Equilibrium Study of Propylenediaminetetraacetato Complexes of Some Divalent Metal Ions

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Smith has reported the stability constants of propylenediaminetetraacetato complexes.[1] However, the experimental details were not given and the values seem to be somewhat questionable.

In this laboratory, the equilibria of substitution reactions involving ethylenediaminetetraacetato complexes have been investigated and the equilibrium constants of these reactions have been determined.[2,3] In this paper, the method developed previously[2] is applied to the systems involving propylenediaminetetraacetato complexes, and the results are compared with the values reported in literature[1] and discussed.

Experimental

Reagents. — Standard solutions of nickel(II) nitrate, copper(II) nitrate, lead(II) nitrate, cadmium(II) nitrate[2,3] and zinc(II) nitrate[4] were obtained by the same procedures as reported previously. To remove a small amount of contaminant of nickel, a standard solution of cobalt(II) nitrate was prepared in the following way: Hexamminecobalt(III) chloride which was recrystallized three times from water was heated at 400°C in an electric furnace. The residue was dissolved into a dilute nitric acid solution, evaporated to dryness and the same procedure was repeated several times to convert cobalt(II) chloride to cobalt(II) nitrate. Cobalt(II) nitrate thus obtained was dissolved into distilled water and the residue was removed by filtration. The concentration of cobalt(II) was determined with a standardized EDTA (disodium dihydrogen ethylenediaminetetraacetate) solution by amperometric titration.

Propylenediaminetetraacetic acid (H_4pdta) was prepared according to the method of Dwyer and Garvan.[5] The stock solution of Na_2H_2pdta was prepared from equimolar quantities of H_4pdta and sodium carbonate. The concentration of PDTA was determined with all of the standard metal nitrate solutions mentioned above by amperometric titration. The values thus obtained were consistent with each other within experimental error and were in good agreement with the value expected from the weight of H_4pdta. Therefore, it may be considered that PDTA can be used in complexometric titration in the same way as in the case of EDTA.

All other chemicals used were of analytical reagent grade.

Apparatus and Procedure.—A Yanagimoto PB-4 pen-recording polarograph was used for the measurement of the current-voltage and current-time curves. The dropping mercury electrodes used had the characteristics given in Table I, being measured in an air-free 0.2 M potassium nitrate solution containing 0.01% gelatin at 25°C.

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

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

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

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

[5] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).

TABLE I. CHARACTERISTICS OF THE DROPPING MERCURY ELECTRODES

	Flow rate of mercury (m) mg./sec.	Drop time (t_d), sec.
Electrode A*1,2	2.13_7	3.96
Electrode B*3	1.99_5	4.13

*1 This electrode was used for the systems containing cobalt(II) ions.
*2 Measured at 63.9 cm. of the mercury height.
*3 Measured at 64.8 cm. of the mercury height.

The measurements of the diffusion currents of copper(II) in acetate buffer solutions were carried out with the following five reaction mixtures at 25°C:

(a) copper(II)-cobalt(II)-PDTA
(b) copper(II)-nickel(II)-PDTA
(c) copper(II)-zinc(II)-PDTA
(d) copper(II)-cadmium(II)-PDTA
(e) copper(II)-lead(II)-PDTA

The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration.

It was found in the preliminary experiments that the substitution reactions between copper(II) ions and various kinds of metal(II)-PDTA complexes were more sluggish than those of the corresponding reactions involving EDTA.2,3) In Fig. 1, a typical example is given. Therefore, in system b, reaction mixtures were kept in a thermostat for 50 days before being subjected to the polarographic measurements. In other systems, as the substitution reactions were completed within 7 hrs., measurements were made after the solutions prepared had been kept overnight.

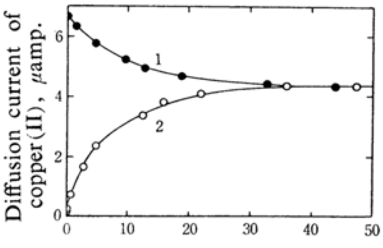

Fig. 1. Diffusion currents of copper(II) as a function of time in the forward (curve 1) and the reverse (curve 2) reactions of the substitution reaction $Cu^{2+}+NiY^{2-} \rightleftarrows CuY^{2-}+Ni^{2+}$, measured in acetate buffer solutions of pH 5.4_5 at 25°C. Total concentrations are: $[Cu]_t=1.00\times10^{-3}$ M; $[Ni]_t=1.00\times10^{-3}$ M; $[PDTA]_t=0.99_0\times10^{-3}$ M.

Results

In the acetate buffer solution which contains two different metal ions, M^{m+} and $M'^{m'+}$, and propylenediaminetetraacetate ions, there exist the following equilibria:

$$\left\{\begin{matrix} M^{m+} \\ \uparrow\downarrow \\ M(OAc)_n{}^{(m-n)+} \end{matrix}\right\} + \left\{\begin{matrix} M'Y^{(m'-4)+} \\ \uparrow\downarrow \\ M'HY^{(m'-3)+} \end{matrix}\right\} \rightleftarrows \left\{\begin{matrix} MY^{(m-4)+} \\ \uparrow\downarrow \\ MHY^{(m-3)+} \end{matrix}\right\} + \left\{\begin{matrix} M'^{m'+} \\ \uparrow\downarrow \\ M'(OAc)_{n'}{}^{(m'-n')+} \end{matrix}\right\} \quad (1)$$

where Y^{4-} denotes quadrivalent PDTA ions.

The values of $[Cu^{2+}]_{app}$ in the reaction mixtures of systems a to e which are given by2)

$$[Cu^{2+}]_{app}=[Cu^{2+}]+\sum_1^n[Cu(OAc)_n{}^{(2-n)+}] \quad (2)$$

were determined at various concentrations of acetate. Then, the apparent equilibrium constants for Eq. 1,

$$K^{M}_{M',\,app} = \frac{[M'^{m'+}]_{app}\{[MY^{(m-4)+}]+[MHY^{(m-3)+}]\}}{[M^{m+}]_{app}\{[M'Y^{(m'-4)+}]+[M'HY^{(m'-3)+}]\}} \quad (3)$$

were calculated and plotted against the acetate ion concentration. These plots for systems a to e are shown in Fig. 2 to Fig. 4.

$K^{M}_{M',\,app}$ is rewritten as2)

$$K^{M}_{M',\,app} = K^{M}_{M'}\frac{\alpha_{MHY(H)}}{\alpha_{M'HY(H)}} \times \frac{1+\sum_1^{n'}K_{M'(OAc)_{n'}}[OAc^-]^{n'}}{1+\sum_1^{n}K_{M(OAc)_n}[OAc^-]^{n}} \quad (4)^*$$

where

$$\alpha_{MHY(H)}=1+K^{H}_{MHY}[H^+] \quad (5)$$

$$\alpha_{M'HY(H)}=1+K^{H}_{M'HY}[H^+] \quad (6)$$

$$K^{M}_{M'} = \frac{[M'^{m'+}][MY^{(m-4)+}]}{[M^{m+}][M'Y^{(m'-4)+}]} \quad (7)$$

$K_{M(OAc)_n}$ and $K_{M'(OAc)_{n'}}$ represent the overall formation constants of $M(OAc)_n{}^{(m-n)+}$ and

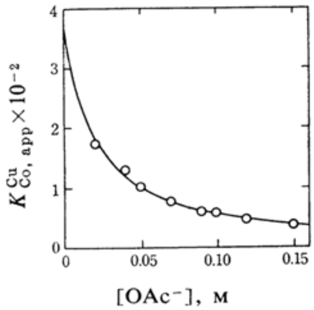

Fig. 2. $K^{Cu}_{Co,\,app}$ at pH 4.56 as a function of acetate ion concentration.

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* β and β', the symbols that are given in previous papers2,3) are replaced by $\alpha_{MHY(H)}$ and $\alpha_{M'HY(H)}$ respectively.

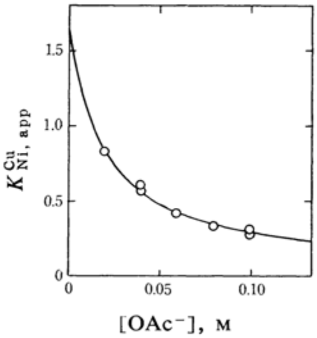

Fig. 3. $K^{Cu}_{Ni, app}$ at pH 4.9 as a function of acetate ion concentration.

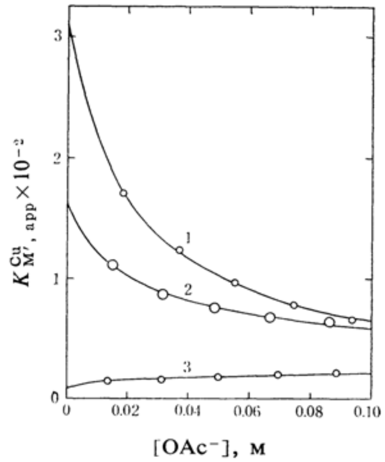

Fig. 4. $K^{Cu}_{Zn, app}$ (1), $K^{Cu}_{Cd, app}$ (2) and $K^{Cu}_{Pb, app}$ (3) at pH 5.4 as a function of acetate ion concentration.

$M'(OAc)_{n'}^{(m'-n')+}$, respectively, and $K^{M}_{M'}$ means the equilibrium constant of reaction given by the equation

$$M^{m+} + M'Y^{(m'-4)+} \rightleftarrows MY^{(m-4)+} + M'^{m'+} \tag{8}$$

It may be reasonable to consider the values of $\alpha_{MHY(H)}/\alpha_{M'HY(H)}$ as being approximately unity under these experimental conditions (pH 4.5—5.5), because this is true in the case of the EDTA complexes,⁶⁾ to which the PDTA complexes are closely related.

The experimental values in Figs. 2 to 4 were treated by a least square method with the aid of Eq. 4 and the formation constants of acetato complexes obtained previously,²·³·⁷⁾ the values of the equilibrium constants for Eq. 8 ($K^{Cu}_{M'}$) were determined. They are given in Table II.

TABLE II. EQUILIBRIUM CONSTANTS FOR THE SUBSTITUTION REACTION (Eq. 8) INVOLVING PDTA COMPLEXES AT 25°C AND IONIC STRENGTH 0.2

K^{Cu}_{Co}	K^{Cu}_{Ni}	K^{Cu}_{Zn}	K^{Cu}_{Cd}	K^{Cu}_{Pb}
3.7×10^2	1.6_6	3.2×10^2	$1.6_1\times10^2$	8.8

The values of $K^{Cu}_{M', app}$ can be calculated as a function of acetate concentration using the $K^{Cu}_{M'}$ values given in Table II, the formation constants of acetato complexes²·³·⁷⁾ and Eq. 4. The solid curves in Figs. 2 to 4 are the calculated ones, which are in satisfactory agreement with the $K^{Cu}_{M', app}$ obtained experimentally at various acetate concentrations. This fact indicates that the values of the formation constants of acetato complexes obtained previously²·³·⁷⁾ are reliable.

Discussion

Equation 7 means that $K^{M}_{M'}$ is equal to the ratio of the stability constant of the M^{m+}-PDTA complex to that of the $M'^{m'+}$-PDTA complex:

$$K^{M}_{M'} = \frac{K_{MY}}{K_{M'Y}} \tag{9}$$

For the sake of comparison, the $K^{Cu}_{M'}$ values in Table II are converted to the relative stability constants to the stability constant of zinc(II)-PDTA complex and the resulting values are given in Table III.

Smith has reported the stability constants of various PDTA complexes.¹⁾ The K^{M}_{Zn} values

TABLE III. THE VALUES OF K^{M}_{Zn} OF PDTA COMPLEXES

	Temp. °C	Ionic strength	K^{Co}_{Zn}	K^{Ni}_{Zn}	K^{Cu}_{Zn}	K^{Zn}_{Zn}	K^{Cd}_{Zn}	K^{Pb}_{Zn}
I	25	0.2	0.85	$1.9_0\times10^2$	3.2×10^2	1	1.9_6	3.6×10
II	20	0.1	1.6×10^{-2}	$1.0_0\times10^{-2}$	3.2×10	1	0.63	$1.2_6\times10$

I. Values obtained in the present investigation.
II. Values calculated from the Smith's values.¹⁾

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

7) N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).

obtained from his stability constants are also given in Table III. Table IV shows the $K_{\mathrm{Zn}}^{\mathrm{M}}$ values calculated from the $K_{\mathrm{M'}}^{\mathrm{M}}$ values of the EDTA complexes obtained previously.[2,3] The $K_{\mathrm{Zn}}^{\mathrm{M}}$ values of the PDTA complexes obtained in this study do not agree with those calculated from the Smith's data, but are quite similar to the $K_{\mathrm{Zn}}^{\mathrm{M}}$ values of the EDTA complexs given in Table IV.

TABLE IV. THE VALUES OF $K_{\mathrm{Zn}}^{\mathrm{M}}$ OF EDTA COMPLEXES AT 25°C AND IONIC STRENGTH 0.2[2,3]

$K_{\mathrm{Zn}}^{\mathrm{Co}}$	$K_{\mathrm{Zn}}^{\mathrm{Ni}}$	$K_{\mathrm{Zn}}^{\mathrm{Cu}}$	$K_{\mathrm{Zn}}^{\mathrm{Zn}}$	$K_{\mathrm{Zn}}^{\mathrm{Cd}}$	$K_{\mathrm{Zn}}^{\mathrm{Pb}}$
0.59	1.5×10^2	3.3×10^2	1	1.1	6.6×10

Recently, the stability constants of alkaline earth chelates and the acid dissociation constants (pK) of PDTA have been determined by Grimes et al.[8] They reported that the fourth dissociation constant (pK_4) of PDTA is higher than that of EDTA, and the stability constants of alkaline earth chelates of PDTA are larger than those of EDTA,[8] explaining that these are attributed to the inductive effect of the methyl group in PDTA.

Nevertheless, it is considered that the increase of stability constants in the presence of methyl group is considered to affect slightly the values of $K_{\mathrm{M'}}^{\mathrm{M}}$, because it may be considerably compensated. Actually, the change in the stability constants of alkaline earth chelates of PDTA[8] with increase in atomic number is parallel to those of EDTA[9] as shown in Fig. 5. Therefore, the similarity between our data of $K_{\mathrm{M'}}^{\mathrm{M}}$ values of PDTA complexes and those of EDTA complexes seems to be reasonable.

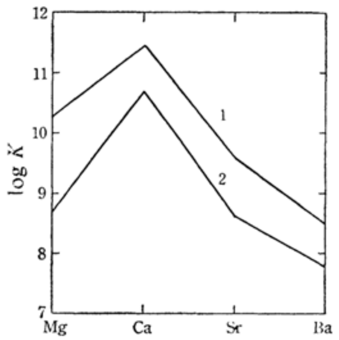

Fig. 5. Logarithms of the stability constants of alkaline earth chelate at ionic strength 0.1: (1) PDTA chelate at 30°C,[8] (2) EDTA chelate at 20°C.[9]

The values reported by Smith are considered to be somewhat erroneous, because his values for $K_{\mathrm{Zn}}^{\mathrm{Co}}$, $K_{\mathrm{Zn}}^{\mathrm{Ni}}$ and $K_{\mathrm{Zn}}^{\mathrm{Cu}}$ are too small.

Summary

The relative stability constants of propylenediaminetetraacetato complexes ($K_{\mathrm{M'}}^{\mathrm{M}}=K_{\mathrm{MY}}/K_{\mathrm{M'Y}}$) of six metal ions were determined at 25°C and ionic strength 0.2 by the polarographic method reported previously.[2] The values obtained are $K_{\mathrm{Co}}^{\mathrm{Cu}}=3.7\times10^2$, $K_{\mathrm{Ni}}^{\mathrm{Cu}}=1.6_6$, $K_{\mathrm{Zn}}^{\mathrm{Cu}}=3.2\times10^2$, $K_{\mathrm{Cd}}^{\mathrm{Cu}}=1.6_1\times10^2$ and $K_{\mathrm{Pb}}^{\mathrm{Cu}}=8.8$ and are quite similar to the corresponding values of the ethylenediaminetetraacetato complexes respectively.

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

[9] G. Schwarzenbach and H. Ackermann, *Helv. Chem. Acta*, **30**, 1798 (1947).