The Formation Constants of Metal Acetate Complexes. II. Polarographic Determination of the Formation Constants of Acetatocopper(II), Acetatolead(II) and Acetatozinc(II) Complexes

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In the previous paper[1], a new method for the determination of the formation constants of metal acetate complexes and its application to the study of acetatonickel(II) complexes were presented. The method is based on the polarographic measurement of the sum of the equilibrium concentrations of hydrated metal ions and metal acetate complexes in the presence of an appropriate auxiliary complex-forming substance. Although it has advantages over the conventional methods, its application to other metal acetate complexes seems to be difficult.

In this paper are presented the procedure and the results of the determination of the formation constants of acetatocopper(II), acetatolead(II) and acetatozinc(II) complexes. The procedure is applicable when the formation constants of certain metal acetate complexes are known and can be used as standards.

Theoretical

Let us consider the acetate buffer solution which contains two different metal ions, M^{m+} and $M'^{m'+}$, and ethylenediaminetetraacetate (EDTA) ions. There exist the following equilibria:

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

$$MY^{(m-4)+} + H^{+} \rightleftarrows MHY^{(m-3)+} \quad (2)$$

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

$$M'Y^{(m'-4)+}+H^+ \rightleftarrows M'HY^{(m'-3)+} \qquad (3)$$

$$M^{m+}+nOAc^- \rightleftarrows M(OAc)_n{}^{(m-n)+} \qquad (4)$$

$$M'^{m'+}+n'OAc^- \rightleftarrows M'(OAc)_{n'}{}^{(m'-n')+} \qquad (5)$$

where Y^{4-} means a completely dissociated EDTA anion. The overall substitution reaction between M^{m+} and $M'Y^{(m'-4)+}$ in the acetate buffer solution, therefore, may be represented as

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

$$\left\{\begin{array}{l} M'^{m'+} \\ \uparrow\downarrow \\ M'(OAc)_{n'}{}^{(m'-n')+} \end{array}\right\} + \left\{\begin{array}{l} MY^{(m-4)+} \\ \uparrow\downarrow \\ MHY^{(m-3)+} \end{array}\right\} \qquad (6)$$

In the polarographic measurement, the diffusion current of metal ions obtained in acetate media corresponds to the sum of the diffusion current of the hydrated metal ions and that of the acetato complexes[1]. Consequently, the concentrations that can be determined polarographically are $[M^{m+}]_{app}$ and $[M'^{m'+}]_{app}$ given by the equations

$$[M^{m+}]_{app}=[M^{m+}]+\sum_1^n[M(OAc)_n{}^{(m-n)+}] \qquad (7)$$

and

$$[M'^{m'+}]_{app}=[M'^{m'+}] + \sum_1^{n'}[M'(OAc)_{n'}{}^{(m'-n')+}] \qquad (8)$$

respectively.

The total concentrations of metals and EDTA, $[M]_t$, $[M']_t$ and $[EDTA]_t$, in the solution are given in terms of the concentrations of the ionic and molecular species present:

$$[M]_t=[M^{m+}]_{app}+[MY^{(m-4)+}] + [MHY^{(m-3)+}] \qquad (9)$$

$$[M']_t=[M'^{m'+}]_{app}+[M'Y^{(m'-4)+}] + [M'HY^{(m'-3)+}] \qquad (10)$$

$$[EDTA]_t=[EDTA]_f+[MY^{(m-4)+}] + [MHY^{(m-3)+}]+[M'Y^{(m'-4)+}] + [M'HY^{(m'-3)+}] \qquad (11)$$

where $[EDTA]_f$ represents the concentration of the uncomplexed EDTA. Under the condition that $[M]_t+[M']_t>[EDTA]_t$, $[EDTA]_f$ is negligibly small as compared with the concentrations of other species in the solution.

From the polarographic measurement of either $[M^{m+}]_{app}$ or $[M'^{m'+}]_{app}$, the equilibrium constant of Eq. 6

$$K_{M,\,app}^{M'} = \frac{[M'^{m'+}]_{app}\{[MY^{(m-4)+}]+[MHY^{(m-3)+}]\}}{[M^{m+}]_{app}\{[M'Y^{(m'-4)+}]+[M'HY^{(m'-3)+}]\}} \qquad (12)$$

is obtained with the relations given by Eqs. 9 to 11, provided that the values of $[M]_t$, $[M']_t$, and $[EDTA]_t$ are known. The constant $K_{M',\,app}^{M}$ may be called the apparent equilibrium constant of the substitution reaction in question. On the other hand, the equilibrium constant of the substitution reaction given by Eq. 1 is expressed as

$$K_{M'}^{M}=\frac{[M'^{m'+}]\,[MY^{(m-4)+}]}{[M^{m+}]\,[M'Y^{(m'-4)+}]} \qquad (13)$$

Introducing Eqs. 7, 8 and 13 into Eq. 12, $K_{M',\,app}^{M}$ is rewritten as

$$K_{M',\,app}^{M}=K_{M'}^{M}\,\frac{\beta}{\beta'}\,\frac{1+\sum_1^{n'}K_{M'(OAc)_{n'}}[OAc^-]^{n'}}{1+\sum_1^{n}K_{M(OAc)_n}[OAc^-]^{n}} \qquad (14)$$

$$\beta=1+K_{MHY}^{H}[H^+]$$

$$\beta'=1+K_{M'HY}^{H}[H^+]$$

where $K_{M(OAc)_n}$ and $K_{M'(OAc)_{n'}}$ represent the overall formation constants of $M(OAc)_n{}^{(m-n)+}$ and $M'(OAc)_{n'}{}^{(m'-n')+}$, respectively, and K_{MHY}^{H} and $K_{M'HY}^{H}$, the equilibrium constants of the reactions of Eqs. 2 and 3, respectively.

If the formation constants of acetato complexes of one of the metals are known, those of the other can be determined with Eq. 14 by the measurement of $K_{M',\,app}^{M}$ at various acetate concentrations. When the values of $K_{M(OAc)_n}$ are known, Eq. 14 is conveniently arranged as

$$F_0 \equiv K_{M',\,app}^{M}\left\{1+\sum_1^{n}K_{M(OAc)_n}[OAc^-]^{n}\right\}$$

$$=K_{M'}^{M}\,\frac{\beta}{\beta'}\left\{1+\sum_1^{n'}K_{M'(OAc)_{n'}}[OAc^-]^{n'}\right\} \qquad (15)$$

From the extrapolation of the plot of F_0 vs. $[OAc^-]$ to zero acetate concentration, $\frac{\beta}{\beta'}K_{M'}^{M}$ is obtained. Then, the functions $F_1, F_2, \cdots, F_{n'}$ are defined, which are written as follows:

$$F_1 \equiv \frac{F_0-\frac{\beta}{\beta'}K_{M'}^{M}}{\frac{\beta}{\beta'}K_{M'}^{M}[OAc^-]} = K_{M'OAc}+K_{M'(OAc)_2}[OAc^-]+\cdots\cdots \qquad (16)$$

$$F_2 \equiv \frac{F_1-K_{M'OAc}}{[OAc^-]} = K_{M'(OAc)_2}+K_{M'(OAc)_3}[OAc^-]+\cdots\cdots \qquad (17)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$F_{n'} \equiv \frac{F_{n'-1} - K_{\mathrm{M'(OAc)}_{n'-1}}}{[\mathrm{OAc}^-]} = K_{\mathrm{M'(OAc)}_{n'}} \qquad (18)$$

F_1 is plotted against $[\mathrm{OAc}^-]$ and the value of $K_{\mathrm{M'OAc}}$ is determined by extrapolating the plot to zero acetate concentration. Further treatment leads to the determination of $K_{\mathrm{M'(OAc)}_{n'}}$, if higher acetato complexes are present in the solution.

When the formation constants of $\mathrm{M'(OAc)}_{n'}{}^{(m'-n')+}$ are known, similar relations are derived:

$$F_0' \equiv \frac{1+\sum_1^{n'} K_{\mathrm{M'(OAc)}_{n'}} [\mathrm{OAc}^-]^{n'}}{K^{\mathrm{M}}_{\mathrm{M'},\mathrm{app}}} = \frac{\beta'}{\beta K^{\mathrm{M}}_{\mathrm{M'}}} \left\{ 1+\sum_1^{n} K_{\mathrm{M(OAc)}_n} [\mathrm{OAc}^-]^{n} \right\} \qquad (15')$$

$$F_1' \equiv \frac{F_0' - \dfrac{\beta'}{\beta K^{\mathrm{M}}_{\mathrm{M'}}}}{\dfrac{\beta'}{\beta K^{\mathrm{M}}_{\mathrm{M'}}} [\mathrm{OAc}^-]} = K_{\mathrm{MOAc}} + K_{\mathrm{M(OAc)}_2} [\mathrm{OAc}^-] + \cdots\cdots \qquad (16')$$

$$F_2' \equiv \frac{F_1' - K_{\mathrm{MOAc}}}{[\mathrm{OAc}^-]} = K_{\mathrm{M(OAc)}_2} + K_{\mathrm{M(OAc)}_3} [\mathrm{OAc}^-] + \cdots\cdots \qquad (17')$$

The values of $K_{\mathrm{M(OAc)}_n}$ can be determined by the same procedure as for those of $K_{\mathrm{M'(OAc)}n'}$.

Experimental

Reagent. — Standard solutions of copper(II) nitrate and zinc nitrate were prepared by dissolving known amounts of pure copper and zinc metals, respectively, in a reagent-grade nitric acid. A standard solution of nickel nitrate was the same as used in the previous study¹⁾. The solution of disodium ethylenediaminetetraacetate was standardized against the standard solution of copper(II) nitrate by amperometric titration²⁾. A standard solution of lead nitrate was prepared by dissolving an appropriate quantity of reagent-grade lead nitrate. Its concentration was determined amperometrically with the standardized EDTA solution²⁾. For buffers and supporting electrolytes, guaranteed reagents were used without further purification.

Apparatus and Procedure. — The polarograph and the dropping mercury electrode used were the same as those described in the previous paper¹⁾. The dropping mercury electrode had an m value of 1.27 mg./sec. and a drop time τ of 3.69 sec. in an air-free 0.1 M potassium chloride solution at 25°C with open circuit. The measurements of the diffusion currents of copper(II) in acetate buffer solutions were carried out with the following three reaction mixtures:

(a) copper(II)-nickel(II)-EDTA
(b) copper(II)-lead(II)-EDTA
(c) copper(II)-zinc(II)-EDTA

The measurements were made at 15, 25 and 35°C in acetate buffers of pH 4.7±0.1 in which the acetate concentrations were varied from 0.01 M to 0.2 M. The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration.

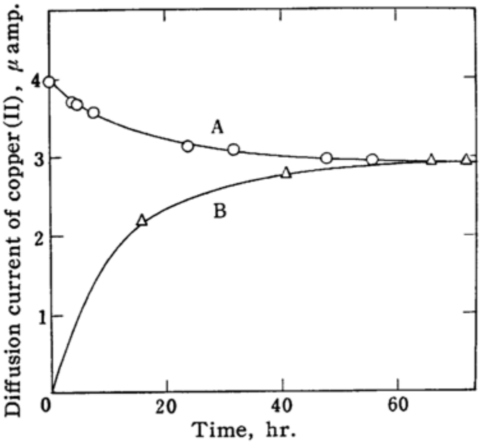

Fig. 1. Relation between the diffusion current of copper(II) and time in the forward (curve A) and the reverse (curve B) reactions of the substitution reaction $\mathrm{Cu^{2+} + NiY^{2-} \rightleftarrows CuY^{2-} + Ni^{2+}}$, measured in acetate buffer solutions of pH 4.7 at 15°C. Total concentrations are: $[\mathrm{Cu}]_t = 1.00\times10^{-3}$ M; $[\mathrm{Ni}]_t = 1.50\times10^{-3}$ M; $[\mathrm{EDTA}]_t = 1.00\times10^{-3}$ M.

The substitution reactions involving the EDTA complexes are not always completed instantaneously. The rates of these reactions vary widely according to the system investigated. In systems (b) and (c), the reactions are nearly completed within a few minutes under the experimental conditions. The reaction mixtures, therefore, were subjected to the measurement approximately 3 hours after the preparation. On the other hand, it has often been stated that the exchange or substitution reactions involving the nickel-EDTA complexes proceed at a relatively slow rate³⁻⁷⁾. This was confirmed also in this study by the fact that the reaction mixtures of system (a) reach the equilibrium extremely slowly. One of the examples is given in Fig. 1, where the change of the polarographic diffusion current of copper(II) in the reaction mixture is plotted against

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

3) F. A. Long, S. S. Jones and M. Burke, *Brookhaven Conf. Rept. BNE-C-8*, **2**, 106 (1948).

4) C. M. Cook, Jr. and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958).

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

6) K. Bril and P. Krumholz, *J. Phys. Chem.*, **57**, 874 (1953).

7) N. Tanaka and Y. Sakuma, This Bulletin, **32**, 578 (1959).

the time for the forward and reverse reactions. Fig. 1 shows that the reaction equilibrates approximately 60 hours after the initiation of the reaction. In system (a), therefore, all measurements were made about 3 days after the solutions had been prepared.

Results

The apparent diffusion current constants of copper(II) were determined by measuring the diffusion current at various acetate concentrations. The values of $[Cu^{2+}]_{app}$ were calculated with the aid of those apparent diffusion current constants from the diffusion currents obtained with the reaction mixtures of systems (a), (b) and (c). Then, the apparent equilibrium constants $K^{M}_{M',app}$ given by Eq. 12 were calculated, with which F_0, $F_1 \cdots\cdots F_{n'}$ (or F_0', $F_1' \cdots\cdots F_n'$) were successively obtained. The results obtained for systems (a), (b) and (c) are given below. The values of β/β' (or β'/β) in Eq. 14 were calculated with the equilibrium constants K^{H}_{MHY} and $K^{H}_{M'HY}$ given by Schwarzenbach et al.⁵⁾, with the result that they are approximately unity for all three systems at pH of the present experiments.

Copper(II) - Nickel(II) - EDTA System. — In the solution containing acetate up to 0.2 M in concentration, nickel(II) forms only a monoacetato complex, its formation constant K_{NiOAc} at ionic strength 0.2 being 2.6, 2.6 and 2.4 at 15, 25 and 35°C, respectively¹⁾. With the aid of these values, the formation constants of acetatocopper(II) complexes were obtained by determining the values for $K^{Cu}_{Ni,app}$ at various acetate concentrations. The $K^{Cu}_{Ni,app}$ is given by the equation

$$K^{Cu}_{Ni,app}=\frac{[Ni^{2+}]_{app}[CuY^{2-}]}{[Cu^{2+}]_{app}[NiY^{2-}]}$$

F_0' and F_1' given by Eqs. 15′ and 16′ respectively were calculated and plotted against the acetate ion concentration. These plots for 25°C are shown in Fig. 2, in which the F_1' plot gives a straight line. This fact clearly indicates that no appreciable amount of complexes with three acetates or more co-ordinated is present in the solution under the experimental conditions. From the F_1' plot the formation constants of mono- and diacetatocopper(II) complexes, K_{CuOAc} and $K_{Cu(OAc)_2}$, were determined, the former being determined by the intercept at zero acetate concentration and the latter, by the slope.

Similar relations were also found at 15 and 35°C. The formation constants obtained at various temperatures are given in Table I.

Copper(II)-Lead(II)-EDTA System. — The formation constants of acetatolead(II) complexes were determined by the measurement of $K^{Cu}_{Pb,app}$ at various acetate concentrations with the aid of the formation constants of $CuOAc^+$ and $Cu(OAc)_2$ obtained in this study, where $K^{Cu}_{Pb,app}$ is given by the equation

$$K^{Cu}_{Pb,app}=\frac{[Pb^{2+}]_{app}[CuY^{2-}]}{[Cu^{2+}]_{app}[PbY^{2-}]}$$

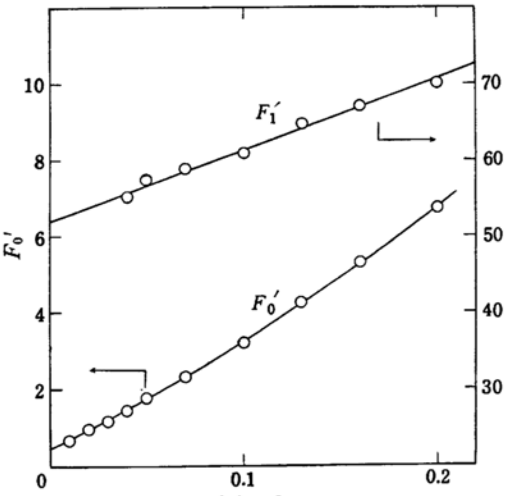

Fig. 2. F_0' (Eq. 15′) and F_1' (Eq. 16′) as a function of the acetate ion concentration in copper(II)-nickel(II)-EDTA system at 25°C.

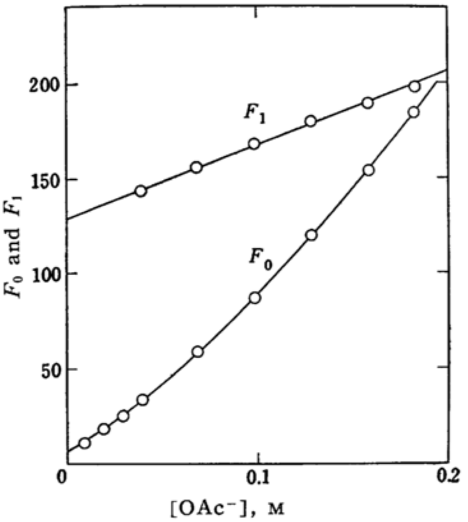

Fig. 3. F_0 (Eq. 15) and F_1 (Eq. 16) as a function of the acetate ion concentration in copper(II)-lead(II)-EDTA system at 25°C.

In this case F_0 and F_1 given by Eqs. 15 and 16 were calculated and plotted instead of F_0' and F_1'. In Fig. 3 these plots for 25°C are shown, where the F_1 plot gives a straight line indicating that $PbOAc^+$ and $Pb(OAc)_2$ are appreciable species of acetatolead(II) complexes present in the solution. Similar plots were obtained at 15 and 35°C. The formation constants of $PbOAc^+$ and $Pb(OAc)_2$ were determined. These are given in Table I.

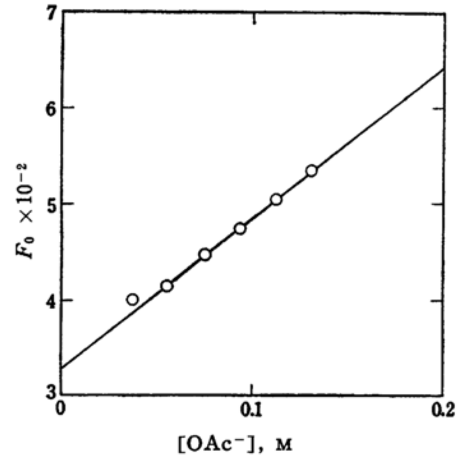

Fig. 4. F_0 (Eq. 15) as a function of the acetate ion concentration in copper(II)-zinc(II)-EDTA system at 25°C.

Copper(II) - Zinc(II) - EDTA System. — The formation constants of acetatozinc(II) complexes were determined with the same procedure as for the acetatolead(II) complexes. $K^{Cu}_{Zn,\,app}$ which is given by the equation

$$K^{Cu}_{Zn,\,app}=\frac{[Zn^{2+}]_{app}[CuY^{2-}]}{[Cu^{2+}]_{app}[ZnY^{2-}]}$$

was determined at various acetate concentrations. In this case it was found that

TABLE I. FORMATION CONSTANTS OF ACETATOCOPPER(II), ACETATOLEAD(II) AND ACETATOZINC(II) COMPLEXES AT VARIOUS TEMPERATURES

Metal ion	Temp., °C	K_{MOAc}	$K_{M(OAc)_2}$
Copper(II)	15	41	190
	25	52	93
	35	69	82
Lead(II)	15	130	750
	25	130	390
	35	120	380
Zinc(II)	15	5.7	—
	25	4.6	—
	35	3.7	—

TABLE II. SOME EXAMPLES OF THE REPORTED VALUES OF FORMATION CONSTANTS OF ACETATOCOPPER(II), ACETATOLEAD(II) AND ACETATOZINC(II) COMPLEXES

Metal ion	Investigator	Method	Temp., °C	Ionic strength	K_{MOAc}	$K_{M(OAc)_2}$	Ref.
Copper(II)	Pedersen	Potentiometric	18	0.2	46.7	316	8
	Fronæus	Ion-exchange	20	1	45	440	9
	Sircar et al.	Potentiometric	29～33	0	250	2000	10
				0.2	83*	350*	(10)
Lead(II)	Aditya et al.	Potentiometric	30	0	270	9000	11, 12
				0.2	76*	1300*	(11, 12)
	Burns et al.	Polarographic	25	1.98	150	840	13
	Siddhanta et al.	Potentiometric	31～34.5	0	302	9700	14
				0.2	85*	1500*	(14)
Zinc(II)	Cannan et al.	Potentiometric	—	0.2	10.7	—	15
	Bardhan et al.	Solubility	35	0	39	—	16
				0.2	13*		(16)
	Bardhan et al.	Potentiometric	35	0	29	—	16
				0.2	9.6*		(16)

* 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 copper(II), lead(II), zinc(II) and acetate ions were estimated to be 0.33, 0.28, 0.33 and 0.73, respectively, and the activity coefficient of monoacetato complexes was assumed to be equal to that of acetate ions.

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9) S. Fronæus, *Acta Chem. Scand.*, **5**. 859 (1951).

10) S. C. Sircar. S. Aditya and B. Prasad, *J. Indian Chem. Soc.*, **30**, 633 (1953).

11) N. K. Das, S. Aditya and B. Prasad, ibid., **29**, 169 (1952).

12) S. Aditya and B. Prasad, ibid., **30**, 213 (1953).

13) E. A. Burns and D. N. Hume, *J. Am. Chem. Soc.*, **78**, 3958 (1956).

14) S. K. Siddhanta and S. N. Banerjee, *J. Indian Chem. Soc.*, **35**, 323 (1958).

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

		15°C	20°C	25°C	35°C
Copper(II)-Nickel(II)	$K_{\rm Ni}^{\rm Cu}$ a)	2.0	—	2.2	2.5
	$K_{\rm Ni,app}^{\rm Cu}$ b)	—	1.5	—	—
	$K_{\rm Ni,cor}^{\rm Cu}$ c)	—	2.1	—	—
Copper(II)-Lead(II)	$K_{\rm Pb}^{\rm Cu}$ a)	3.2	—	5.0	8.0
	$K_{\rm Pb,app}^{\rm Cu}$ b)	—	6.3	—	—
	$K_{\rm Pb,cor}^{\rm Cu}$ c)	—	4.4	—	—
Copper(II)-Zinc(II)	$K_{\rm Zn}^{\rm Cu}$ a)	3.2×10^2	—	3.3×10^2	3.4×10^2
	$K_{\rm Zn,app}^{\rm Cu}$ b)	—	2.1×10^2	—	—
	$K_{\rm Zn,cor}^{\rm Cu}$ c)	—	2.9×10^2	—	—

a) Values obtained in the present investigation.
b) Values obtained by Schwarzenbach et al.
c) Values calculated from Schwarzenbach's values with Eq. 14.

the F_0 plot gave a straight line, which is shown in Fig. 4. This fact led to the conclusion that at acetate concentration up to 0.2 M, $\rm ZnOAc^+$ is the only species which exists in the solution at an appreciable concentration. Similar relations were obtained also at 15 and 35°C. The formation constants of $\rm ZnOAc^+$ are listed in Table I.

Discussion

The formation constants of the acetato complexes of copper(II), lead(II) and zinc(II) have been determined by various researchers. Some of them are given in Table II. These are compared with the formation constants given in Table I.

Recently, Yasuda and Yamasaki[18] studied the complex formation of some carboxylic acids by the pH titration method. They compared the stabilities of the complexes of bivalent metal ions and found that the order of Pb > Cu > Zn, Cd > Ni is valid for the complexes which contain co-ordinating groups such as benzoate, phthalate and succinate. The magnitude of the first formation constants of acetato complexes of nickel(II), copper(II), lead(II) and zinc(II) determined by the present authors are in accordance with the above order. This fact supports the validity of the rule proposed by Yasuda and Yamasaki.

The equilibria of the substitution reaction represented by Eq. 1 have been studied. The equilibrium constants so far obtained, however, are considered to be not $K_{\rm M'}^{\rm M}$, but $K_{\rm M',app}^{\rm M}$, because they were determined in the acetate media but not corrected for the effect of acetate ions on the equilibria. In the present paper, the values of $K_{\rm M'}^{\rm M}$ given in Eq. 13 were determined by the extrapolation of the F_0 (or F_0') plot to zero acetate concentration. In Table III, the values of $K_{\rm M'}^{\rm M}$ for the three substitution reactions obtained in this study are summarized together with those obtained by Schwarzenbach et al.[5] for the same reactions. Schwarzenbach and his co-workers studied these equilibria at 20°C in the solution of ionic strength 0.1 with 8×10^{-3} M sodium acetate. The effect of acetato complex formation can be corrected with the relation given by Eq. 14. The original values given by Schwarzenbach et al. were converted to the $K_{\rm M'}^{\rm M}$ values using the formation constants $K_{\rm M(OAc)_n}$ and $K_{\rm M'(OAc)_{n'}}$ determined in this study. The resulting constants are also given in Table III, which are in satisfactory agreement with the $K_{\rm M'}^{\rm M}$ values observed experimentally in this study. This fact proves clearly the validity of the procedure and the results presented in this paper.

Summary

A new procedure for the determination of the formation constants of metal acetate complexes was developed. The procedure is

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[17] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

[18] M. Yasuda and K. Yamasaki, presented at the Symposium on Metal Complexes, Tokyo, November, 1958.

based on the polarographic measurements of the sum of the equilibrium concentrations of the hydrated metal ions and the metal acetate complexes in the presence of an appropriate auxiliary complex-forming substance and of the reference metal ions of which the formation constants of acetate complexes are known.

The procedure was applied to the study of acetatocopper(II), acetatolead(II) and acetatozinc(II) complexes, EDTA being used as an auxiliary complex-forming substance. The overall formation constants $K_{\mathrm{M(OAc)}_n}$ (n=1 and 2) for these metal acetate complexes were determined at an ionic strength of 0.2 at 15, 25 and 35°C.

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