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Potentiometric Study on the Complex Formation of Cobalt(II) Ion with Ethylenediamine-*N*-acetic Acid, Diethylenetriamine, and Iminodiacetic Acid

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The formation constants of Co(II)-ethylenediamine-*N*-acetate (edma), -diethylenetriamine (dien) and -iminodiacetate (ida) complexes were determined by potentiometric titration in 1.0 M $NaClO_4$ solution at 25 °C. The following results were obtained. Edma: $\log \beta_{101}=7.51$, $\log \beta_{102}=14.05$; dien: $\log \beta_{101}=9.34$, $\log \beta_{102}=16.89$; ida: $\log \beta_{101}=6.54$, $\log \beta_{102}=11.95$, β_{pqr} being the overall formation constant defined in the text. The relative effects of amino and carboxyl groups on the affinity of ligands to Co(II) ion are discussed.

Ethylenediamine-*N*-acetic acid (edma) is a simple, artificial and basic amino acid in products formed during the carboxymethylation of ethylenediamine;[1] Nevertheless, only a few papers have appeared on the complex formation equilibria between metal ions and edma$^-$ anion, in contrast to those of ethylenediaminetetraacetic acid (EDTA). Fujii *et al.*[2-6] have prepared this ligand by a new, simple method and studied the complex formation with Cd(II), Pb(II), Cu(II), and Tl(I) ions by d.c. polarography and with Ni(II) by spectrophotometry. Oyama *et al.*[7] reexamined the Cd(II)-edma system in detail by means of potentiometric titration as well as the d.c. polarographic method. However, no data of complex formation equilibria between Co(II) ion and edma$^-$ anion seem to have been reported.

We have examined the electrode kinetics of the redox couples of Co(II)/Co(III) complexes with tridentate ligands which contain nitrogen and/or oxygen as coordinating atoms, *e.g.*, edma, diethylenetriamine (dien), iminodiacetate (ida). For analysis of electrode kinetics, it is necessary to obtain the equilibrium data of Co(II)-edma, -dien, and -ida complexes under the same conditions as for the examination of electrode kinetics. We have determined the stepwise formation constants of (a) Co(II)-edma, (b) -dien, and (c) -ida complexes in 1.0 M (1 M=1 mol dm^{-3}) $NaClO_4$ solution by potentiometric titration. The formation constants of (b) and (c) for different solution compositions have been reported.[8-10] On the basis of the formation constants, relative effects of amino and acetate groups on the affinity of ligands to Co(II) ion are discussed.

Symbols

h	Concentration of hydrogen ion at equilibrium
c_{Co}	Total concentration of Co(II) ion
L	Ligand (edma$^-$, dien or ida^{2-})
c_L	Total concentration of L
l	Concentration of free ligand
X	Degree of neutralization of ligand, defined by $(-H+h-K_w/h)/c_L$, where H denotes the analytical excess of hydrogen ion in a test solution and K_w the autoprotolysis constant of water in 1.0 M $NaClO_4$ solution ($10^{-13.95}$ mol^2 dm^{-6})[11]
$\bar{n}$	Average number of protons bound to one L
$\bar{Z}$	Average number of ligand anions bound to one Co(II) ion
β_{pqr}	Equilibrium constant for the reaction: $p\mathrm{Co}^{2+}+q\mathrm{H}^{+}+r\mathrm{L}^{a-}=\mathrm{Co}_p\mathrm{H}_q\mathrm{L}_r^{(2p+q-ra)+}$

Experimental

Reagents. *Cobalt(II) perchlorate* was purified by recrystallizing $Co(ClO_4)_2$ three times, which was prepared from $HClO_4$ and $CoCO_3$, the latter being precipitated from $Co(NO_3)_2$ solution with Na_2CO_3 and then thoroughly decanted. The stock solution contained a small amount of $HClO_4$ to prevent the hydrolysis of Co(II) ion, where the amount of excess $HClO_4$ was determined from the location of end point of neutralization by means of a Gran-plot. The concentration of Co(II) ion in the stock solution was determined by EDTA titration using a murexide indicator. *Diethylenetriamine* was vacuumdistilled twice at ca. 59 °C. *Iminodiacetic acid* was purified by recrystallization twice from water. All other chemicals used were prepared and purified by the method described previously.[7,12]

Potentiometric Measurements. The measurements were performed in a paraffin oil thermostat at 25.00±0.02 °C with use of a glass electrode. Sodium perchlorate was used as an indifferent salt to keep the perchlorate concentration at 1.0 mol dm^{-3} in all runs. The titration vessel and burets were filled with Ar gas before the test, solutions being then introduced. The solutions were deaerated with Ar gas, a vigorous stream of Ar gas being passed through the solution during the course of titration. The Ar gas was freed from O_2 by being passed through hot activated copper and then led through three washing bottles filled with 10% NaOH, 10% $HClO_4$ and 1.0 M $NaClO_4$ solutions, respectively. The apparatus and experimental procedure for potentiometric titration were reported.[12]

Results and Discussion

Evaluation of Protonation Constants of Ligands. The potentiometric titration curves of the Hedma, dien and H_2ida solutions are given in Figs. 1, 2, and 3, respec-

Table 1. Protonation constants of edma, dien, and ida bases in 1.0 M $NaClO_4$ solution at 25 °C

Base	$\log \beta_{011}$	$\log \beta_{021}$	$\log \beta_{031}$
edma	9.97±0.02	16.71±0.02	18.76±0.02
dien	10.76±0.02	20.56±0.02	25.40±0.02
ida	9.05±0.02	11.60±0.02	13.58±0.02

tively. Overall protonation constants of these ligand bases, β_{0q1}, were determined from the formation function, $\bar{n}$, by means of the generalized least squares method.[12] The results are given in Table 1. The values for the edma base are the same as obtained previously.[7] For the dien base Evtimova *et al.*[13] obtained the values log $\beta_{011}=10.03$, log $\beta_{021}=19.39$, and log $\beta_{031}=24.26$ in 1 M NH_4NO_3 solution at 25 °C. Grenthe and Gardhammar[14] obtained log $\beta_{011}=9.32$, log $\beta_{021}=11.89$ and log $\beta_{031}=13.77$ for the ida base under the same experimental conditions as in the present work.

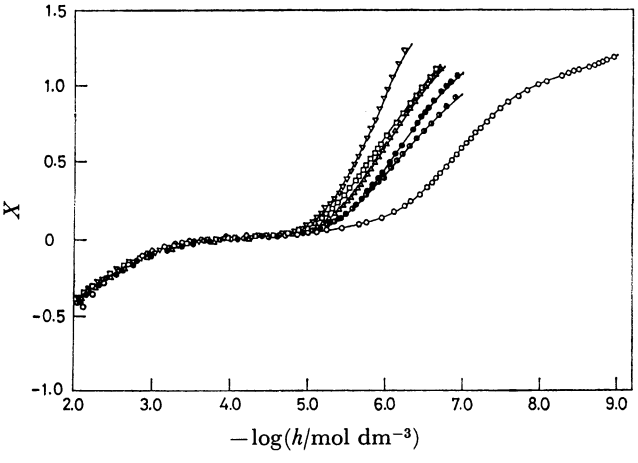

Fig. 1. Degree of neutralization, X, of edma solutions for the Co(II)–edma system.
(○): $c_{Co}=0.0$ mol dm^{-3}, $c_L=0.002200$ mol dm^{-3},
(▽): $c_{Co}=0.004381$ mol dm^{-3}, $c_L=0.008462$ mol dm^{-3},
(□): $c_{Co}=0.004504$ mol dm^{-3}, $c_L=0.01979$ mol dm^{-3},
(△): $c_{Co}=0.003079$ mol dm^{-3}, $c_L=0.01355$ mol dm^{-3},
(●): $c_{Co}=0.001503$ mol dm^{-3}, $c_L=0.008135$ mol dm^{-3},
(◑): $c_{Co}=0.001852$ mol dm^{-3}, $c_L=0.01360$ mol dm^{-3}.
Solid lines are the values of X calulated by the use of the for mation constants given in Table 2.

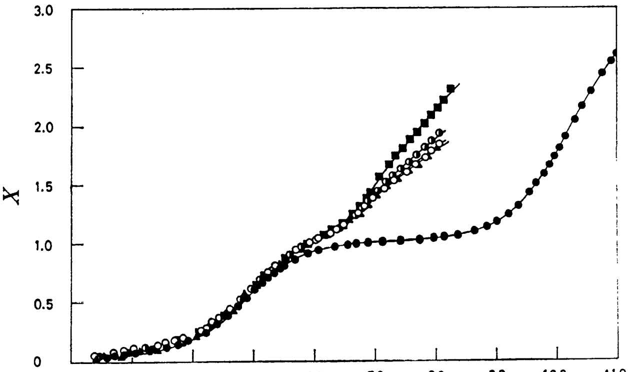

Fig. 2. Degree of neutralization, X, of dien solutions for the Co(II)–dien system.
(●): $c_{Co}=0.0$ mol dm^{-3}, $c_L=0.02000$ mol dm^{-3},
(■): $c_{Co}=0.003639$ mol dm^{-3}, $c_L=0.01086$ mol dm^{-3},
(◑): $c_{Co}=0.002898$ mol dm^{-3}, $c_L=0.01165$ mol dm^{-3},
(○): $c_{Co}=0.003139$ mol dm^{-3}, $c_L=0.01581$ mol dm^{-3},
(▲): $c_{Co}=0.002388$ mol dm^{-3}, $c_L=0.01259$ mol dm^{-3}.
Solid lines are the values of X calculated by the use of the formation constants given in Table 2.

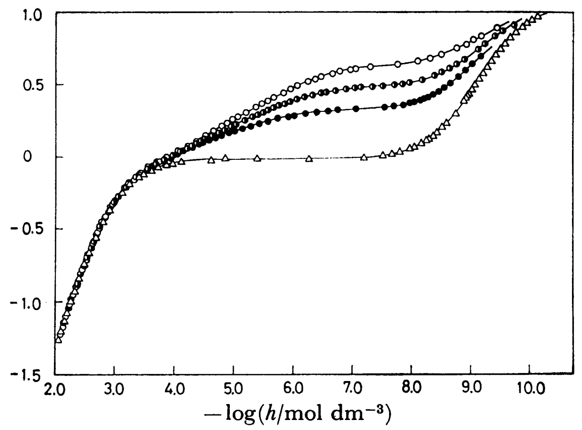

Fig. 3. Degree of neutralization, X, of ida solutions for the Co(II)–ida system.
(△): $c_{Co}=0.0$ mol dm^{-3}, $c_L=0.01004$ mol dm^{-3},
(○): $c_{Co}=0.002945$ mol dm^{-3}, $c_L=0.008965$ mol dm^{-3},
(◑): $c_{Co}=0.002990$ mol dm^{-3}, $c_L=0.01193$ mol dm^{-3},
(●): $c_{Co}=0.003051$ mol dm^{-3}, $c_L=0.01791$ mol dm^{-3}.
Solid lines are the values of X calculated by the use of the formation constants given in Table 2.

We see that the third protonation constant of edma, log $(\beta_{031}/\beta_{021})=2.05$, is almost equal to the average value of the second and third ones of ida, log $(\beta_{021}/\beta_{011})=2.57$ and log $(\beta_{031}/\beta_{021})=1.88$, indicating that these constants correspond to protonation of the carboxyl group. The carboxyl group bound to the imino group of edma and ida is acidic to a greater extent than the acetate (log $\beta_{011}=4.6$).

Determination of the Composition and Formation Constants of the Complexes. Titration curves for the Co(II)–edma, –dien, and –ida solutions are shown in Figs. 1, 2, and 3, respectively. The experiments were performed with the c_L/c_{Co} ratio in the range 2—7, c_{Co} and c_L being varied from 1.5 to 4.5 mmol dm^{-3} and from 8 to 27 mmol dm^{-3}, respectively. In high pH regions above pH 7.5 for the edma system and above pH 8.5 for the dien system, the potential of glass electrode becomes unstable. Thus measured points corresponding to such pH regions are not given in the figures. The instability of glass electrode might result from the interaction of Co(II)L_2 with a very small amount of oxygen remaining in the solutions. Miller *et al.*[15] reported that for Co(II)–dien complexes this interaction may occur even at oxygen concentration below 10^{-8} mol dm^{-3}.

In the pH range 2—5 the values of X for edma system are independent of c_{Co} and c_L, no proton being released from the ligand by complex formation (Fig. 1). On the other hand, above pH 5 the titration curves of solution containing Co(II) ion deviate from that of solution containing only the ligand, indicating that some protons are released from the ligand by the complex formation. As a first approximation for analyzing data we assumed that neither protonated nor polynuclear species are formed, since this was found to be the case for the Cd(II)–edma system.[7] The concentration of the free ligand l and the complex formation function $\bar{Z}$ can be expressed by Eqs. 8 and 9 of Ref. 7, respectively. The plot of $\bar{Z}$ *vs.* log l is shown by curve II in

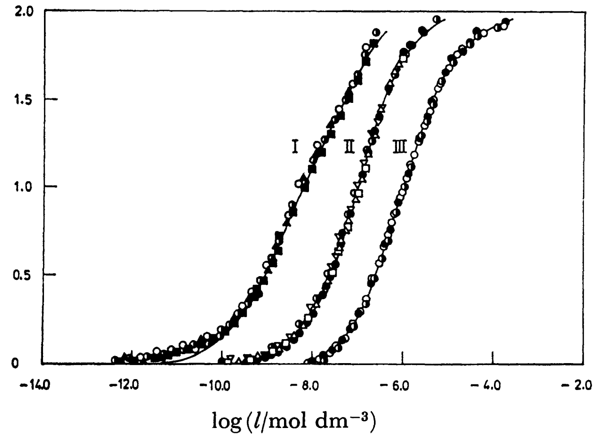

Fig. 4. Relationships between the complex formation function $\bar{Z}$ and log l for the Co(II)–dien, –edma, and –ida systems.
(I): Co(II)–dien, (II): Co(II)–edma, (III): Co(II)–ida. Solid lines are the best fit curves calculated by Eq. 11 of Ref. 7.

Fig. 4. We see that a single curve is obtained regardless of variation of c_L/c_{Co}, c_{Co}, and c_L, satisfying the above assumption, and also that the values of $\bar{Z}$ approach to 2 when the values of log l increase, showing that the complex species of $Co(edma)^+$ and $Co(edma)_2{}^0$ are formed in the pH range 5—7.

Similarly, for the dien and ida systems, the following conclusion may be deduced from the behavior of curves I and III (Fig. 4): the complex species of 1 to 1 and 1 to 2 compositions are formed in the pH ranges 6—8 (for dien) and 4—10 (for ida). No evidence of the formation of protonated complex species was detected for both systems, although for the dien system a slight deviation from the best fit curve (solid curve) was observed in the region $\log l = -12 - -10.5$. This suggests the formation of protonated complex species. For dien complexes, Miller *et al.*[15] postulated the formation of monoprotonated species such as Co(II)-(dien)(Hdien)$^{3+}$ for interpreting the pH dependence of the rate constant for oxygen uptake by the bis species.

The formation constants of the Co(II)–edma, –dien, and –ida complexes were evaluated by curve fitting using the generalized least squares method.[7] The results are summarized in Table 2. The solid curves in Figs. 1—4 represent the theoretical curves calculated by using these formation constants, which are seen to reproduce the experimental results.

Table 2 indicates that the first step formation constants, K_1 $(=\beta_{101})$, are somewhat larger than the second ones, K_2 $(=\beta_{201}/\beta_{101})$, and also that the coordinating ability of the ligands to Co(II) ion is reduced with increase in the number of replacement of amino group in dien by carboxyl group. Further we see that the following relation holds approximately among the successive formation constants, K_n $(n=1, 2)$:

Table 2. Formation constants of Co(II)–edma, –dien, and –ida complexes in 1.0 M $NaClO_4$ solution at 25 °C

Complex	log β_{101}	log β_{102}
Co(II)–edma	7.51±0.02	14.05±0.05
Co(II)–dien	9.34±0.02	16.89±0.05
Co(II)–ida	6.54±0.02	11.95±0.05

$$\log K_n(\text{edma}) = \frac{1}{2}[\log K_n(\text{dien}) + \log K_n(\text{ida})]. \quad (1)$$

This can be understood from the following consideration: The ligands we used are typical tridentate ones of (N,N,N)-, (N,N,O)-, and (O,N,O)-types, forming the five-membered chelate rings. Their chelate entropy effect[16] as well as steric effect on complex formation may be almost the same. If we assume that the contributions of amino, imino and carboxyl groups to the free energy change, ΔG_n°, of succesive complex formation are constitutive and additive, and denote them by ΔG_n(amino), ΔG_n(imino), and ΔG_n(carboxyl), respectively, ΔG_n° can be given by

$$\Delta G_n^\circ(\text{dien}) = \Delta G_n(\text{imino}) + 2\Delta G_n(\text{amino}) \quad (2)$$

$$\Delta G_n^\circ(\text{edma}) = \Delta G_n(\text{imino}) + \Delta G_n(\text{amino}) + \Delta G_n(\text{carboxyl}) \quad (3)$$

$$\Delta G_n^\circ(\text{ida}) = \Delta G_n(\text{imino}) + 2\Delta G_n(\text{carboxyl}). \quad (4)$$

Combining Eqs. 2—4, we obtain

$$\Delta G_n^\circ(\text{edma}) = \frac{1}{2}[\Delta G_n^\circ(\text{dien}) + \Delta G_n^\circ(\text{ida})]. \quad (5)$$

Equation 5 is identical with Eq. 1. By using the values of successive formation constants available,[8,9] we can show that Eq. 1 holds for Ni(II) and Cu(II) (only for $n=1$) complexes with dien, edma and ida, with somewhat larger deviations, partly because the conditions relevant to each measurement are not the same. A similar relation can be deduced for complexes of some divalent metal ions, such as Co(II), Ni(II), and Cu(II) ions, with the bidentate ligands containing amino and/or carboxyl groups, *e.g.*, ethylenediamine, glycinate and oxalate.[8,9]

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