The Formation Constants of Metal Acetate Complexes. III. Polarographic Determination of the Formation Constants of Acetatocadmium(II) and Acetatocobalt(II) Complexes

By Nobuyuki TANAKA, MINORU KAMADA, Hisao OSAWA and Gen SATÔ

(Received May 18, 1960)

In the previous papers[1,2], the formation constants of acetato complexes of nickel(II), copper(II), lead(II) and zinc(II) were reported. They were determined by the newly devised methods, which are based on the polarographic measurement of the sum of the equilibrium concentrations of hydrated metal ions and metal acetate complexes. In the case of acetatocopper(II), acetatolead(II) and acetatozinc(II) complexes, the substitution reaction of the type,

$$M^{m+}+M'Y^{(m'-4)+} \rightleftarrows MY^{(m-4)+}+M'^{m'+} \quad (1)$$

where Y^{4-} means a completely dissociated ethylenediaminetetraacetate(EDTA) anion, was used for the determination of the formation constants. This was based on the fact that, in acetate buffers, the substitution reaction (Eq. 1) was considered to be

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

$$\left\{\begin{matrix} MY^{(m-4)+} \\ \uparrow\downarrow \\ MHY^{(m-3)+} \end{matrix}\right\} + \left\{\begin{matrix} M'^{m'+} \\ \uparrow\downarrow \\ M'(OAc)_{n'}{}^{(m'-n')+} \end{matrix}\right\} \quad (2)$$

In this paper are presented the formation constants of acetatocadmium(II) and acetatocobalt(II) complexes which have been determined by the same procedure as used for the acetato complexes of copper(II), lead(II) and zinc(II).

Experimental

Reagent.—Standard solutions of copper(II) nitrate and cadmium(II) nitrate were prepared by dissolving known amounts of pure copper and pure cadmium metals (Merck Co. Ltd.), respectively, in reagent-grade nitric acid. In the case of cadmium metal, the oxide layer on the metal surface was removed with hydrochloric acid. This cadmium metal was found by the a. c. polarographic method to contain 0.08% of lead as impurity. The careful examination, however, showed that this minute quantity of lead would give no appreciable effect on the equilibrium determination, and therefore no further purification was carried out. The solution of disodium ethylenediaminetetraacetate (EDTA) was standardized against the standard solution of copper(II) nitrate by amperometric titration with the dropping mercury electrode[3]. A standard solution of cobalt(II) nitrate was prepared by dissolving an appropriate

---

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

[2] N. Tanaka and K. Kato, ibid., 33, 417 (1960).

[3] N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), 6, 86 (1957).

amount of cobalt metal in reagent-grade nitric acid. Its concentration was determined with the standardized EDTA solution volumetrically using murexide as an indicator[4] and also amperometrically using the dropping mercury electrode as an indicator electrode[3]. The polarographic analysis showed that the cobalt metal contained 0.2% of nickel as impurity. Therefore, the equilibrium study of the reaction involving cobalt(II) ions or cobalt(II)-EDTA complexes was carried out, taking into consideration the substitution reaction involving nickel(II)-EDTA complexes (see below).

Sodium acetate-acetic acid buffers were prepared by mixing the solutions of sodium carbonate and acetic acid. Sodium carbonate, acetic acid and other reagents used for the supporting electrolyte were of guaranteed reagent grade and used without further purification.

Apparatus and procedure. — A Shimadzu RP-2 pen-recording polarograph and a manual apparatus similar to that of Kolthoff and Lingane[5] were used for the measurement of current-voltage curves. Two dropping mercury electrodes were used. One had an m value of 2.57 mg./sec. and a drop time τ of 3.52 sec. in an air-free acetate buffer of pH 4.7 containing 0.1 M acetate, 0.1 M potassium nitrate and 0.01% gelatin at 25°C with open circuit. The other had an m value of 2.93 mg./sec. and a drop time τ of 3.16 sec. in an air-free 0.1 M potassium nitrate solution at 25°C with open circuit. A saturated calomel electrode with a large area was used as the anode, which was connected to the electrolytic solution by a Hume and Harris-type agar bridge[6]. A Hitachi Model EHP-1 pH meter was used for the pH measurement. Dissolved oxygen in the solution was removed by bubbling pure tank nitrogen through the solution.

The measurements of the diffusion current of copper(II) in acetate buffer solutions were carried out with the following two reaction mixtures:

(a) copper(II)—cadmium(II)—EDTA

(b) copper(II)—cobalt(II)—EDTA.

The measurements were made at 15, 25 and 35°C in acetate buffers of pH 4.75 (for cadmium(II)) and pH 4.70 (for cobalt(II)) of which the acetate concentrations were varied from 0.02 M to 0.10 M (for cobalt(II)) or to 0.15 M (for cadmium(II)). The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration.

In the preliminary experiments, it was found that the substitution reactions between copper(II) ions and cadmium(II)-EDTA complexes and those between copper(II) ions and cobalt(II)-EDTA complexes proceeded at considerable reaction rates. The reaction mixtures of the copper(II)-cadmium(II)-EDTA system were kept standing at the given temperature for ten to twenty hours after the preparation and were subjected to the measurement, though they were found to reach nearly the equilibrium within 60 minutes. In the case of the copper(II)-cobalt(II)-EDTA system, the diffusion currents of the copper(II) in the reaction mixtures were measured 45 min. after the preparation at 15°C, 30 min. at 25°C and 25 min. at 35°C. This was decided from the consideration of the effect of the reaction between copper(II) and nickel(II)-EDTA complexes on the equilibrium under consideration, because the cobalt(II) solution used in this experiment contained a small amount of nickel as impurity. It was found in the preliminary experiments that the reaction between copper(II) and nickel(II)-EDTA complexes affect more or less the equilibrium concentration of copper(II) in the substitution reaction between copper(II) and cobalt(II)-EDTA complexes after the above-mentioned period, though the former reaction proceeds at much slower rate than the latter[7].

Results

The apparent diffusion current constants[2] of copper(II) were determined by measuring the diffusion current at various acetate concentrations. The values of $[\mathrm{Cu}^{2+}]_{\mathrm{app}}$ which is given by[2]

$$[\mathrm{Cu}^{2+}]_{\mathrm{app}} = [\mathrm{Cu}^{2+}] + \sum_{1}^{n} [\mathrm{Cu(OAc)}_n{}^{(2-n)+}] \tag{3}$$

were determined with the aid of those apparent diffusion current constants from the diffusion currents obtained with the reaction mixtures of systems a and b. Then, the apparent equilibrium constants ($K^{\mathrm{M}}_{\mathrm{M}',\mathrm{app}}$) for Eq. 2, expressed as[2]

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

were culculated. The F_n functions expressed as[2]

$$F_0 \equiv K^{\mathrm{M}}_{\mathrm{M}',\,\mathrm{app}}\left\{1 + \sum_{1}^{n} K_{\mathrm{M(OAc)}}[\mathrm{OAc}^-]^n\right\}$$

$$= K^{\mathrm{M}}_{\mathrm{M}'}\frac{\beta}{\beta'}\left\{1 + \sum_{1}^{n'} K_{\mathrm{M}'(\mathrm{OAc})_{n'}}[\mathrm{OAc}^-]^{n'}\right\} \tag{5}$$

$$F_1 = \frac{F_0 - \dfrac{\beta}{\beta'}K^{\mathrm{M}}_{\mathrm{M}'}}{\dfrac{\beta}{\beta'}K^{\mathrm{M}}_{\mathrm{M}'}[\mathrm{OAc}^-]}$$

$$= K_{\mathrm{M'OAc}} + K_{\mathrm{M}'(\mathrm{OAc})_2}[\mathrm{OAc}^-] + \cdots\cdots \tag{6}$$

$$F_2 \equiv \frac{F_1 - K_{\mathrm{M'OAc}}}{[\mathrm{OAc}^-]}$$

$$= K_{\mathrm{M}'(\mathrm{OAc})_2} + K_{\mathrm{M}'(\mathrm{OAc})_3}[\mathrm{OAc}^-] + \cdots\cdots \tag{7}$$

....

---

[4] G. Schwarzenbach, "Complexometric Titrations" translated by H. Irving, Methuen & Co. Ltd., London (1957), p. 78.

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, New York (1952), p. 297.

[6] D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, 15, 465 (1943).

[7] unpublished work.

$$F_{n'} \equiv \frac{F_{n'-1} - K_{\mathrm{M'(OAc)}_{n'-1}}}{[\mathrm{OAc}^-]} = K_{\mathrm{M'(OAc)}n'} \qquad (8)$$

were successively obtained, where $K^{\mathrm{M}}_{\mathrm{M'}}$ means the true equilibrium constant given by

$$K^{\mathrm{M}}_{\mathrm{M'}} = \frac{[\mathrm{M'}^{m'+}]\,[\mathrm{MY}^{(m-4)+}]}{[\mathrm{M}^{m+}]\,[\mathrm{M'Y}^{(m'-4)+}]} \qquad (9)$$

and β and β' are

$$\beta = 1 + K^{\mathrm{H}}_{\mathrm{MHY}}[\mathrm{H}^+]$$

$$\beta' = 1 + K^{\mathrm{H}}_{\mathrm{M'HY}}[\mathrm{H}^+]$$

The results obtained for systems a and b are given below. The values of β/β' were calculated to be approximately unity for both a and b systems at the pH's in the present experiments, using the equilibrium constants $K^{\mathrm{H}}_{\mathrm{MHY}}$ and $K^{\mathrm{H}}_{\mathrm{M'HY}}$ given by Schwarzenbach, Gut and Anderegg[8].

(a) Copper(II)-Cadmium(II)-EDTA System. —The formation constants of acetatocadmium(II) complexes were determined by the measurement of $K^{\mathrm{Cu}}_{\mathrm{Cd,\,app}}$ at various acetate concentrations with the aid of the formation constants of CuOAc^+ and $\mathrm{Cu(OAc)_2}$ obtained in the previous paper[2], where, under the experimental condition, $K^{\mathrm{Cu}}_{\mathrm{Cd,\,app}}$ is given by the equation

$$K^{\mathrm{Cu}}_{\mathrm{Cd,\,app}} = \frac{[\mathrm{Cd}^{2+}]_{\mathrm{app}}\{[\mathrm{CuY}^{2-}] + [\mathrm{CuHY}^-]\}}{[\mathrm{Cu}^{2+}]_{\mathrm{app}}\{[\mathrm{CdY}^{2-}] + [\mathrm{CdHY}^-]\}}$$

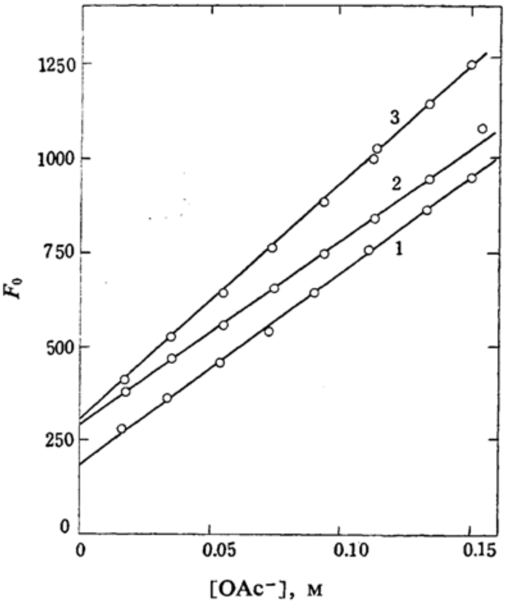

Fig. 1. F_0 (Eq. 5) as a function of the acetate ion concentration in copper(II)-cadmium(II)-EDTA system: 1, at 15°C; 2, at 25°C; 3, at 35°C.

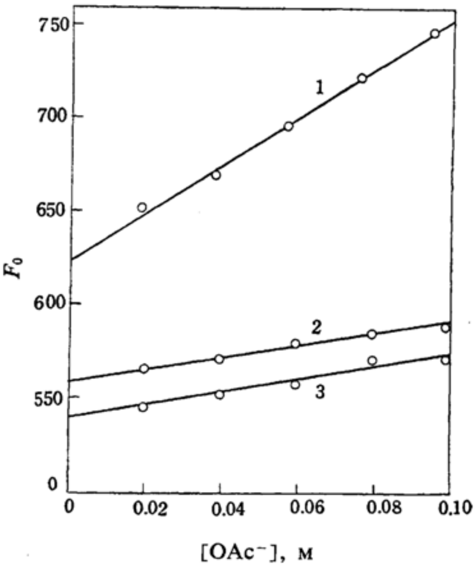

Fig. 2. F_0 (Eq. 5) as a function of the acetate ion concentration in copper(II)-cobalt(II)-EDTA system: 1, at 15°C; 2, at 25°C; 3, at 35°C.

The values of F_0 given by Eq. 5 were calculated and plotted against the acetate ion concentration. These plots for 15, 25 and 35°C are shown in Fig. 1, in which all F_0 plots give straight lines indicating that at acetate concentrations up to 0.15 M CdOAc^+ is only species of acetatocadmium(II) complex which exists in the solution at an appreciable concentration. The formation constants of CdOAc^+ are listed in Table I.

(b) Copper(II)-Cobalt(II)-EDTA System. —The formation constants of acetatocobalt(II) complexes were determined with the same procedure as for the acetatocadmium(II) complexes. $K^{\mathrm{Cu}}_{\mathrm{Co,\,app}}$ which is given by the equation

$$K^{\mathrm{Cu}}_{\mathrm{Co,\,apq}} = \frac{[\mathrm{Co}^{2+}]_{\mathrm{app}}\{[\mathrm{CuY}^{2-}] + [\mathrm{CuHY}^-]\}}{[\mathrm{Cu}^{2+}]_{\mathrm{app}}\{[\mathrm{CoY}^{2-}] + [\mathrm{CoHY}^-]\}}$$

was determined at various acetate concentrations. In this case also, the F_0 plots gave straight lines as shown in Fig. 2. From these plots the formation constants of CoOAc^+ were determined, which are given in Table I.

TABLE I. FORMATION CONSTANTS OF ACETATOCADMIUM(II) AND ACETATOCOBALT(II) COMPLEXES AT VARIOUS TEMPERATURES

Metal ions	Temp., °C	K_{MOAc} (μ=0.2)
Cadmium(II)	15	27
	25	16
	35	20
Cobalt(II)	15	2.1
	25	0.6
	35	0.6

---

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

TABLE II. SOME EXAMPLES OF THE REPORTED VALUES OF FORMATION CONSTANTS OF ACETATOCADMIUM(II) AND ACETATOCOBALT(II) COMPLEXES

Metal ion	Investigator	Method	Temp., °C	Ionic strength	K_{MOAc}	$K_{M(OAc)_2}$	Ref.
Cadmium(II)	I. Leden et al.	Potentiometric	25	3	20	190	9, 10
	A. Jacques	〃	25	$\simeq 0.5$	100	~150	11
	E. Ferrell et al.	〃	20	≤ 0.55	50	—	9, 12
Cobalt(II)	S. Bardhan et al.	Potentiometric	35	0	23	—	13
				0.2	7.6*		(13)
	S. K. Siddhanta et al.	〃	30~35	0	33	127	14
				0.2	11*	22*	(14)

* Those values are the formation constants which were calculated by the present authors with the values reported in the literature referred to. In the calculation, the activity coefficients of cadmium(II), cobalt(II) and acetate ions were estimated to be 0.30, 0.33 and 0.73, respectively, and the activity coefficient of monoacetato complexes was assumed to be equal to that of acetate ions[2,15].

Discussion

The formatiom constants of the acetato complexes of cadmium(II) and cobalt(II) have been reported by several researchers. In Table II some of them are given, which are compared with the formation constants listed in Table I.

Recently, Yasuda and Yamasaki[16] determined the formation constants of acetato complexes of some bivalent metal ions and found that the stabilities of those complexes decreased in the order of Pb > Cu > Cd > Zn > Ni. The formation constants of K_{MOAc} obtained in the previous[1,2] and present investigations agree with the above order.

The equilibria of the substitution reaction represented by Eq. 1 have been studied with the same procedure as that reported previously[2]. The equilibrium constants, K^{Cu}_{Cd} and K^{Cu}_{Co}, are given in Table III. Schwarzenbach and his co-workers[8] studied the substitution reaction of copper(II) ions and cadmium(II)-EDTA complexes at 20°C in the solution of ionic strength 0.1 with 8×10^{-3} M sodium acetate. The equilibrium constant which was reported by those researchers was corrected for the acetato complex formation using the formation constants K_{CuOAc}, $K_{Cu(OAc)_2}$ and K_{CdOAc}. The resulting constant is also given in Table III. On the other hand, no investigation had been reported on the substitution reaction between copper(II) ions and cobalt(II)-EDTA complexes. Therefore, the equilibrium constant of the reaction was calculated with the formation constants of copper(II)-EDTA and cobalt(II)-EDTA complexes[8]. This is also shown in Table III. It is seen that the $K^{M}_{M'}$ values obtained in this study are in satisfactory agreement with those calculated from the equilibrium or the formation constants reported by Schwarzenbach et al.

TABLE III. EQUILIBRIUM CONSTANTS FOR THE SUBSTITUTION REACTION (EQ. 1) AT IONIC STRENGTH 0.2 COMPARED WITH SCHWARZENBACH'S VALUES

Temp., °C	$K^{Cu}_{Cd}\times10^{-2}$		$K^{Cu}_{Co}\times10^{-2}$	
	I	II	I	III
15	1.9	—	6.2	—
20	—	2.6±0.5	—	4.4±2.0
25	3.0	—	5.6	—
35	3.1	—	5.4	—

I. Values obtained in the present investigation.

II. Values calcuated from the Schwarzenbach's $K^{Cu}_{Cd,\,app}$[8].

III. Values calculated from the formation constants[8].

Summary

The formation constants of acetatocadmium(II) and acetatocobalt(II) complexes were determined at ionic strength of 0.2 at 15, 25 and 35°C with the procedure that is based on the polarographic measurement of the sum of the equilibrium concentrations of the hydrated metal ions and the metal acetate complexes in the substitution reaction involving EDTA complexes. The resulting formation constants K_{CdOAc} and K_{CoOAc} are 27 and 2.1 at 15°C, 16 and 0.6 at 25°C and 20 and 0.6 at 35°C, respectively.

---

9) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal Ion Complexes, Part I, Organic Ligands," the Chemical Society, London (1957), Special Publ. No. 6, p. 3.

10) I. Leden, *Svensk Kem. Tidskr.*, **58**, 129 (1946); Doctoral Diss., Lund, 1943, 89.

11) A. Jacques, *Trans. Faraday Soc.*, **5**, 225 (1910).

12) E. Ferrell, J. M. Ridgion and H. L. Riley, *J. Chem. Soc.*, **1934**, 1440.

13) S. Bardhan and S. Aditya, *J. Indian. Chem. Soc.*, **32**, 109 (1955).

14) S. K. Siddhanta and S. N. Banerjee, *Ibid.*, **35**, 343 (1958).

15) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

16) M. Yasuda and K. Yamasaki, presented at the Symposium on Metal Complexes, Fukuoka, October, 1959.

The authors thank the Ministry of Education for the financial support granted for this research.

Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai