The Kinetics of Substitution Reactions Involving Metal Complexes. IV. Reaction between Lead and Zinc-Ethylenediaminetetraacetate Complexes in Aqueous Solutions

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The substitution reaction of lead ions and zinc-ethylenediaminetetraacetate (EDTA) complexes was investigated by Bril, Bril and Krumholz[1]. The rate of the reaction was followed by measuring the change of the polarographic diffusion current of lead ions with time in acetate buffer solutions using the streaming mercury electrode. The reaction was found to proceed, under the experimental conditions, through three different reaction paths simultaneously, and the rate constants of several reactions were determined.

Although Bril et al.[1] measured the reaction rate in acetate buffer solutions, they did not take consideration of the effect of acetate ions on the reaction rate. Recently, the present authors[2,3] dealt with the substitution reaction of copper ions and lead-EDTA complexes and that of copper ions and zinc-EDTA complexes, and explained the decrease of the reaction rate with increasing concentration of acetate by assuming that the substitution reaction proceeds only through the hydrated metal ions.

In this situation it seems worth while to reinvestigate the substitution reaction of lead ions and zinc-EDTA complexs from the same viewpoint as given in the previous papers[2,3].

Experimental

The preparation of the solutions of lead nitrate, zinc nitrate and disodium ethylenediaminetetraacetate was described in the previous papers[3,4].

The rate of the reaction between lead ions and zinc-EDTA complexes was followed by measuring the change of the polarographic diffusion current of lead ions with time in acetate buffer solutions. Current-time curves were obtained with a Shimadzu RP-2 pen-recording polarograph and a dropping mercury electrode. The latter was the same as described in the previous papers[2-4] and had an m value of 1.27 mg./sec. and a drop time of 3.69 sec. in an air-free 0.1 M potassium chloride solution at 25°C with open circuit.

Measurements were made at 15 and 25°C in acetate buffers of pH 4.8 to 5.7 which contained 0.1 M of sodium acetate. The ionic strength was adjusted to be 0.2 with potassium nitrate, unless otherwise stated. Gelatin was added as a maximum suppressor by 0.01% in concentration.

Results and Discussion

In the solution containing acetate ions less than 0.2 M in concentration, lead(II) forms mono- and diacetato complexes, whereas zinc(II) forms only a monoacetato complex[5]. Therefore, the overall substitution reaction of lead ions and zinc-EDTA complexes in acetate buffer solutions is represented with the equations

$$\mathrm{Pb^{2+} + 2\,OAc^- \rightleftharpoons PbOAc^+ + OAc^- \rightleftharpoons Pb(OAc)_2} \qquad (1)$$

$$\mathrm{Pb^{2+} + ZnY^{2-} \rightleftharpoons PbY^{2-} + Zn^{2+}} \qquad (2)$$

$$\mathrm{Zn^{2+} + OAc^- \rightleftharpoons ZnOAc^+} \qquad (3)$$

where $\mathrm{Y^{4-}}$ means a completely dissociated EDTA anion. Under the condition that both zinc ions and zinc-EDTA complexes are present in a large excess over lead ions, the substitution reaction 2 can be treated simply as

$$\mathrm{Pb^{2+}} \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \mathrm{PbY^{2-}} \qquad (4)$$

The rate equation for the reaction 4 is expressed as[2]

$$-\frac{\mathrm{d}[\mathrm{Pb^{2+}}]_{\mathrm{app}}}{\mathrm{d}t} = k^+[\mathrm{Pb^{2+}}]_{\mathrm{app}} - k^-[\mathrm{PbY^{2-}}] \qquad (5)$$

where $[\mathrm{Pb^{2+}}]_{\mathrm{app}}$ is the concentration of lead ions that can be determined polarographically, and given by the equation

$$[\mathrm{Pb^{2+}}]_{\mathrm{app}} = [\mathrm{Pb^{2+}}] + [\mathrm{PbOAc^+}] + [\mathrm{Pb(OAc)_2}] \qquad (6)$$

Integrating Eq. 5,

$$\ln\{[\mathrm{Pb^{2+}}]_{\mathrm{app}} - [\mathrm{Pb^{2+}}]_{\mathrm{e,app}}\} = -(k^+ + k^-)t + \ln\{[\mathrm{Pb^{2+}}]_{\mathrm{0,app}} - [\mathrm{Pb^{2+}}]_{\mathrm{e,app}}\}$$

is obtained, where subscripts o and e denote

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[1] K. Bril, S. Bril and P. Krumholz, *J. Phys. Chem.*, **59**, 596 (1955); **60**, 251 (1956).

[2] N. Tanaka and K. Kato, This Bulletin, **32**, 1376 (1959).

[3] K. Kato, ibid., **33**, 600 (1960).

[4] N. Tanaka, K. Kato and R. Tamamushi, ibid., **31**, 283 (1958).

[5] N. Tanaka and K. Kato, This Bulletin, **33**, 417 (1960).

the initial and the equilibrium condition, respectively. At the equilibrium of the reaction, the relation

$$\frac{k^+}{k^-}=\frac{[\mathrm{PbY}^{2-}]_e}{[\mathrm{Pb}^{2+}]_{e,\mathrm{app}}}\doteqdot K^{\mathrm{Pb}}_{\mathrm{Zn,app}}\frac{[\mathrm{ZnY}^{2-}]_0}{[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}}$$

may be satisfied, where $K^{\mathrm{Pb}}_{\mathrm{Zn,app}}$ represents the apparent equilibrium constant expressed as

$$K^{\mathrm{Pb}}_{\mathrm{Zn,app}}=\frac{[\mathrm{Zn}^{2+}]_{e,\mathrm{app}}[\mathrm{PbY}^{2-}]_e}{[\mathrm{Pb}^{2+}]_{e,\mathrm{app}}[\mathrm{ZnY}^{2-}]_e}$$

The values of $K^{\mathrm{Pb}}_{\mathrm{Zn,app}}$ were determined polarographically to be 9.0 at 15°C and 5.4 at 25°C in acetate buffer solutions which contained 0.1 M of sodium acetate.

The apparent rate constant, $k^+/[\mathrm{ZnY}^{2-}]_0$, was obtained at varied pH's at two different concentrations of zinc ions but at the same concentrations of other species. The values obtained were plotted against the hydrogen ion concentration. The plots obtained for 15°C are given in Fig. 1, which clearly indicate linear relations existing between $k^+/[\mathrm{ZnY}^{2-}]_0$ and $[\mathrm{H}^+]$. Similar relations were also found at 25°C.

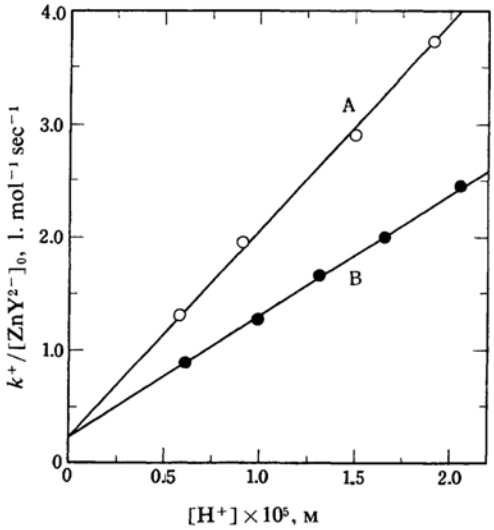

Fig. 1. $k^+/[\mathrm{ZnY}^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}=1.60\times10^{-4}$ M; $[\mathrm{ZnY}^{2-}]_0=5.04\times10^{-3}$ M; $[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}=5.10\times10^{-3}$ M (curve A) and 1.02×10^{-2} M (curve B). Concentrations of free acetate are: 0.098 M (A) and 0.096 M (B).

According to Bril, Bril and Krumholz$^{1)}$, the substitution reaction between lead ions and zinc-EDTA complexes is supposed to proceed simultaneously through the following three reaction paths:

$$\text{(i)}\quad \mathrm{Pb}^{2+}+\mathrm{ZnY}^{2-}\rightleftharpoons\mathrm{PbY}^{2-}+\mathrm{Zn}^{2+}\qquad(7)$$

$$\text{(ii)}\quad \mathrm{ZnY}^{2-}+\mathrm{H}^+\rightleftharpoons\mathrm{ZnHY}^-\qquad(8a)$$

$$\mathrm{Pb}^{2+}+\mathrm{ZnHY}^-\rightleftharpoons\mathrm{PbHY}^-+\mathrm{Zn}^{2+}\qquad(8b)$$

$$\mathrm{PbHY}^-\rightleftharpoons\mathrm{PbY}^{2-}+\mathrm{H}^+\qquad(8c)$$

$$\text{(iii)}\quad \mathrm{ZnY}^{2-}+\mathrm{H}^+\rightleftharpoons\mathrm{Zn}^{2+}+\mathrm{HY}^{3-}\qquad(9a)$$

$$\mathrm{Pb}^{2+}+\mathrm{HY}^{3-}\rightleftharpoons\mathrm{PbY}^{2-}+\mathrm{H}^+\qquad(9b)$$

In the polarographic measurement in acetate media, the concentration of lead ions that is actually measured polarogrphically is not the concentration of hydrated lead ions but the sum of the concentrations of hydrated ions and acetato complexes$^{2)}$. Therefore, if it is assumed that the substitution reaction proceeds only through the hydrated ions which are in equilibrium with the acetato complexes, the apparent rate of the forward reaction ($v^+=k^+[\mathrm{Pb}^{2+}]_{\mathrm{app}}$) determined polarographically is represented by Eq. 10$^{2,3)}$.

$$v^+=k^+[\mathrm{Pb}^{2+}]_{\mathrm{app}}$$

$$=\left\{\frac{k_1{}^+ + k_2{}^+[\mathrm{H}^+]+k_3{}^+[\mathrm{H}^+]\dfrac{1+K_{\mathrm{ZnOAc}}[\mathrm{OAc}^-]}{[\mathrm{Zn}^{2+}]_{\mathrm{app}}}}{1+\sum\limits_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n}\right\}\times[\mathrm{Pb}^{2+}]_{\mathrm{app}}[\mathrm{ZnY}^{2-}]\qquad(10)$$

In Eq. 10

$$\left.\begin{aligned}k_2{}^+&=k_{\mathrm{II}}{}^+K^{\mathrm{H}}_{\mathrm{ZnHY}}\\ k_3{}^+&=k_{\mathrm{III}}{}^+/K_{\mathrm{ZnY}}K_{\mathrm{HY}}\end{aligned}\right\}\qquad(11)$$

where $K^{\mathrm{H}}_{\mathrm{ZnHY}}$ represents the equilibrium constant of the reaction 8a, K_{ZnY}, the formation constant of ZnY^{2-} and K_{HY}, the fourth dissociation constant of ethylenediaminetetraacetic acid. $K_{\mathrm{Pb(OAc)}_n}$ and K_{ZnOAc} represent the overall formation constants of acetatolead(II) and acetatozinc(II) complexes, respectively.

From Eq. 10, Eq. 12 is obtained, where the initial concentrations, $[\mathrm{Zn}^{2+}]_0$ and $[\mathrm{ZnY}^{2-}]_0$, are substituted for $[\mathrm{Zn}^{2+}]$ and $[\mathrm{ZnY}^{2-}]$,

$$\frac{k^+}{[\mathrm{ZnY}^{2-}]_0}=\frac{k_1{}^+ + k_2{}^+[\mathrm{H}^+]+k_3{}^+[\mathrm{H}^+]\dfrac{1+K_{\mathrm{ZnOAc}}[\mathrm{OAc}^-]}{[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}}}{1+\sum\limits_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n}\qquad(12)$$

respectively. Since both Zn^{2+} and ZnY^{2-} are present in the reaction mixture in a large excess over concentration of lead ions, the change of their concentrations during the reaction can be neglected.

The rate constants in Eq. 10 were calculated from the plots of $k^+/[ZnY^{2-}]_0$ against the hydrogen ion concentration, which are tabulated in Table I. The formation constants of acetatolead(II) and acetatozinc(II) complexes which were used in the calculation are those that were determined polarographically at ionic strength 0.2 at 15 and 25°C5). The concentration of uncomplexed acetate in the solution was calculated by successive approximation.

The rate constants of both elementary reactions 8b and 9b were calculated from the relations given in Eqs. 11, using the values of K^{H}_{ZnHY}, K_{ZnY} and K_{HY} which were obtained with the same procedure as described previously3,4) and are given in Table II. The rate constants of three elementary reactions 7, 8b and 9b thus calculated are summarized in Table III.

TABLE I. RATE CONSTANTS IN EQ. 10 OBTAINED EXPERIMENTALLY AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp., °C	Rate constant, l. mol⁻¹ sec⁻¹		
	k_1^+	k_2^+	k_3^+
15	4.6	6×10^5	1.1×10^4
25	8.9	9×10^5	2.4×10^4

TABLE II. EQUILIBRIUM CONSTANTS AT IONIC STRENGTH 0.2 AT VARIUS TEMPERATURES

Temp., °C	$\log K_{ZnY}$	pK_{HY}	$\log K^{H}_{ZnHY}$
15	16.17	10.20	—
20	—	—	2.9
25	15.94	10.04	—

TABLE III. RATE CONSTANTS FOR REACTIONS 7, 8b AND 9b AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp., °C	Rate constant, l. mol⁻¹ sec⁻¹		
	k_1^+	k_{II}^+	k_{III}^+
15	4.6	8×10^2	1.0×10^{10}
25	8.9	1×10^3	1.9×10^{10}

From these results, the rate constants expressed in the form of the Arrhenius equation were derived and the heats of activation and entropies of activation were calculated for three elementary reactions 7, 8b and 9b. The results are given in Table IV.

Bril et al. determined the rate constants of this substitution reaction in acetate buffer solutions of ionic strength 1.0 containing 0.1 M acetate at 25°C1), but they took no account of the effect of acetate ion on the reaction rate. Therefore, the rate constants reported by Bril et al., R_1, R_2 and $R_3$6), correspond to those given by the equations,

$$\left.\begin{aligned} R_1 &= \frac{k_1^+}{1+\sum_{n=1}^{2} K_{Pb(OAc)_n}[OAc^-]^n} \\ R_2 &= \frac{k_2^+}{f_H\{1+\sum_{n=1}^{2} K_{Pb(OAc)_n}[OAc^-]^n\}} \\ R_3 &= \frac{k_3^+\{1+K_{ZnOAc}[OAc^-]\}}{f_H\{1+\sum_{n=1}^{2} K_{Pb(OAc)_n}[OAc^-]^n\}} \end{aligned}\right\} \qquad (13)$$

where f_H means the activity coefficient of hydrogen ions. Since the values of K_{PbOAc}, $K_{Pb(OAc)_2}$, K_{ZnOAc}, K^{H}_{ZnHY}, K_{ZnY} and K_{HY} and f_H are all unknown at ionic strength 1.0 at 25°C, it seems impossible to calculate the rate constants R_1, R_2 and R_3 in Eq. 13, using the values of k_1^+, k_2^+ and k_3^+ obtained in this study.

In the measurement of the reaction rate, Bril et al. employed the streaming mercury electrode. They stated that the streaming electrode had an advantage over the conventional dropping mercury electrode when used as an indicator electrode for kinetic measurements. However, the diffusion current obtained with the streaming mercury electrode was considered less accurate and less reproducible than that obtained with the dropping mercury electrode. For comparison, therefore, the measurements were made under the same condition as Bril et al.'s but with the dropping mercury electrode, and the values of R_1, R_2 and R_3 were determined with the same procedure as mentioned above. The results are given in Table V and compared with the values reported by Bril et al. An agreement between both results seems to indicate no significant discrepancy between the two methods7).

TABLE IV. RATE CONSTANTS, HEATS OF ACTIVATION AND ENTROPIES OF ACTIVATION FOR REACTIONS 7, 8b AND 9b

Reaction	Rate constant, expressed in l. mol⁻¹ sec⁻¹	$\Delta H^{\neq}$, kcal. mol⁻¹	$\Delta S^{\neq}$, e. u.
$Pb^{2+} + ZnY^{2-} \rightarrow PbY^{2-} + Zn^{2+}$	$k_1^+ = 1.1\times10^9 \exp(-11{,}000/RT)$	10	−19
$Pb^{2+} + ZnHY^{-} \rightarrow PbHY^{-} + Zn^{2+}$	$k_{II}^+ = 9.3\times10^7 \exp(-6{,}700/RT)$	6.1	−24
$Pb^{2+} + HY^{3-} \rightarrow PbY^{2-} + H^+$	$k_{III}^+ = 1.2\times10^{18} \exp(-11{,}000/RT)$	10	22

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6) R_1, R_2 and R_3 correspond to k_0^+, k_1^+ and k_2^+, respectively, given in the first paper of Bril, Bril and Krumholz1).

7) The values of R_2 are considerably less accurate than those of R_1 and $R_3$4).

TABLE V. RATE CONSTANTS EXPRESSED IN EQS. 13 OBTAINED EXPERIMENTALLY AT IONIC STRENGTH 1.0 AT 25°C

	Rate constant, l. mol^{-1} sec^{-1}, obtained	
	by Bril et al.	by the present authors
R_1	0.34	0.30
R_2	2×10^4	8×10^4
R_3	1.1×10^3	1.5×10^3

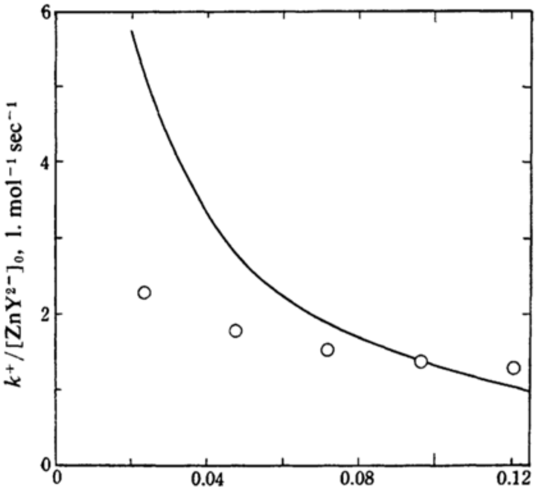

Fig. 2. $k^+/[ZnY^{2-}]_0$ as a function of the acetate concentration in acetate buffer-potassium nitrate solutions of pH 5.09 and ionic strength 0.2 at 15°C. Initial concentrations are: $[Pb^{2+}]_{0,app}=1.65\times10^{-4}$ M; $[ZnY^{2-}]_0=5.00\times10^{-3}$ M; $[Zn^{2+}]_{0,app}=1.00\times10^{-2}$ M. —— indicates the theoretical curve and ○, the experimental value.

From Eq. 10, it is predicted that the reaction rate decreases with increasing concentrations of acetate ions. Using Eq. 12, the values of $k^+/[ZnY^{2-}]_0$ were calculated at various acetate concentrations with the rate constants given in Table I and the formation constants of the acetato complexes. They are plotted against the acetate ion concentration as shown in Fig. 2. The overall rate constants ($k^+/[ZnY^{2-}]_0$) were actually measured at varied acetate concentrations under the conditions in which the theoretical values were calculated. They are also given in Fig. 2. Both the calculated and the experimental values increase with decreasing concentrations of aetate. The discrepancy existing between the calculated and experimental values is considered probably to be due to the contribution of the reaction in which acetato complexes participate.

Summary

The kinetic study of the substitution reaction of lead ions and zinc-EDTA complexs in acetate buffer solutions has been carried out with the same procedure as that reported previously[2-4]. Under the experimental conditions, the reaction is found to proceed simultaneously through three different reaction paths, and the rate constants for three elementary reactions of those reaction paths are determined at ionic strength 0.2 at 15 and 25°C. The heats of activation and the entropies of activation for the three elementary reactions are calculated.

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