The Stability Constants of Ethylenediaminetetraacetato, Trimethylenediaminetetraacetato and Propylenediaminetetraacetato Complexes of Some Divalent Metal Ions

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The equilibrium constants of substitution reactions involving ethylenediaminetetraacetato[1,2] and propylenediaminetetraacetato complexes[3] have been reported previously. Although Smith has reported the stability constants of propylenediaminetetraacetato complexes,[4] the values seem to be somewhat questionable.[3] Schwarzenbach et al. obtained the stability constants of trimethylenediaminetetraacetato complexes,[5,6] with which the ethylenediaminetetraacetato complexes are closely related. However, their study was restricted to alkaline earth metal, cadmium(II) and mercury(II) ions. Therefore, it seems worthwhile to clarify the relationships between the stability constants of ethylenediaminetetraacetato, trimethylenediaminetetraacetato and propylenediaminetetraacetato complexes of some divalent metal ions containing transition metal ions.

In this paper, these stability constants are determined by two methods. One is a new method which is based on the polarographic measurement of the concentration of an uncomplexed ligand in a solution containing two kinds of ligands and an appropriate metal ion. The other, a modification of the method described in the previous paper,[1] is used for the determination of the relative stability constants of trimethylenediaminetetraacetato complexes.

Theoretical

The Determination of the Relative Stability Constants of the Complexes with Different Ligands.—Let us consider an equilibrated solution which contains a metal (M^{m+}) ion and two kinds of ligands (anions of H_4Y and H_4Z).* There exist the following equilibria:

$$MY^{(m-4)+} + Z^{4-} \rightleftarrows MZ^{(m-4)+} + Y^{4-} \qquad (1)$$

$$Y^{4-} + nH^{+} \rightleftarrows H_nY^{(4-n)-} \qquad (2)$$

$$Z^{4-} + n'H^{+} \rightleftarrows H_{n'}Z^{(4-n')-} \qquad (3)$$

The overall reaction, therefore, may be expressed as:

$$MY^{(m-4)+} + \left\{\begin{matrix} H_4Z \\ \uparrow\downarrow \\ H_3Z^{-} \\ \uparrow\downarrow \\ \vdots \\ \uparrow\downarrow \\ Z^{4-} \end{matrix}\right\} \rightleftarrows MZ^{(m-4)+} + \left\{\begin{matrix} H_4Y \\ \uparrow\downarrow \\ H_3Y^{-} \\ \uparrow\downarrow \\ \vdots \\ \uparrow\downarrow \\ Y^{4-} \end{matrix}\right\} \qquad (4)$$

When $[M]_t<[Y]_t+[Z]_t$, the total concentrations of metal and ligands, $[M]_t$, $[Y]_t$ and $[Z]_t$, in the solution are given as,

$$[M]_t=[MY^{(m-4)+}] + [MZ^{(m-4)+}] \qquad (5)$$

$$[Y]_t=[MY^{(m-4)+}] + [Y]_f \qquad (6)$$

$$[Z]_t=[MZ^{(m-4)+}] + [Z]_f \qquad (7)$$

where

$$[Y]_f=\sum_0^4[H_iY^{(4-i)-}]$$

$$[Z]_f=\sum_0^4[H_jZ^{(4-j)-}]$$

The equilibrium constant of Eq. 4,

$$K_{Z,\mathrm{app}}^{Y}=\frac{[Z]_f[MY^{(m-4)+}]}{[Y]_f[MZ^{(m-4)+}]} \qquad (8)$$

can be calculated by means of the relations given by Eqs. 5 to 7, provided that the value of one term on the right-hand sides of Eqs. 5 to 7 is known. In this study, the values of $K_{Z,\mathrm{app}}^{Y}$ were determined from the polarographic measurements of the concentrations of uncomplexed ethylenediaminetetraacetate or propylenediaminetetraacetate.

Equation 8 is rewritten as,

$$K_{Z,\mathrm{app}}^{Y}=K_{Z}^{Y}\frac{\alpha_Z}{\alpha_Y} \qquad (9)$$

where

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[1] N. Tanaka and K. Kato, This Bulletin, 33, 417 (1960).

[2] N. Tanaka, M. Kamada, H. Osawa and G. Satô, ibid., 33, 1412 (1960).

[3] N. Tanaka and H. Ogino, ibid., 38, 439 (1965).

[4] R. L. Smith, "The Sequestration of Metals," Chapman and Hall, London (1959).

[5] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 31, 1029 (1948).

[6] G. Schwarzenbach, H, Senn and G. Anderegg, ibid., 40, 1886 (1957).

* Although H_4Y and H_4Z represent alkylenediaminetetraacetic acids, they may be replaced by other appropriate ligands.

$$\alpha_{\mathrm{Y}}=1+\frac{[\mathrm{H}^+]}{K_{\mathrm{HY}}}+\frac{[\mathrm{H}^+]^2}{K_{\mathrm{H_2Y}}K_{\mathrm{HY}}}+\frac{[\mathrm{H}^+]^3}{K_{\mathrm{H_3Y}}K_{\mathrm{H_2Y}}K_{\mathrm{HY}}}$$

$$+\frac{[\mathrm{H}^+]^4}{K_{\mathrm{H_4Y}}K_{\mathrm{H_3Y}}K_{\mathrm{H_2Y}}K_{\mathrm{HY}}}$$

$$\alpha_{\mathrm{Z}}=1+\frac{[\mathrm{H}^+]}{K_{\mathrm{HZ}}}+\frac{[\mathrm{H}^+]^2}{K_{\mathrm{H_2Z}}K_{\mathrm{HZ}}}+\frac{[\mathrm{H}^+]^3}{K_{\mathrm{H_3Z}}K_{\mathrm{H_2Z}}K_{\mathrm{HZ}}}$$

$$+\frac{[\mathrm{H}^+]^4}{K_{\mathrm{H_4Z}}K_{\mathrm{H_3Z}}K_{\mathrm{H_2Z}}K_{\mathrm{HZ}}}$$

$$K^{\mathrm{Y}}_{\mathrm{Z}}=\frac{[\mathrm{Z}^{4-}][\mathrm{MY}^{(m-4)+}]}{[\mathrm{Y}^{4-}][\mathrm{MZ}^{(m-4)+}]}=\frac{K_{\mathrm{MY}}}{K_{\mathrm{MZ}}} \tag{10}$$

$K_{\mathrm{H_4Y}}$, $K_{\mathrm{H_3Y}}$, $K_{\mathrm{H_2Y}}$ and K_{HY} represent, respectively, the first, the second, the third and the fourth dissociation constant of $\mathrm{H_4Y}$, and $K_{\mathrm{H_4Z}}$, $K_{\mathrm{H_3Z}}$, $K_{\mathrm{H_2Z}}$ and K_{HZ}, those of $\mathrm{H_4Z}$, respectively.

Therefore, $K^{\mathrm{Y}}_{\mathrm{Z}}$, which is the ratio of the stability constant of $\mathrm{MY}^{(m-4)+}$ to that of $\mathrm{MZ}^{(m-4)+}$, can be determined from the value of $K^{\mathrm{Y}}_{\mathrm{Z,app}}$ by the use of the dissociation constants of $\mathrm{H_4Y}$ and $\mathrm{H_4Z}$.

The Determination of the Relative Stability Constants of Trimethylenediaminetetraacetato Complexes.*—In the course of this study, it was found that the trimethylenediaminetetraacetatocobaltate(II) complex gives a polarographic one-electron oxidation wave.[7] In order to determine the relative stability constants of trimethylenediaminetetraacetato complexes, this anodic wave was utilized.

In an acetate buffer solution which contains cobalt(II) ions, other appropriate metal ions, and trimethylenediaminetetraacetate ions, there exist the following equilibria:**

$$\left\{\begin{matrix}\mathrm{Co}^{2+}\\ \downarrow\uparrow\\ \mathrm{CoOAc}^{+}\end{matrix}\right\}+\mathrm{Mtrdta}^{(m-4)+}\rightleftarrows$$

$$\mathrm{Cotrdta}^{2-}+\left\{\begin{matrix}\mathrm{M}^{m+}\\ \uparrow\downarrow\\ \mathrm{M(OAc)}_n{}^{(m-n)+}\end{matrix}\right\} \tag{11}$$

where trdta^{4-} denotes the quadrivalent trimethylenediaminetetraacetate anion.

The total concentrations of metals and TRDTA, $[\mathrm{Co}]_\mathrm{t}$, $[\mathrm{M}]_\mathrm{t}$ and $[\mathrm{TRDTA}]_\mathrm{t}$, in the solution are given as follows:

$$[\mathrm{Co}]_\mathrm{t}=[\mathrm{Co}^{2+}]_{\mathrm{app}}+[\mathrm{Cotrdta}^{2-}] \tag{12}$$

$$[\mathrm{M}]_\mathrm{t}=[\mathrm{M}^{m+}]_{\mathrm{app}}+[\mathrm{Mtrdta}^{(m-4)+}] \tag{13}$$

$$[\mathrm{TRDTA}]_\mathrm{t}=[\mathrm{TRDTA}]_\mathrm{f}+[\mathrm{Cotrdta}^{2-}]+[\mathrm{Mtrdta}^{(m-4)+}] \tag{14}$$

where

$$[\mathrm{Co}^{2+}]_{\mathrm{app}}=[\mathrm{Co}^{2+}]+[\mathrm{CoOAc}^{+}]$$

$$[\mathrm{M}^{m+}]_{\mathrm{app}}=[\mathrm{M}^{m+}]+\sum_{1}^{n}[\mathrm{M(OAc)}_n{}^{(m-n)+}]$$

When $[\mathrm{Co}]_\mathrm{t}+[\mathrm{M}]_\mathrm{t}>[\mathrm{TRDTA}]_\mathrm{t}$, $[\mathrm{TRDTA}]_\mathrm{f}$ is negligibly small compared with the concentrations of other species present in the solution.

From the polarographic measurement of $[\mathrm{Cotrdta}^{2-}]$, the equilibrium constant of Eq. 11

$$K^{\mathrm{M}}_{\mathrm{Co,app}}=\frac{[\mathrm{Co}^{2+}]_{\mathrm{app}}[\mathrm{Mtrdta}^{(m-4)+}]}{[\mathrm{M}^{m+}]_{\mathrm{app}}[\mathrm{Cotrdta}^{2-}]} \tag{15}$$

is obtained with the relations given by Eqs. 12 to 14.

Equation 15 is rewritten as,

$$K^{\mathrm{M}}_{\mathrm{Co,app}}=K^{\mathrm{M}}_{\mathrm{Co}}\times\frac{1+K_{\mathrm{CoOAc}}[\mathrm{OAc}^-]}{1+\sum_{1}^{n}K_{\mathrm{M(OAc)}_n}[\mathrm{OAc}^-]^n} \tag{16}$$

where

$$K^{\mathrm{M}}_{\mathrm{Co}}=\frac{[\mathrm{Co}^{2+}][\mathrm{Mtrdta}^{(m-4)+}]}{[\mathrm{M}^{m+}][\mathrm{Cotrdta}^{2-}]} \tag{17}$$

Equation 17 means that $K^{\mathrm{M}}_{\mathrm{Co}}$ is equal to the ratio of the stability constant of the M^{m+}-TRDTA complex to that of the Co^{2+}-TRDTA complex:

$$K^{\mathrm{M}}_{\mathrm{Co}}=\frac{K_{\mathrm{MY}}}{K_{\mathrm{CoY}}} \tag{18}$$

The values of $K^{\mathrm{M}}_{\mathrm{Co}}$ can be calculated from Eq. 16 using the values of $K^{\mathrm{M}}_{\mathrm{Co,app}}$ and the formation constants of the acetato complexes.[1,2,8]

Experimental

Reagents. — Standard solutions of metal(II) nitrate, disodium dihydrogen ethylenediaminetetraacetate ($\mathrm{Na_2H_2edta}$) and disodium dihydrogen propylenediaminetetraacetate ($\mathrm{Na_2H_2pdta}$) were obtained by procedures reported previously.[1-3,9]

Trimethylenediaminetetraacetic acid ($\mathrm{H_4trdta}$) was prepared according to the method described in the previous paper.[10] A stock solution of $\mathrm{Na_2H_2trdta}$ was prepared from equimolar quantities of $\mathrm{H_4trdta}$ and sodium carbonate. The concentration of TRDTA was determined by amperometric titration with standard solutions of copper(II) nitrate, cobalt(II) nitrate and nickel(II) nitrate in acetate buffer solutions of pH 5.4, and that of cadmium(II) nitrate, in ammonia-ammonium nitrate buffer solutions of pH 8.7. The values thus obtained were consistent with each other within the range of experimental error and were in good agreement with the value expected from the weight of $\mathrm{H_4trdta}$.

All the other chemicals used were of analytical reagent grade.

Apparatus and Procedure. — The polarograph used was the same as that described in the previous paper.[3] The dropping mercury electrode had an m value of 2.13_7 mg./sec. and a drop time, t_d, of

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[7] The details will be published elsewhere.

* Trimethylenediaminetetraacetate may be replaced by other, appropriate ligands.

** It is known that cobalt(II) forms only a monoacetato complex in a solution containing acetate up to 0.2 M in concentration at ionic strength 0.2.[2]

[8] N. Tanaka and K. Kato, This Bulletin, 32, 516 (1959).

[9] N. Tanaka and H. Ogino, ibid., 36, 175 (1963).

[10] N. Tanaka and H. Ogino, ibid., 37, 877 (1964).

3.96 sec., as measured in an air-free 0.2 M potassium nitrate solution containing 0.01% gelatin at 25°C. The pH of the solution was measured, after the polarographic measurement, with a Hitachi Horiba Model P pH meter.

In order to determine the relative stability constants of ethylenediaminetetraacetatocuprate(II), propylenediaminetetraacetatocuprate(II) and trimethylenediaminetetraacetatocuprate(II) complexes, measurements of the diffusion currents of ethylenediaminetetraacetate or propylenediaminetetraacetate in acetate buffer solutions were carried out with the following two reaction mixtures at 25°C:

(a) copper(II)-EDTA-TRDTA

(b) copper(II)-PDTA-TRDTA

The ionic strength was adjusted to be 0.2 with sodium perchlorate. Gelatin was added as a maximum suppressor by 0.01% in concentration. It was found in the preliminary experiments that the equilibria of systems a and b were attained within 30 min.

In order to determine the relative stability constants of trimethylenediaminetetraacetato complexes, measurements of the diffusion currents of the trimethylenediaminetetraacetatocobaltate(II) complex in the acetate buffer solutions were carried out with the following five reaction mixtures at 25°C:

(c) cobalt(II)-nickel(II)-TRDTA

(d) cobalt(II)-copper(II)-TRDTA

(e) cobalt(II)-zinc(II)-TRDTA

(f) cobalt(II)-cadmium(II)-TRDTA

(g) cobalt(II)-lead(II)-TRDTA

The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.005% in concentration. Since it was found that the substitution reactions between cobalt(II) ions and various kinds of metal(II)-TRDTA complexes were attained within 40 hr., measurements were made with solutions which had been kept in a thermostat for 2 days after preparation.

Results

The Determination of the Relative Stability Constants of Ethylenediaminetetraacetatocuprate(II), Propylenediaminetetraacetatocuprate(II) and Trimethylenediaminetetraacetatocuprate(II) Complexes.—It is well known that EDTA gives a polarographic anodic wave[11] as a result of the following electrode reaction:

$$\mathrm{Hg} + \mathrm{H}_n\mathrm{Y}^{(4-n)-} \rightleftarrows \mathrm{HgY}^{2-} + n\mathrm{H}^+ + 2\mathrm{e}$$

In the course of this study, it was found that PDTA gave a similar anodic wave and that its half-wave potential was slightly more negative than that of EDTA. TRDTA, on the other hand, was found to produce an ill-defined wave at a more positive potential than EDTA. These facts suggested that the concentrations of free EDTA and PDTA can be determined in systems a and b respectively. In Fig. 1 typical examples are given.

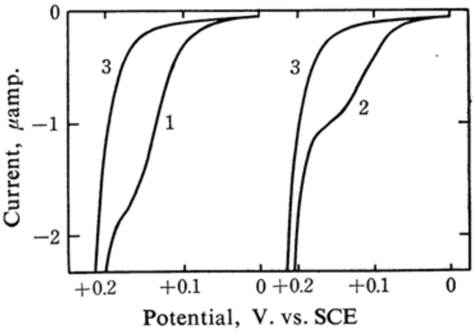

Fig. 1. Polarograms of systems a and b in the acetate buffer solutions of pH 5.38 at 25°C. Total concentrations are: 2.00 mM copper(II), 1.98_8 mM EDTA, 4.09_6 mM TRDTA (curve 1); 2.00 mM copper(II), 1.98_8 mM PDTA, 4.09_6 mM TRDTA (curve 2); 4.09_6 mM TRDTA (curve 3).

The diffusion current constants of EDTA and PDTA were determined by measuring the diffusion currents at various pH's. The values of $[\mathrm{EDTA}]_f$ and $[\mathrm{PDTA}]_f$ were calculated, with the aid of these diffusion current constants, from the diffusion currents obtained with the reaction mixtures of systems a and b respectively. Then, the equilibrium constants, $K^{\mathrm{Y}}_{\mathrm{Z,app}}$, given by Eq. 8 were calculated. The results obtained for systems a and b are given in Table I.

The reported values of the acid dissociation constants (pK) of EDTA, TRDTA and PDTA are summarized in Table II. The relative stability constants of the copper(II)-EDTA complex to the copper(II)-TRDTA complex, $K^{\mathrm{EDTA}}_{\mathrm{TRDTA}}$, were calculated from the $K^{\mathrm{EDTA}}_{\mathrm{TRDTA,app}}$ given in Table I and from the pK values of EDTA and TRDTA reported by Schwarzenbach et al.[6] The resulting values at various pH's are presented in Table III.

It seems not appropriate to calculate the values of $K^{\mathrm{PDTA}}_{\mathrm{TRDTA}}$ from the observed values of $K^{\mathrm{PDTA}}_{\mathrm{TRDTA,app}}$ with the reported pK values of TRDTA and PDTA, because these pK values have not all been determined under the same conditions. However, a $K^{\mathrm{PDTA}}_{\mathrm{TRDTA,app}}$ value at a given pH can be converted to a $K^{\mathrm{PDTA}}_{\mathrm{EDTA,app}}$ value with the aid of a $K^{\mathrm{EDTA}}_{\mathrm{TRDTA,app}}$ value obtained at the same pH according to the equation,

$$K^{\mathrm{PDTA}}_{\mathrm{EDTA,app}} = K^{\mathrm{PDTA}}_{\mathrm{TRDTA,app}} / K^{\mathrm{EDTA}}_{\mathrm{TRDTA,app}} \tag{19}$$

From the $K^{\mathrm{PDTA}}_{\mathrm{EDTA,app}}$ thus obtained and the pK

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[11] For instance, J. Goffart, G. Michel and G. Duyckaerts, *Anal. Chim. Acta*, **9**, 184 (1953); C. N. Reilley, W. G. Scribner and C. Temple, *Anal. Chem.*, **28**, 450 (1956).

Table I. Equilibrium constants for the substitution reaction (Eq. 4) at 25°C and ionic strength 0.2

System a*			System b**		
pH	$[\mathrm{EDTA}]_{\mathrm{f,mM}}$	$K^{\mathrm{EDTA}}_{\mathrm{TRDTA,app}}$	pH	$[\mathrm{PDTA}]_{\mathrm{f,mM}}$	$K^{\mathrm{PDTA}}_{\mathrm{TRDTA,app}}$
5.39	0.201	1.6×10^2	5.36	0.099	6.9×10^2
5.28	0.232	1.2×10^2	5.26	0.117	4.9×10^2
5.06	0.220	1.3×10^2	5.06	0.113	5.3×10^2
4.84	0.211	1.5×10^2	4.88	0.113	5.3×10^2

* Total concentrations are: $[\mathrm{Cu}]_t=2.00$ mM, $[\mathrm{EDTA}]_t=1.98_8$ mM, $[\mathrm{TRDTA}]_t=4.09_6$ mM.

** Total concentrations are: $[\mathrm{Cu}]_t=2.00$ mM, $[\mathrm{PDTA}]_t=1.98_8$ mM, $[\mathrm{TRDTA}]_t=4.09_6$ mM.

Table II. The reported values of the acid dissociation constants of EDTA, TRDTA and PDTA at ionic strength 0.1

Chelating agent	Temp., °C	$\mathrm{p}K_1$	$\mathrm{p}K_2$	$\mathrm{p}K_3$	$\mathrm{p}K_4$	Ref.
EDTA	20	2.0	2.67	6.16	10.26	6
	30	2.4	2.86	6.22	10.25	12
TRDTA	20	2.0	2.67	7.90	10.27	6
PDTA	30	2.60	3.03	6.20	10.84	12

Table III. The determination of the value of $K^{\mathrm{EDTA}}_{\mathrm{TRDTA}}$ of copper(II) complexes at 25°C and ionic strength 0.2

pH	$\alpha_{\mathrm{TRDTA}}/\alpha_{\mathrm{EDTA}}$	$K^{\mathrm{EDTA}}_{\mathrm{TRDTA}}$
5.39	50.8	3.2
5.28	52.2	2.3
5.06	54.2	2.5
4.84	55.5	2.6
		2.7 (av.)

Table IV. The determination of the value of $K^{\mathrm{PDTA}}_{\mathrm{EDTA}}$ of copper(II) complexes at 25°C and ionic strength 0.2

pH*	$K^{\mathrm{PDTA}}_{\mathrm{EDTA,app}}$	$\alpha_{\mathrm{PDTA}}/\alpha_{\mathrm{EDTA}}$	$K^{\mathrm{PDTA}}_{\mathrm{EDTA}}$
5.37_5	4.2	3.74	16
5.27	4.1	3.74	15
5.06	4.0	3.74	15
4.86	3.7	3.74	14
			15 (av.)

* The pH values of the same line of system a and system b in Table I are averaged.

values of EDTA and PDTA reported by Grimes et al.,[12] the $K^{\mathrm{PDTA}}_{\mathrm{EDTA}}$ values were determined; they are given in Table IV.

The hydrogen ion concentration used in this calculation was obtained from the observed pH and the activity coefficient of the hydrogen ion, which was assumed to be 0.80 at ionic strength 0.2.

The Determination of the Relative Stability Constants of Trimethylenediaminetetraacetato Complexes.—Cobalt(II)-TRDTA complex gave a reversible anodic wave with the half-wave potential of about +0.05 V. vs. SCE in the acetate media, independent of pH from 4.7 to 5.5. The limiting current of the wave was found to be diffusion-controlled.

The diffusion current constants of the cobalt(II)-TRDTA complex were determined by measuring the diffusion current under various acetate concentrations and pH's. The values of $[\mathrm{Cotrdta}^{2-}]$ were calculated, with the aid of these diffusion current constants, from the diffusion currents obtained with systems c to g. Then, the values of $K^{\mathrm{M}}_{\mathrm{Co,app}}$ given by Eq. 15 and those of $K^{\mathrm{M}}_{\mathrm{Co}}$ were calculated according to the procedures described above.

The results obtained for systems c to g are summarized in Table V.

Although the measurements were carried out for the cobalt(II)-manganese(II)-TRDTA system, no detectable decrease in the wave height of the cobalt(II)-TRDTA complex was observed. The value of $K^{\mathrm{Mn}}_{\mathrm{Co}}$, therefore, was calculated to be less than 2×10^{-4} from the experimental errors and from the total concentrations of cobalt(II), manganese(II) and trimethylenediaminetetraacetate ions.

Discussion

The reported values of the acid dissociation constants of EDTA, TRDTA and PDTA[6,12] ($\mu=0.1$, 20°C or 30°C) were used without correction when $K^{\mathrm{Y}}_{\mathrm{Z}}$ was calculated from $K^{\mathrm{Y}}_{\mathrm{Z,app}}$.

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[12] J. H. Grimes, A. J. Huggard and S. P. Wilford, *J. Inorg. Nucl. Chem.*, **25**, 1225 (1963).

TABLE V. THE DETERMINATION OF THE VALUES OF $K_{\mathrm{Co}}^{\mathrm{M}}$ OF TRDTA COMPLEXES AT 25°C AND IONIC STRENGTH 0.2

pH	$[\mathrm{OAc}^-]_{\mathrm{add}}$, M	$[\mathrm{OAc}^-]$, M*	$K_{\mathrm{Co,app}}^{\mathrm{M}}$	$K_{\mathrm{Co}}^{\mathrm{M}}$
		Cobalt(II)-copper(II)-TRDTA system		
5.29	0.100	0.099_0	4.59×10^2	3.06×10^3
5.22	0.100	0.098_3	6.08×10^2	4.02×10^3
5.19	0.0400	0.039_3	1.05×10^3	3.26×10^3
5.17	0.0500	0.049_1	1.15×10^3	4.23×10^3
				$K_{\mathrm{Co}}^{\mathrm{Cu}}=3.6\times10^3$ (av.)
		Cobalt(II)-nickel(II)-TRDTA system		
5.28	0.100	0.099_1	5.30×10^2	6.24×10^2
5.28	0.100	0.099_1	5.68×10^2	6.69×10^2
5.23	0.100	0.098_4	5.32×10^2	6.26×10^2
				$K_{\mathrm{Co}}^{\mathrm{Ni}}=6.4\times10^2$ (av.)
		Cobalt(II)-zinc(II)-TRDTA system		
5.34	0.100	0.099_6	0.433	0.596
5.34	0.100	0.099_6	0.438	0.603
				$K_{\mathrm{Co}}^{\mathrm{Zn}}=0.60$ (av.)
		Cobalt(II)-cadmium(II)-TRDTA system		
5.22	0.100	0.097_2	1.49×10^{-2}	1.63×10^{-2}
5.20	0.100	0.097_2	1.49×10^{-2}	1.63×10^{-2}
				$K_{\mathrm{Co}}^{\mathrm{Cd}}=1.6\times10^{-2}$ (av.)
		Cobalt(II)-lead(II)-TRDTA system		
5.02	0.0400	0.0205	9.33×10^{-3}	3.52×10^{-2}
4.84	0.0200	0.0074	1.89×10^{-2}	3.73×10^{-2}
				$K_{\mathrm{Co}}^{\mathrm{Pb}}=3.6\times10^{-2}$ (av.)

* The concentration of uncomplexed acetate in the solution was calculated by successive approximation.

This procedure, however, does not seem to introduce any appreciable error into the values of $K_{\mathrm{Z}}^{\mathrm{Y}}$ thus obtained, because the predominant species of uncomplexed ligands are always $\mathrm{H_2Y^{2-}}$ for EDTA, TRDTA and PDTA under the present experimental conditions, and their abundances are more than 88%. From this fact, we may approximately express $\alpha_{\mathrm{Z}}/\alpha_{\mathrm{Y}}$ in Eq. 9 by the equation:

$$\frac{\alpha_{\mathrm{Z}}}{\alpha_{\mathrm{Y}}}=\frac{K_{\mathrm{H_2Y}}K_{\mathrm{HY}}}{K_{\mathrm{H_2Z}}K_{\mathrm{HZ}}} \tag{20}$$

indicating that the values of $\alpha_{\mathrm{Z}}/\alpha_{\mathrm{Y}}$ are mainly dependent on the values of the third and fourth dissociation constants of ligands. According to the Debye-Hückel equation, at a given temperature and ionic strength the activity coefficients of the ions with the same charge are determined only by ion-size parameters. Since EDTA, TRDTA and PDTA are closely related compounds, the changes in the activity coefficients of the corresponding ionic species of these compounds with the changes in temperature and ionic strength are considered to be almost identical. Therefore, the values of $\alpha_{\mathrm{Z}}/\alpha_{\mathrm{Y}}$ would not be affected appreciably by the changes in temperature and ionic strength, as long as the acid dissociation constants are determined under the same conditions.

If $\mathrm{MHY}^{(m-3)+}$ and $\mathrm{MHZ}^{(m-3)+}$ are formed, the equation corresponding to Eq. 9 is given as follows:

$$K_{\mathrm{Z,app}}^{\mathrm{Y}}=K_{\mathrm{Z}}^{\mathrm{Y}}\times\frac{\alpha_{\mathrm{Z}}\alpha_{\mathrm{MHY(H)}}}{\alpha_{\mathrm{Y}}\alpha_{\mathrm{MHZ(H)}}} \tag{21}$$

where

$$\alpha_{\mathrm{MHY(H)}}=1+K_{\mathrm{MHY}}^{\mathrm{H}}[\mathrm{H^+}]$$

$$\alpha_{\mathrm{MHZ(H)}}=1+K_{\mathrm{MHZ}}^{\mathrm{H}}[\mathrm{H^+}]$$

$K_{\mathrm{MHY}}^{\mathrm{H}}$ and $K_{\mathrm{MHZ}}^{\mathrm{H}}$ represent the formation constants of $\mathrm{MHY^-}$ and $\mathrm{MHZ^-}$ respectively. Schwarzenbach et al.[13] have reported that $\log K_{\mathrm{CuHedta}}^{\mathrm{H}}$ was 3.0 at 20°C and ionic strength 0.1. This value indicates that no appreciable amount of $\mathrm{CuHedta^-}$ is present in systems a and b. The values of neither $K_{\mathrm{TRDTA}}^{\mathrm{EDTA}}$ nor $K_{\mathrm{EDTA}}^{\mathrm{PDTA}}$ are dependent on pH, as is shown in Table III and Table IV respectively. These also suggest that no appreciable amounts of

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[13] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

CuHtrdta⁻ and CuHpdta⁻ are present under the experimental conditions.

The stability constants of the copper(II)-TRDTA complex and the copper(II)-PDTA complex were calculated by using the $K^{\mathrm{EDTA}}_{\mathrm{TRDTA}}$ value in Table III, the $K^{\mathrm{PDTA}}_{\mathrm{EDTA}}$ value in Table IV and the value of K_{Cuedta}, which was evaluated with a procedure which has been described previously.[14] The stability constants of the trimethylenediaminetetraacetato complexes of some divalent metal ions were calculated from the K_{Cutrdta} value thus obtained and from the $K^{\mathrm{M}}_{\mathrm{Co}}$ values of TRDTA in Table V. The $K^{\mathrm{M}}_{\mathrm{M'}}$ values of EDTA and PDTA complexes determined previously[1-3] were used for the determination of the stability constants of ethylenediaminetetraacetato and propylenediaminetetraacetato complexes. The scheme for the determination of the stability constants is given in Fig. 2. The results obtained are shown in Table VI and Fig. 3.

TABLE VI. THE LOGARITHMIC STABILITY CONSTANTS OF EDTA, PDTA AND TRDTA COMPLEXES AT 25°C AND IONIC STRENGTH 0.2[15]

Metal ion	EDTA complex	PDTA complex	TRDTA complex
Manganese(II)	13.64*	14.85*	<10.8
Cobalt(II)	15.71	17.07	14.48
Nickel(II)	18.12	19.42	17.29
Copper(II)	18.46**	19.64	18.04
Zinc(II)	15.94	17.14	14.26
Cadmium(II)	15.98	17.43	12.69
Lead(II)	17.76	18.69	13.04

* These values were calculated from unpublished results.

** This value was evaluated with the same procedure as described previously.[14]

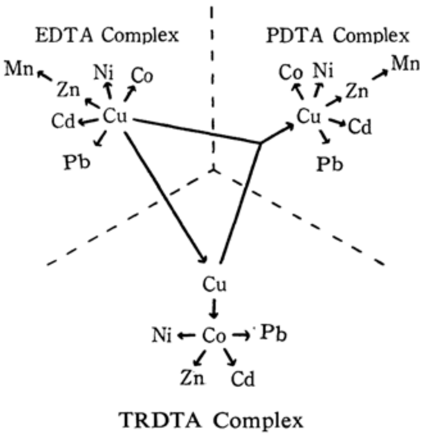

Fig. 2. Scheme for the determination of the stability constants of EDTA, TRDTA and PDTA complexes.

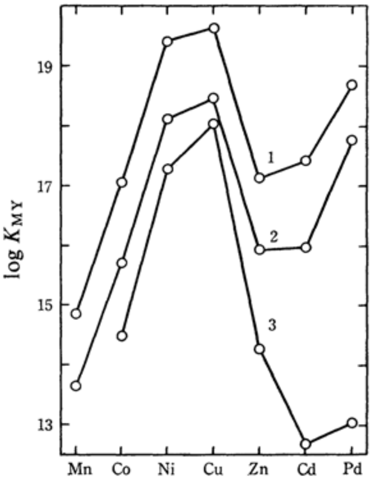

Fig. 3. The logarithmic stability constants of PDTA (1), EDTA (2) and TRDTA (3) complexes at 25°C and ionic strength 0.2.

The stability constants of EDTA complexes and the cadmium(II)-TRDTA complex obtained in this study seem to be in satisfactory agreement with those reported by Schwarzenbach et al.,[6,13] provided that the differences in temperature and ionic strength between the two sets of results are considered.

For the sake of comparison, the calculations shown in Table VII were carried out. The differences between the logarithmic stability constants of PDTA and EDTA complexes, which are expressed with $\log K^{\mathrm{PDTA}}_{\mathrm{EDTA}}$ in Table VII, indicate that the stability constants of PDTA complexes are larger than those of

TABLE VII. COMPARISON OF THE STABILITY CONSTANTS OF EDTA, PDTA AND TRDTA COMPLEXES AT 25°C AND IONIC STRENGTH 0.2

	Mn	Co	Ni	Cu	Zn	Cd	Pb
$\log K^{\mathrm{PDTA}}_{\mathrm{EDTA}}$	1.21	1.36	1.30	1.18	1.20	1.45	0.93
$\log K^{\mathrm{EDTA}}_{\mathrm{TRDTA}}$	>2.8	1.23	0.83	0.42	1.68	3.29	4.72

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[14] N. Tanaka and K. Kato, This Bulletin, **32**, 1376 (1959).

[15] Note added in proof: Recently, stability constants of PDTA complexes[a] and TRDTA complexes[b-d] were reported. They seem to be in good agreement with the values obtained in this study, when the differences in the experimental conditions and in the values of acid dissociation constants used in the calculation are taken into consideration. Irving and Conesa[a] determined $K^{\mathrm{Pb}}_{\mathrm{Cu}}$ and $K^{\mathrm{Cd}}_{\mathrm{Pb}}$ of PDTA complexes in acetate media, but they did not consider the effects of acetate ions on the equilibria. The better agreement can be obtained between their values and those obtained in this study by considering the formation of acetato complexes of copper, cadmium and lead.

a) H. M. N. H. Irving and J. P. Conesa, *J. Inorg. Nucl. Chem.*, **26**, 1945 (1964); b) G. Anderegg and F. L'Eplattenier, *Chimia*, **18**, 186 (1964); c) F. L'Eplattenier and G. Anderegg, *Helv. Chim. Acta*, **47**, 1792 (1964); d) G. Anderegg, ibid., **47**, 1801 (1964).

EDTA complexes by about 1.2 $\log K$ unit, without regard to the kind of metal ions. It was found that the fourth dissociation constant of PDTA is higher than that of EDTA, and that the stability constants of alkaline earth chelates of PDTA are larger than those of EDTA.(12) Grimes et al. concluded that these results are attributable to the inductive effect of the methyl group in PDTA.(12) Therefore, the values of $\log K^{\mathrm{PDTA}}_{\mathrm{EDTA}}$ indicate that the increase in the basicity of the ligand has almost the same effect on the stability constants of the PDTA complexes compared with the EDTA complexes. On the other hand, the values of $\log K^{\mathrm{EDTA}}_{\mathrm{TRDTA}}$ are considerably dependent on the kind of metal ions. It may be considered that the values of $\log K^{\mathrm{EDTA}}_{\mathrm{TRDTA}}$ are affected by two factors. The first one is that the increase in basicity due to the third dissociation constant of TRDTA being higher than that of EDTA(5,6) causes the stabilization of TRDTA complexes. The second factor is that the TRDTA complexes are instabilized by the presence of a six-membered chelate ring involving two nitrogen atoms. The first factor may have almost the same effect on the $\log K^{\mathrm{EDTA}}_{\mathrm{TRDTA}}$ values of various metal ions, as is true in the case of $\log K^{\mathrm{PDTA}}_{\mathrm{EDTA}}$ values. Therefore, the orders of the instabilization by the presence of a six-membered ring may be given as:

$$\mathrm{Cu} < \mathrm{Ni} < \mathrm{Co} < \mathrm{Zn} < \mathrm{Mn}\,;\ \mathrm{Zn} < \mathrm{Cd} < \mathrm{Pb}$$

These orders agree with the order of the ionic (crystal) radii(16) of metal ions. This fact indicates that the decrease in the size of metal ions is favorable for the formation of TRDTA complex.

Summary

Two methods are presented for the determination of the stability constants of ethylenediaminetetraacetato, trimethylenediaminetetraacetato and propylenediaminetetraacetato complexes of some divalent metal ions. One is a new method which is based on the polarographic measurement of the concentration of an uncomplexed ligand in a solution containing two kinds of ligands and an appropriate metal ion. The other is a modification of the method described in the previous paper.(1) From the results obtained by these methods and those obtained previously,(1-3) the individual stability constants have been calculated. The values of the logarithmic stability constants of complexes at 25°C and ionic strength 0.2 are: Mn 13.64, Co 15.71, Ni 18.12, Cu 18.46, Zn 15.94, Cd 15.98 and Pb 17.76 for ethylenediaminetetraacetato complexes; Mn <10.8, Co 14.48, Ni 17.29, Cu 18.04, Zn 14.26, Cd 12.69 and Pb 13.04 for trimethylenediaminetetraacetato complexes, and Mn 14.85, Co 17.07, Ni 19.42, Cu 19.64, Zn 17.14, Cd 17.43 and Pb 18.69 for propylenediaminetetraacetato complexes.

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16) T. Moeller, "Inorganic Chemistry," John Wiley & Sons, New York, N. Y. (1952), p. 140.