The Binding of Free Calcium Ions in Aqueous Solution Using Chelating Agents, Phosphates and Poly(Acrylic Acid)

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ABSTRACT

Organic chelating agents, phosphates, and polyelectrolytes were studied to determine their calcium ion binding power (CBP) and binding mechanism. A calcium ion electrode was used to measure the equilibrium calcium ion concentrations from which stability constants were calculated. Except for EDTA and NTA, the binding power did not correspond to the formation of complexes with a simple stoichiometry. In most cases, more than one equilibrium is involved. Increase in the level of binding agent decreased CBP, especially for those agents which formed complexes with low stability constants. CBP calculated on the basis of weight should be used to measure the relative cost effectiveness of commercial calcium binding agents. At an amount lower than required to form stable stoichiometric complexes, poly(acrylic acid) had a higher CBP than traditional organic chelating agents. The electrostatic effect accounts for the excellent CBP of poly(acrylic acid) at low concentrations. To get maximum efficiency in detergent and water treatment applications, use of low levels is recommended.

INTRODUCTION

Organic chelating agents such as EDTA have been used to control water hardness. Because of cost, it is replaced mostly by inorganic tripolyphosphates. In the 1960s, tripolyphosphates were found to cause environmental problems (1). During the past 15 years, great efforts have been made to replace phosphates. Many organic materials, including organic polymers, were promising (1-3). NTA was a successful candidate. However, it was found later to be potentially carcinogenic (2). Polymers such as poly(acrylic acid) are also good candidates. This report describes and compares the calcium ion binding power and binding mechanism of organic chelating agents, phosphates, organic oligomers and polymers, using a calcium ion electrode to measure the equilibrium calcium ion concentrations (4).

EXPERIMENTAL

Apparatus

A calcium ion electrode (Model 93-20, Orion Research, Inc.) and a digital pH/MV meter (Fisher Accument Model 144) were used to measure the equilibrium calcium ion concentrations.

Standard Solution Preparation

A standard calcium ion solution (2.00×10^{-3} M, 80 mg/L in calcium ion, 200 mg/L in calcium carbonate) was freshly prepared by diluting Orion standard calcium ion solution (0.100M) with a 0.03M ammonium chloride/0.07M ammonium hydroxide buffer (pH 9.70, ionic strength 0.10M). Standard calcium binding agent solutions (2.00×10^{-3} M) were prepared in the same way. Triple distilled water was used.

Calibration Curve

The electrodes were immersed in a standard calcium ion solution (80 mg/L in calcium ion) and the solution was stirred. The meter reading was adjusted to read 63.5 mV at 25 C. Other points on the calibration curve were obtained by successively diluting the standard calcium ion solution with the ammonium chloride/ammonium hydroxide buffer. The logarithm of calcium ion concentration (mg/L) vs the potential (mV) plot showed a linear relation above 3 mg/L hardness. The accuracy of the hardness measurement is reduced at 2 mg/L, but the calcium electrode was still sensitive to the calcium ion concentration.

Titrations

The electrodes were immersed in 50 mL of 80 mg/L calcium hardness solution at 25 C and the meter reading was adjusted to read 63.5 mV, according to the calibration curve. The calcium binding agent solution was added in small increments and the equilibrium-free calcium ion concentrations were measured. At free calcium ion concentra-

TABLE I

Calcium Binding Power of Common Chelating Agents and Polymers[a]

Material[b]	Theoretical CBP[c]	Actual CBP	Log K[e]
EDTA	342	340	7.0
Citric Acid	520	391	4.1
STPP-Na 5	272	269	7.0
CMOS-Na3	240	237	6.8
NTA	523	509	6.1
MAO	861	539	3.7
PAA	695[d]	869/620[d]	5.3

[a]Calcium binding powers (CBP) were determined in NH_4OH/NH_4Cl buffer, pH = 9.7, ionic strength 0.10M. See text for calculation.

[b]See Figure 1.

[c]Calculated from stoichiometry amount.

[d]Data at 1:2 molar ratio.

[e]See text for calculation.

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tions higher than 10 mg/L, the meter reading stabilized rapidly. As the free calcium ion concentration became lower than 10 mg/L, it took a few minutes before the reading became steady. The titration was stopped when the concentration was ca. 1 mg/L. The experimentally determined calcium binding powers for the different chelating and binding agents are given in Table I.

Materials

EDTA and citric acid were reagent grade. All others are commercial grades. Good-rite K-702 poly(acrylic acid) was from the B F Goodrich Company and Belclene 200 maleic acid oligomer from Ciba-Geigy. Total solids (TS, %) were determined by drying a sample at 82 C for 2 hr in vacuum. Acid contents were determined by titration using an automatic titrator (from Brinkmann). Molar quantities and weights indicated in the table and figures are based on dry weights of pure agents.

RESULTS

The chemical structures of some calcium binding agents are shown in Figure 1. It includes organic chelating agents, oligomer, polymers, and inorganic polyphosphate. The effect of the level of calcium binding agents (mmol) on the free calcium ions concentration is shown in Figure 2.

Since the total volume at any particular incremental addition is the same for all titrations, level (mmol) and concentration are closely related. In all cases, the equilibrium calcium ion concentrations decreased rapidly. EDTA, NTA, STPP, and CMOS have the capability of binding nearly all calcium ions at the equivalent point. They are also known as chelating agents. On the other hand, citric acid, poly(acrylic acid), maleic acid oligomer (MAO) bound only 80-90% of calcium ions at the stoichiometric equivalent point.

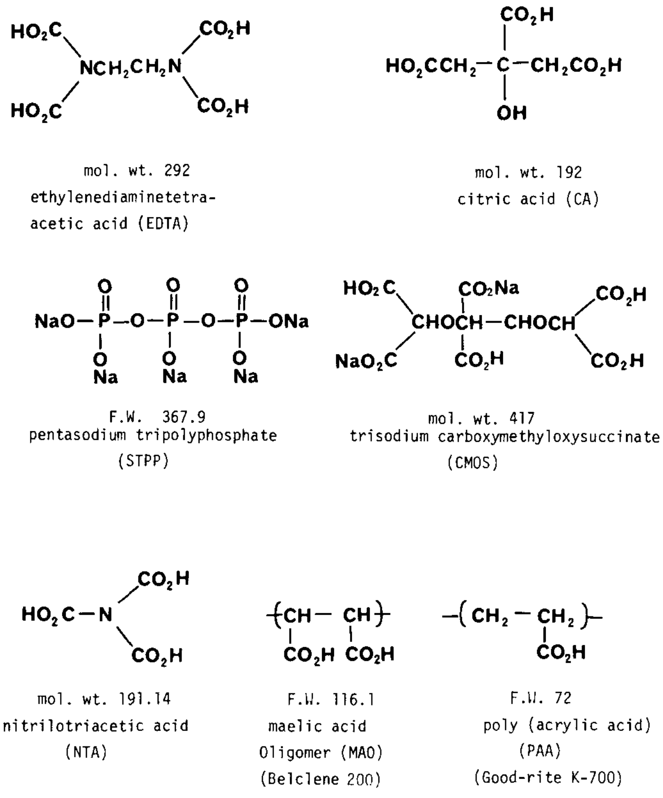


FIG. 1. Chemical structures of calcium binding agents.

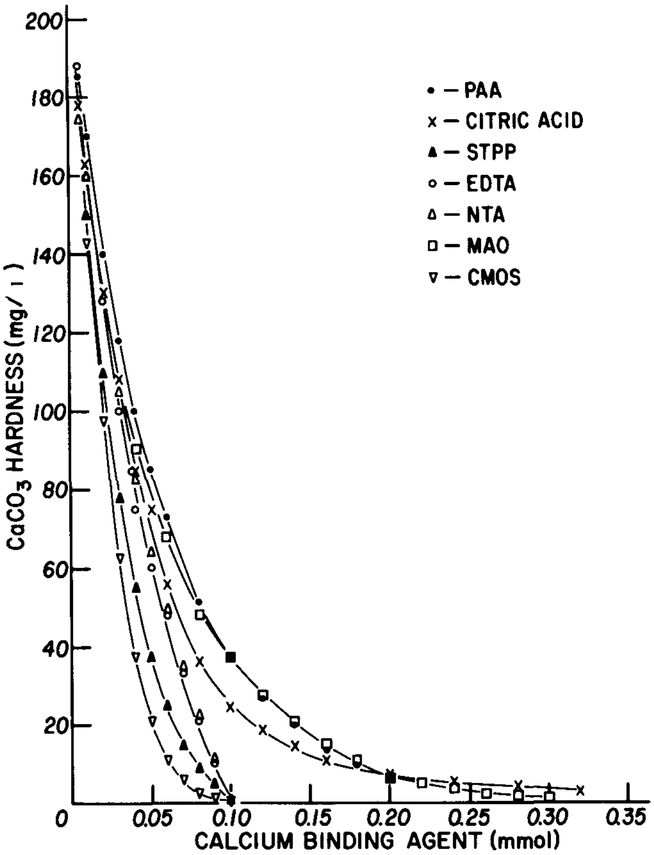


FIG. 2. Titration of calcium ions with calcium binding agents.

DISCUSSION

Calcium Binding Ratio

The amount of bound calcium (mmol) can be calculated by subtracting the free calcium ions from the total (0.10 mmol) as

$$\text{bound Ca (mmol)} = 0.10 - [Ca^{2+}]\ [50 + V] \qquad [1]$$

in which 50 is the total volume (mL) of calcium ion solution before the titration starts and V is the cumulative volume (mL) of calcium binding agent solution added. Figure 3 shows that the bound calcium increased as the calcium binding agents were added. However, the increase was not exactly linear, even for EDTA and NTA which almost followed a 1:1 binding molar ratio straight line. Note that the slopes of these curves at any point are calculated as the molar binding ratio. To study the effect of the total amount of added binding agent on the binding ratio, Figure 3 was rearranged to Figure 4. Ca/A represents the molar binding ratio of calcium ion and binding agents. In the case of polymers or oligomers, formula weights of repeating units (see Figure 1) are used to determine A. For STPP, citric acid, CMOS, maleic acid oligomer and poly(acrylic acid), the binding ratios are a function of the amount added. STPP and CMOS showed a binding ratio higher than 1 at low levels and lower than 1 near the stoichiometric end

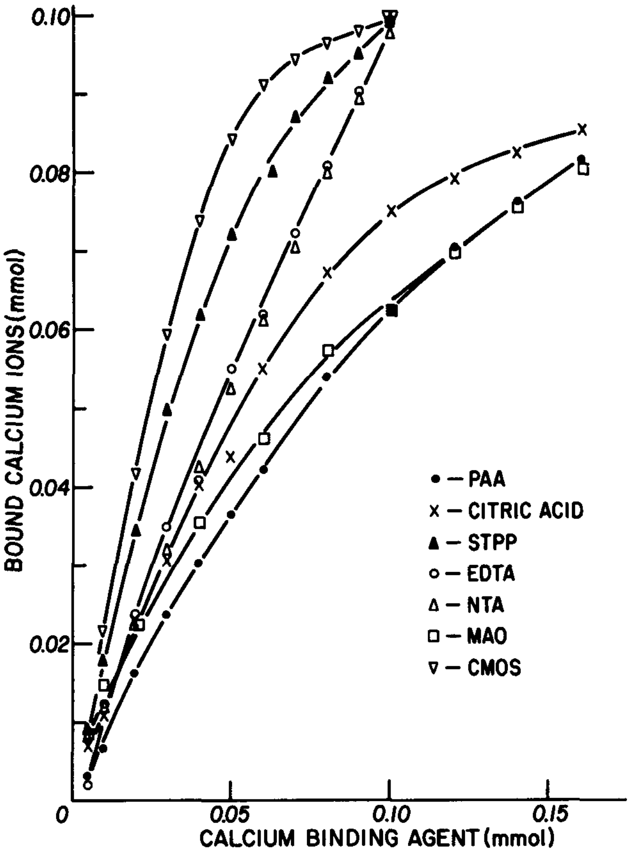


FIG. 3. Binding of calcium ions with calcium ion binding.

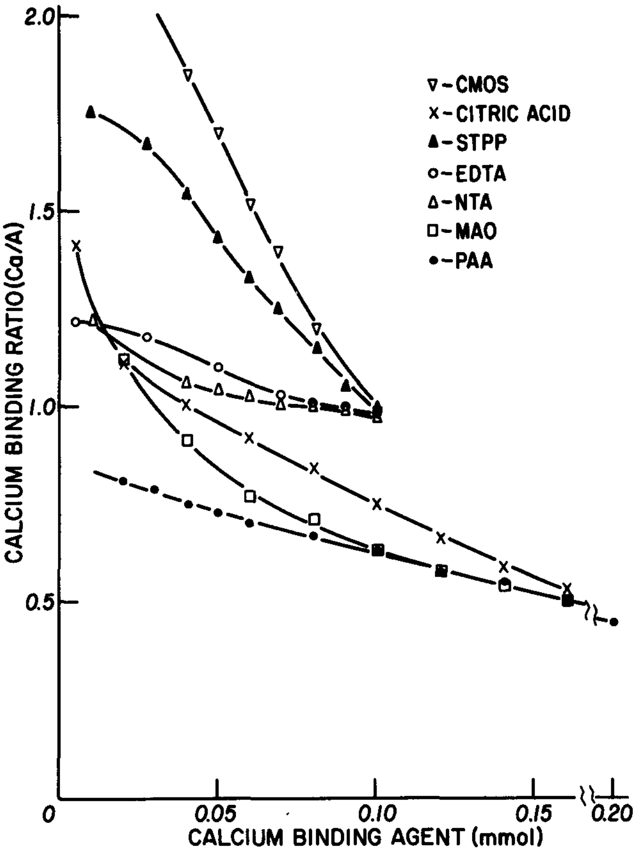


FIG. 4. Effect of calcium ion binding agent level on binding ratio.

point. Citric acid, maleic acid oligomer and PAA always possessed a binding ratio smaller than 1. Even though the binding ratio is ca. 1 for NTA and EDTA, it was still higher than 1.0 at low levels. CMOS, a hexacarboxylic acid formed a 2:1 complex at low levels and the ratio decreased to 1:1 and lower, gradually, with further addition of CMOS. This can be explained by the following equilibria:

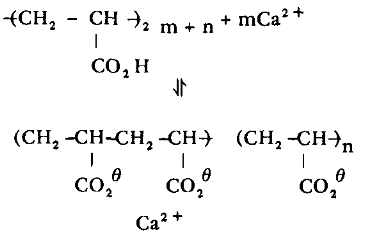
$[R(CO_2)_6\,Ca_2]^{2-}$ $\rightleftharpoons$	$R(CO_2)_6\,Ca]^{4-}$ $\rightleftharpoons$
binding ratio	binding ratio
2 : 1	1 : 1
chelate	chelate

$$R(CO_2)_6^{6-} + Ca^{2+}$$

Similar equilibria were observed in the case of STPP. Citric acid, a hydroxy-tricarboxylic acid formed a 3:2 binding ratio chelate at low levels and the ratio decreased to 1.0 and lower gradually as more citric acid was added. The following equilibria apparently are related.

$ROH(CO_2)_3^{3-}Ca^{2+}$	$[ROH\,(CO_2)_3\,Ca]^{1-}$
citric acid	binding ratio 1:1 complex
	Ca^{2+} $\rightleftharpoons$ citric acid
	$[ROH(CO_2)_3]_2Ca_3$ salt-complex binding ratio 3:2

The binding of calcium ions to poly(acrylic acid) in aqueous solutions is, at least in part, a polyelectrolyte effect (5,6). Simple chelation or salt formation cannot account for the calcium binding quantitatively. The theoretical binding ratio (Ca/A) is 0.5. At low levels, the electrostatic effect predominated and the binding ratio was higher than 0.5. As the PAA levels increased, the binding ratio decreased to 0.5. It can be explained by the following equilibrium:



$$\underset{\displaystyle CO_2H}{-\!(CH_2-\overset{}{CH}\!-\!)_{2\,m+n}} + mCa^{2+} \rightleftharpoons (CH_2\text{-}\underset{CO_2^{\theta}}{CH}\text{-}CH_2\text{-}\underset{CO_2^{\theta}}{CH}\text{-})\;Ca^{2+}\;(CH_2\text{-}\underset{CO_2^{\theta}}{CH}\text{-})_n$$

Poly(acrylic acid) showed an electrostatic effect over a wide range of levels (0 – 0.10 mmol) when the binding ratio is equivalent or above 0.5. The PAA calcium salt may precipitate or remain in suspension such as in the water treatment area where low levels are used. Since the polymer-calcium salt is amorphous, it does not form a crystalline structure and would interfere with the calcium carbonate crystal formation. This may partly explain the inhibition and retardation of scale formation on the heat exchanger surfaces.

The maleic acid oligomer (MAO) formed a salt with calcium at a theoretical binding ratio of 1.0. Figure 4 shows insignificant electrostatic effect except at extremely low concentration. The calcium ion binding behavior is similar to that of citric acid. In fact, the maleic acid oligomer has a degree of polymerization of ca. 10, which may be too low to show a significant electrostatic effect.

Stability Constant

The stability constant or chelation constant of 1 to 1 organic chelate with Ca^{2+} can be written as

$$K = \frac{[CaA^{(n-2)^-}]}{[Ca^{2+}]\,[A^{n-}]} \qquad [2]$$

where A represents the chelating agente and n is the anionic charge on the chelator. The values of log K calculated at the stoichiometric points for the chelators in this study are included in Table I. The stability constant of poly(acrylic acid) is defined herein as

$$K = \frac{[CaA_2]}{[Ca^{2+}]\,[A_2]} \qquad [3]$$

because 2 equivalents of carboxyl group bind one mole of calcium ions. The data in Table I can be divided into two groups: those chelators with log K larger than 6 and smaller than 6. EDTA, STPP, CMOS, and NTA which form chelates with calcium ions belong to the former group. Citric acid MAO and PAA belong to the latter group. The higher the log K, the stronger the binding force for calcium ions.

Rechnitz and Lin (7) reported log K of 5.1 at pH 7.8-8.1, and 6.5 at pH 8.4-8.5 for NTA. The log K for STPP was reported (2) as 6.0, and for citric acid as 4.6 (8). The data in Table I compare favorably to those reported in the literature considering the dependence of log K on temperature, pH and ionic strength.

Calcium Binding Power

Molar quantities have been used in the previous discussion. However, it is very appropriate and practically useful to discuss the results on a weight basis as is common practice in industrial water treatment and detergent applications. Figure 2 is replotted on a weight basis in Figure 5. Although EDTA, STPP, and NTA are excellent chelating agents as discussed before, their efficiencies to reduce calcium hardness on the weight basis are not as good as PAA and MAO. One of the reasons is the low formula weights of PAA and MAO.

Figure 5 also nicely illustrates the practical consequence of the polyelectrolyte effect exhibited by PAA. At low levels, PAA is much more effective than MAO in removing free calcium ions from solution. The difference in formula weight between PAA (72) and MAO (116.1) does not offer a satisfactory explanation. This is because, as shown in Figure 1, MAO has two carboxylic acid groups per repeating unit whereas PAA only has one. This means the effective formula weight of PAA for comparison with MAO is 144, not 72. Therefore, if no other factors are important, MAO should be much more effective than PAA. The fact that it is not, can be attributed to the electrostatic polyelectrolyte effect which enhances the ability of PAA to remove free calcium ions from solution.

Chelation value has been used in industry to describe the calcium binding power (CBP) of organic chelating agents. The "calcium binding power" is used here because it can be applied to both strong and weak chelating calcium binding agents. It is defined as

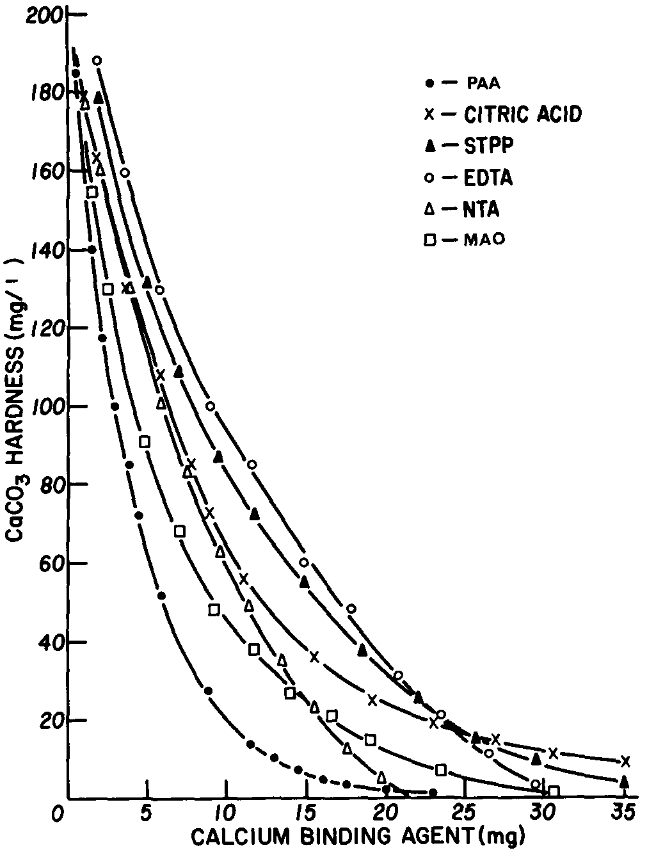


FIG. 5. Binding of calcium ions with calcium binding agents on weight basis.

$$\text{calcium binding power (CBP)} = \frac{\text{bound } CaCO_3 \text{ (mg)}}{\text{total calcium binding agent (g)}} \qquad [4]$$

and equals to the slope of $CaCO_3$ hardness/calcium binding agent plot (Fig. 5) at the equivalent point times one thousand.

It is interesting to compare the experimental and theoretical calcium binding powers at the equivalent point which is defined as

$$\text{theoretical calcium} = \frac{\text{eq wt of } CaCO_3 \text{ (mg)}}{\text{eq wt of CB agent (g)}} \times 1000 \qquad [5]$$

For those having high stability constants, the experimental calcium binding power should approach the theoretical data as shown in Table I. EDTA, STPP, CMOS, and NTA have log K higher than 6 and their experimental and theoretical CBP were almost identical. On the other hand, PAA, MAO, and citric acid have log K lower than 6 and the experimental CBP were much lower than their theoretical values.

We have mentioned that calcium binding power is a function of the amount of calcium binding agent. Experimental CBP at the equivalent point is not a practical method of comparing calcium binding agents because they are rarely used in stoichiometric amounts in industrial practice. Instead, the experimental CBP at a particular concentration or a CBP-concentration profile should be used to compare commercial calcium binding agents.

Although PAA and MAO have low stability constants, their CBP are the highest over a broad concentration range partly because of the low formula weight. PAA is even much better than MAO because of the electrostatic effect possessed by polyelectrolytes.

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