Calcium and Magnesium Sequestration by Sodium and Potassium Polyphosphates

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Abstract

The sequestration of calcium by polyphosphates in the presence of oxalate as a precipitating agent is reported at 25 and 60C in the pH range of 5–12. Sequestration increased with temperature. The sensitivity of sequestration to pH changes decreased with increase in the chain length of the polyphosphates.

Magnesium sequestration by polyphosphates in the presence of sodium oleate is given at pH values of 10.5 and 9.0.

In dilute solution with pH values higher than 9.5, tripolyphosphate and pyrophosphate were found to be the most effective calcium and magnesium polyphosphate sequestrants on a weight basis, respectively.

The results are discussed from a semi-theoretical viewpoint.

Introduction

EVEN THOUGH sodium and potassium polyphosphates have been used for many years as detergent builders and water softeners, their relative effectiveness in sequestering calcium and magnesium has not been rigorously established. Thus, in the early 1940's, German investigators disagreed among themselves on the relative effectiveness and temperature coefficient of calcium sequestration by sodium tripolyphosphate and sodium hexametaphosphate (1–5). This is probably due in part to differences in composition of the phosphates they used.

Later, Hafford et al. (6) measured calcium sequestration using the calcium oxalate precipitation endpoint, but no extensive study was made regarding the equilibrium status of the system and the nature of the precipitate. The depression of soap foam in the presence of hard water has been utilized also (7) in a limited pH range to measure the concentration of free calcium ion in the presence of sequestering agents. Bobtelsky and Kertes (8) titrated metal ions directly with the phosphates and in the absence of other precipitating anions.

Sequestration is a phenomenon in which the precipitation of a metal cation by a precipitating anion is prohibited by the formation of a soluble cation-sequestering anion complex. Since this is a competition-type reaction for the metal cation between the sequestrant and the precipitating anion, reported data are critically dependent upon several variables. These variables are 1) attainment of equilibrium, 2) specific metal cation and its concentration, 3) specific sequestering anion and its concentration, 4) specific precipitating anion and its concentration, 5) presence of other metal ions, 6) total ionic strength, 7) pH of solution, and 8) temperature. A review of metal complexing by phosphates up to 1958 has been published (9).

The thermodynamics of association of calcium and magnesium by the polyphosphates has been established by the authors and reported in the Journal of Physical Chemistry. However, those data were obtained in the absence of alkali metal ions because of the tendency of the latter cations to form complexes of their own with the phosphates (9). The data reported in this article represent the more practical phase of the work, namely, in the presence of sodium, potassium, or ammonium ions.

Experimental Procedure

Materials. Since commercial polyphosphates differ in composition, purified and well-defined materials were used in this study. The sodium orthophosphate was Baker reagent grade. Mallinckrodt grade tetrasodium pyrophosphate decahydrate was used. The commercial tetrapotassium pyrophosphate sample analyzed to be better than 99.5% $K_4P_2O_7$.

Sodium tripolyphosphate hexahydrate was used as the source of $Na_5P_3O_{10}$. It was prepared by four repeated fractional crystallizations of commercial tripolyphosphate from aqueous solutions of ethyl alcohol. The phosphorus analyzed to better than 99.7% $Na_5P_3O_{10}$ (10).

The three anhydrous long chain sodium polyphosphates that were investigated were randomly reorganized products having Na_2O/P_2O_5 ratios of 1.34, 1.15, and 1.033. These ratios (11) as well as end-groups titration (12) established these polyphosphates to have average chain lengths of 6, 14, and 60 phosphorus atoms per molecule.

Other chemicals were C. P. grade.

Nephelometric Titrations. The semi-automatic nephelometer, previously described (13), was used. However, temperature was controlled during titrations to ± 0.1C using a heater in combination with a heat-sensing Thermatrol unit, manufactured by Hallikainen Instruments, Berkeley, Calif. The pH was continuously controlled to within ± 0.02 units from the desired value by the addition of 2M NaOH. A block diagram of the apparatus is shown in Figure 1.

Procedure. Aliquot volumes of the polyphosphate stock solution and the precipitating anion solution (sodium oxalate or sodium laurate) were pipetted into a 400 cc beaker. Aqueous NaOH and distilled water were added to give a total volume of 250 cc, having a desired pH value.

The beaker containing the solution was placed in the nephelometer and allowed to reach temperature equilibrium. Either 0.1M calcium or magnesium nitrate was then added to an unstirred solution automatically and periodically in cycles. In the other portion of the cycle the solution was stirred. The volume of titrant required to reach the point of incipient precipitation of calcium oxalate or magnesium laurate was determined as previously described (13).

Results and Discussion

Equilibration. A serious problem in nephelometric titrations is the attainment of equilibrium, whereby the endpoint is independent of time, mode of addition of the components, or their relative concentration. Thus, some workers (14,15) have reported sequestration values that were different by factors as high as ten, depending upon the time of equilibration.
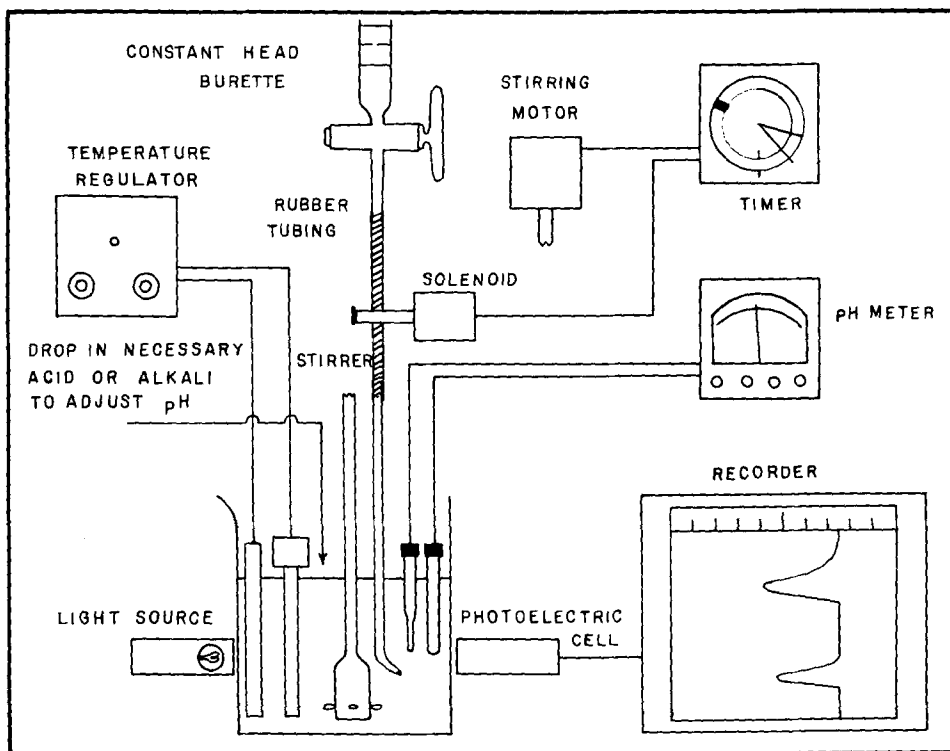
FIG. 1. Block diagram of semi-automatic nephelometer.

In the present procedure, calcium or magnesium were periodically and automatically added to give a high localized concentration in the unstirred solution that contained the precipitating anion, followed by agitation. Thus, equilibrium was attained from the precipitate end and supersaturation is very unlikely. Moreover, since the precipitates were very fresh, their rate of dissolution in the presence of an excess complexing agent was fast.

To further prove equilibration, the precipitate end-point was approached many times from both ends. First, 6 to 7 solutions with controlled pH values hav-

ing various amounts of calcium, but the same amount of polyphosphate and precipitating anion were prepared and stirred with a magnetic stirrer for 10 days. In this time period no significant hydrolytic regradation is expected. The point of incipient precipitation was determined from light intensity measurements. Many solutions, originally clear due to supersaturation, became turbid with time. In a second procedure, excess calcium was added to form a precipitate. Various amounts of the same sodium polyphosphate were then added, and the solutions stirred for a week. The endpoint was again noted from light intensity meas-
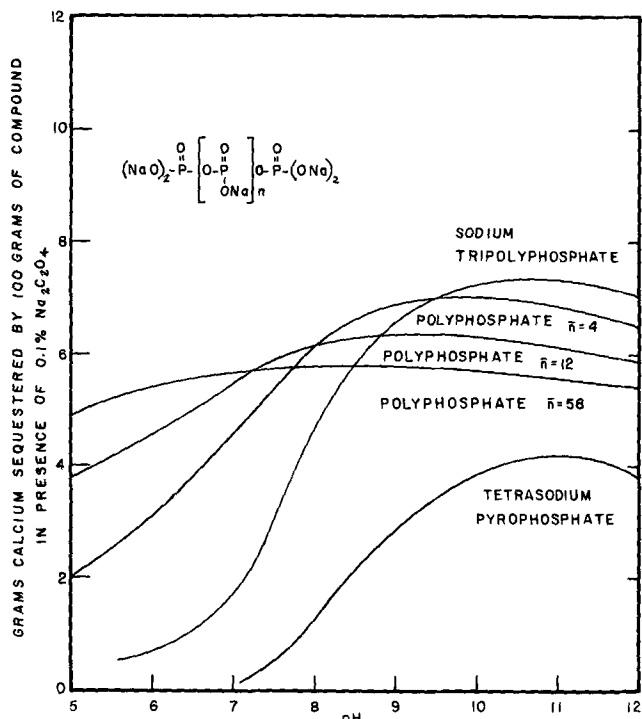

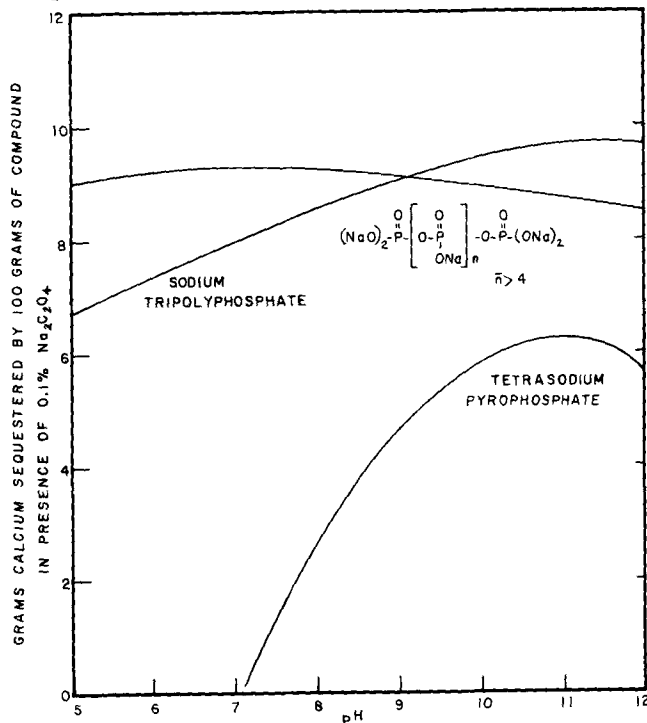FIG. 2. Sequestration of calcium by sodium polyphosphates at 25C.

FIG. 3. Sequestration of calcium by sodium polyphosphates at 60C.

urements. In both procedures the results agreed within experimental error ($\pm$ 0.2 cc) with those from the rapid (10 min) semi-automatic titration method.

Under the conditions of the present experiments, the precipitates were proven to be either calcium oxalate monohydrate or magnesium laurate from X-ray diffraction measurements and wet chemical analyses. Less than 1% P_2O_5 was detected in the unwashed precipitates, and this amount is probably due to sorption.

Calcium Sequestration. Figures 2 and 3 show the number of g of calcium, G, sequestered by 100 g of sodium polyphosphate in the presence of 0.1% sodium oxalate as a function of pH and phosphate chain length at 25 and 60C, respectively. These values were calculated as follows

$$G = \frac{1.6 \times M \times y}{X}$$

where M is the molarity of the calcium solution being added, y the number of cc of the calcium sodution that had to be added to reach the point of incipient precipitation, and X is the weight % concentration of the phosphate in the 250 ml solution being titrated. It was found that if M and X were independently varied, y would come out to give a constant value for the product My/X, and hence a constant G value. This again indicates proper equilibration. Nevertheless, in the bulk of the experiments, M was 0.1 molar and X, 0.1%. When X was zero, the value of G was found to be zero, due to the immediate precipitation of calcium oxalate.

The data for higher concentrations of precipitating agent were similar to those at the lower concentration, except that the values of G were all lower due to the increased tendency for precipitate formation. The reason for presenting sequestration data in the presence of 0.1% $Na_2C_2O_4$ is that the solubility product of CaC_2O_4 is intermediate between that of calcium carbonate and the more insoluble calcium soaps. The interaction of calcium with surfactants, e.g., dodecylbenzene sulfonate, is weaker than that with the polyphosphates (13), so that in a solution containing all three ions, the calcium is preferentially held by the polyphosphates.

The higher sequestration values at 60C as compared with 25C can be explained as follows. The thermodynamic stabilities of the calcium polyphosphate complexes have been shown (13) to be independent of temperature, whereas the solubility of calcium oxalate increases with temperature. In general, the solubility of other precipitates, such as the calcium soaps (16), increases with temperature. Therefore, there is effectively less resistance for the polyphosphates to dissolve calcium precipitates at higher temperature. This is not true with sequestering agents that form so-called chelates, which are complicated structural complexes. For example, the stability of the calcium ethylenediamine tetraacetate complex decreases with temperature (17), and consequently its sequestration efficiency drops with temperature rise. And indeed, at a pH of 10 in the presence of 0.1% $Na_2C_2O_4$, 100 g of tetrasodium ethylenediamine tetraacetate sequester 9.90 and 9.65 g of calcium at 25 and 60C, respectively.

Normally, the sequestration of metal ions drops with decrease in pH due to the competition for the sequestering anion by the hydrogen ion. For the family of the polyphosphates, Figures 2 and 3 show that the sensitivity of sequestration to changes in pH decreases with increase in the chain length of the polyphosphate. This is not unexpected, because down to a pH value of 4–5 only the end phosphorus atoms in a phosphate chain become hydrogen bound (18). And as the length of the polyphosphate chain increases, per cent of end phosphorus atoms decreases.

Although the alkali metal ions are known (9) to form weak complexes of their own with the polyphosphates, the sequestration capacity on a weight basis for tetrasodium, tetrapotassium, and triammonium pyrophosphate were found to be inversely proportional to their molecular weight. Thus, $K_4P_2O_7$ was found to sequester 81% as much calcium as $Na_4P_2O_7$ at all pH values. This is because the stabilities of the various complexes of alkali metals with polyphosphates are not too different.

The sodium phosphates are shown to slightly decrease in their ability to sequester calcium as the pH is increased above 10.5. This is because the stability of the calcium polyphosphate complexes is affected more with increase in ionic strength than does the solubility of calcium oxalate.

Sequestration of calcium by mixtures of phosphates has been shown to be additive (13). Therefore, if a commercial sodium tripolyphosphate contains n% tetrasodium pyrophosphate, its sequestration capacity can be easily calculated at any pH value from the data presented here.

Since orthophosphate in alkaline solutions is a calcium precipitating agent, its sequestration value by definition is zero. Yet in water treatment the precipitation of calcium orthophosphate is occasionally used to release a desirable anion which on its own forms a more soluble calcium precipitate than calcium orthophosphate.

Magnesium Sequestration. Table I is a tabulation of the number of grams of magnesium sequestered by 100 g of polyphosphate at a pH of 10.5 and 9.0 in the presence of 0.004% sodium oleate. Sodium oxalate could not be used as a precipitating agent due to the relatively high solubility of MgC_2O_4.

The stabilities of magnesium complexes with the polyphosphates are comparable (19) to those of the calcium polyphosphates and they are also temperature independent (20). Therefore, magnesium sequestration by polyphosphates is also expected to increase with increase in temperature. However, since magnesium precipitates are usually more soluble than the corresponding calcium precipitates (21), the numerical value of the weight of magnesium sequestered per unit weight of polyphosphates comes out to be larger than that with calcium. If calcium and magnesium precipitates having equal solubility products are utilized in a sequestration study, the numerical values

TABLE I
Magnesium Complexing by Polyphosphates at 25C

Material [a]	g Magnesium sequestered by 100 g of material in the presence of 0.004% sodium oleate	
	pH = 10.5	pH = 9.0
$Na_4P_2O_7$	8.4	6.5
$Na_5P_3O_{10}$	6.2	6.0
$(NaO)_2\text{-}P(\!=\!O)\text{-}O\text{-}[\text{-}P(\!=\!O)(ONa)\text{-}O\text{-}]_n\text{-}P(\!=\!O)\text{-}(ONa)_2$		
$\bar{n} = 4$	5.2	5.5
$\bar{n} = 12$	5.0	5.2
$\bar{n} = 58$	5.7	....

[a] $\bar{n}$ is the average of all the n values that exist in the random mixture (11).

for the seqeustration of either metal ion would not turn out to be much different.

In contrast with results on calcium sequestration, tetrasodium pyrophosphate on a weight basis is found to be the most effective magnesium sequestrant among the polyphosphates. This can be explained from the fact that the thermodynamic stabilities of magnesium pyrophosphates and tripolyphosphates are not much different (19,20). Yet, the molecular weight of $Na_4P_2O_7$ is smaller than $Na_5P_3O_{10}$, so that on a weight basis it turns out to be a better magnesium sequestrant.

In most hard waters a mixture of calcium and magnesium is normally encountered. Although in mixtures calcium precipitates come out first because of their lower solubility, the magnesium ions consume polyphosphates in forming complexes. Therefore, it is not unrealistic to express total hardness as calcium. In practice, more sequestrant is usually required to dissolve a calcium precipitate than its magnesium analogue.

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[Received September 28, 1961]

Thermal Oxidation of Synthetic Triglycerides.

II. Analysis of the Volatile Condensable and Noncondensable Phases[1,2]

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Tripalmitin, 1-lauryl dipalmitin, 2-lauryl dipalmitin, 1-oleyl dipalmitin and 2-oleyl dipalmitin were subjected to thermal oxidation at 200 C in the presence of air. The volatile condensable products of oxidation collected after 3 and 24 hours were analyzed for carbonyl and carboxyl compounds. The volatile non-condensable products were quantitatively examined for carbon monoxide, carbon dioxide, and hydrogen. The results indicated that long chain carbonyls were formed in the initial stages of oxidation. When the oxidation was allowed to proceed for 24 hours, saturated aldehydes from C_1 to C_{16}, methyl ketones, and other ketones were found in the volatile oxidation products. A variety of fatty acids from C_4 to C_{16} were identified in the volatile fatty acids. The presence of dicarboxylic acids indicated that oxygen attacked the double bond of oleic acid in 1-oleyl dipalmitin. Possible mechanisms for the formation of the decomposition products were discussed.

THERMAL OXIDATION of a fat is known to produce a variety of decomposition products. A study of the types of carbonyl compounds and the fatty acids produced is of great importance in elucidation of the type of reactions taking place in a fat during thermal oxidation. The volatile condensable and noncondensable products in the thermal oxidation of synthetic triglycerides at 200C in the presence of air were therefore collected and characterized in order to gain a better insight into the mechanism of oxidation.

Experimental Procedure and Data

Tripalmitin, 1- and 2-lauryl dipalmitin, and 1- and 2-oleyl dipalmitin were thermally oxidized at 200C

in the presence of air. The synthetic triglycerides as well as the method of oxidation have been described in a preceding paper (1). The triglycerides were oxidized for periods of 3, 8, 15, and 24 hr. The condensable and noncondensable volatile products were collected for periods of 0–3, 3–8, 8–15, 15–24, and 0–24 hr. Upon completion of the reaction period, the absorption traps were detached and closed. The method for collection of volatile noncondensable products namely carbon monoxide, carbon dioxide. and hydrogen and their quantitative determination has been described in a previous paper (1). The volatile noncondensable decomposition products, namely carbon monoxide, carbon dioxide, and hydrogen, were calculated on a molar basis, and the amounts of carbon monoxide and hydrogen were calculated as equivalent to the carbon dioxide and water collected in the absorption tubes.

The cold traps containing the condensable products were removed from the −75C bath, the contents immediately taken up in carbonyl-free methanol, and the short connecting tube between the cold traps and the reaction flask rinsed with two 5 ml portions of carbonyl-free methanol. The condensate and washings were transferred to a 50 ml volumetric flask and made up to volume with carbonyl-free methanol; aliquots of this solution were used for further analysis.

Thirty ml of the methanolic solution which contained the condensable phase was neutralized with 0.1 N NaOH to the phenolphthalein end point, and extracted with three 20 ml. portions of ethyl ether. The ether extracts were combined and divided into two equal portions. Twenty ml of 2,4-dinitrophenyl-hydrazine reagent prepared in carbonyl-free methanol was added to one portion of the ether solution. The ether was allowed to evaporate slowly and the volume