# *Stability of Condensed Phosphate Complexes. I. Alkaline-earth Metal Complexes*

By Akira ROPPONGI and Takio KATO

(Received August 23, 1961)

It has been reported that a mixture of soap and a condensed phosphate such as hexametaphosphate is more effective than soap alone for removing radioactive contaminations on surfaces of concrete, glass, various metals and films(1). It has been further found that EDTA and condensed phosphate are more useful as complexing agents than surface active agents for cleaning cotton goods contaminated with radioactive nuclides(2).

Condensed phosphate has been used as a boiler cleaner. In this case, the addition is very minute compared with the amount necessary to keep metallic ions as soluble complexes in hard water. Thus, the condensed phosphate is thought to have two different functions: complex formation and surface activity.

Many investigators have measured the ability of condensed phosphates to make complex formations by using various methods, but the metal elements used were limited to alkali and alkaline-earth metals. Furthermore, the stability constants measured by different methods do not agree with each other(3).

In order to obtain fundamental information about the washing ability of condensed phosphates, as well as about their usefulness as decontaminating agents, the stability constants of the complexes formed between condensed phosphates and metals were measured in this experiment.

## Theoretical

The stabilty constants were measured either by acid-base titration using a glass electrode or by the replacement reaction. Schwarzenbach et al.(4) and Watters et al.(5-6) have evaluated the stability constants of magnesium and calcium complexes with triphosphoric acid by method A.

**Method A.** — If triphosphoric acid in the presence of a relatively large excess of metal ions can be titrated without precipitation, the decrease in pH should be attributed to the complex formation, as is expressed by the reaction:

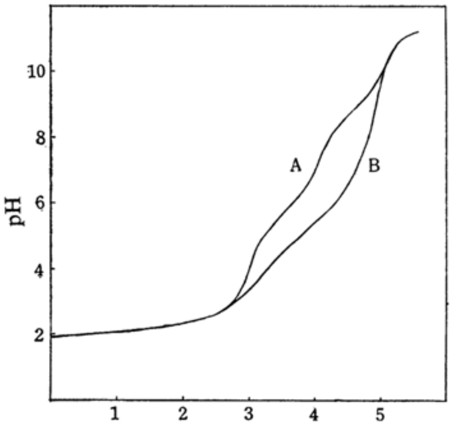

Fig. 1. The effects of metal ion on titration curve of triphosphoric acid with alkali solution.
Curve A: $10^{-3}$ M triphosphoric acid titrated with 0.1 M KOH solution, Curve B: $10^{-3}$ M triphosphoric acid containing $10^{-3}$ M alkaline-earth metal ion titrated with 0.1 M KOH solution.

---

1) F. D. Snell et al., *Soap sanit. Chemicals*, **1**, Oct. (1953).

2) Y. Tajima and Y. Wadachi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 891 (1960).

3) J. R. Van Wazer et al., *Chem Revs.*, **58**, 1011 (1958).

4) G. Schwarzenbach et al., *Helv. Chim. Acta*, **38**, 653 (1955).

5) J. I. Watters et al., *J. Am. Chem. Soc.*, **79**, 5606 (1957).

6) J. I. Watters et al., ibid., **81**, 3201 (1959).

$$mM^{+p}+l(H_{n+1}P_3O_{10})^{-(5-n-1)} \rightleftarrows M_m(H_nP_3O_{10})_l{}^{-((5-n)l-pm)} + lH^+ \qquad (1)$$

As the metal ions are present in a large excess and as no pH change is observed in the region $a<3$ in Fig. 1, it is probable that only a 1 to 1 complex exists in the corresponding region, $a>3$. In such a case, the stability constants of the normal complex, $K_{ML}$, and the acidic complex, $K_{MHL}$, can be evaluated by Eqs. 2 and 3:

$$K_4{}'=K_4+K_{MHL}K_4[M] \qquad (2)$$

$$K_5{}'=\frac{K_5+K_{ML}K_6[M]}{1+K_{MHL}[M]} \qquad (3)$$

where [M] is the free metal ion concentration, $K_n$ is the dissociation constant of triphosphoric acid, and $K_n{}'$ is the apparent dissociation constant defined by Eq. 4 or 5.

$$K_4{}'=\frac{(H)\{[MHP_3O_{10}]+[HP_3O_{10}]\}}{[H_2P_3O_{10}]} \qquad (4)$$

$$K_5{}'=\frac{H\{[MP_3O_{10}]+[P_3O_{10}]\}}{\{[MHP_3O_{10}]+[HP_3O_{10}]\}} \qquad (5)$$

As the metal ion is present in a large excess, the free metal ion concentration can be considered to be equal to the total metal concentration. The apparent dissociation constants can be evaluated by Eq. 6 in a way similar to that used for acid-base titration. When the acid is not too dilute, $pK_{5-n}{}'$ has the same value as the pH at the point where $a$ is $5-(n+0.5)$.

$$K_{5-n}{}'=\frac{(H)\left[(5-n-a)\cdot C_L-\dfrac{K_W}{(H)\cdot f}+\dfrac{(H)}{f}\right]}{\left[(a-4+n)\cdot C_L+\dfrac{K_W}{(H)\cdot f}-\dfrac{(H)}{f}\right]} \qquad (6)$$

**Method B.**—In Schwarzenbach's method, the constants are evaluated only in a system in which no precipitate is formed and in which metal ions can exist in a large excess compared with triphosphate ions. In the system of triphosphate and alkaline-earth metal, a precipitate is formed unless the system is kept under such conditions that triphosphate ions are present in an excess over the metal ions. Thus, the number of ligands bound with metal ions will increase to 1, 2,……, $n$, and the complexes of $M(HP_3O_{10})_n$ and $M(P_3O_{10})_m$ may coexist. In the investigation of polyamino complexes, Schwarzenbach[7] proposed general formulae to evaluate stability constants for the case where the ligand is the only one in the presence of an excess of amines.

The present authors tried to evaluate the stability constants of triphosphate complexes formed in a system in which triphosphate is present in an excess as compared with metal ions.

In the $a>3$ region, the total triphosphate concentration is expressed as

$$C_L=[H_2L]+[HL]+[L]+\sum n[M(HL)_n] + \sum m[ML\,m] \qquad (7)$$

where L represents the $P_3O_{10}$ ion. The concentration of replaceable hydrogen is given by

$$C_H=2[H_2L]+[HL]+[H]+\sum n[M(HL)_n] \qquad (8)$$

Subtracting Eq. 7 from 8 gives

$$C_H-C_L=[H_2L]+[H]-[L]-\sum m[ML\,m] \qquad (9)$$

If $C_L$ is greater than $C_M$ and $[H_2L]-[L]$ is much greater than $\sum m[ML\,m]$, we obtain the following approximate expression:

$$C_H-C_L=[H_2L]+[H]-[L] \qquad (10)$$

The mean ligand number per metal ion, $\bar{n}$, is expressed by Eq. 11, obtained by combining Eq. 10 with $\alpha$ defined by Eq. 12:

$$\bar{n}=\frac{[MHL]+2[M(HL)_2]+\cdots\cdots+[ML]+2[ML_2]+\cdots}{[M]+[MHL]+[M(HL)_2]+\cdots\cdots+[ML]+[ML_2]+\cdots} =\frac{C_L-\dfrac{C_H-C_L-[H]}{\alpha}}{C_M} \qquad (11)$$

$$\alpha=\frac{[H_2L]-[L]}{[H_2L]+[HL]+[L]} \qquad (12)$$

$\bar{n}$ is also expressed in the following way by using successive stability constants:

$$\bar{n}=\frac{k_1\cdot[HL]+2\cdot k_1\cdot k_2\cdot[HL]^2+\cdots+k_1{}'\cdot[L]+2\cdot k_1{}'\cdot k_2{}'\cdot[L]^2+\cdots}{1+k_1\cdot[HL]+k_1\cdot k_2\cdot[HL]^2+\cdots+k_1{}'\cdot[L]+k_1{}'\cdot k_2{}'\cdot[L]+\cdots} \qquad (13)$$

where $k_n{}'$ and $k_n$ are the $n$-th successive stability constants of the normal and the acidic complexes respectively. The spreading factors of $k_n$ and $k_n{}'$ being different, Bjerrum's successive approximation method can not be applied. Thus the authors employed the following method. In the $\bar{n}<1$ region, $\bar{n}$ is expressed by

$$\bar{n}=\frac{k_1\cdot[HL]+k_1{}'\cdot[L]}{1+k_1\cdot[HL]+k_1{}'\cdot[L]} \qquad (14)$$

As both [HL] and [L] are known, $k_1$ and $k_1{}'$ are calculated at the same time. In the $1<\bar{n}<2$ region, $\bar{n}$ is expressed by

$$\bar{n}=\frac{k_1\cdot[HL]+2\cdot k_1\cdot k_2\cdot[HL]^2+k_1{}'\cdot[L]+2\cdot k_1{}'\cdot k_2{}'\cdot[L]}{1+k_1\cdot[HL]+k_1\cdot k_2\cdot[HL]^2+k_1{}'\cdot[L]+k_1{}'\cdot k_2{}'\cdot[L]} \qquad (15)$$

---

[7] G. Schwarzenbach et al., *Helv. Chim. Acta*, 33, 985 (1950).

Using the values of $k_1$ and $k_1'$ calculated from Eq. 14, $k_2$ and $k_2'$ can also be evaluated. Repeating the above calculation allows the determination of $k_n$ and $k_n'$.

**Method C.**—In method B, the existence of ML is neglected in the calculation of $\bar{n}$. Therefore, the error become naturally greater with the increasing ML concentration. In the present calculation, $\bar{n}$ was found in the following manner.

In the $a>3$ region, if the complexes are formed according to reaction 16, the difference in the amounts of alkali required for the titrations of the triphosphate solution and of the solution containing metal ions and triphosphate ions is equal to the amount of triphosphate combined with the metal.

$$\begin{aligned} \mathrm{M}+n\mathrm{H_2L} &\rightleftarrows \mathrm{M(HL)}n+n\mathrm{H} \\ \mathrm{M}+m\mathrm{HL} &\rightleftarrows \mathrm{ML}m+m\mathrm{H} \end{aligned} \qquad (16)$$

$\bar{n}$ is then expressed as

$$\bar{n}=\frac{C_{\mathrm{L}}\cdot \varDelta a}{C_{\mathrm{M}}} \qquad (17)$$

where $\varDelta a$ is the difference in the amounts ot alkali explained above. Furthermore, $k_n$ and $k_n'$ are calculated in a way similar to method B.

The dissociation of the acidic complexes may be considered as

$$\mathrm{M(HL)}_n \rightleftarrows \mathrm{M(HL)}_p\mathrm{L}_q+q\mathrm{H} \qquad (18)$$

where $p$, $q>0$ and $p+q=n$.

In such a case, $\bar{n}$ will become greater than the true value, and mixed complexes are formed. If the formation of such mixed complexes is considered, it is not so easy to evaluate the stability constants of the acidic, normal and mixed complexes.

**Method D.**—*Replacement Reaction Method.*—The equilibrium constant between two kinds of ligands and a metal is given by Eq. 19:

$$K=\frac{[\mathrm{ML_2}]\cdot[\mathrm{L_1}]}{[\mathrm{L_2}]\cdot[\mathrm{ML_1}]} \qquad (19)$$

The constant is further expressed as the ratio of the stability constant of each complex.

$$K=\frac{K_2}{K_1} \qquad (20)$$

In the case where one ligand is a dye such as a metal indicator and the other is condensed phosphate, the concentration of ligands and complexes can be measured spectrophotometrically; therefore, $K$ can be calculated. From $K$ and the stability constant of the dye complex, the stability constant of the condensed phosphate complex is evaluated.

## Experimental

Recrystallization of commercial anhydrous sodium triphosphate, Nippori, with ethanol was carried out three times according to the procedure described by Quimby[8]. The purified triphosphate, when tested by the X-ray diffraction method, showed only patterns of sodium triphosphate hexahydrate.

Trimetaphosphate was prepared from monosodium di-hydrogen orthophosphate by heating it for 5 hr. at 530°C[9] and recrystallizing it three times with ethanol. The dehydrated salt showed the X-ray patterns of anhydrous trimetaphosphate.

Tetrametaphosphate was prepared as follows[10]. Diphosphorous pentoxide, 100 g., was dissolved in 600 ml. of water at 15°C, and the solution was neutralized with sodium hydroxide. After ethanol was added to 50 $^{\mathrm{V}}/_{\mathrm{O}}$, the precipitated salt was filtered and redissolved in water. Repeating these procedures three times yielded crystalline tetrametaphosphate tetrahydrate, whose X-ray diffraction patterns showed no evidence of the existence of any other substances except tetrametaphosphate tetrahydrate.

EBT and Phthalein Complexon, obtained from the Dozin Yakukagaku Research Institute, were used as metal indicators for the replacement reaction.

A solution of triphosphoric acid was prepared by passing a solution of sodium triphosphate through an ion exchange column filled with an Amberlite IR-120 H-form. To avoid the effect of the complex formation of alkali metal with triphosphate, Watters used tetramethyl ammonium hydroxide and chloride. The stability constants obtained by Schwarzenbach in the titration of the triphosphate complex with potassium hydroxide in the presence of potassium chloride were not greatly different from Watters' values. Therefore, 20 ml. of the eluate from the column was mixed with 10 ml. of the metal standard solution and 3.3 ml. of 1 M potassium chloride solution, and the solution was finally titrated with a standard potassium hydroxide solution. The pH measurements were made by using a Hitachi EHP-1 pH meter with a glass electrode. The concentration of triphosphoric acid was determined by tiration prior to the experiment. Solutions of magnesium and calcium were prepared by dissolving magnesium bicarbonate and calcium carbonate in hydrochloric acid and by removing the free acid respectively. Solutions of strontium and barium were further prepared by dissolving their chloride salts in distilled water.

Replacement reactions were performed as follows. The dissociation constant of EBT was evaluated from the change in the absorbance of the EBT solution with a pH value at the maximum absorption in the visible range of the spectrum; the molar extinction coefficient was also evaluated from the change in concentration. The stability constants of phosphate complexes were found from the equilibrium constants and the stability constants

---

8) O. T. Quimby, *J. Phys. Chem.*, **58**, 603 (1954).

9) L. F. Audrieth, " Inorganic Syntheses ", Vol. 3, (1950), p. 104.

10) R. N. Bell et al., *Ind. Eng. Chem.*, **44**, 568 (1952).

of the dye complexes. On calcium, strontium and barium, the measurements of the constants were performed in replacement reactions of phosphate with Phthalein Complexon in a way similar to that used for the EBT-magnesium system, since the stability of EBT complexes with the metals is too low and the complexes are not formed in a concentration suitable for the replacement reaction. The measurements were performed at an ionic strength of 0.1 with a buffer solution consisting of ammonium hydroxide and chloride.

## Results

Though the results obtained by Watters show that the $M_2L$-type complex is present in the system of triphosphate and magnesium, the following experimental results make it seem probable that the main species of soluble complexes is a 1 to 1 complex. That is, the relations of the pH value and the volume of the 0.01 M sodium triphosphate solution which was added to 10 ml. of 0.01 M alkaline-earth metal solution are as shown in Fig. 2. As can be seen in Fig. 2, the precipitated salt is normal salt ($P_3O_{10}/M=2/5$), and it redissolves in the form of a 1 to 1 complex in a higher region of the ratio of L/M than 2/5.

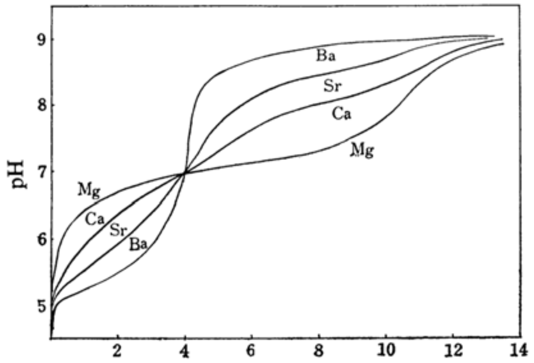

Fig. 2. The titration curves of 10 ml. of 0.01 M alkaline-earth metal solutions with 0.01 M sodium triphosphate solution.

The stability constants calculated by method A, as given in Table I, are found at various

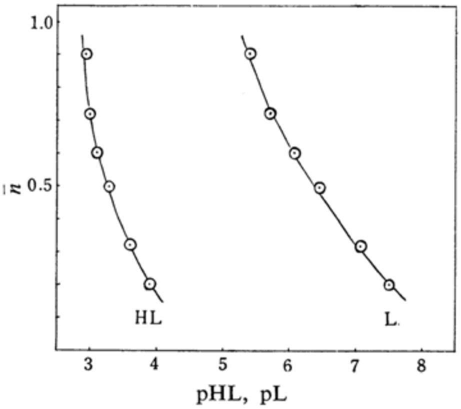

Fig. 3. Correlation of $\bar{n}$ with pHL and pL for Mg.

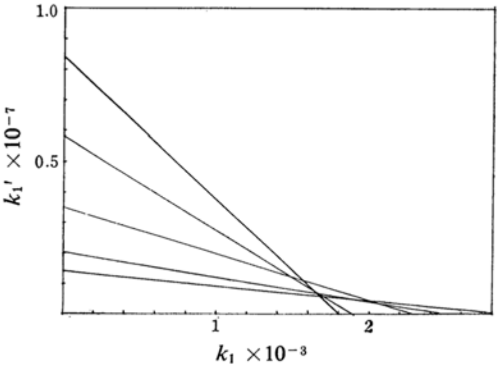

Fig. 4. Graphical solution of $k_1$ and $k_1'$ for Mg.

TABLE I. STABILITY CONSTANTS CALCULATED BY METHOD A

| | $C_L\times10^3$ M | $C_M\times10^3$ M | log $K_{MHL}$ | $C_L\times10^3$ M | $C_M\times10^3$ M | log $K_{ML}$ |
|---|---|---|---|---|---|---|
| Mg | 4.53 | 2.78 | 3.23 | 4.34 | 2.66 | 4.83 |
| | | 5.55 | 3.37 | | 5.32 | 5.36 |
| | | 11.1 | 3.33 | | 10.6 | 5.36 |
| | | 22.2 | 3.23 | | 21.6 | 5.80 |
| | 3.78 | 64.7 | 3.00 | 3.62 | 62.0 | 5.92 |
| Ca | 4.53 | 1.29 | 2.74 | 4.34 | 1.24 | 3.55 |
| | | 2.59 | 2.91 | | 2.48 | 4.18 |
| | | 3.89 | 2.97 | | 3.72 | 4.47 |
| Sr | 4.03 | 0.35 | 2.18 | 3.88 | 0.34 | 3.02 |
| | | 0.58 | 2.33 | | 0.57 | 3.09 |
| | | 1.16 | 2.45 | | 1.12 | 3.19 |
| | | 1.74 | 2.53 | | 1.67 | 3.51 |
| | | 2.32 | 2.57 | | 2.23 | 3.63 |
| Ba | 4.51 | 0.42 | 2.47 | 4.32 | 0.40 | 2.85 |
| | | 0.70 | 2.47 | | 0.67 | 2.98 |
| | | 1.41 | 2·59 | | | |

metal concentrations at which no precipitation occurs. The results on magnesium obtained by method B are plotted in Fig. 3, in which the relation between $\bar{n}$, pHL and pL is illustratrated. In the range where $\bar{n}$ is less than unity, both $k_1$ and $k_1'$ are found graphically from the intersection of the lines corresponding to Eq. 21, as is seen in Fig. 4.

$$\left.\begin{aligned}0.191&=0.809\times 1.28\times 10^{-4}\times k_1\\&\quad+0.809\times 2.81\times 10^{-8}\times k_1'\\0.319&=0.681\times 2.48\times 10^{-4}\times k_1\\&\quad+0.681\times 7.86\times 10^{-8}\times k_1'\\0.517&=0.483\times 4.59\times 10^{-4}\times k_1\\&\quad+0.483\times 2.96\times 10^{-7}\times k_1'\\0.601&=0.399\times 7.28\times 10^{-4}\times k_1\\&\quad+0.399\times 8.37\times 10^{-7}\times k_1'\\0.731&=0.269\times 9.91\times 10^{-4}\times k_1\\&\quad+0.269\times 1.76\times 10^{-6}\times k_1'\end{aligned}\right\}\qquad(21)$$

The mean values of $k_1$ and $k_1'$ are 3.24 and 5.69 respectively.

The results obtained by method C with magnesium, calcium, strontium and barium are plotted in Fig. 5. In the region where $\bar{n}$ is below unity, the $k_1$ and $k_1'$ of magnesium are evaluated as mentioned above; their logarithms were found to be 3.63 and 5.41 respectively. In the case of calcium, strontium and barium, $k_1'$ in Eq. 14 becomes zero, indicating that the concentration of ML is negligible compared with that of MHL.

TABLE II. STABILITY CONSTANTS OF ACIDIC COMPLEXES CALCULATED BY METHOD C

| | Mg | Ca | Sr | Ba |
|---|---|---|---|---|
| $\log k_1$ | 3.63 | 3.29 | 2.95 | 2.69 |
| $\log k_1'$ | 5.41 | | | |

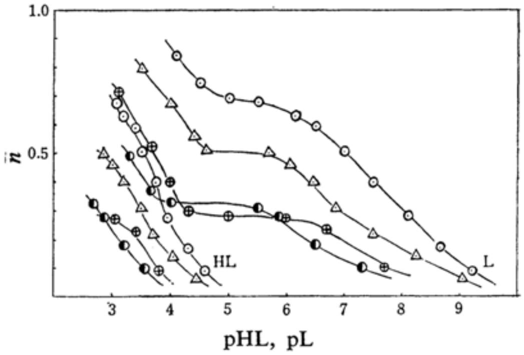

Fig. 5. Correlation of $\bar{n}$ with pHL and pL.
⊙ : Mg, △ : Ca, ⊕ : Sr, ◐ : Ba

Therefore, in the region where $\bar{n}$ is below unity, Eq. 22 gives the relation between $\bar{n}$, $k_1$ and HL. The values of $k_1$ are listed in Table II.

$$\bar{n}=\frac{k_1\cdot[\mathrm{HL}]}{1+k_1\cdot[\mathrm{HL}]}\qquad(22)$$

As ring phosphoric acids are comparatively strong acids, the stability constants of the complexes between alkaline-earth metals and ring phosphoric acids cannot be evaluated by the usual titration method. In place of the titration method, the replacement reaction was utilized in the present experiments. The stability constants of magnesium complexes of ring phosphate and triphosphate are given in Table III.

The dissociation constants of phthalein complexon ($H_6F$) and the stability constants of the dye complexes with calcium and barium were reported by Schwarzenbach[11]. According to his data, the ratio of the concentration of CaF and CaHF is 0.01 at pH 9. At this pH,

TABLE III. STABILITY CONSTANTS OF RING PHOSPHATES AND TRIPHOSPHATE COMPLEXES WITH MAGNESIUM

| | pH | $C_{L1}\times 10^5$ M | $C_M\times 10^5$ M | $C_{L2}\times 10^3$ M | $\log K_{ML}$ |
|---|---|---|---|---|---|
| Trimetaphosphate | 9.31 | 2.28 | 1.16 | 2.30 | 2.84 |
| | 9.31 | 2.28 | 1.56 | 2.30 | 2.73 |
| | 9.31 | 2.28 | 1.94 | 2.30 | 2.64 |
| | | | | | 2.74 |
| | pH | $C_{L1}\times 10^5$ M | $C_M\times 10^5$ M | $C_{L2}\times 10^5$ M | $\log K_{ML}$ |
| Tetrametaphosphate | 9.29 | 2.27 | 1.16 | 1.87 | 4.57 |
| | 9.28 | 2.27 | 1.56 | 2.80 | 4.51 |
| | 9.27 | 2.27 | 1.94 | 3.74 | 4.41 |
| | | | | | 4.51 |
| | pH | $C_{L1}\times 10^5$ M | $C_M\times 10^5$ M | $C_{L2}\times 10^5$ M | $\log K_{ML}$ |
| Triphosphate | 9.32 | 1.60 | 1.56 | 1.06 | 5.69 |
| | 9.28 | 2.00 | 1.56 | 1.06 | 5.95 |
| | 9.27 | 2.40 | 1.56 | 1.06 | 6.12 |
| | | | | | 5.92 |

$L_1$ : EBT, $L_2$ : Phosphate

---

[11] G. Schwarzenbach et al., *Helv. Chim. Acta*, **37**, 113 (1954).

only the acidic complex can exist. As both the complexes and HF exhibit the maximum absorption at the same wavelength, 570 m$\mu$, the concentration of MHF was determined after correction for the absorption due to HF. The stability constants thus obtained are listed in Table IV.

TABLE IV. STABLITY CONSTANTS OF RING PHOSPHATES AND TRIPHOSPHATE COMPLEXES OBTAINED BY METHOD D

| | log $K_{ML}$ | | |
|---|---|---|---|
| | Ca | Sr | Ba |
| Trimetaphosphate | 1.68 | 0.62 | 0.08 |
| Tetrametaphosphate | 3.77 | 1.46 | 1.00 |
| Triphosphate | 4.59 | | |

## Discussion

Because of the formation of precipitate at high pH values, the stability constants of triphosphate complexes cannot be evaluated by method A. The logarithmic values of the stability constants reported by Schwarzenbach and his coworkers are 3.7 and 3.1 respectively for magnesium and calcium acidic complexes MHL, and 5.80 and 4.85 for magnesium and calcium complexes ML. The values obtained by Watters are 3.34 and 3.01 respectively for magnesium and calcium acidic complexes, and 5.83 and 5.44 for magnesium and calcium complexes at an ionic strength of 0.1. With calcium, however, titration cannot be continued up to the alkaline region without causing precipitation. Therefore, the values for calcium complexes reported by them do not seem reasonable. However, if the stability of the complex is low, the amount of metal present in the form of the complex is negligible compared with the total concentration of metal ion, even if the latter is smaller than the concentration of acid.

In method B, the error becomes greater with the increasing concentration of ML, as can be seen from Eq. 9. In method C, the value of $\bar{n}$ becomes greater with the increasing dissociation of MHL as acid, as is evident from Eq. 18.

Our values found by methods B and C indicate that the dissociation of MHL is not very great; therefore, the assumption involved in the above methods is considered to be quite reasonable. The values obtained by the replacement reactions are consistent with the results found by using methods B and C. Further, the values evaluated at the largest metal concentration in the measurements by method A are nearly equal to those evaluated by the other methods, and the values summarized in Table V seem to be near to the true values.

Figure 6 shows the relation of the stability constants of the complexes to the ratio of the square of the charge of metal ions to the

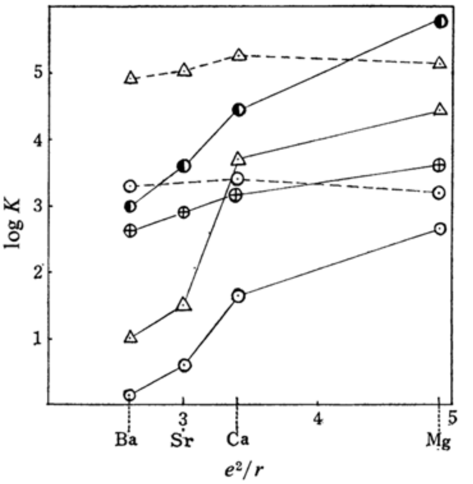

Fig. 6. Correlation of stability constants of condensed phosphate complexes of alkaline-earth metals with $e^2/r$ of metals.

⊙ : Trimetaphosphate
△ : Tetrametaphosphate
◐ : Triphosphate (ML)
⊕ : Triphosphate (MHL)
—— : Measured values
- - - : Reported values by Monk et al.

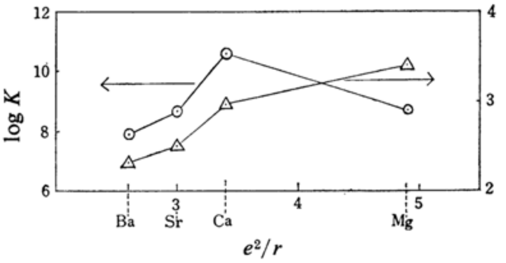

Fig. 7. Correlation of stability constants of alkaline-earth metal complex of EDTA or oxalic acid with $e^2/r$ of metals.
⊙ : EDTA, △ : Oxalic acid

TABLE V. STABILITY CONSTANTS OF ALKALINE-EARTH METALS WITH TRIPHOSPHATE AND RING PHOSPHATES

| | log $K_{ML}$ | log $K_{MHL}$ | log $K_{ML}$ | log $K_{MHL}$ | log $K_{ML}$ | log $K_{MHL}$ | log $K_{ML}$ | log $K_{MHL}$ | Method |
|---|---|---|---|---|---|---|---|---|---|
| Trimetaphosphate | 2.74 | | 1.68 | | 0.62 | | 0.08 | | D |
| Tetrametraphosphate | 4.52 | | 3.77 | | 1.46 | | 1.00 | | D |
| Triphosphate | 5.8 | 3.6 | 4.6 | 3.3 | 3.6 | 3.0 | 3.0 | 2.7 | A,B,C,D |

ionic radius. The stability of principally ionic complexes of alkali and alkaline-earth metals is affected by both the charge and the ionic radius of the metal ions. Figure 7 shows the relation between $\log K$ and $e^2/r$ for the series of alkaline-earth metal complexes. The two different trends are also observed with other ligands(12). One group of ligands exhibits a maximum stability with calcium, while the stability of complexes with the other group of ligands increases monotonously from barium to magnesium. Ligands belonging to the former group possess a greater number of functional groups and form a greater number of chelate rings (e. g., EDTA) than do those belonging to the latter group.

As the stability of the condensed phosphate complexes increases monotonously from barium to magnesium, they do not seem to form complicated rings.

In Fig. 6, the values measured by electroconductivity and solubility methods by Monk et al.(13) are also included. The curves show a maximum at calcium, but there are no significant differences between the metals. Our data are different from theirs, and the values of Monk have already been criticized as too great by Gross(14).

It is already known that the complexes with ring phosphate are less stable than the chain phosphate complexes. This difference is attributed to the steric hindrance, which acts against the formation of chlelate rings, and to the stronger acidity of ring phosphate than chain phosphate. The results obtained by us also show that ring phosphate complexes are less stable than chain phosphates.

*Department of Applied Chemistry*
*Faculty of Engineering*
*Tohoku University*
*Sakurakoji, Sendai*

---

12) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall Inc., Englewood Cliffs, New York (1952), p. 160.

13) C. B. Monk et al., *J. Chem. Soc.*, **1949**, 413.

14) R. J. Gross et al., *J. Am. Chem. Soc.*, **77**, 3695 (1955).