November, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (11), 3047—3052 (1976) 3047

A Potentiometric Study on Complex Formation of Cadmium(II) and Lead(II) Ions with *N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic Acid

Noboru Oyama, Takehide Shirato, Hiroaki Matsuda, and Hitoshi Ohtaki

Department of Electronic Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152

(Received May 13, 1976)

The complex formation of cadmium(II) and lead(II) ions with *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid (HEDTA) has been studied potentiometrically in a 1.0 M $NaClO_4$ medium at 25.0 °C by using glass and metal-amalgam electrodes. The emf data obtained over the pH range 1 to 10 were explained in terms of the formation of the following species: for the Cd–HEDTA system, CdL^- ($\log \beta_{101}=13.21\pm0.04$), CdHL ($\log \beta_{111}=15.61\pm0.02$) and CdH_2L^+ ($\log \beta_{121}=16.68\pm0.04$); for the Pb–HEDTA system, PbL^- ($\log \beta_{101}=14.83\pm0.02$), PbHL ($\log \beta_{111}=16.97\pm0.02$), PbH_2L^+ ($\log \beta_{121}=17.89\pm0.02$) and PbH_3L^{2+} ($\log \beta_{131}=18.67\pm0.02$), where $\beta_{pqr}=[M_pH_qL_r{}^{(2p+q-3r)+}]/[M^{2+}]^p[H^+]^q[L^{3-}]^r$ and L denotes the unprotonated molecule of HEDTA. Protonation constants of HEDTA were determined as $\log \beta_{011}=9.20\pm0.01$, $\log \beta_{021}=14.72\pm0.01$, $\log \beta_{031}=17.06\pm0.01$, $\log \beta_{041}=18.52\pm0.01$ and $\log \beta_{051}=18.65\pm0.05$.

The complex formation reaction of Cd(II) and Pb(II) ions with polyamino-*N*-polycarboxylic acids has been quantitatively studied by many investigators, and numerous results for the formation constants of unprotonated complexes have been reported.[1)] Nevertheless, a relatively few attentions have been focused on the formation reactions of protonated complexes.

Earlier works on equilibrium studies of metal–HEDTA compounds have been described for systems of some divalent heavy metals and rare-earth elements.[2,3)] The complexes of Cd(II) and Pb(II) ions with HEDTA have also been examined by some investigators, but formation constants of protonated complexes have scarcely been reported.[2,4,5)] Although protonated complexes are expected to be present in an acidic region, most of previous experiments have only been performed in a relatively high pH region where no protonated complexes were formed.

Recently, we have studied the electrode reactions of Cd(II) and Pb(II) complexes with HEDTA and it was concluded from the d.c. polarographic behavior of the complexes in these systems that the protonated complexes MH_2L and MHL should significantly participate in the charge transfer processes.[6,7)] Therefore, it is expected that such protonated complexes are also present in the bulk of the solution. The aim of the present investigation is to search the formation of protonated complexes in these systems, and thus to carry out potentiometric measurements on complex equilibrium over a wide range of pH, especially in an acidic region.

Symbols

h	Concentration of hydrogen ion at equilibrium
m	Concentration of metal ion at equilibrium
H	Analytical excess of hydrogen ion in a test solution
$H_1{}^T$	Analytical excess of hydrogen ion in the T_1 solution
$c_B{}^T$	Hydroxide ion concentration in the T_2 solution
M	Cd(II) or Pb(II)
c_M	Total concentration of M
L	*N*-(2-Hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate anion ($hedta^{3-}$)
c_L	Total concentration of L
l	Concentration of free L
X	Degree of neutralization of H_3L: $(-H+[H]-[OH])/c_L$
p	Number of metal atoms bound to complex species
q	Number of protons bound to complex species
r	Number of ligands bound to complex species
β_{pqr}	Equilibrium constant for the reaction $pM+qH+rL=M_pH_qL_r$
$\bar{n}$	Average number of protons bound to one L
y_h, y_m	Activity coefficients of hydrogen and metal ions, respectively
E_g, E_m	Emf of the cells defined by the subscripts of Eqs. 1 and 2
$E_j(h,m)$	Liquid junction potential as a function of h and m
[ ]	Concentration

All charges are omitted for the sake of convenience.

Experimental

Reagents. N-*(2-Hydroxyethyl)ethylenediamine*-N,N′,N′-*triacetic acid* was purchased from Dojindo Laboratories, recrystallized from distilled water and dried under a reduced pressure in a desiccator over silica gel. Found: C, 43.41%; H, 6.74%; N, 10.16%; O, 39.78%. Calcd for $C_{10}H_{18}N_2O_7$: C, 43.17%; H, 6.52%; N, 10.07%; O, 40.25%.

Cadmium(II) perchlorate was prepared by dissolving CdO (99.99%, Mitsuwa Pure Chemicals Co.) in a $HClO_4$ solution and was purified by recrystallizing twice from water. The stock solution contained a small amount of perchloric acid to prevent the hydrolysis of cadmium ion. The concentration of cadmium ion in the stock solution was determined by electrogravimetry. The concentration of excess $HClO_4$ in the solution was determined from the location of the end point of neutralization by means of a Gran-plot.

Lead(II) perchlorate was prepared by dissolving $PbCO_3$ in $HClO_4$ solution and purified by recrystallizing twice from water. The concentration of lead(II) ion in the stock solution was determined by electrogravimetry as PbO_2.

Sodium perchlorate was prepared according to Biedermann and Civatta.[8)]

Sodium hydroxide solution was prepared by electrolysis of sodium perchlorate solution. A 1.0 M sodium perchlorate solution was taken in a polyethylene bottle and electrolyzed at about 4 mA cm^{-2} with platinum foil electrodes. The concentration of hydroxide ion was determined by titrating the stock solution with a standard perchloric acid using a bromcresol green-methyl red mixed indicator.

Perchloric acid solution was used without further purification of $HClO_4$ (E. Merck Co., reagent grade). The concentration of hydrogen ion in the stock solution was determined by means of titration with a standard $KHCO_3$ solution using the same mixed indicator as described above. The total concentration of ClO_4^- in the $HClO_4$ solution was adjusted to 1.0 M by the addition of some $NaClO_4$ crystals.

Potassium hydrogen carbonate was prepared by recrystallizing $KHCO_3$ (reagent grade) twice from water and kept in a vessel filled with CO_2 gas.

Silver perchlorate solution used for preparation of Ag–AgCl electrodes was prepared from $HClO_4$ and Ag_2CO_3, the latter being precipitated from $AgNO_3$ solution with Na_2CO_3 and then thoroughly decanted.

Cadmium- and lead-amalgams were prepared by electrolysis of cadmium(II) perchlorate and lead(II) nitrate solution respectively, with a Metrohm E211A type coulometer. The metal content of the amalgams was about 3% (weight). Before each experiment, the tap in the amalgam delivery line was opened to supply the amalgam and an appropriate amount of the amalgam was then transferred to a separate glass tube of the J-shape. This J-type amalgam electrode was originally described by Holloway and Reilley[4] and used with slight modification. Oxidation of the amalgam was avoided by preparing and storing it in an atmosphere of nitrogen.

The measurements were performed in a paraffin-oil thermostat at 25.00±0.02 °C, which was kept in a room thermostated at 25.0±1.0 °C.

Apparatus. *Glass electrodes* (Beckman Nos. 40495 and 40498) were used.

A silver–silver chloride electrode was made according to Brown.[9] The half-cell of the "Kawai" type[10] was set for emf measurements.

A digital pH/mV meter (Orion Research, Model 801) was used for pH measurements. Potentials at each point of measurements were determined with an accuracy of±0.1 mV.

A digital voltmeter (Takeda Riken, Model TR-6656) was used for measurements of potentials of the amalgam electrodes. The potentials were determined with an accuracy of ±0.01 mV.

The titration vessel was set with a glass electrode, an amalgam electrode, an Ag–AgCl reference electrode, burets, and glass tubes for nitrogen gas inlet and outlet. Nitrogen gas was freed from O_2 and CO_2 by passing through bottles containing 10% NaOH, 10% H_2SO_4–VSO_4–Zn–amalgam and 1.0 M $NaClO_4$ solutions. The titration vessel and burets were filled with nitrogen gas before the test and titrating solutions were introduced. A stream of nitrogen gas was passed through the test solution during the course of the titration.

Methods of emf Measurements. The concentrations of hydrogen and metal (II) ions were measured with the following cell:

Indicator Electrode	Test Solution	1.00 M $NaClO_4$ aqueous solution	0.01 M $AgClO_4$ 0.99 M $NaClO_4$ aqueous solution	AgCl-Ag

where the glass or amalgam electrode was used as the indicator electrode. The emf at equilibrium can be written by the following equation at 25 °C:

$$E_g = E_g^{\circ\prime} + 59.16 \log h + 59.16 \log y_h + E_j(h, m) \quad (1)$$

$$E_m = E_m^{\circ\prime} + 29.58 \log m + 29.58 \log y_m + E_j(h, m) \quad (2)$$

where $E_g^{\circ\prime}$ and $E_m^{\circ\prime}$ are constants.

In a constant ionic medium, y_h and y_m may reasonably be assumed to be constant. The liquid junction potential $E_j(h,m)$ which is given as a function of the concentrations of hydrogen and metal ions may be independent of m, as long as the concentration of metal ion is low. Under the present experimental conditions Eqs. 1 and 2 may be rewritten, respectively, as

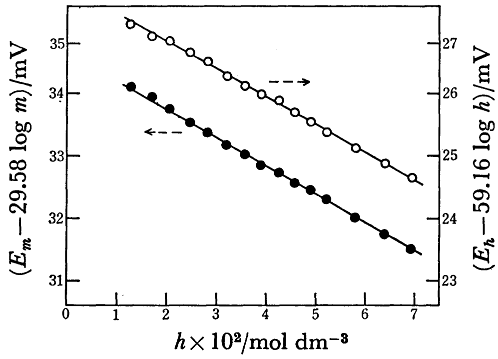

Fig. 1. Plots of $E_g-59.16 \log h$, (○), and $E_m-29.58 \log m$, (●), against h in 1.0 M (Na, H) ClO_4.

$$E_g = E_g^{\circ} + 59.16 \log h + E_j(h) \quad (3)$$

$$E_m = E_m^{\circ} + 29.58 \log m + E_j(h) \quad (4)$$

where $E_g^{\circ}=E_g^{\circ\prime}+59.16 \log y_h$ and $E_m^{\circ}=E_m^{\circ\prime}+29.58 \log y_m$. Equations 3 and 4 are transformed to

$$E_g - 59.16 \log h = E_j(h) + E_g^{\circ} \quad (5)$$

$$E_m - 29.58 \log m = E_j(h) + E_m^{\circ} \quad (6)$$

The values of $E_j(h)$, E_g° and E_m° were experimentally determined before each titration. $E_j(h)$ was estimated to be $-45\,h$ mV/mol dm^{-3}, as seen in Fig. 1, independent of the indicator electrodes used. Substituting the value of $E_j(h)$ thus obtained into Eqs. 3 and 4, the values of E_g° and E_m° were determined by means of Gran-plots. After the determination of E_g° and E_m° of the electrodes in a given solution, a suitable amount of HEDTA was added to allow to form complexes in the test solution, which has the following composition:

$$|c_M\, Cd^{2+} \text{ or } Pb^{2+},\ c_L\, \text{HEDTA},\ H H^+,$$
$$(1.0 - 2c_M - H)\ NaClO_4| \quad (7)$$

During the course of the potentiometric titrations, equal volumes of T_1 and T_2 solutions,

$$T_1 = 2c_M\, Cd^{2+} \text{ or } Pb^{2+},\ 2c_L\, \text{HEDTA},\ H_1^T H^+,$$
$$(1.0 - 4c_M - H_1^T)\ NaClO_4$$
$$T_2 = c_B^T\, OH^-,\ (1.0 - c_B^T)\ NaClO_4$$

were added into the test solution in order to keep constant the total concentrations of the metal ion c_M and the ligand c_L during the titration. The total concentration of perchlorate ion was also kept constant, 1.0 M. The values of h and m were obtained by using Eqs. 3 and 4, successive approximations being employed.

An emf of the amalgam electrode required about 5 min to attain a constant value after the addition of the titrants, while an emf of the glass electrode became constant within a few minutes. The potentials remained unchanged for several hours. The emf's of the amalgam electrode were determined within an accuracy of ±0.02 mV at $-\log h$ below 3.0, but at $-\log h$ above 3.5 the emf's became unstable so that the results obtained by the amalgam electrode were rather unreliable.

Results and Discussion

Evaluation of Protonation Constans of HEDTA. Overall protonation constants of the HEDTA base, β_{0q1}, were determined from the formation function $\bar{n}$. A generalized least squares method was applied to make the error squares sum $U=\sum(\bar{n}-\bar{n}_{\text{calc}})^2$ a minimum for the set of overall acid association (protonation) constants,

β_{011}, β_{021}, β_{031}, β_{041} and β_{051}. The calculation was performed with the help of an electronic computer HITAC 8700 at the Computer Center of the Tokyo Institute of Technology. $\bar{n}_{\rm calc}$ and $\bar{n}$ denote

$$\bar{n}_{\rm calc} = \frac{(\beta_{011}h+2\beta_{021}h^2+3\beta_{031}h^3+4\beta_{041}h^4+5\beta_{051}h^5)}{(1+\beta_{011}h+\beta_{021}h^2+\beta_{031}h^3+\beta_{041}h^4+\beta_{051}h^5)} \qquad (8)$$

and

$$\bar{n} = \frac{3c_{\rm L} + H - h + (K_{\rm W}/h)}{c_{\rm L}} \qquad (9)$$

where $K_{\rm W}$ is the autoprotolysis constant of water in 1 M $NaClO_4$ solution: $10^{-13.95}$.[11] The protonation constants thus obtained were $\log \beta_{011}=9.20\pm0.01$, $\log \beta_{021}=14.72\pm0.01$, $\log \beta_{031}=17.06\pm0.01$, $\log \beta_{041}=18.52\pm0.01$ and $\log \beta_{051}=18.65\pm0.05$. Bhat *et al.*[12] reported the values of $\log \beta_{011}=8.65$, $\log \beta_{021}=13.76$ and $\log \beta_{031}=16.06$ in a 1.0 M $NaClO_4$ medium at 25 °C but not those of $\log \beta_{041}$ and $\log \beta_{051}$.

Determination of the Composition and the Stability Constants of Complexes. Titration curves of the Cd(II)- and Pb(II)-HEDTA solutions are shown in Figs. 2 and 3.

From the material balance for the metal ion, we obtained Eq. 10:

$$c_{\rm M} = [{\rm M}] + \sum_p\sum_q\sum_r p\,[{\rm M}_p{\rm H}_q{\rm L}_r]$$
$$= m + \sum_p\sum_q\sum_r p\beta_{pqr}m^p h^q l^r \qquad (10)$$

The summation may include hydrolyzed species of the metal ion and the metal complexes ($q<0$).

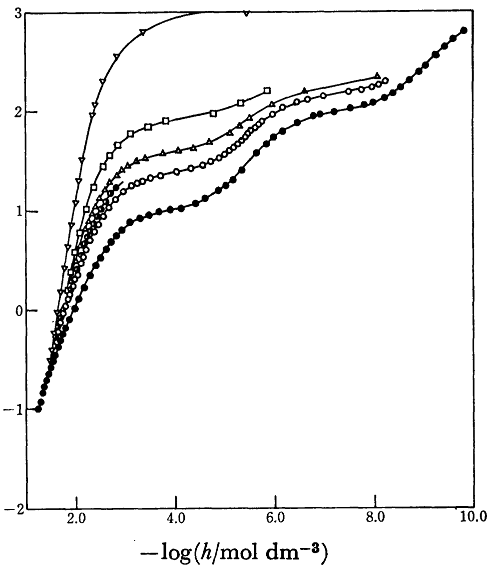

Fig. 2. Degrees of neutralization, X, of *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetic acid (HEDTA) solutions for the Cd(II)–HEDTA system.
(●); $c_{\rm M}=0.0$ M, $c_{\rm L}=0.01351$ M:
(○); $c_{\rm M}=0.002701$ M, $c_{\rm L}=0.01252$ M:
(◑); $c_{\rm M}=0.003440$ M*, $c_{\rm L}=0.012771$ M*:
(△); $c_{\rm M}=0.002699$ M, $c_{\rm L}=0.007508$ M:
(□); $c_{\rm M}=0.002564$ M, $c_{\rm L}=0.005000$ M:
(▽); $c_{\rm M}=0.007508$ M, $c_{\rm L}=0.007579$ M.
Solid lines are the values of X calculated by the use of the stability constants in Table 1. *$c_{\rm M}$ and $c_{\rm L}$ are the initial concentrations of the metal and the ligand, and $c_{\rm M}$ and $c_{\rm L}$ are slightly changed during the course of titration by the addition of the titrants.

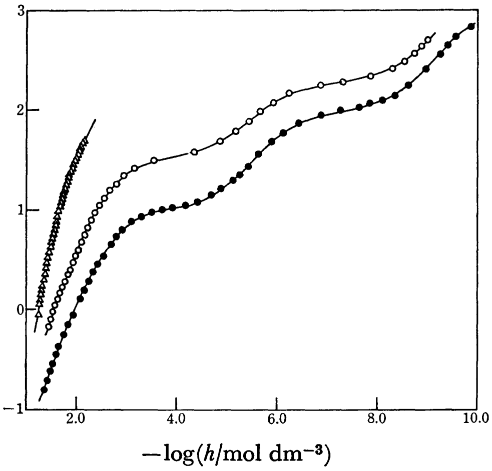

Fig. 3. Degrees of neutralization, X, of HEDTA solutions for the Pb(II)–HEDTA system.
(●); $c_{\rm M}=0.0$ M, $c_{\rm L}=0.007050$ M:
(○); $c_{\rm M}=0.002650$ M, $c_{\rm L}=0.01008$ M:
(△); $c_{\rm M}=0.01007$ M, $c_{\rm L}=0.01523$ M.
Solid lines are the values of X calculated by the use of the stability constants in Table 1.

Thus, we derive Eqs. 11 and 12:

$$\eta = \log\,(c_{\rm M}/m) = \log\{1 + \sum_p\sum_q\sum_r p\beta_{pqr}m^{p-1}h^q l^r\} \qquad (11)$$

and

$$\xi = \log\{(c_{\rm M} - m)/m\} = \log\{\sum_p\sum_q\sum_r p[{\rm M}_p{\rm H}_q{\rm L}_r]/[{\rm M}]\}$$
$$= \log\{\sum_p\sum_q\sum_r p\beta_{pqr}m^{p-1}h^q l^r\} \qquad (12)$$

The quantity η is a measure of the degree of complexation of the metal ion and $\eta>0$ at $-\log h>1.5$ (see Fig. 4). This fact shows that the complexes between the metal ions and HEDTA are formed even in an acid solution of minimum pH examined in this experiment.

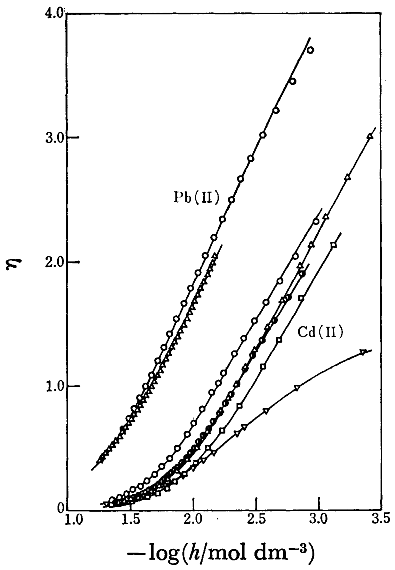

Fig. 4. Relationships between η and $-\log h$ for the Cd(II) and Pb(II) systems.
Symbols are the same as those in Figs. 2 and 3.
Solid lines are curves calculated by the use of the stability constants in Table 1.

As the first approach for analyzing data, we assume that only one kind of the complex $M_pH_qL_r$ is formed in the solution. Thus, Eq. 12 may be simplified as follows:

$$\xi = \log p\beta_{pqr} + (p-1)\log m + q\log h + r\log l \qquad (13)$$

Since $c_M < c_L$ in most cases and the degree of complexation is rather small in a relatively low and narrow pH range, we can assume that l is proportional to c_L at a constant pH and inversely proportional to h^n at a given c_L; that is,

$$c_L \simeq l + \sum_{n=1}^{N}\beta_{0n1}lh^n \qquad (14)$$

$$l \simeq c_L/(1+\sum_{n=1}^{N}\beta_{0n1}h^n) \simeq c_L/\beta_{0n1}h^n \qquad (15)$$

From the knowledge of the association constants of the HEDTA molecules with protons, we know that most of the ligand molecules are present in the form of H_3L and H_2L^- and partially H_4L^+ in the pH range of 1.5 to 3. Therefore, the value of n may become 2—3 and may slightly change with pH. However, the assumption of an averaged constant value of n over this pH range may not introduce a serious error in the following argument at the stage of the first approximation.

Substitution of Eq. 15 into Eq. 13 leads to Eq. 16:

$$\xi \simeq \log p\beta_{pqr} + (p-1)\log m + (q-n)\log h + r\log c_L - \log\beta_{0n1} \qquad (16)$$

The plots ($\xi - \log c_L$) *vs.* $-\log h$ are shown for the Cd(II)-system in Fig. 5. Points obtained at different c_L fell on an approximately single curve and the points were practically independent of c_M except for the case where $c_M = c_L$ and $-\log h > 2$. Thus, we conclude that the main species formed in this pH range has the composition of $p=1$ and $r=1$, and thus MH_qL. The slope of the line corresponds to $-(q-n)$ according to the above consideration, and we have found from Fig. 5 that the slope is about 2. Since $n=2\sim3$, q would become 0—1. Therefore, we can estimate the composition of the main species to be MHL and/or ML in the pH range discussed.

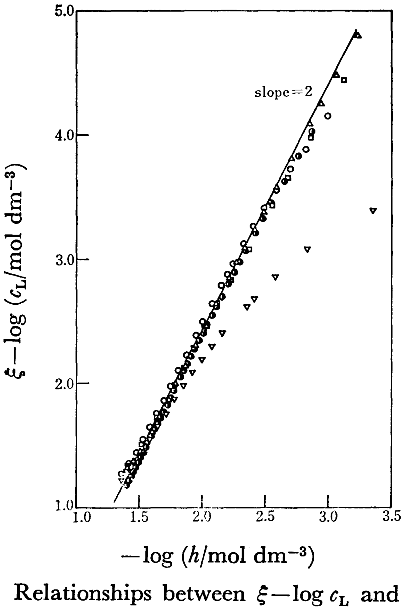

Fig. 5. Relationships between $\xi - \log c_L$ and $-\log h$ for the Cd(II)–HEDTA system.

The estimation for the compositions of the complexes formed in the solution may be made more quantitatively than in the above treatment, if the formation of mononuclear and monoligand complexes with various numbers of protons is assumed.

From the assumption, we obtained the following relationships:

$$c_M = m + \sum_{q=0}^{Q}[MH_qL] \qquad (17)$$

$$c_L = l + \sum_{n=1}^{N}[H_nL] + \sum_{q=0}^{Q}[MH_qL] \qquad (18)$$

Insertion of Eq. 17 into Eq. 18 and rearrangement lead to Eq. 19:

$$l = (c_L - c_M + m)/(1+\sum_{n=1}^{N}\beta_{0n1}h^n) \qquad (19)$$

A function F_0 is defined as follows:

$$F_0 = (c_M - m)/ml = \sum_{q=0}^{Q}[MH_qL]/ml = \sum_{q=0}^{Q}\beta_{1q1}h^q \qquad (20)$$

The plot of $\log F_0$ against $-\log h$ is shown in Fig. 6 for both systems of Cd(II)- and Pb(II)-HEDTA. In each system a single curve was obtained and the curve was independent of c_M, c_L and c_M/c_L. Therefore, the assumption of the formation of a series of MH_qL complexes is confirmed to be reasonable.

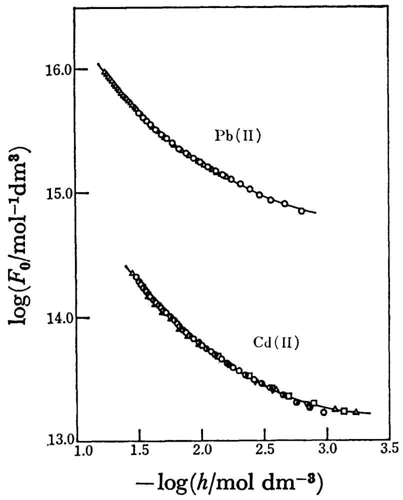

Fig. 6. Plot of $\log F_0$ against $-\log h$ for both systems. Each solid line is the curve calculated with the values of the stability constants in Table 1.

The plot of F_0 against h was extrapolated toward $h=0$ to give an intercept corresponding to β_{101}.

A new function

$$F_1 = (F_0 - \beta_{101})/h = \sum_{q=1}^{Q}\beta_{1q1}h^{q-1} \qquad (21)$$

was plotted against h and then extrapolated toward $h=0$ in order to obtain β_{111}. The procedure was repeated until a horizontal line was obtained. The sets of the plots carried out to obtain β_{1q1} are shown in Figs. 7 and 8 for the Cd(II) and Pb(II) systems, respectively. The values of β_{1q1} thus found are given for the Cd(II)–HEDTA complexes as follows:

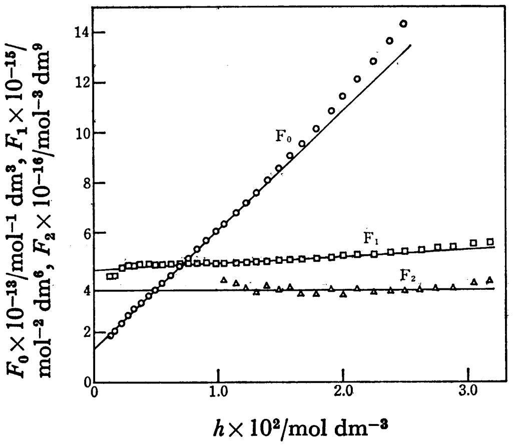

Fig. 7. A typical set of the plot of F_q *vs.* h in the system of Cd(II)-HEDTA complexes (c_M=0.002873 M, c_L= 0.01021 M). (○): F_0; (□): F_1; (△): F_2.

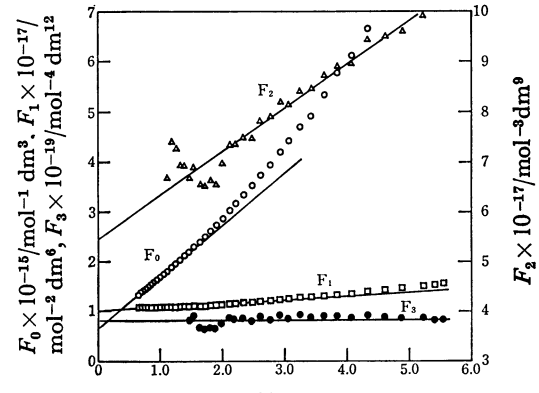

Fig. 8. A typical set of the plot of F_q *vs.* h in the system of Pb(II)-HEDTA complexes (c_M=0.01007 M, c_L= 0.01523 M). (○): F_0; (□): F_1; (△): F_2; (●): F_3.

$$\beta_{101} = 1.5\times10^{13}\,\text{mol}^{-1}\,\text{dm}^3$$
$$\beta_{111} = 4.4\times10^{15}\,\text{mol}^{-2}\,\text{dm}^6$$
$$\beta_{121} = 3.7\times10^{16}\,\text{mol}^{-3}\,\text{dm}^9$$

and for the Pb(II)-HEDTA complexes

$$\beta_{101} = 6.7\times10^{14}\,\text{mol}^{-1}\,\text{dm}^3$$
$$\beta_{111} = 1.0\times10^{17}\,\text{mol}^{-2}\,\text{dm}^6$$
$$\beta_{121} = 5.5\times10^{17}\,\text{mol}^{-3}\,\text{dm}^9$$
$$\beta_{131} = 8.0\times10^{18}\,\text{mol}^{-4}\,\text{dm}^{12}$$

The formation constants of the complexes were refined by means of a generalized least squares method. The method was applied to make the error squares sum $U=\sum\{\log F_0-\log F_{0,\text{calcd}}\}^2$ minimum for the set of the formation constants over the pH range 1.5 to 3, where $F_{0,\text{calcd}}$ denotes the value of F_0 calculated for a particular set of the formation constants. The formation constants thus determined are given in Table 1.

Since the metal amalgam electrode did not function well at a high pH range, data of X obtained in the high pH range were not analyzed by the extrapolation method described above. However, the constants reproduced the experimental results fairly well as seen from Figs. 2 and 3, and no polynuclear, polyligand and hydrolyzed species are formed.

Table 1. Stability constants of Cd(II)- and Pb(II)-HEDTA complexes (log β_{pqr})

log β_{011}=9.20±0.01, log β_{021}=14.72±0.01, log β_{031}= 17.06±0.01, log β_{041}=18.52±0.01, log β_{051}=18.65±0.05

Complexes	ML^-	MHL^0	MH_2L^+	MH_3L^{2+}
Cd(II)	13.21±0.04	15.61±0.02	16.68±0.04	—
Pb(II)	14.83±0.02	16.97±0.02	17.89±0.02	18.67±0.02

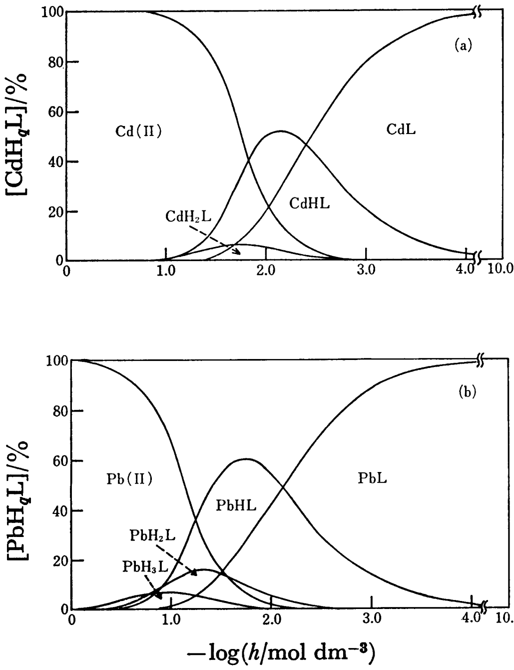

Fig. 9. The distribution of metal-HEDTA complexes *vs.* −log h (c_M=0.001M, c_L=0.01M).
(a): for the Cd(II)-HEDTA system. (b): for the Pb(II)-HEDTA system.

The distributions of the Cd(II)- and Pb(II)-HEDTA complexes are graphically represented in Fig. 9.

The Pb(II)-HEDTA complexes are stronger by 1—1.5 in log β unit than the corresponding Cd(II)-HEDTA complexes, like in other cases of the complexes of these metals with ligands containing oxygen or oxygen and nitrogen as the ligating atoms. Lead(II) ion forms the PbH_3L complex at a high concentration of hydrogen ion, whereas cadmium(II) ion does not.

The stepwise association constants of the complexes with protons are log K_H^{MHL}=log {[MHL]/[ML][H]}= 2.40 and log $K_H^{MH_2L}$=log {[MH_2L]/[MHL][H]}=1.07 for the Cd(II)-HEDTA complexes and log K_H^{MHL}= 2.13, log $K_H^{MH_2L}$=0.92 and log $K_H^{MH_3L}$=0.78 for the Pb(II)-HEDTA complexes. The association constants may be compared with the corresponding values of the ligand; log $K_H^{H_3L}$=log $(\beta_{031}/\beta_{021})$=log {[$H_3L$]/ [$H_2L$][H]}=2.34, log $K_H^{H_4L}$=log $(\beta_{041}/\beta_{031})$=1.46 and log $K_H^{H_5L}$=log $(\beta_{051}/\beta_{041})$=0.13.

The authors wish to thank Dr. Takayoshi Kawai for his kind help in potentiometric measurements.

References

1) L. G. Sillén and A. E. Martell, "Stability Constants," Chemical Society, London (1964), Supplement No. 1, (1971).

2) S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 1477 (1955).

3) F. H. Spedding, J. E. Powell, and E. J. Wheelwright, *J. Am. Chem. Soc.*, **78**, 34 (1956).

4) J. H. Holloway and E. N. Reilley, *Anal. Chem.*, **32**, 249 (1960).

5) M. Kodama, K. Namekawa, and T. Horiuchi, *Bull. Chem. Soc. Jpn.*, **47**, 2011 (1974).

6) N. Oyama and H. Matsuda, *J. Electroanal. Chem.*, in press.

7) N. Oyama, T. Shirato, and H. Matsuda, *J. Electroanal. Chem.*, in press.

8) G. Biedermann and L. Civatta, *Acta Chem. Scand.*, **15**, 1347 (1961).

9) A. S. Brown, *J. Am. Chem. Soc.*, **56**, 646 (1934).

10) H. Tsukuda, T. Kawai, M. Maeda, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **48**, 691 (1975).

11) G. Anderegg, *Helv. Chim. Acta*, **50**, 2333 (1967).

12) T. R. Bhat, R. K. Iyer, and J. Schankar, *Z. Anorg. Chem.*, **343**, 329 (1966).