Polarographic Studies of Metal Complexes. V. Ethylenediamine Complexes of Cadmium, Nickel and Zinc[*]

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Introduction

The complex salts hitherto studied by polarographic methods were mostly confined to the so-called polarographically reversible systems and there are found very few studies on the irreversible complex systems. In the previous papers¹⁾, the author reported the polarographic behaviour of the ammonia complexes of cadmium, nickel and zinc. The polarographic reductions of the ethylenediamine complexes of these metals, in 0.1 N potassium nitrate medium with various concentrations of the complexing agent, were investigated in the present paper. While the reductions of nickel and zinc were irreversible, the reduction of cadmium complex was found to be reversible, and it was possible to determine the number of coordinated ligands and the overall complex formation constant for the cadmium complex, which existed in the solution under investigation. The attempt was also made to interpret the irreversible polarographic waves with the aid of the theoretical treatment of the current-voltage curves developed recently by Matsuda and Ayabe²⁾, and the number of ligands in the complex ions which participated in the electron transfer process could be determined. The forward rate constants of the electron transfer process could also be

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[*] This paper was read at the 2nd Symposium on Polarography held on November 22, 1955 at Hiroshima University by the Chemical Society of Japan and the Electrochemical Society of Japan.

1) K. Morinaga, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **75**, 627 (1954); **76**, 133, 136 (1955).

2) H. Matsuda and Y. Ayabe, This Bulletin, **29**, 134 (1956).

calculated using the known complex formation constants.

Experimental Part

The Heyrovsky-Shikata type polarograph with the circuit for extendable and adjustable e.m.f. was employed to record the enlarged polarograms, from which the half-wave potentials were determined by the log plot method. The span voltage applied to a potentiometer-drum was selected in the range of 0.24 to 0.60 v. The H-cell with a saturated calomel electrode was used, the internal resistance of which was found to be about 400 Ω. The reproducibility of the values for the half-wave potential was ± 1 mV. for cadmium and was ± 3 mV. for nickel and zinc. The capillary used had an m value of 2.11$_9$ mg./sec. and a drop time of 4.61 sec./drop at the mercury height of 68.5 cm., in distilled water with an open circuit. All polarographic measurements were carried out in a thermostat of 25.0±0.1°C.

The solutions of cadmium, nickel and zinc sulfates, and the 1 N stock solution of potassium nitrate used as a supporting electrolyte, were all prepared from reagent grade materials. The 2 and 4 M solutions of ethylenediamine were prepared by dilution of twice distilled reagent and was standardized with hydrochloric acid using B.P.B. as an indicator. The concentration of gelatine solution which was employed as a maximum suppressor, had considerable influence on the characteristics of the reduction waves for nickel as seen below; therefore the greatest care was taken with its preparation. The electrolytic solutions were prepared by adding the stock solutions of metal sulfates, potassium nitrate, ethylenediamine and lastly a fresh solution of 0.1% gelatine in a measuring flask. Oxygen was removed from the electrolytic solution by passing nitrogen gas through it for half an hour.

Experimental Results

The Relation between E and log $(i/(i_l-i))$.—The waves were analyzed by the log plot method from the observed current i at the potential E of the dropping mercury electrode and the limiting current i_l. The reciprocal slope of cadmium waves was 31.$_6$ mV. in average, as shown in Table II, and the reduction was reversible. Two examples of the plot of E against log $(i/(i_l-i))$ are illustrated in Fig. 1. The reciprocal slope of zinc waves was found to be 34.$_2$ mV. and a little larger than the one expected for the reversible waves. For nickel waves a slight deviation from the linearity was observed, but five points which are gathered around the half-wave potential, gave a straight line, from which the reciprocal slope was estimated as a first approximation. It is probable that the deviation from the linearity may be partly due to an inappropriate concentration of gelatine, and partly due to an experimental error caused by a rather large span voltage applied to the potentiometer-drum*.

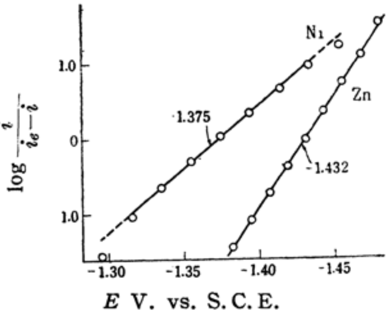

Fig. 1. Plot of E against log $(i/(i_l-i))$.
Concentration of ethylenediamine:
0.966 M for nickel and 1.05 M for zinc

The Dependence of the Limiting Currents on the Heights of Mercury Column. — The limiting currents were measured at various heights of mercury column. If the limiting current is diffusion-controlled, it should be proportional to the square root of the height of mercury column H_{corr}, corrected for the back pressure. Data given in Table I indicate that the limiting currents are determined by a diffusion process for the reductions of these complex metal ions.

TABLE I

DEPENDENCE OF LIMITING CURRENTS ON HEIGHT OF MERCURY COLUMN

		Cd		Ni		Zn	
		0.5×10^{-3} M 0.15 M en 0.01% gel.		0.6×10^{-3} M 1.15 M en 0.02% gel.		0.46×10^{-3} M 1.05 M en 0.02% gel.	
$H_{corr.}$ (cm.)	$\sqrt{H_{corr.}}$	i_l (μA)	$i_l/\sqrt{H_{corr.}}$	i_l (μA)	$i_l/\sqrt{H_{corr.}}$	i_l (μA)	$i_l/\sqrt{H_{corr.}}$
68.5	8.28	3.61	0.436	3.52	0.425	2.98	0.360
64.5	8.03	3.51	0.437	3.40	0.423	2.88	0.359
60.5	7.78	3.41	0.438	3.31	0.425	2.80	0.360
56.5	7.52	3.30	0.439	3.19	0.424	2.72	0.362

The Variation of the Half-wave Potential as a Function of the Ethylenediamine Concentration.—The characteristics of waves at various concentrations of ethylenediamine C_{en} are given in Tables II, III and IV.

The half-wave potentials for cadmium and zinc

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* The log plot of nickel wave, shown in Fig. 1, appears to give a convex curve, but this is not always the case.

were independent of the concentrations of the depolarizers, as shown in Tables II and IV, and the reciprocal slopes remained constant in the concentration range of 0.1 to 2.5 M ethylenediamine.

The same was no longer the case for nickel. The reciprocal slope decreased with the increase of concentration of ethylenediamine. Moreover, the concentration of gelatine had considerable influence on the slope and the half-wave potential. At the lower concentration of gelatine, the slope was smaller and the half-wave potential was more positive.

TABLE II

VARIATION OF $(E_{1/2})_c$ AS A FUNCTION OF ETHYLENEDIAMINE CONCENTRATION 0.1 N KNO_3, 0.01% GELATINE, $m=2.12$ mg./sec., $t=4.12$ sec./drop., $H=68.5$ cm.

C_{en} (M)	log C_{en}	Concn. of Cadmium (10^{-3} M)	$E/\log(i/(i_a-i))$ (mV.)	i_a (μA)	$-(E_{1/2})_c$ (V.vs.S.C.E.)
0		0.5	32	3.85	0.581
0.115	$\bar{1}.061$	0.5	32	3.65	0.845
0.154	$\bar{1}.187$	0.5	32	3.61	0.856
0.231	$\bar{1}.363$	0.5	$31._5$	3.59	0.873
0.308	$\bar{1}.488$	0.5	30	3.55	0.882
0.308	$\bar{1}.488$	0.2	32	1.43	0.884
0.308	$\bar{1}.488$	0.7	31	4.99	0.885
0.462	$\bar{1}.665$	0.5	32	3.51	0.902
0.616	$\bar{1}.789$	0.5	32	3.44	0.914
0.770	$\bar{1}.886$	0.5	31	3.39	0.922
0.866	$\bar{1}.937$	0.5	33	3.34	0.928
0.924	$\bar{1}.965$	0.5	31	3.30	0.930
1.15	0.061	0.5	31	3.26	0.940
1.44	0.158	0.5	33	3.15	0.950
1.79	0.253	0.5	31	3.07	0.960
2.02	0.305	0.5	31	2.94	0.967
2.31	0.363	0.5	31	2.84	0.974
2.60	0.415	0.5	32	2.75	0.980
2.89	0.460	0.5	32	2.66	0.987

TABLE III

VARIATION OF $(E_{1/2})_c$ AS A FUNCTION OF ETHYLENEDIAMINE CONCENTRATION

0.1 N KNO_3, $m=2.01$ mg./sec., $t=3.72$ sec./drop, $H=64.5$ cm.

C_{en} (M)	Concn. of Nickel (10^{-3} M)	Concn. of Gelatine (%)	$E/\log(i/i_a-i))$ (mV.)	i_a (μA)	$-(E_{1/2})_c$ (V.vs.S.C.E)
0	0.6			(4.01)	
0.146	0.6	0.013	78	3.86	1.327
0.146	0.6	0.020	90	3.77	1.351
0.219	0.6	0.020	82	3.73	1.353
0.292	0.6	0.015	72	3.77	1.342
0.292	0.6	0.016	74	3.73	1.346
0.292	0.6	0.020	80	3.69	1.355
0.365	0.6	0.020	76	3.67	1.358
0.438	0.6	0.016	70	3.69	1.353
0.438	0.6	0.020	74	3.64	1.361
0.584	0.6	0.020	70	3.60	1.365
0.730	0.6	0.020	67	3.54	1.369
0.876	0.6	0.020	63	3.50	1.373
0.966	0.6	0.020	60	3.47	1.375
0.966	0.4_3	0.020	55	2.46	1.370
0.966	0.2_4	0.020	52	1.42	1.363
1.21	0.6	0.020	59	3.37	1.381
1.45	0.6	0.020	56	3.31	1.385
1.69	0.6	0.020	54	3.20	1.391
1.93	0.6	0.020	52	3.12	1.394

TABLE IV

VARIATION OF $(E_{1/2})_c$ AS A FUNCTION OF ETHYLENEDIAMINE CONCENTRATION

0.1 N KNO_3, 0.02% Gelatine, $m=2.01$ mg./sec., $t=3.65$ sec./drop, $H=64.5$ cm.

C_{en} (M)	$\log C_{en}$	Concn. of Zinc (10^{-3} M)	$E/\log(i/(i_a-i))$ (mV.)	i_a (μA)	$-(E_{1/2})_c$ (V.vs.S.C.E.)
0		0.46		(3.39)	
0.103	$\bar{1}.013$	0.46	$34._5$	3.26	1.356
0.154	$\bar{1}.187$	0.46	$34._5$	3.18	1.370
0.231	$\bar{1}.363$	0.46	34	3.14	1.383
0.308	$\bar{1}.488$	0.46	34	3.12	1.391
0.384	$\bar{1}.585$	0.46	$34._5$	3.10	1.399
0.461	$\bar{1}.664$	0.46	34	3.09	1.404
0.615	$\bar{1}.789$	0.46	34	3.01	1.413
0.769	$\bar{1}.886$	0.46	$34._5$	2.97	1.421
0.923	$\bar{1}.965$	0.46	$34._5$	2.92	1.426
1.05	0.020	0.46	34	2.88	1.432
1.05	0.020	0.55	34	3.43	1.434
1.05	0.020	0.27	$33._5$	1.72	1.431
1.31	0.117	0.46	$34._5$	2.80	1.440
1.57	0.196	0.46	$34._5$	2.69	1.446
1.83	0.263	0.46	$34._5$	2.61	1.452
2.10	0.321	0.46	34	2.53	1.458
2.36	0.372	0.46	34	2.41	1.463
2.62	0.418	0.46	34	2.36	1.466

The Viscosities of the Electolytic Solutions. —Diffusion currents i_d in each case decreased with the increase of concentration of ethylenediamine. The viscosities of the solutions η were measured with Ostwald viscometer, taking distilled water as a standard, and the observed diffusion currents were plotted against the inverse square root of the relative viscosities. As illustrated in Fig. 2, The product of the diffusion current and the square root of the viscosity remained constant at each concentration of ethylenediamine. Thus the decrease of the diffusion current was found to be due to the increase of the viscosities of the electrolytic solutions³⁾. The extrapolated points at relative viscosity of 1 may represent the apparent diffusion currents of the complex ions, comparable to those of the simple ions. So the square roots of the apparent polarographic diffusion coefficients of these complex metal ions may be estimated to be ca. 4% less than those of the simple metal ions*.

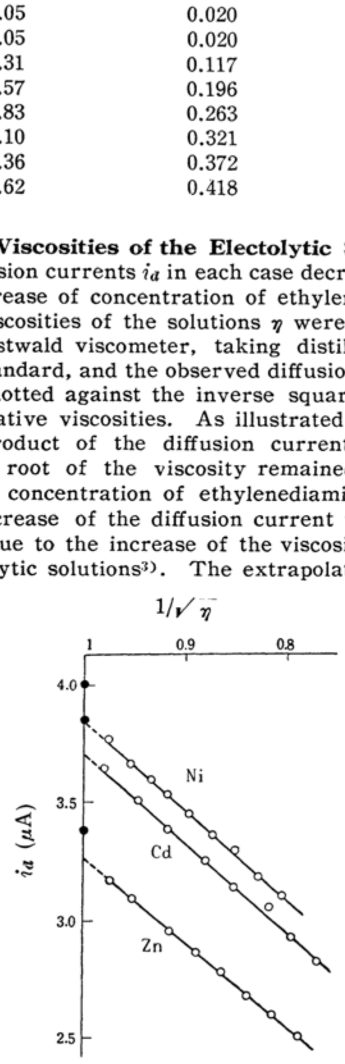

Fig. 2. Plot of i_d against $1/\sqrt{\eta}$.
The black circles represent the diffusion currents of the simple metal ions.

Discussion

Matsuda and Ayabe²⁾ have recently derived a general expression for the polarographic current-voltage curves of complex metal ions, by assuming that the net electrode reaction

$$MX_{\nu}^{(n-\nu b)+}+ne+Hg=M(Hg)+\nu X^{-b}$$

($\nu=N, N-1, \cdots\cdots, 1, 0$: N is the maximum number of ligands which can be combined)

take place according to the following scheme:

(1) dissociation and association processes

$$MX_{\nu}^{(n-\nu b)+}=MX_{\nu-1}^{[n-(\nu-1)b]+}+X^{-b}$$

$(\nu=N,\ N-1, \cdots\cdots,\ p+1)$

$$MX_{\mu-1}^{[n-(\mu-1)b]+}+X^{-b}=MX_{\mu}^{(n-\mu b)+}$$

$(\mu=p,\ p-1,\ \cdots\cdots,\ 1)$

(2) electron transfer process

$$MX_{p}^{(n-pb)+}+ne+Hg=M(Hg)+pX^{-b}$$

In the above equations M(Hg) represents the amalgam formed on the electrode surface and n is the number of electrons associated with the electrode reaction; X^{-b} represents the complexing agent and

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3) I. M. Kolthoff and J. J. Lingane. "Polarography", Vol. I, Interscience Pub., New York, London (1952), p. 97.

* Usually the presence of gelatine causes the lowering of the limiting current, so the observed limiting current in the presence of gelatine is not the true diffusion current. But, in the meaning that the limiting current is diffusion-controlled, the apparent polarographic diffusion coefficient may be estimated from the observed diffusion current.

$MX_p^{(n-pb)+}$ represents the complex which participates in the electron transfer process, among various complex species $MX_\nu^{(n-\nu b)+}$ ($\nu=N, N-1, \cdots\cdots, 1, 0$) which exist in the bulk of the solution.

If the reaction rates of dissociation and association are sufficiently rapid, that is, the limiting current is diffusion-controlled, the wave for the reversible system may be expressed:

$$E=E_0-2.3\frac{RT}{nF}\log\frac{\sqrt{D}}{\sqrt{D_a}}-2.3\frac{RT}{nF}\log\frac{i}{i_d-i}$$
$$-2.3\frac{RT}{nF}\log\left\{1+\sum_{\nu=1}^{N}(C_X)^\nu\left(\prod_{\mu=1}^{\nu}k_\mu\right)\right\}. \qquad (1)$$

The wave for the irreversible system may be expressed:

$$E^*=2.3\frac{RT}{\alpha nF}\left\{\log\frac{k_f^0}{\sqrt{D}}\sqrt{\tau}-0.049-\log\frac{i}{i_d-i}\right.$$
$$\left.-\log\left[\sum_{\nu=0}^{N}(C_X)^{\nu-p}\left(\prod_{\mu=0}^{\nu}k_\mu\right)\Big/\left(\prod_{\mu=1}^{p}k_\mu\right)\right]\right\}, \qquad (2)$$

where E_0 is the standard potential for the reduction of the simple metal ion M^{n+} to the amalgam state; D and D_a are the diffusion coefficients of the complex metal ions $MX_\nu^{(n-\nu b)+}$ in the solution and of the metal atoms M(Hg) in the amalgam, respectively; C_X is the concentration of the complexing agent and k_μ is the successive formation constants defined by Bjerrum[4]; α is the transfer coefficient and τ is the drop time and k_f^0 is the forward (reduction) rate constant of the electron transfer process at the potential of the normal hydrogen electrode. (All activity coefficients are assumed to be equal to 1 in the above equations.)

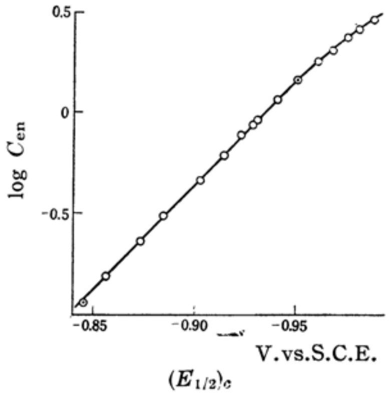

Fig. 3. Variation of $(E_{1/2})_c$ for cadmium as a function of log C_{en}.

Cadmium Complexes.—In Fig. 3 the half-wave potentials are plotted against the logarithm of the concentrations of ethylenediamine. As the activity coefficients of ethylenediamine are unknown at the ionic strength of 0.1 (KNO_3), they are all assumed as equal to 1 in the following calculations. The values found are lying on the line:

$$(E_{1/2})_c=-0.934-0.096\log C_{en}$$

This system belongs to a reversible type and Eq. (1) can be used. From the above data it can be concluded that the complex ion $[Cd\ en_3]^{++}$ predominates in the concentration range of 0.1 to 2.0 M ethylenediamine and its formation constant is equal to $10^{12.01}$. This value is in good agreement with the value of $10^{12.18}$ determined polarographically by Douglas, Laitinen and Bailar[5].

Nickel Complexes. — The reduction of nickel is irreversible and we have attempted to interpret the waves by Eq. (2). When only the complex $MX_S^{(n-Sb)+}$, which predominates in the bulk of the solution, dissociates very rapidly into the complex $MX_p^{(n-pb)+}$ in the vicinity of the electrode surface and the complex $MX_p^{(n-pb)+}$ is reduced irreversibly at the dropping electrode, Eq. (2) can be reduced to the more simple form:

$$E=2.3\frac{RT}{\alpha nF}\left\{\log\frac{k_f^0}{\sqrt{D}}\sqrt{\tau}-0.049-\log\frac{i}{i_d-i}\right.$$
$$\left.-\log\left[\left(\prod_{\mu=0}^{S}k_\mu\right)\Big/\left(\prod_{\mu=1}^{p}k_\mu\right)\right]-(S-p)\log C_X\right\} \qquad (3)$$

Since the successive formation constants of nickel-ethylenediamine complexes[6] are $k_1=10^{7.52}$, $k_2=10^{6.28}$ and $k_3=10^{4.26}$, the overall stability constant $K_3(\equiv k_1k_2k_3=10^{18.06})$ is much larger than $K_2(\equiv k_1k_2=10^{13.80})$ or $K_1(\equiv k_1)$ and therefore the concentrations of the complexes $[Ni\ en_2]^{++}$ and $[Ni\ en]^{++}$ are negligibly small in comparison to that of the complex $[Ni\ en_3]^{++}$ in the concentration range of 0.1 to 2.0 M ethylenediamine. Thus S in Eq. (3) are equal to 3 in the present case.

If Eq. (3) is valid for the reduction of nickel complexes, the value of α can be estimated from the log plot shown in Fig. 1 and the value of $(3-p)$ can be obtained by plotting the half-wave potentials against the logarithm of the ethylenediamine concentrations. It is to be noted that the value of α is dependent on the concentration of ethylenediamine and it is not easy to determine $(3-p)$

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* E in Eq. (2) is measured with reference to the normal hydrogen electrode.

[4] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase and Son, Copenhagen (1941), p. 20.

[5] B.E. Douglas, H.A. Laitinen and J.C. Bailar, *J. Am. Chem. Soc.*, 72, 2484 (1950).

[6] A.E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, New York (1952), p. 518, 519.

so definitely as in the nickel-ammonia system[2]. But, as shown in Fig. 4, the value of $(3-p)$ may be estimated as approximately equal to 1, that is, $p\simeq 2$. This value seems reasonable, considering the higher stability of the ethylenediamine complex than that of the ammonia complex, for which p was found to be equal to 2*. Thus the complex $[\mathrm{Ni\ en_3}]^{++}$ in the solution may dissociate into the complex $[\mathrm{Ni\ en_2}]^{++}$ in the vicinity of the electrode surface, and then it will be reduced at the dropping electrode.

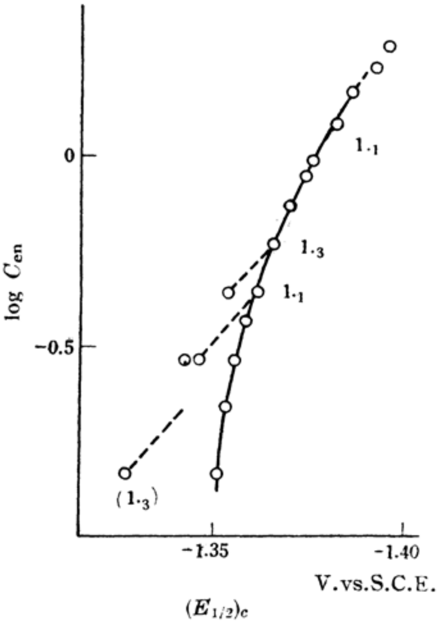

Fig. 4. Variation of $(E_{1/2})_c$ for nickel as a function of log C_{en}.

Figures of $1._1$, $1._3$ and $1._0$ represent values of $(S-p)$ at the reciprocal slopes of 74, 70 and 60 mV., respectively.

The forward rate constant of this electron transfer process can also be calculated by Eq. (3)**. The results are given in Table V. Since α depends on the concentration of ethylenediamine and gelatine, $k_f{}^0$ thus calculated no longer remains constant. The values of α greatly influence the calculated values of the rate constant. The relation between α and $k_f{}^0$ is not yet clear, but Table V shows that the larger α is, the smaller $k_f{}^0$ is. Moreover, the equal value for α gave the nearly consistent value for $k_f{}^0$ even at the different concentrations of ethylenediamine. This suggests that estimation of α from the log plot (Fig. 1) may be allowed as a first approximation. At the concentration of 1 M ethylenediamine, the values of α and $k_f{}^0$ may be close to 0.5 and $10^{-17.5}$ cm./sec., respectively**. For the ammonia complexes, the values $\alpha\simeq 0.7$ and $k_f{}^0\simeq 10^{-16.8}$ cm./sec. were found in the solution of 1 M ammonia and 0.1 N KNO_3. Comparing these values, it seems that in the ethylenediamine system the transfer coefficient and the reduction rate constant of the electron transfer process at the normal hydrogen electrode are smaller than those in the ammonia system.

TABLE V
VALUES OF α AND $k_f{}^0$ FOR NICKEL
(in 0.1 N KNO_3)

C_{en} (M)	Concn. of Nickel (10^{-3} M)	Concn. of Gelatine (%)	α	$-\log k_f{}^0$ ($k_f{}^0$: cm./sec.)
0.146	0.6	0.020	0.33	$11._6$
0.146	0.6	0.013	0.38	$13._3$
0.219	0.6	0.020	0.36	$12._8$
0.292	0.6	0.020	0.37	$13._0$
0.292	0.6	0.016	0.40	$14._0$
0.292	0.6	0.015	0.41	$14._3$
0.365	0.6	0.020	0.39	$13._7$
0.438	0.6	0.020	0.40	$14._0$
0.438	0.6	0.016	0.42	$14._6$
0.584	0.6	0.020	0.42	$14._8$
0.730	0.6	0.020	0.44	$15._5$
0.876	0.6	0.020	0.47	$16._6$
0.966	0.6	0.020	0.49	$17._5$
0.966	0.4_2	0.020	0.54	$19._1$
0.966	0.2_4	0.020	0.57	$20._1$
1.21	0.6	0.020	0.50	$17._8$
1.45	0.6	0.020	0.53	$18._8$
1.69	0.6	0.020	0.55	$19._7$
1.93	0.6	0.020	0.57	$20._5$

Zinc Complexes.—This system belongs also to an irreversible type and Eq. (1) can not be used to interpret the waves[7]. The plot of $(E_{1/2})_c$ against $\log C_{en}$ are given in Fig. 5.

In the range of 0.1 to 2.0 M ethylenediamine α, taken from the log plot, remains constant to be equal to 0.86. Since the successive complex formation constants for zinc-ethylenediamine system[6] are $k_1=10^{5.71}$, $k_2=10^{4.33}$ and $k_3=10^{1.72}$, K_3 is larger than K_2 or

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* Ethylenediamine is a bidentate group, while ammonia is a monodentate group. The successive formation constants for nickel-ammonia system are $k_1=10^{2.80}$, $k_2=10^{2.24}$, $k_3=10^{1.78}$, $k_4=10^{1.19}$, $k_5=10^{0.75}$ and $k_6=10^{0.04}$.

** The ratio of the diffusion current of the complex ion to that of the simple ion is taken from Tables III and IV. D may be calculated using this ratio and the diffusion coefficient of the simple ion at infinite dilution (0.69×10^{-5} cm.²/sec. for nickel and 0.72×10^{-5} cm.²/sec. for zinc).

** Since $\alpha\simeq 0.5$ is used in the calculation of the rate constant, the values given here may be allowed as approximate values, although it is found that the slope and the half-wave potential are dependent on the concentration of nickel.

7) C. J. Nyman, E. W. Murbach and G. B. Millard, *J. Am. Chem. Soc.*, 77, 4194 (1955).

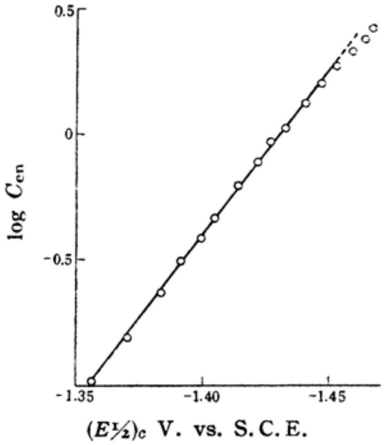

Fig. 5. Variation of $(E_{1/2})_c$ for zinc as a function of $\log C_{en}$.

K_1 and therefore the complex $[Zn\ en_3]^{++}$ predominates in the solution under investigation. So Eq. (3) can be used to interpret the waves. From the plot shown in Fig. 5 the value of $(3-p)$ is obtained as equal to $2._2$, that is, $p \simeq 1$. Thus the complex $[Zn\ en_3]^{++}$ in the solution may dissociate into the complex $[Zn\ en]^{++}$ and then it will participate in the electron transfer process. The forward rate constant of the electron transfer process at the concentration of 1 M ethylenediamine can be calculated to be nearly equal to $10^{-31.2}$ cm./sec. The reduction rate constant of the electron transfer process at the equilibrium potential ($E_G=-0.930$ V. vs. N.H.E.*) can be obtained as $k_G \simeq 10^{-4.0}$ cm./sec. This value seems reasonable in comparison to the rate constant $k_G \simeq 10^{-2.4}$ cm./sec. for zinc ion in the solution of 1 M KCl found by Randles and Somerton[8], since the ethylenediamine complex is much more stable than the chloride complex.

Summary

1. The reduction of cadmium-ethylenediamine complexes is reversible. In the concentration range of 0.1 to 2.0 M ethylenediamine $[Cd\ en_3]^{++}$ predominates in the solution, of which complex formation constant is equal to $10^{12.01}$.

2. The reduction of nickel-ethylenediamine complexes is irreversible. With the aid of the theoretical treatment developed by Matsuda and Ayabe, it was found that at the concentration of 1 M ethylenediamine $[Ni\ en_2]^{++}$ participated in the electron transfer process with the forward rate constant nearly equal to $10^{-17.6}$ cm./sec. and the transfer coefficient nearly equal to 0.5.

3. The reduction of zinc-ethylenediamine complexes is irreversible. It was found that in the concentration range of 0.1 to 2.0 M ethylenediamine $[Zn\ en]^{++}$ participated in the electron transfer process with the forward rate constant nearly equal to $10^{-31.2}$ cm./sec. and the transfer coefficient equal to 0.86.

4. The decrease of the diffusion currents are due to the increase of the viscosities of the solutions. The apparent polarographic diffusion coefficients of these complex metal ions are ca. 8% smaller than those of the simple metal ions.

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* This value was estimated using $E_G=-0.762$ V. vs. N.H.E. for the reduction of simple zinc ion in 1 N KNO_3 and $K_1=10^{5.71}$.

[8] J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 951 (1952).