Journal of the American Oil Chemists' Society **Surfactants & Detergents**

Technical

Disodium Dicarboxy Methyl Starch as a Calcium Sequestrant

S. SANTHANAGOPALAN, Hindustan Lever Research Centre, Andheri East, Bombay 400 099, India, **H. RAMAN**, Lupin Laboratories, Santa Cruz (E), Bombay 400 098, India and **S.K. SURI**,* Chemistry Department, Indian Institute of Technology, New Delhi 110016, India

ABSTRACT

Disodium dicarboxy methyl starch (DDMS), the malonate derivative of starch with varying degrees of substitution (DS = 0.22, 1.1 and 1.8), have been prepared and examined for their calcium-sequestrating ability. These derivatives form relatively stronger chelates with calcium ($\log K_{Ca} = 4.7$) than sodium citrate ($\log K_{Ca} = 3.8$). A degree of substitution (DS) ca. 1 appears to be most effective from structural consideration. On a weight basis, the chelating value of DDMS with DS ca. 1 was determined to be ca. 1/3 of that of STPP and EDTA and comparable with that of sodium citrate.

INTRODUCTION

Sodium tripolyphosphate has been in use in detergent formulations for many years as a builder. Of late, awareness has been growing about the eutrophication problems arising from the increased use of phosphate (1). Various alternate materials have been developed that are capable of deactivating calcium ions in wash liquor (1-6). Attempts have also been made to develop starch- and cellulose-based detergent builders by introducing plurality of carboxyl groups (in appropriate proportion to hydroxyl groups) to aid effective sequestration of hardness ions (7-9). Starch-based products appear to be attractive in view of their reported complete biodegradability (10-13). This manuscript deals with the study of the calcium-sequesterating ability of disodium dicarboxy methyl starch (DDMS). The synthesis of DDMS comprises the preparation of bromomalonic acid (disodium salt) followed by its condensation with starch.

EXPERIMENTAL

All chemicals and solvents used in the present studies were of reagent grade. Infrared (IR) spectra were taken on Perkin-Elmer 197 and nuclear magnetic resonance (NMR) on Bruker WP-80.

The degree of substitution (DS) of disodium malonate on hexose moiety of starch was determined by following a procedure similar to the one described by Wilson (14).

Preparation of Disodium Bromomalonate

A mixture of dry ether (500 mL), malonic acid (52 g, 0.5 mol) and acetamide (41.3 g, 0.7 mol) was placed in a three-necked round bottom flask fitted with a mechanical stirrer, condenser and addition funnel. The contents of the flask were gently refluxed and 80 g of bromine was added to it by drops in one hour, stirring constantly. After the addition was complete, the stirring was continued for another 30 min. The reaction mixture was cooled to room temperature and filtered to remove the solids. The solvents were evaporated from the filtrate and the light yellow liquid residue obtained was dissolved in water and neutralized with an aqueous solution of sodium hydroxide

---

*To whom correspondence should be addressed.

(20%) using phenol phthalein as indicator. The temperature of the reaction mixture was maintained at ca. 10 C during neutralization. To the neutralized solution, 100 g potassium acetate was added and the contents warmed till the solution was clear. The mixture was cooled and rectified spirit was added to it to precipitate disodium bromomalonate. The complete precipitation of the product was ensured by the absence of the precipitate formation when further rectified spirit was added to the filtrate. The white solid obtained was added to rectified spirit, stirred and filtered. Finally, it was washed with acetone and dried (yield = 66 g, IR [Nujol] = 1601 Cm^{-1} [$-CO_2^- M^+$]).

Preparation of Disodium Dicarboxy Methyl Starch

To a mixture of 16 g of warm sodium hydroxide in 250 mL of n-propanol in the autoclave vessel, 16.2 g of starch, then 68.3 g of disodium bromomalonate were added and allowed to react at 130 C for 6 hr. The reaction mixture was cooled to ambient temperature and filtered. The solid obtained was dissolved in water (300 mL) and the resultant solution was filtered to remove insolubles. The filtrate was added to a beaker containing 1.5 L of methanol to precipitate the product. The solid obtained was washed by suspending it in methanol (500 mL) and filtered through a Buchner funnel. The material was finally washed with acetone (2 x 500 mL) and dried (yield = 26.1 g, DS = 1.8; IR [Nujol] = 1610 Cm^{-1} [broad, $-CO_2^- M^+$]; ^{13}C-NMR [D_2O]: 170.1 ppm [$-\overset{*}{C}O_2^- M^+$]). A similar procedure was followed to prepare DDMS with DS of 1.1 and 0.22.

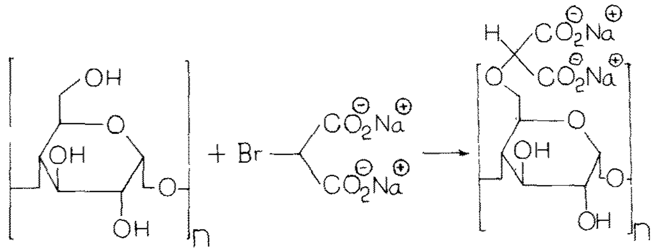
Determination of Calcium Chelating Activity (15)

A known weight (ca. 1 g) of DDMS was dissolved in ca. 80 mL of distilled water at room temperature and the pH of the solution was adjusted to ca. 11.5 using an aqueous solution of sodium hydroxide (10%). Ten mL of 2% sodium oxalate was added to it and the resultant solution was titrated with a standard calcium chloride solution (0.2 N) until a slight haziness was observed in the solution. The amount of calcium added is a measure of the calcium-sequestering power of DDMS and is expressed as mg calcium carbonate/g DDMS.

The procedure was repeated with sodium citrate, STPP and disodium salt of EDTA to compare the chelating value of DDMS with these chelating agents.

RESULTS AND DISCUSSION

The reaction of disodium bromomalonate with starch (resulting in DDMS with DS = 1) can be represented as in Scheme 1.



SCHEME 1

The malonic acid derivatives of starch with DS = 1.1 and 1.8 are fairly soluble in water (solubility >2%). The sample with lower DS (i.e. = 0.22), however, exhibited relatively poor aqueous solubility (ca. 0.3%). All 3 samples gave clear, nonviscous aqueous solutions.

The chelating functions of DDMS are similar to those of citric acid and CMOS (Fig. 1). The formation constant values reveal that although DDMS, like CMOS, is a weak sequestrant, it forms a relatively stronger chelate with calcium ions than citric acid. The possible structure for the calcium chelates of the 3 sequestering agents are shown in Figure 2.

The calcium-sequestrating ability of the 3 DDMS samples (DS = 0.22, 1.1 and 1.8) are given in Table I. The sequestrating ability for the sample with a lower degree of substitution (DS = 0.22) is very small. This agrees with the structural features of the sequestrant. A lower degree of substitution corresponds to the relatively larger distances between 2 substituent malonate groups in DDMS rendering them either ineffective or less active for sequestering the

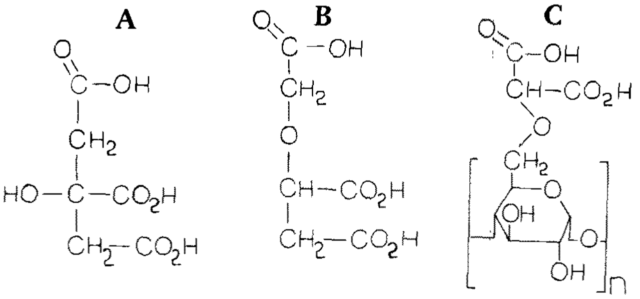


FIG. 1. (a) Citric Acid, log K_{Ca} = 3.8*, (b) CMOS, log K_{Ca} = 4.4*, (c) Dicarboxy Methyl Starch log K_{Ca} = 4.7+.

*From reference.

+Estimated for sample with d.s. = 1.1 using Calcium ion Selective Electrode (17).

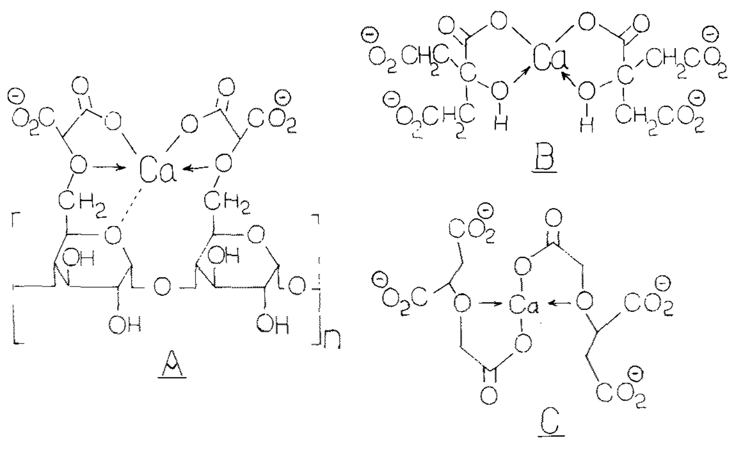


FIG. 2. Calcium chelates of: (a) DDMS; (b) citric acid; (c) CMOS.

TABLE I

Calcium-Chelating Value for Various Builders

Compound	Molecular weight	Chelating value (mg $CaCO_3$/g)		Chelating efficiency (%)
		Experimental	Theoretical	
DDMS (DS = 0.22)	194[a]	12	56	27
(DS = 1.1)	325[a]	105	169	62
(DS = 1.8)	427[a]	91	211	43
Sodium citrate ($2H_2O$)	294	89 94[b]	170	52
EDTA ($2H_2O$)	372	272	269	100
STPP ($6H_2O$)	368	273	272	100

[a]Average molecular weight per hexose unit.
[b]From ref. 6.

metal ions. Therefore, samples with DS ca. 1.0 are expected to be more effective from structural considerations. On a weight basis, the chelating power of DDMS with DS = 1.1 was determined to be ca. 1/3 that of STPP and EDTA, and is comparable to that of sodium citrate (Table I).

Molecular models show that replacing both the primary and secondary hydroxyl of the monomer unit of starch by malonic function (i.e., DS = 2.0) significantly restricts the chain flexibility. This decreases the feasibility of chelation of a second calcium ion with the dimer unit of the polyelectrolyte. The malonic acid substitution beyond DS = 1, therefore, has relatively less chelating affinity. It, however, increases the unit molecular weight of the polyelectrolyte, which (for the same effective chelating affinity) corresponds to a lower calcium-sequestration value. This agrees with our experimental results.

The experimentally obtained calcium-chelating values for various compounds have been compared with the theoretical values in the third column of Table I. The theoretical values for DDMS samples were calculated by assuming that the substitution of 2 malonate functions in the polyelectrolyte can hold one calcium ion. We observed that for STPP and EDTA, the chelating efficiency is ca. 100% whereas for the 3 DDMS samples and for sodium citrate, it is relatively low. Among 3 DDMS samples, the one with DS = 1 exhibits the maximum chelating efficiency and appears to be attractive as a detergent builder. Further studies on this builder are underway.

REFERENCES

1. Schaffer, J.F., and R.T. Woodhams, Ind. Eng. Chem. Prod. Res. Dev. 16:3 (1977).
2. Berth, P., G. Jakobi, E. Schmadel, M.J. Schwuger and C.H. Krauch, Angew. Chem. 87:115 (1975).
3. H.C. Kemper, R.J. Martens, J.R. Nooi and C.E. Stubbs, Tenside Detergents 12:47 (1975).
4. Rutkowski, Beverly J. in Detergency—Theory & Test Methods, Part III, edited by Cutler, W.G. and R.C. Davis, Marcel Dekker Inc., NY, 1981, Chapter 23.
5. Schweiker, G.C., JAOCS 58:170A (1981).
6. Wilham, C.A. and C.L. Mehltretter, Ibid. 48:682 (1971).
7. Wilham, C.A., T.A. McCuire, A.M. Mark and C.L. Mehltretter, Ibid. 47:522 (1970).
8. Diamantoglou, M., H. Magerlein and R. Zielke, Tenside Detergents 14(5):250 (1977).
9. Cornelissens, E.G.P., M. Diamantoglou, A. Malgerlein and R. Zielke, Ger. Offent. 2,410,560 (1975).
10. Hofreiter, B.T., I.A. Wolff and C.L. Mehltretter, U.S. Patent 2,894,945 (1959).
11. Eldib, I.A., Oil Paint Drug Rep. 194(19):5 (1968).
12. Eldib, I.A., Chem. Engr. News. 46(47):16 (1968).
13. Eldib, I.A., U.S. Patent 9,629,121 (1971).
14. Wilson, K., Svensk Papper Stidn. 59:218 (1956).
15. Morgenthaler, W.W. in Detergency—Theory and Test Methods, Part II, edited by Cutler, W.G. and R.C. Davis, Marcel Dekker Inc., NY, 1975, Chapter 11.
16. Chang, D.M., JAOCS 60:618 (1983).

[Received January 16, 1984]