (the thermodynamic equilibrium constant for the hardness ion sequestrant complex formation reaction) are usually reported. These are determined through turbidimetric (e.g. oxalate) titrations (5), pH-lowering acidimetric titrations (6) and ion-selective electrode titrations (7,8). In the case of a precipitant builder, (e.g. sodium carbonate) the solubility product of the insoluble calcium-builder salt (which is the ion-product concentrations in equilibrium with the insoluble calcium carbonate, for example) is generally deemed a

measure of the builder's ability to control water hardness ions. This is determined by conventional physico-chemical techniques like turbidimetry, conductometry, etc. (9,10). Zeolite, the principal ion-exchange builder used in detergents, is usually characterized (11) by its Ca^{+2}/Na^+ selectivity coefficient which defines the equilibrium between unit weight in grams of the insoluble solid builder and molar concentrations of Ca^{+2} and Na^+ ions. It is, therefore, apparent that the definitions, the units and the experimental techniques used in evaluating the water hardness control performances of various detergent builders vary with the builder-type. Even within one class of materials the reported experimental conditions like concentrations of calcium ions and of the sequestrant, ionic strength, buffer strength, pH, etc., rarely overlap. While it is possible that a uniform, common method for evaluating the relative effectiveness of water hardness controlling agents of different types is being used by detergent-product manufacturers, no such data with a common experimental base are available in the published literature. We report here the relative water hardness control performances of several detergent-builders determined under the same experimental conditions. The builders examined include the newly emerging class of organic polymeric detergent builders, e.g. sodium polyacrylates (M_W=2000 to 220,000).

EXPERIMENTAL PROCEDURES

Materials

Pentasodium tripolyphosphate, trisodium citrate, disodium ethylene diamine tetraacetate, sodium carbonate (all Fisher); trisodium carboxymethyl oxysuccinate (Ethyl Corporation); Type-A Zeolite (PQ Corporation); monosodium nitriloriacetate (Eastman Kodak), and six sodium polyacrylates (B. F. Goodrich Chemical; weight average molecular weights by gel-permeation chromatography: 2030, 5260, 20,000, 60,000, 155,000 and 211,000) were used without further purification. All experimental results reported are on 100% dry builder basis. Calcium chloride dihydrate, magnesium chloride hexahydrate, 0.1N sodium hydroxide, 0.1N hydrochloric acid and sodium sulfate were Fisher certified reagent grade materials.

The method reported here for evaluating the water hardness control performance of detergent builders involved the measurement of free hardness ion concentration in equilibrium with varying amounts of builder (gm per 100 ml of solution) under experimental conditions closely simulating practical use conditions of detergents viz., hardness ions: $2Ca^{+2}$: $1Mg^{+2}$ mole ratio; starting water hardness: 2.00 × 10^{-3} M or 200 ppm total hardness expressed as $CaCO_3$; additional electrolyte: 0.10 gm sodium sulfate per 100 ml; builder concentrations (100% dry builder basis): 0, 0.005, 0.010, 0.020, 0.030, 0.040, 0.060, 0.080 and 0.100 gm per 100 ml. Individual 100 ml solutions were made up (using demineralized water) to correspond to each of the above mentioned builder concentrations. The pH of each solution was adjusted to 10.50 ± 0.05 using either 0.1N NaOH or 0.1N HCl. No pH adjustments were made in the case of sodium carbonate, since it is not possible to adjust the pH down to 10.50 using 0.1N HCl without irreversible decomposition of sodium carbonate. The free hardness ion concentration of each solution was determined electrometrically employing a Radiometer F2112 Ca electrode, K-801 silver/silver chloride reference electrode and Fisher pH meter model No. 144. The builder concentration required to lower the (initial) 2.00 × 10^{-3} M calcium-magnesium hardness to 10^{-4} M (or below) is obtained from a 5-cycle semilogarithmic plot of the electrometric data and is taken as the common measure of the water hardness controlling

ability of the builder, irrespective of the builder-type.

Calibration

Eleven standard samples containing water hardness ions ($2Ca^{+2}$: $1Mg^{+2}$ mole ratio) of varying concentration (C_h) between 10^{-2} M and 10^{-7} M and in the presence of 0.10 gm sodium sulfate per 100 ml, were prepared in demineralized water and their pH adjusted to 10.50 ± 0.05. The electrode potentials in millivolts (E) of each standard solution were measured at room temperature (25 C) with constant agitation by a magnetic stirrer. These measurements were repeated four times and their mean values were fitted to the following non-linear second-degree equation: C_h = exp. ($A + B.E + C.E^2$), where A = -4.781, B = 0.0654 and C = 0.000147 and C_h is expressed in ppm as $CaCO_3$ (1 ppm $CaCO_3$ = 1.0 × 10^{-5} M hardness ion). The calibration data are plotted in Figure 1, and the Nernstian slope of the straight portion of the curve (viz. approximately between 2.0 × 10^{-3} M and 1.0 × 10^{-4} M hardness ion concentration) is 24.0 millivolts per decade. The curvature in E vs. concentration plot below about 10^{-4} M hardness ions concentration agrees favorably with that given by the electrode manufacturers (12). The error in reproducibility of the measurement of hardness ion concentrations by this analytic method was less than ±0.5 per cent at the high concentration end (i.e. 10^{-3} M) and not more than ±2.0 per cent at concentrations below about 10^{-4} M.

RESULTS AND DISCUSSION

The decrease in the free hardness ion ($2Ca^{+2}/1Mg^{+2}$ mole ratio) concentration observed with increasing builder concentrations in solution for the different builder-types investigated is shown in Figure 2. It is seen from Figure 2
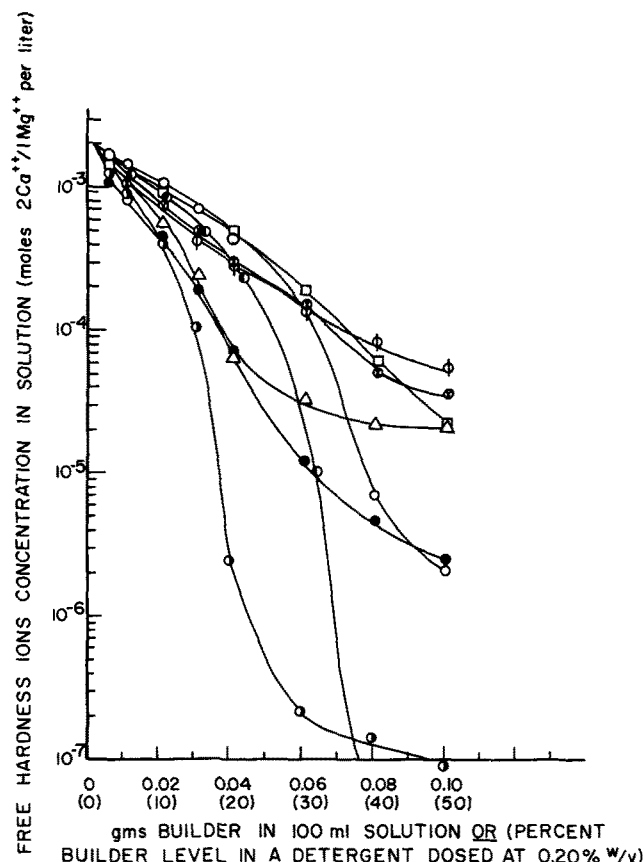

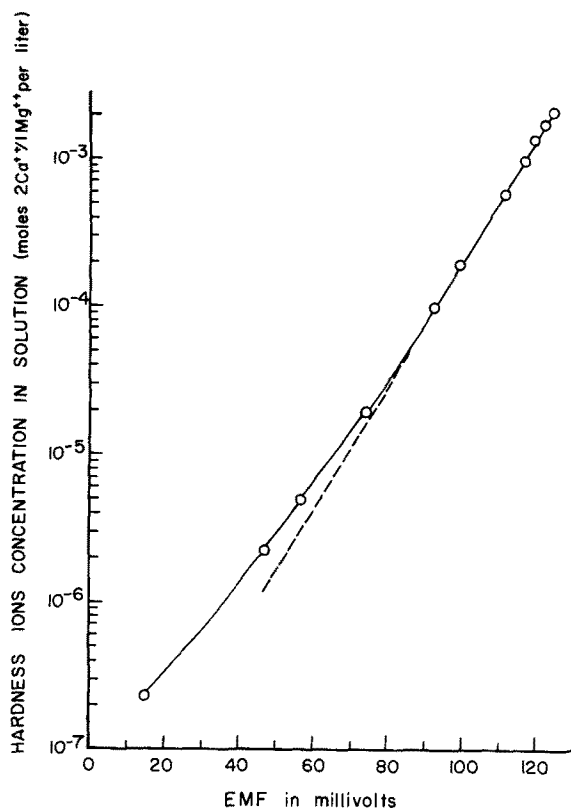
FIG. 1. Calibration data. pH: 10.5 ± 0.05; 25.0 C ± 0.5 C; 0.10% Na_2SO_4.

FIG. 2. Free hardness vs. builder level (different builder-types). ⦶ Na-NTA; ◐ Na$_2$-EDTA; ● Na-PAA (M$_w$=155,000) (K-752); ○ Na$_5$-STPP; ∅ Na$_3$-Citrate; ⊗ Na$_3$-CMOS; △ Na$_2$CO$_3$; □ Type A Zeolite. pH 10.50 ± 0.05; 25 C ± 0.5 C; 0.1% Na$_2$SO$_4$.
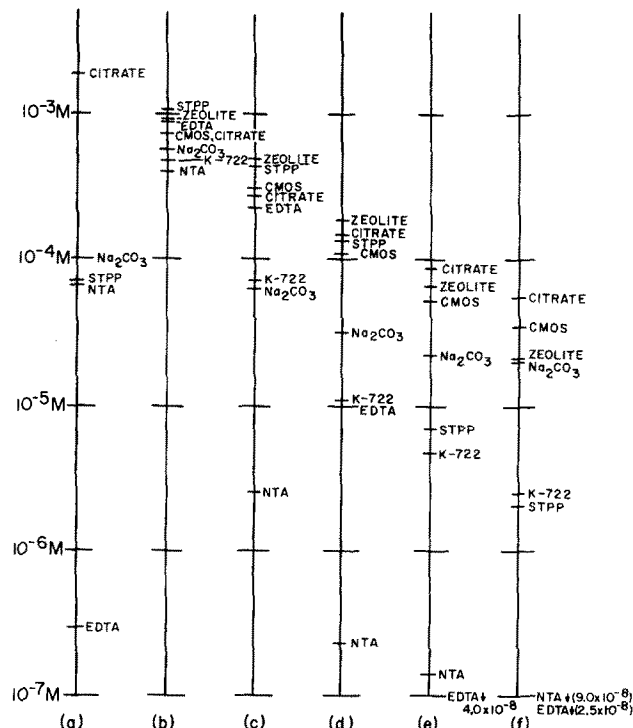

FIG. 3. Relative ranks of builders at different builder levels in detergent. (a) Data from Ref. 10; (b) 0.020 gm/100 ml; (c) 0.040 gm/100 ml; (d) 0.060 gm/100 ml; (e) 0.080 gm/100 ml; (f) 0.100 gm/100 ml. Y-axis denotes free hardness ion (2Ca^{+2}/1Mg^{+2}) concentration (lower the better) observed at specified builder-level.

that the shape of the curves differs with the builder-type. In the case of sequestrant builders like STPP, NTA, EDTA, CMOS, PAA and citric acid, the curves approximately resemble an inverse-S shape, i.e. small gradual decrease in the free hardness at low builder concentrations, large (sharp) decrease at an intermediate builder concentration and, again, small gradual decrease at high builder concentration. In the case of a precipitant builder like Na$_2$CO$_3$, the free hardness decreases more or less uniformly with an increase in the builder concentration, reaching asymptotically a constant low value related to the solubility product of the insoluble CaCO$_3$ precipate. In the case of an ion exchange type builder like Zeolite, Type A, the decrease in free hardness is gradual and, more or less, uniform with increase in the builder concentration.

From a practical detergent formulation point of view, these differences in shapes of the free hardness vs. builder concentration curves result in significantly altered rankings of hardness ions controlling abilities of the detergent additives. This is illustrated in Figure 3, where the various builders are ranked according to the free hardness ion concentrations reached at different builder concentrations. At a given builder concentration, the lower the free hardness ion concentration reached, the better is the ability of that builder in controlling water hardness in detergent-use situations. Thus, at 0.020 gm per 100 ml use-level concentration of the builer (cf. Fig. 3b), none of the builders investigated exhibit a hardness ion control performance necessary for achieving good detergency (4). At 0.040 gm per 100 ml (cf. Fig. 3c), only NTA, Na$_2$CO$_3$ and PAA exhibit satisfactory hardness ion control; their relative rankings are NTA > Na$_2$CO$_3$ > PAA ≫ EDTA > Citrate > CMOS > STPP > Zeolite. At 0.060 gm per 100 ml (cf. Fig. 3d) the relative rankings change to NTA > EDTA > PAA >

Na$_2$CO$_3$ ≫ CMOS > STPP > Citrate > Zeolite. Only the first four builders exhibit satisfactory hardness ion control performance required for good detergency at this use-level concentration of the builder. At 0.080 gm per 100 ml (cf. Fig. 3e), all the eight builders investigated exhibit satisfactory hardness ion control performance necessary for good detergency, and their relative rankings change to EDTA > NTA > PAA > STPP > Na$_2$CO$_3$ > CMOS > Zeolite > Citrate. At 1.00 gm per 100 ml (cf. Fig. 3f), all the eight builders perform satisfactorily with respect to hardness ion control, and their relative rankings now are: EDTA > NTA > STPP > PAA > Na$_2$CO$_3$ > Zeolite > CMOS > Citrate. It is interesting to note that only at and above 0.080 gm per 100 ml use-level concentration of the builder, the relative rankings of five of the detergent builders studied here approach that predicted (cf. Fig. 3a) by considering either the calcium-sequestrant complex stability constant or the solubility product of the (precipitated) calcium-builder salt (10): EDTA > NTA > STPP > Na$_2$CO$_3$ > Citrate.

The data reported here also can be used in a practical manner by converting the minimum builder concentration required to lower the initial water hardness (200 ppm as CaCO$_3$) to the free hardness level (10 ppm CaCO$_3$) necessary for achieving good detergency (4) to the mimimum builder level in a hypothetical detergent assumed to be dosed at 0.200 percent. The relationship between these two units of expression is shown below:

Builder concentration gm/100 ml.	0, 0.005, 0.010, 0.020, 0.030, 0.040, 0.060, 0.080, 0.100
Builder level in detergent weight per cent:	0, 2.5, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, 50.0.

Table I summarizes the data obtained in this study according to the above two units of expressing the builder level. It is important to note here that the data given in Table I signify only the builder levels required for adequate

TABLE I

Builder Levels for Adequate Water Hardness Control Function in Detergents (See text for explanation of the terms used)

Builder	Minimum level required for adequate water hardness control	
	Concentration in solution (gm per 100 ml)	Level in detergent (weight per cent)
Sequestrant builders		
NTA	0.029	14.5
PAA (M_W = 211,000)	0.037	18.5
PAA (M_W = 155,000)	0.037	18.5
PAA (M_W = 60,000)	0.036	18.0
PAA (M_W = 20,000)	0.045	22.5
PAA (M_W = 5,260)	0.043	21.5
PAA (M_W = 2,030)	0.061	30.5
EDTA	0.051	25.5
STPP	0.062	31.0
CMOS	0.067	33.5
Na-Citrate	0.071	35.5
Precipitant builder		
Na_2CO_3	0.037	18.5
Ion-exchange builder		
Type A Zeolite	0.071	35.5

water hardness control. These levels do not necessarily correlate with detergency performances obtained under practical detergent-use situations. Water hardness removal rate, soil dispersion/solubilization, anti-redeposition and several other factors need to be considered together with the hardness ion removal capacities reported here, in order to arrive at a practically meaningful minimum builder lever necessary for achieving good detergency.

Figure 4 illustrates the application of the method reported here to the selection of the optimum (weight average) molecular weight range of sodium polyacrylate polymers for water hardness control applications in detergent formulations. From the experimental curves shown in Figure 4, the data in Table I, this optimum (weight average) molecular weight range seems to be between 60,000-211,000 and (probably) above.

ACKNOWLEDGMENT

REFERENCES

1. Morgenthaler, W.W. in "Detergency, Theory and Test Methods", Surfactant Science Series, Vol. 5, Part II, edited by W.G. Cutler and R.C. Davies, Marcel Dekker Inc., New York, 1975, pp. 475-479.
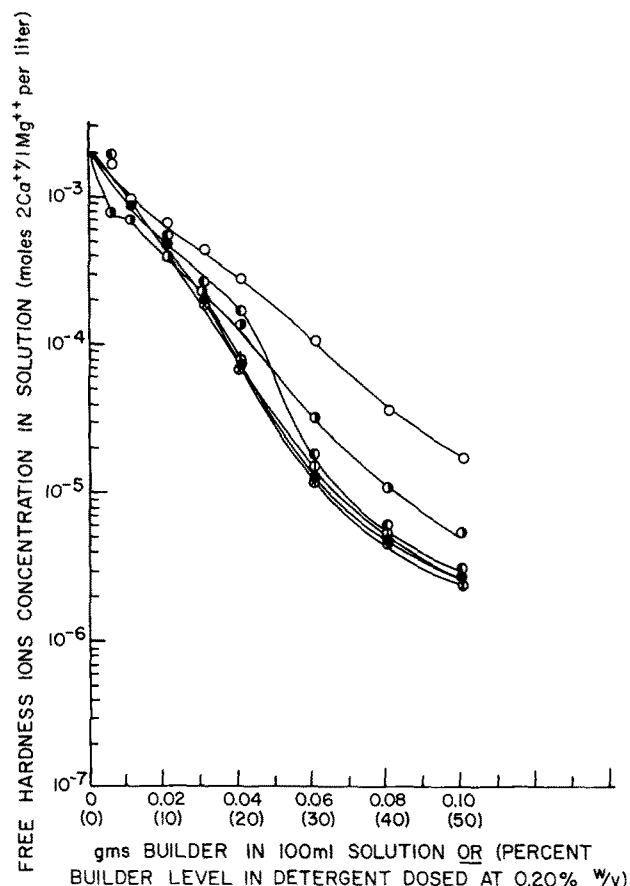
FIG. 4. Free hardness vs builder level (Na-polyacrylates). ⊙ K-752 (PAA of M_W = 2030); ◑ K-732 (PAA of M_W = 5260); ◐ XP-11 (PAA of M_W = 20,000); ● XP-18 (PAA of M_W = 60,000); ⊗ K-722 (PAA of M_W = 155,000); ∅ K-702 (PAA of M_W = 211,000). pH: 10.50 ± 0.50; 25.0 C ± 0.5 C; 0.1% Na_2SO_4.

2. Porter, A.S., 4th International Congress on Surface Activity, Sec. C/II, Vol. 3, 1964, p. 187.
3. Nagarajan, M.K., Ind. Jour. of Chem Edn., 7, 22 (1980).
4. Jones, T.G., and J.P. Parke, 3rd International Congress on Surface Activity, Sec. D/III, Vol. 4, 1960, p. 178.
5. Irani, R.R., and C.F. Callis, J. Phys. Chem., 64:1398 (1960).
6. Irani, R.R., and C.F. Callis, Ibid. 65:1463 (1961).
7. Blay, J.A., and J.H. Ryland, Anal. Letters, 4:653 (1971).
8. Chang, D.M., JAOCS, 60:618 (1983).
9. Irani, R.R., and C.F. Callis, J. Phys. Chem., 64;1741 (1960).
10. Van Wazer, J.R., and C.F. Callis, Chem. Revs., 58, 1011 (1958).
11. Berth, P., JAOCS, 55:52 (1978).
12. Instruction manuals for calcium ion or divalent cation sensing electrodes published by Radiometer A/S, Denmark and Orion Research Inc., U.S.A. (1977).

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