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Kinetic Study of Poly(acrylic acid)-Copper(II) Complex Formation

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The kinetics of poly(acrylic acid)-copper(II) (PAA–Cu) complex formation has been studied by a relaxation method. It was found that the greater stability of PAA–Cu complex than that of a monomeric analog is due to the increase of forward rate constant (k_f(PAA)/k_f(GA)=4) and decrease of the reverse rate constant (k_r(PAA)/k_r(GA)=1/4) in the polymer system. The results are explained in terms of an electrostatic effect of polyelectrolyte and a conformational change of the polymer ligand.

Several reports have appeared on the kinetics of complexation reactions of labile metal ions.[1–4] However, reaction with a polymer ligand has not been studied due to the complexity of the polymer system. Although polymer metal complexes, in particular polymer–copper(II) complexes exhibit high activity in the catalytic reaction in solution,[5,6] the mechanism of the catalysis has not been elucidated. In order to study the polymer–copper(II) complex catalyzed reaction in detail, it is necessary to clarify the effect of the polymer ligand on the complexation reaction. Static studies have been carried out on formation reaction of the polymer–copper(II) complexes by several investigators,[7–10] but the kinetics remains unclarified. The complexation reaction of copper(II) being very rapid, a relaxation method can be utilized for determining the reaction rate constant.

This paper deals with a kinetic study of the reaction of copper(II) ion with poly(acrylic acid) by means of the temperature-jump method. Discussion is given on the effect of polymer ligands in the kinetics of the complexation reaction.

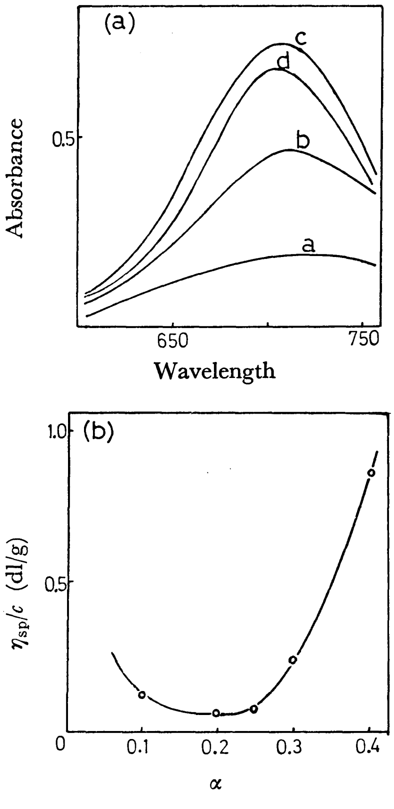


Fig. 1. Viscometric and spectroscopic change of poly(acrylic acid)-copper(II) solution with neutralization. [PAA]$=1.0\times10^{-2}$ unit·mol/l, [Cu]/[PAA]=1/10
(a) a: $\alpha=0.05$, b: $\alpha=0.15$, c: $\alpha=0.25$, d: $\alpha=0.35$

Experimental

Materials. Poly(acrylic acid) (PAA) was prepared by radical polymerization of acrylic acid, its average molecular weight being 1.2×10^5 as determined by viscometric measurement.

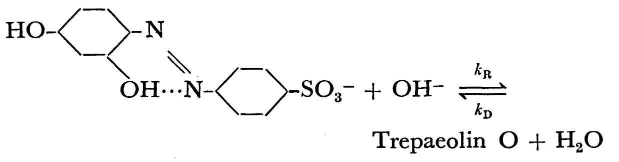
Commercial $CuCl_2\cdot H_2O$, gultaric acid, malonic acid, and other salts were used. The concentration of Cu(II) ion in solution was determined by chelate titration with use of EDTA.

All the solutions were prepared with freshly distilled water.

Methods. The acid dissociation constant of poly(acrylic acid) was determined by Henderson-Haselbach's method[7] by potentiometric titration with a Hitachi-Horiba M-1 pH-meter.

The viscosity of the polymer complex solution was measured at 25 °C with an Ubbelohde viscometer. Visible spectra of the polymer complex solutions were observed with a Shimadzu MPS50 spectrophotometer.

The complexation reaction of Cu(II)–PAA was followed with a temperature-jump apparatus (Union Giken RA-1200), the optical change in the indicator added (bromocresol green and bromochlorophenol blue) being observed. The rise-time of the temperature-jump apparatus is below 1 μs as confirmed from the discharge-curve, the other functions of the apparatus being checked through the reaction of proton exchange on trepaeolin 0,



k_R: $3.8\times10^5\ M^{-1}\cdot s^{-1}$ ($3.6\times10^5\ M^{-1}\cdot s^{-1}$)
k_D: $7.6\times10^3\ s^{-1}$ ($8\times10^3\ s^{-1}$)

where the values in parentheses were taken from the work of Eigen *et al.*[11]

The complexation reaction of each monomeric analog was studied by the same way as in the polymer system.

Result and Discussion

The spectroscopic result showing that the maximum wavelength of d-d absorption spectra of poly(acrylic acid)-copper(II) (PAA–Cu) complex is observed at 700 nm (Fig. 1(a)), near that of malonato copper(II) (MA–Cu) complex (659 nm), suggests that two acrylate units of PAA coordinate to a copper(II) ion, a chelate complex being formed. Thus the complexation reaction of PAA with copper(II) can be expressed by Eq. 1, where L is a coordination unit consisting of two acrylate anions, and HL one consisting of an acrylate anion and an undissociated acrylic acid.

$$\mathrm{M^{2+}} + \mathrm{L^{2-}} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{ML} \qquad k_f/k_r = K$$

$$\mathrm{M^{2+}} + \mathrm{HL^{-}} \underset{k_r'}{\overset{k_f'}{\rightleftharpoons}} \mathrm{ML} + \mathrm{H^+} \tag{1}$$

Analysis of the temperature-jump data requires a prior knowledge of appropriate equilibrium constants. The stability constant of polymer metal complex was determined by a modified Bjerrum's method reported by Gregor *et al.*[7] The acid dissociation constant of polyacid being affected by the charge on the partially dissociated polymer chain, the dissociation constant of PAA was determined by the following equations,

$$K' = \frac{[\mathrm{H^+}][\mathrm{A}]}{[\mathrm{N}]}(\mathrm{Z})^{n-1} \qquad \mathrm{Z} = \frac{\text{charged unit}}{\text{uncharged unit}}$$

$$K_1^{\mathrm{a}} = \frac{[\mathrm{H^+}][\mathrm{HL^-}]}{[\mathrm{H_2L}]} \qquad K_2^{\mathrm{a}} = \frac{[\mathrm{H^+}][\mathrm{L^{2-}}]}{[\mathrm{HL^-}]} \tag{2}$$

$$[\mathrm{A}] = 2[\mathrm{L^{2-}}] + [\mathrm{HL^-}], \quad [\mathrm{N}] = [\mathrm{HL^-}] + 2[\mathrm{H_2L}],$$

$$[\mathrm{L^{2-}}] = \left[\frac{[\mathrm{A}]}{[\mathrm{N}] + [\mathrm{A}]}\right]^2 [\mathrm{L}]_\mathrm{t}$$

where K' and n are given by Henderson-Haselbach plots, and [A], [N], and $[\mathrm{L}]_\mathrm{t}$ are concentration of acrylate anion unit, undissociated acrylic acid unit, and total concentration of uncoordinated ligand unit, respectively. Average coordination number, $\bar{n}$, is given by Eq. 3, where $[\mathrm{H_2L}]_\mathrm{t}$ and $[\mathrm{Cu(II)}]_\mathrm{t}$ are initial concentrations of ligand unit and copper(II) ion, the stability constant K of each system being given by the $\bar{n}$ *vs.* p[$\mathrm{L^{2-}}$] plots according to Bjerrum's theory.

$$\bar{n} = \frac{[\mathrm{H_2L}]_\mathrm{t} - [\mathrm{H_2L}] - [\mathrm{HL^-}] - [\mathrm{L^{2-}}]}{[\mathrm{Cu(II)}]_\mathrm{t}} \tag{3}$$

The equilibrium constants used for analysis of PAA-Cu(II) system and its monomeric analog are given in Table 1.

The ranges of pH and concentrations of PAA and copper(II) ion available are strictly restricted by three factors: (1) decomposition of the chelate structure due to the electrostatic repulsion between carboxylate anions (Figs. 1(a) and 1(b)), (2) olation of the complex or copper ion, and (3) relatively small absorption change in the lower pH region.

TABLE 1. EQUILIBRIUM CONSTANTS (μ=0.1, 25 °C)

Ligand[a]	Equilibrium constant	
PAA(5.0×10^{-3} M) PAA(1.0×10^{-2} M)	pK'=5.91, n=1.83	log K=3.6 log K=3.1
GA[b]	pK_1^{a} = 4.1 pK_2^{a} = 5.0	log K=2.4
MA[b]	pK_1^{a} = 2.8 pK_2^{a} = 5.3	log K=5.0
Indicator	pK_{In}	
Bromocresol green	4.7	
Bromochlorophenol blue	4.0	

a) PAA: Poly(acrylic acid), GA: Glutaric acid, MA: Malonic acid. b) *Cf.* M. Yasuda, K. Yamasaki, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **33**, 1067 (1960).

By applying standard techniques for deriving relaxation time expressions,[3,12] we have

$$1/\tau = Ak_\mathrm{f} + Bk_\mathrm{f}'$$

$$A = \frac{[\mathrm{M^{2+}}]}{1+\alpha} + [\mathrm{L^{2-}}] + \frac{1}{K}$$

$$B = \frac{[\mathrm{M^{2+}}]}{1+\alpha} + [\mathrm{HL^-}] + \frac{1}{K\cdot K_2^{\mathrm{a}}}\left([\mathrm{H^+}] + \alpha\beta\frac{[\mathrm{ML}]}{1+\alpha}\right)$$

$$\alpha = \frac{K_1^{\mathrm{a}}[\mathrm{H^+}] + \beta[\mathrm{H^+}][\mathrm{HL^-}] + [\mathrm{H^+}]^2}{K_1^{\mathrm{a}}K_2^{\mathrm{a}} + 4\beta K_2^{\mathrm{a}}[\mathrm{HL^-}] + \beta K_2^{\mathrm{a}}[\mathrm{L^{2-}}]} \tag{4}$$

$$\beta = \frac{K_{\mathrm{In}} + [\mathrm{H^+}]}{K_{\mathrm{In}} + [\mathrm{H^+}] + [\mathrm{In^-}]}$$

Since acid dissociation "constant" K_1^{a} or K_2^{a} changes in the polymer system with the charge on the polymer, K_1^{a} and K_2^{a} were calculated separately by Eq. 2 for each experimental point.

Plots $(\tau B)^{-1}$ *vs.* AB^{-1} for PAA-Cu(II) at the concentrations of PAA 1.0×10^{-2} M and 0.5×10^{-2} M (Fig. 2). The plots are almost linear, indicating that the standard relaxation techniques can be used for the polymer system. The same plots for the monomeric analog, glutarato-copper(II) (GA-Cu) and malonato-copper(II) (MA-Cu) complexes are illustrated in Figs. 3 and 4. The slopes give k_f's and intercepts k_f' respectively. The rate constants obtained are summarized in Table 2.

When the k_f values of Cu-PAA were compared with those of monomeric analog, the order acetic acid(AA)-Cu>MA-Cu>PAA-Cu>GA-Cu, was observed, which

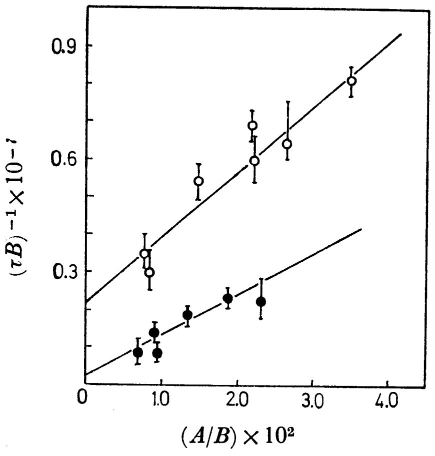


Fig. 2. Plots of $(\tau B)^{-1}$ *vs.* A/B for Cu(II)-PAA system. ○: [PAA]=0.5×10^{-2} M, ●: [PAA]=1.0×10^{-2} M.

TABLE 2. RATE CONSTANTS FOR COMPLEXATION OF Cu(II) WITH CARBOXYLIC ACIDS

Ligand	k_f($\mathrm{M^{-1}\,s^{-1}}$)	k_r($\mathrm{s^{-1}}$)	k_f'($\mathrm{M^{-1}\,s^{-1}}$)
PAA(5.0×10^{-3} M)	1.7×10^8	4.5×10^4	2.2×10^6
PAA(1.0×10^{-2} M)	9.3×10^7	6.8×10^4	4.2×10^5
GA	4.1×10^7	1.6×10^5	3.0×10^5
MA	1.2×10^9	1.2×10^4	3.2×10^7
AA[a]	1.5×10^9	—	—

a) AA: Acetic acid; *cf.* G. Maass, *Z. Phys. Chem., Fraukfurt*, **60**, 131 (1968).

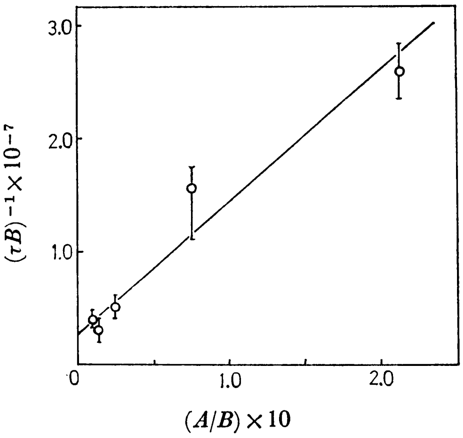


Fig. 3. Plots of $(\tau B)^{-1}$ *vs.* A/B for Cu(II)–GA system.

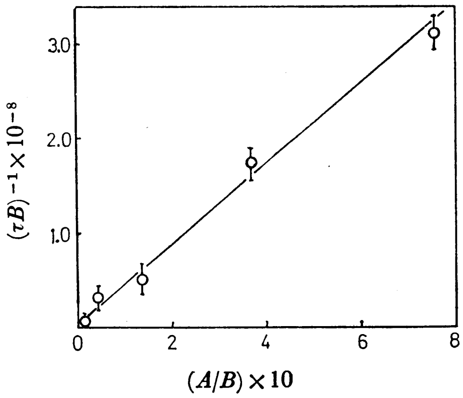


Fig. 4. Plots of $(\tau B)^{-1}$ *vs.* A/B for Cu(II)–MA system.

agrees with that of the stability constants except for the AA–Cu system.

Eigen and Wilkins proposed the following mechanism for bidentate complex formation.[1)]

$$\begin{array}{ccc}
W_2M\ W_1 + A\text{-}B & \overset{K_{os}}{\rightleftharpoons} & W_2M\ W_1A\text{-}B \\
\text{I} & & \text{II} \\
W_2M\ W_1A\text{-}B & \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} & W_2M\text{-}A\text{-}B + W_1 \\
\text{II} & & \text{III} \\
W_2M\text{-}A\text{-}B & \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} & M\langle{}^{A}_{B}\rangle + W_2 \\
\text{III} & & \text{IV}
\end{array} \qquad (5)$$

The first outer sphere complex formation step is very fast and diffusion controlled. If we assume that the outer sphere complex formation is in an equilibrium the forward rate constant k_f is given by

$$k_f = K_{os}k_1\frac{1}{1+(k_1'/k_2)} \qquad (6)$$

The equilibrium constant K_{os} for the outer sphere complex formation is affected by charge on both the metal ion and the ligand, the approximate value being given by[13)]

$$K_{os} = 4Na^3/3000\exp\frac{z_M z_L e_o^2}{\varepsilon a\kappa T} \qquad (7)$$

where N, a, κ and ε are the Avogadro number, the distance of the closest approach of the two ions, the Boltzmann constant and the dielectric constant, respectively, z_M and z_L being the corresponding net charges of metal and ligand.

Comparing the K_{os} value of each system calculated by Eq. 7, we find that the K_{os} values for MA–Cu and GA–Cu are about 7.5 times larger than that for AA–Cu. The K_{os} value of copper with PAA could not be calculated since the net charge of the ligand was not definite. However, it is certain that the K_{os} value for PAA–Cu is greater than that for the monomeric analog due to increase of ligand's net charge by carboxylate anions on the same chain. The large k_f value for PAA–Cu can be explained partially by the electrostatic effect of the neighboring carboxylate anions on the outer sphere complex formation.

The II→III step of each system examined is the substitution of water by carboxylate anion. If we assume that the k_1 values are the same for all the systems, the k_f/K_{os} value gives a measure of the difficulty of the chelate formation. The stability of the chelate ring is dependent on the number of atoms constituting the chelate and 5-(unconjugated system); 6-(conjugated system) membered ring is the most stable. Since the ligands in the complexes we examined are not conjugated, the chelate ring formation is considered to be rather slow in MA–Cu where a six-membered ring is formed, and much slower in GA–Cu where an eight-membered ring is formed. This is in line with the results obtained by means of Eq. 6 where the k_1'/k_2 value of GA–Cu is 30 times larger than that of MA–Cu.

The reduced viscosity of the polymer solution changes with the complexation (Fig. 1 (b)). This suggests that the conformation of the polymer ligand changes with chelate formation or dissociation. A larger k_1'/k_2 value and a smaller k_f/K_{os} value for polymer system as compared with those of monomeric analog are reasonable. However, the k_f value of PAA–Cu we obtained was larger than that of the GA–Cu system. This can not be explained by the effect of polymer ligand on the chelate formation step (III→IV).

The k_f value decreased with the increase of the polymer concentration. This might be due to the formation of intermolecular complex at higher polymer concentration since the anion concentration per one polymer molecule is lowered.

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