Stability of Condensed Phosphate Complexes. II. Rare-earth Metal Complexes

By Akira ROPPONGI and Takio KATO

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Condensed chain phosphate has become an important commercial product since it has been known that its chemical properties, based on complex formation and surface activity, are useful in many fields of chemical industry.

Its ability of complex formation has been investigated by various methods, but the metal elements studied have been limited to alkali and alkaline-earth metals because of the precipitate formation of heavy metals with condensed chain phosphates over a wide range of pH values.

In order to investigate fundamentally the washing ability of chain phosphate, the present authors evaluated the stability constants of soluble complexes with various metals. As has been reported previously[1], triphosphate forms a precipitate in the presence of an excess of alkaline-earth metal ions except when magnesium is over the phosphate. On rare-earth metals, too, precipitate formation is observed in the presence of excess metal ions[2,3].

Therefore, the authors evaluated the stability constants of triphosphate complexes with the rare-earth metals by a new method to be described in the later part of this paper.

The ratio of triphosphate to metal in the complex was estimated by the following experiment: the change in the pH value of 10 ml. of a 0.01 M metal solution due to the addition of a triphosphate solution was measured by a glass electrode pH meter; the relation of the pH value to the ratio of the phosphate concentration to the metal concentration for several rare-earth metals is shown in Fig. 1. The abrupt change in pH value at the point where C_L/C_M is 3/5 means that the precipitate is normal salt and begins to dissolve as the concentration ratio of the phosphate to the metal becomes greater. The pH value of the solution increases again at the point where

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[1] A. Roppongi and T. Kato, This Bulletin, 35, 1086 (1962).

[2] E. Giesbecht et al., *J. Inorg. Nuclear Chem.*, 6, 308 (1958).

[3] E. Giesbecht, ibid., 15, 265 (1960).

C_L/C_M is 2/1; this means that the greatest number of the phosphates bound with the metal is equal to 2. Between 3/5 and 2/1 of C_L/C_M, 1 to 1 and 2 to 1 complexes may form successively; therefore, the precipitate dissolves in the presence of an excess of triphosphate.

Theoretical

A solution containing triphosphoric acid and rare-earth metal corresponding to one-fourth of the triphosphate concentration can be titrated with an alkaline hydroxide solution without precipitation up to an alkaline region; the pH value of the solution is lower than that of the solution which contains triphosphate only at a certain value in the region between 5 and 3 of a, which is the molar ratio of the added alkali per triphosphate. The decrease in pH value may be attributed to the complex formation of triphosphate with metal.

It is assumed that the species of complexes are only acidic, MHL and $M(HL)_2$, in the low pH region.

The equilibrium constants which are expressed by Eqs. 1 and 2:

$$k_1=\frac{[MHL]\cdot[H]}{[M]\cdot[H_2L]} \tag{1}$$

$$k_2=\frac{[M(HL)_2]\cdot[H]^2}{[M]\cdot[H_2L]^2} \tag{2}$$

are related to known values, that is, the total concentrations of the phosphate, and the metal, the dissociation constants of triphosphoric acid and the hydrogen ion concentration as follows:

The total concentration of triphosphate, C_L, and the replaceable hydrogen ion concentration, C_H, are:

$$C_L=[H_3L]+[H_2L]+[HL]+[MHL]+2[M(HL)_2] \tag{3}$$

$$C_H=3[H_3L]+2[H_2L]+[HL]+[H]+[MHL]+2[M(HL)_2] \tag{4}$$

and C_L is four times as large as the total metal ion concentration, C_M. The free phosphate ion concentration is expressed by

$$[H_3L]+[H_2L]+[HL]=\frac{C_H-C_L-[H]}{\frac{2[H]}{K_3}+1}\times\left(\frac{[H]}{K_3}+1+\frac{K_4}{[H]}\right) \tag{5}$$

where K_3 and K_4 are the third and the fourth dissociation constants of triphosphoric acid. The concentration of triphosphate combined with metal is

$$[MHL]+2[M(HL)_2]=[MHL]\times\left(1+\frac{2k_2}{k_1}\cdot\frac{\frac{C_H-C_L-[H]}{\frac{2[H]}{K_3}+1}}{[H]}\right) \tag{6}$$

Therefore, the concentration of MHL is

$$[MHL]=\frac{C_L-\frac{C_H-C_L-[H]}{\frac{2[H]}{K_3}+1}\cdot\left(\frac{[H]}{K_3}+1+\frac{K_4}{[H]}\right)}{1+\frac{2k_2}{k_1}\cdot\frac{\frac{C_H-C_L-[H]}{\frac{2[H]}{K_3}+1}}{[H]}} \tag{7}$$

By combining the condition that C_L is equal to $4\times C_M$ with Eqs. 5—7, the free metal concentration may be expressed by Eq. 8:

$$[M]=\frac{1}{4}\left[\left\{\frac{2(C_H-C_L-[H])}{\frac{2[H]}{K_3}+1}\times\left(\frac{[H]}{K_3}+1+\frac{K_4}{[H]}\right)-C_L\right\}-2\left\{\frac{C_L-\frac{C_H-C_L-[H]}{\frac{2[H]}{K_3}+1}\cdot\left(\frac{[H]}{K_3}+1+\frac{K_4}{[H]}\right)}{\frac{2k_2}{k_1}\cdot\frac{(C_H-C_L-[H])}{\frac{2[H]}{K_3}+1}\cdot[H]}\right\}\right] \tag{8}$$

By substituting Eqs. 5—8 into Eq. 1, Eq. 9 is obtained; it is then transformed into Eq. 10, in which k_1 is the tangent of the straight line and k_2 is the intercept in the y-axis.

$$k_1=\frac{C_L-\frac{C_H-C_L-[H]}{\frac{2[H]}{K_3}+1}\cdot\left(\frac{[H]}{K_3}+1+\frac{K_4}{[H]}\right)}{1+\frac{2k_2}{k_1}\cdot\frac{(C_H-C_L-[H])}{\frac{2[H]}{K_3}+1}\cdot[H]}\cdot[H]\Bigg/\frac{1}{4}\left[\left\{\frac{2(C_H-C_L-[H])}{\frac{2[H]}{K_3}+1}\cdot\left(\frac{[H]}{K_3}+1+\frac{K_4}{[H]}\right)-C_L\right\}-2\left\{\frac{C_L-\frac{C_H-C_L-[H]}{\frac{2[H]}{K_3}+1}\cdot\left(\frac{[H]}{K_3}+1+\frac{K_4}{[H]}\right)}{1+\frac{2k_2}{k_1}\cdot\frac{(C_H-C_L-[H])}{\frac{2[H]}{K_3}+1}\cdot[H]}\right\}\right]\times\frac{C_H-C_L-[H]}{\frac{2[H]}{K_3}+1} \tag{9}$$

$$k_1\cdot\frac{A}{B}\cdot D+k_2=\frac{C}{B}\cdot D^2 \tag{10}$$

where

$$A=1-\frac{3}{4}\cdot\frac{C_L}{\dfrac{C_H-C_L-[H]}{\dfrac{2[H]}{K_3}+1}\cdot\left(\dfrac{[H]}{K_3}+1+\dfrac{K_4}{[H]}\right)}$$

$$B=1-\frac{1}{2}\cdot\frac{C_L}{\dfrac{C_H-C_L-[H]}{\dfrac{2[H]}{K_3}+1}\cdot\left(\dfrac{[H]}{K_3}+1+\dfrac{K_4}{[H]}\right)}$$

$$C=\frac{C_L}{\dfrac{C_H-C_L-[H]}{\dfrac{2[H]}{K_3}+1}\cdot\left(\dfrac{[H]}{K_3}+1+\dfrac{K_4}{[H]}\right)}-1$$

$$D=\frac{[H]}{\dfrac{C_H-C_L-[H]}{\dfrac{2[H]}{K_3}+1}}$$

Both k_1 and k_2 can be evaluated graphically from the plot of $(A/B)\cdot D$ against $(C/B)\cdot D^2$. The stability constants are calculated from the equilibrium constants and the dissociation constants of triphosphoric acid. With an increase in the pH value of the solution, normal complexes such as ML and ML_2 may coexist, and the plot for Eq. 10 will deviate from a linear relation. In such a region, the stability constants of ML and ML_2 are obtained as follows by using the stability constants of the acidic complexes calculated above.

The constants are calculated on the assumption that the concentration of MHL is much greater than that of ML, since the main species of normal complexes is ML_2, as is seen in Fig. 1.

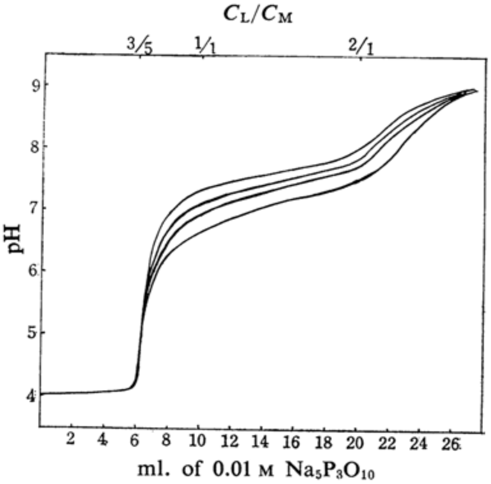

Fig. 1. The titration curves of 10 ml. of 0.01 M rare-earth metal solutions with 0.01 M sodium triphosphate ($Na_5P_3O_{10}$) solution.

Based on this assumption, the free metal ion concentration is derived from Eq. 11, where $K_1{}^*$ is the stability constant of MHL.

$$\begin{aligned}&4[M]+4[MHL]+4[ML]+4[M(HL)_2]\\&\quad+4[ML_2]=[H_2L]+[HL]+[L]+[MHL]\\&\quad+[ML]+2[M(HL)_2]+2[ML_2]\end{aligned}\tag{11}$$

$$[M]=\frac{[H_2L]+[HL]+[L]-\dfrac{C_L}{2}}{K_1{}^*\cdot[HL]+2}\tag{12}$$

The total phosphate concentration, C_L, and the replaceable hydrogen concentration, C_H, are expressed as:

$$\begin{aligned}C_L=&[H_2L]+[HL]+[L]+[MHL]+[ML]\\&+2[M(HL)_2]+2[ML_2]\end{aligned}\tag{13}$$

$$\begin{aligned}C_H=&2[H_2L]+[HL]+[H]+[MHL]\\&+2[M(HL)_2]\end{aligned}\tag{14}$$

Combining Eqs. 12 and 14, Eq. 15, containing the stability constants of the acidic complexes, $K_1{}^*$ and $K_2{}^*$, is induced.

$$\begin{aligned}C_H-[H]=&\left(\frac{2[H]^2}{K_4\cdot K_5}+\frac{[H]}{K_5}\right)\cdot[L]\\&+\frac{\left(\dfrac{[H]^2}{K_4\cdot K_5}+\dfrac{[H]}{K_5}+1\right)[L]-\dfrac{C_L}{2}}{K_1{}^*\cdot\dfrac{[H]}{K_5}\cdot[L]+2}\\&\times\left(K_1{}^*\cdot\frac{[H]}{K_5}\cdot[L]+2K_2{}^*\cdot\left(\frac{[H]}{K_5}\right)^2\cdot[L]^2\right)\end{aligned}\tag{15}$$

Equation 15 is then transformed to Eq. 16, which is the third order equation of [L] and can be solved graphically at a certain pH value.

$$\begin{aligned}&2K_2{}^*\cdot\left(\frac{[H]}{K_5}\right)^2\cdot\left(\frac{[H]^2}{K_4\cdot K_5}+\frac{[H]}{K_5}+1\right)\cdot[L]^3\\&+\left\{K_1{}^*\cdot\frac{[H]}{K_5}\cdot\left(\frac{3[H]^2}{K_4\cdot K_5}+\frac{2[H]}{K_5}+1\right)-K_2{}^*\cdot C_L\right.\\&\left.\times\left(\frac{[H]}{K_5}\right)^2\right\}\cdot[L]^2+\left\{2\left(\frac{2[H]^2}{K_4\cdot K_5}+\frac{[H]}{K_5}\right)\right.\\&\left.-K_1{}^*\cdot\frac{[H]}{K_5}\cdot\left(\frac{C_L}{2}+C_H-[H]\right)\right\}\cdot[L]\\&-2(C_H-[H])=0\end{aligned}\tag{16}$$

Without neglecting the existence of ML, the concentration of ML_2 is expressed as:

$$[ML_2]=\frac{C_L-C_H+2[H]+[H_2L]-[L]}{\dfrac{K_1{}'}{K_2{}'}\cdot\dfrac{1}{[L]}+2}\tag{17}$$

and the concentration of M is:

$$[M]=\frac{[H_2L]+[HL]+[L]-\dfrac{C_L}{2}}{2+K_1{}^*\cdot[HL]+K_1{}'\cdot[L]}\tag{18}$$

where

$$K_1'=\frac{[\mathrm{ML}]}{[\mathrm{M}]\cdot[\mathrm{L}]} \tag{19}$$

$$K_2'=\frac{[\mathrm{ML_2}]}{[\mathrm{M}]\cdot[\mathrm{L}]^2} \tag{20}$$

Substituting Eqs. 17 and 18 into Eq. 20, K_2' is expressed as:

$$K_2'=\frac{\dfrac{C_\mathrm{L}-C_\mathrm{H}+2[\mathrm{H}]+[\mathrm{H_2L}]-[\mathrm{L}]}{\dfrac{K_1'}{K_2'}\cdot\dfrac{1}{[\mathrm{L}]}+2}}{\left(\dfrac{[\mathrm{H_2L}]+[\mathrm{HL}]+[\mathrm{L}]-\dfrac{C_\mathrm{L}}{2}}{2+K_1^*\cdot[\mathrm{HL}]+K_1'\cdot[\mathrm{L}]}\right)\cdot[\mathrm{L}]^2} \tag{21}$$

Equation 21 is transformed into the first order equation for K_1' and K_2', and the constants are evaluated by the plot of variables possible to be calculated from the concentration of L obtained graphically and the pH value measured.

$$\frac{2K_5+K_1^*\cdot[\mathrm{L}]\cdot[\mathrm{H}]}{K_5\cdot[\mathrm{L}]}\times\frac{C_\mathrm{L}-C_\mathrm{H}+[\mathrm{H}]+\left(\dfrac{[\mathrm{H}]^2}{K_4\cdot K_5}-1\right)\cdot[\mathrm{L}]}{C_\mathrm{H}-\dfrac{3}{2}C_\mathrm{L}-[\mathrm{H}]+\left(\dfrac{[\mathrm{H}]}{K_5}+2\right)\cdot[\mathrm{L}]}=K_1'+2K_2'\cdot[\mathrm{L}]\cdot\frac{\left(\dfrac{[\mathrm{H}]^2}{K_4\cdot K_5}+\dfrac{[\mathrm{H}]}{K_5}+1\right)\cdot[\mathrm{L}]-\dfrac{C_\mathrm{L}}{2}}{C_\mathrm{H}-\dfrac{3}{2}C_\mathrm{L}-[\mathrm{H}]+\left(\dfrac{[\mathrm{H}]}{K_5}+2\right)\cdot[\mathrm{L}]} \tag{22}$$

If this assumption is reasonable, the plots should be on a linear line. In a high pH value region, complexes containing a hydroxyl group may be formed, and the difference in pH value for different rare-earth metals decreases. Therefore, it is reasonable that the estimation of the stability constants in the lower pH value region is better.

Experimental

In the case where the triphosphate concentration was twice as much as that of metal, a precipitate was slightly formed in the range of low pH values, approximately in the vicinity of 4. Thus the experiment were performed when the triphosphate concentration was four times the metal concentration.

Rare-earth metal solutions were prepared by dissolving 99.9% oxide in hydrochloric acid and removing the free acid completely by evaporation; the concentration was thus finally kept to 0.005 M.

A solution of 0.02 M sodium triphosphate was prepared by dissolving the recrystallized salt in distilled water; it contained 0.2 M of sodium perchlorate.

After mixing 10 ml. of a metal solution with a sodium triphosphate solution, the resulting solution was titrated with a 0.05 M perchloric acid solution containing 0.1 M sodium perchlorate.

The pH value was measured by a Hitachi pH meter EHP-1 type with a 0.02 unit.

Results and Discussion

The values of the variables in Eq. 10 were calculated by using the dissociation constants of triphosphoric acid, and the hydrogen ion concentration was obtained by dividing the pH values by Kieland's activity coefficient at the ionic strength, $\mu=0.1$.

The dissociation constants are $10^{-2.15}$, $10^{-6.00}$ and $10^{-8.73}$ for K_3, K_4 and K_5 respectively.

The values of the variables in Eq. 10 for lanthanum are shown in Table I, while the values calculated for various rare-earth metals are plotted in Fig. 2. The stability constants for MHL and $\mathrm{M(HL)_2}$ obtained from the lines in Fig. 2 are tabulated in Table II. In order to evaluate the stability constants of normal complexes, the values of [L] at various pH values were obtained from Eq. 16 by using the stability constants of acidic complexes obtained above. By substituting the values of [L] into Eq. 22, the variables were calculated. The values for lanthanum are tabulated in Table III. Further, the values of the left term and the right term in Eq. 22 for various rare-earth metals are plotted in Fig. 3. From the inclination and the intercept of the straight lines giving the relation between K_1' and K_2' for the rare-earth metals, the stability constants of ML and $\mathrm{ML_2}$ were obtained; these results are shown in Table IV.

In Fig. 2, the deviation from linearity in variables of a smaller value may be attributed to the formation of the normal complexes. As the calculated values have a linear relation MHL and $\mathrm{M(HL)_2}$ coexist, and neither ML nor

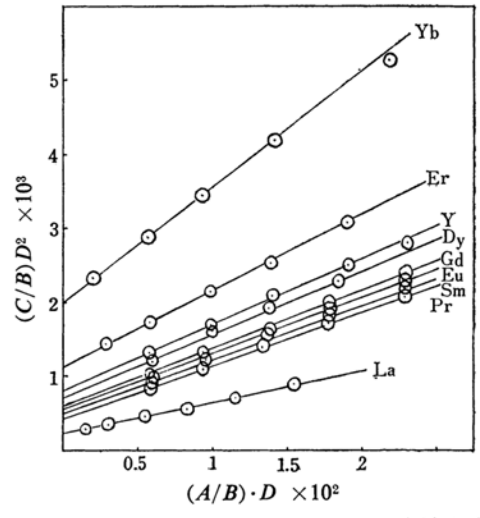

Fig. 2. The relations between $(A/B)\cdot D$ and $(C/B)\cdot D^2$ in Eq. 10 for rare-earth metals.

TABLE I. THE VALUES OF THE VARIABLES IN EQ. 10 FOR LANTHANUM

pH	$HClO_4$, ml.	$C_L\times10^3$ M	$C_H\times10^3$ M	$(A/B)\cdot D$	$(C/B)\cdot D^2$
3.41	6.70	7.49	14.9	2.57×10^{-2}	1.45×10^{-3}
3.49	6.60	7.52	14.8	2.02×10^{-2}	1.14×10^{-3}
3.58	6.50	7.55	14.6	1.54×10^{-2}	8.62×10^{-4}
3.66	6.40	7.58	14.4	1.16×10^{-2}	7.17×10^{-4}
3.75	6.30	7.61	14.3	8.31×10^{-3}	5.70×10^{-4}
3.85	6.20	7.63	14.1	5.48×10^{-3}	4.31×10^{-4}

TABLE II. THE STABILITY CONSTANTS OF THE ACIDIC COMPLEXES WITH RARE-EARTH METALS

	La	Pr	Sm	Eu	Gd	Dy	Er	Yb	Y
$\log K_{MHL}$	4.63	4.86	4.89	4.90	4.91	4.94	5.00	5.20	4.97
$\log K_{M(HL)_2}$	8.32	8.64	8.66	8.68	8.72	8.84	9.05	9.29	8.87

TABLE III. THE VALUES OF THE VARIABLES IN EQ. 22 FOR LANTHANUM

pH	$HClO_4$, ml.	$C_L\times10^3$ M	$C_M\times10^3$ M	[L]	Values of left term	Values of right term
4.41	5.70	7.78	13.2	6.40×10^{-9}	9.51×10^{7}	1.37×10^{-8}
4.50	5.60	7.81	13.0	9.54×10^{-9}	1.86×10^{8}	2.25×10^{-8}
4.58	5.50	7.84	12.8	1.36×10^{-8}	2.68×10^{8}	3.66×10^{-8}
4.66	5.40	7.87	12.7	1.95×10^{-8}	5.73×10^{8}	8.57×10^{-8}

TABLE IV. THE STABILITY CONSTANTS OF THE NORMAL COMPLEXES WITH RARE-EARTH METALS

	La	Pr	Sm	Eu	Gd	Dy	Er	Yb	Y
$\log K_{ML_2}$	15.81	16.95	16.98	16.91	16.92	17.12	17.41	17.95	17.21

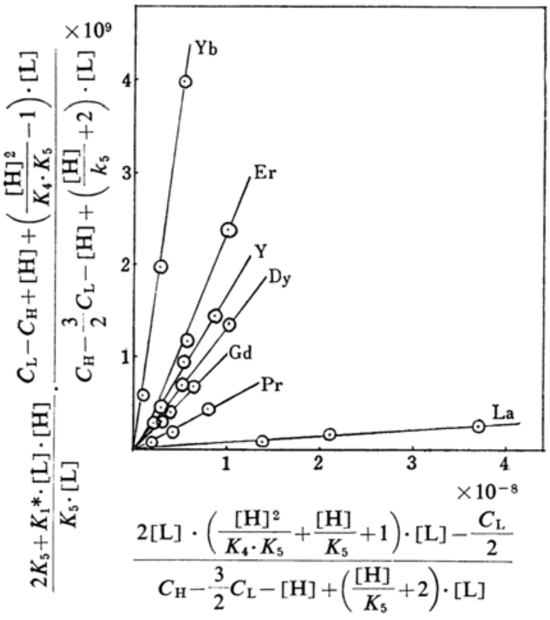

Fig. 3. The relations of K_1' and K_2' in Eq. 22 for rare-earth metals.

ML_2 exist appreciably in the pH range in which calculations were made.

ML and ML_2 may form successively as the value of pH becomes greater. However, as is seen in Fig. 3, the intercepts in the y-axis of the lines are nearly zero for all the metals measured. This shows that the main species of normal complexes is ML_2 under the conditions for which the measurements were made.

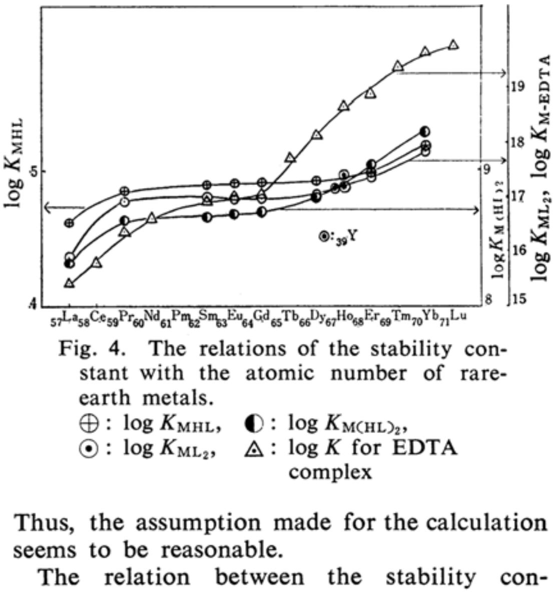

Fig. 4. The relations of the stability constant with the atomic number of rare-earth metals.
⊕ : log K_{MHL}, ◐ : log $K_{M(HL)_2}$,
⊙ : log K_{ML_2}, △ : log K for EDTA complex

Thus, the assumption made for the calculation seems to be reasonable.

The relation between the stability constants and the atomic number of the rare-earth metals is shown in Fig. 4; the tendency is the same as that of the EDTA complex⁽⁴⁾.

Triphosphate can keep the rare-earth metal in solution over a wide range of pH values if it exists in a large excess over the metal.

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

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4) J. E. Powell et al., AL-119, Ames Lab. AEC.