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A Kinetic Study of Poly(acrylic acid)–Copper(II) Interactions in Aqueous Solutions

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Concentration-jump kinetic studies of the aqueous poly(acrylic acid)–copper(II) system reveal the presence of a relaxation phenomenon in the time range of 10^2 ms. Kinetic data under various pH's and compositions, together with the potentiometric results, indicate that this relaxation effect is due to the following complex-formation reaction:

$$\mathrm{CuL_2} + \mathrm{L_2}^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Cu(L_2)_2}^{2-},$$

where $\mathrm{L_2}^{2-}$ is a coordination unit consisting of two adjacent carboxylato side groups on the polymer chain. The specific features of the pH dependence of the τ^{-1} value are discussed in relation to the degree of dissociation of the carboxyl groups. The rate and stability constants of the reaction are determined to be: $k_2=5.6\times10^3\ \mathrm{M^{-1}\ s^{-1}}$ (1 M=1 mol dm^{-3}), $k_{-2}=0.7\ \mathrm{s^{-1}}$, and $K_2\ (=k_2/k_{-2})=7.9\times10^3$, at pH 7.0, $I\approx0$, and 25 °C. The overall complex-formation mechanism, involving the very rapid formation of $\mathrm{CuL_2}$, is discussed.

The metal–polymer complex has been the subject of increasing interest recently[1–3] in the fields of the coordination chemistry, biochemistry, and industrial applications. Although there has been a considerable accumulation of experimental results available about metal–polymer systems, most of them have been limited to the equilibrium properties of the systems (based on the measurements by spectrophotometry, potentiometry, ESR, viscosity, and so on) or their catalytic effects. Only a few kinetic studies[4,5] of metal–polymer interactions have been done up to the present.

In the present work, we studied the kinetics of the poly(acrylic acid)–copper(II) system, since the polymer is one of the simplest polyelectrolytes consisting of a uniform arrangement of carboxyl groups and since the nature of the system has been comparatively well known.[6–11] The stopped-flow experiments on this system revealed the presence of a relaxation effect in the time range of 10^2 ms; this is slower by almost three orders of magnitude than the temperature-jump relaxation phenomenon reported in the same system.[4] The relaxation effect is also unusually slow compared with those for the complex formation of copper(II) with simple ligands.[12] The apparent slowness may reflect the restriction of the movement of the side groups on the polymer as well as electrostatic repulsions between the polymer chains. It is the purpose of this work to elucidate the metal–polymer interactions through the kinetic treatment of the relaxation process. The kinetic information obtained will be helpful in understanding the dynamic behavior of metal–polymer systems.

Experimental

Materials. Poly(sodium acrylate), abbreviated as NaPAA, was synthesized[13] from acrylic acid of a reagent grade (Wako Pure Chem., Ltd.), dialized against deionized-distilled water, lyophilized, and finally vacuum-dried at 60 °C for 12 h. The degree of polymerization was determined to be 1400 from the intrinsic viscosity in 2 M NaOH solution.[14] All the other chemicals were of a reagent grade and were used without further purification.

Sample solutions were prepared from aqueous stock solutions of 0.1 M $\mathrm{CuSO_4}$ and 0.1 M NaPAA. Here and hereafter, the concentration of NaPAA (or PAA) will be expressed by the residue mole. The pH of the solutions was controlled with NaOH. No neutral salt was added to the solutions; thus, all the experiments were carried out under an approximately zero ionic strength ($I\approx0$). Bromophenol Blue, Bromocresol Green, Methyl Red, and Bromocresol Purple were used as colorimetric pH-indicators for the kinetic measurements covering the pH range of 4—7. All the solutions were prepared by using deionized-distilled water.

Equilibrium Measurements. The absorption spectra in the UV range of 190—360 nm were recorded on an Union Giken SM-401 spectrophotometer equipped with a data-processing unit. Quartz cells with a path length of 10 mm were used. The concentration of free copper ions in PAA–copper solutions was potentiometrically determined by using a Hitachi-Horiba M-5 pH-meter equipped with a copper-ion electrode (Model 8006-05T).

Kinetic Measurement. The stopped-flow apparatus was a modification of the Union Giken gas pressure-driven type.[15] It was constructed by assembling a mixing unit (Union Giken UO-001) and an optical detection system. The optical path length of the observation cell, equipped with quartz windows, was 10 mm. The reaction signal (transmittance against the time) was stored in a digital memory and then recorded on an X-Y recorder. The dead time of the apparatus was 1.7 ms at a driving pressure of 5 atm and a mixing volume ratio of 1:1. The flow system was thermostatted at 25.0±0.5 °C.

Results and Discussion

The concentration-jump experiments were carried out by mixing the $\mathrm{CuSO_4}$ solution (containing a pH-indicator) and the NaPAA solution. The pH's of both solutions were adjusted to appropriate values to give a definite pH value after mixing. The observed signal curves exhibited a single exponential time-dependence and enabled us to adopt the usual relaxation treatment. All the relaxation times, τ, quoted in this study are the means of several measurements; the maximum errors are about ±15%. A representative relaxation

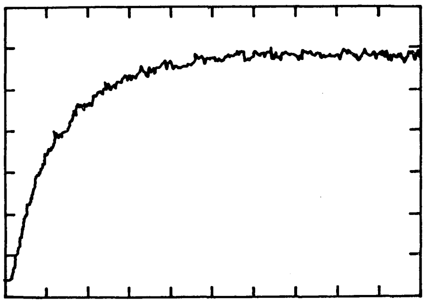

Fig. 1. Relaxation effect in the PAA–copper(II) system; $\Sigma PAA = 1.25 \times 10^{-3}$ M, $\Sigma Cu = 1.25 \times 10^{-4}$ M, pH 7.0, and $I \approx 0$, with 1.0×10^{-5} M Bromocresol Purple as an indicator.
The observation wavelength is 592 nm. The abscissa scale is 200 ms per division, and the vertical scale is in arbitrary unit of absorbance. The relaxation curve corresponds to a decrease in absorbance with time.

effect is shown in Fig. 1. Here, ΣPAA and ΣCu indicate the total concentrations of PAA and copper, respectively. The relaxation curve shows a decrease in the absorbance with the time, indicating a pH decrease due to the deprotonation from carboxyl groups on PAA. The deprotonation can be ascribed to the perturbation of the dissociation equilibrium of the acid groups induced by the complex formation of copper with PAA. Blank experiments of mixing solutions of PAA and an indicator or of diluting a copper-indicator solution with water showed no relaxation effect in the same time range. Therefore, the relaxation phenomenon observed is really to be associated with the PAA–copper interactions.

Additional concentration-jump experiments were carried out without using an indicator. The observation wavelength was 257 nm, at which the PAA–copper(II) system showed an absorption maximum due to complexation, while neither PAA nor copper exhibited any significant absorbance. The relaxation time measured was similar to the τ obtained for the sample with an indicator, but the signal amplitude was much smaller than that in the latter experiment. The relaxation curve showed an increase in the absorbance with the time, indicating the formation of PAA–copper complexes. The above results exhibit that the same phenomenon was observed by the two-type experiments. The presence of another reaction process, which is too fast to be observed by the stopped-flow apparatus, can be conjectured by a comparison of the observed signal amplitude with the total absorption change on mixing the PAA and copper solutions; the faster process contributes most of the absorbance change, while the slower observed process contributes only a small part of it.

Taking into account the results of the earlier equilibrium studies,[6–11] the PAA–copper complexation may proceed *via* the following reaction scheme:

$$\mathrm{Cu} + \mathrm{L_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CuL_2}, \tag{1}$$

$$\mathrm{CuL_2} + \mathrm{L_2} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Cu(L_2)_2}, \tag{2}$$

where the charges are omitted for the sake of simplicity and where L_2 denotes a coordination unit consisting of two adjacent carboxylato groups on a polymer chain. In the above reaction scheme, Eq. 1 is a very fast complex-formation reaction to which the temperature-jump relaxation effect has been ascribed.[4] Therefore, it may be reasonable to ascribe the rapid absorption change, which occurred within the dead time of the present concentration-jump experiments, to the CuL_2 complex formation through Eq. 1.

The result of the potentiometric measurements showed that almost all copper ions bind to PAA and that no free Cu^{2+} remains in the mixed solutions at the pH values higher than 4.5. Therefore, the observed relaxation effect is very likely attributable to the interactions involving uncomplexed carboxylato groups on PAA and copper ions already bound to the polymer sites, *i.e.*, Eq. 2. This assignment was supported by the pH dependence of the reciprocal relaxation time, τ^{-1}, for the solutions of 2.5×10^{-3} M ΣPAA and 2.5×10^{-4} M ΣCu (after mixing). Figure 2 shows the experimental results. In the low pH-region, the τ^{-1} increases with an increase in the pH. With a further increase in pH, the value of τ^{-1} attains its maximum at pH 5.3 and then finally decreases. If we ascribe the observed relaxation effect to Eq. 2, we can easily explain the above features of the pH dependence of τ^{-1}. When the pH increases, the deprotonation of the carboxyl group, HL, on PAA increases the concentration of the uncomplexed carboxylato group, L, resulting in an increase in the L_2 concentration. This effect causes an increase in the τ^{-1} in the lower pH-region. With a further increase in pH, the electrostatic repulsion caused by the high population of the uncomplexed carboxylato groups on PAA prevents the approach of the second coordination unit to form the $Cu(L_2)_2$ complex. This effect explains the decrease in

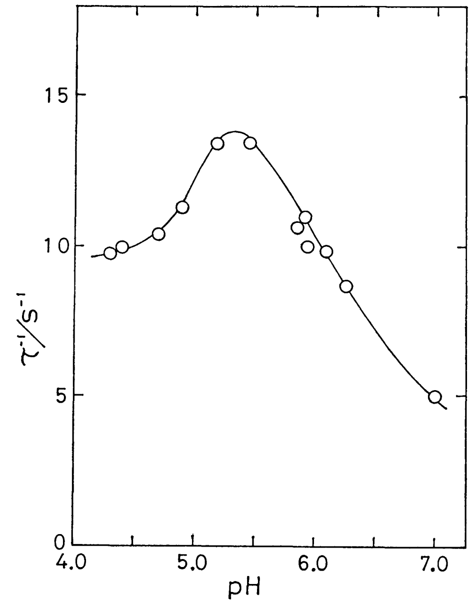

Fig. 2. The pH dependence of the relaxation time for the PAA–copper(II) system; $\Sigma PAA = 2.50 \times 10^{-3}$ M and $\Sigma Cu = 2.50 \times 10^{-4}$ M, at 25 °C and $I \approx 0$.

TABLE 1. KINETIC DATA FOR THE PAA-COPPER(II) SYSTEM[a] AT 25 °C, $I \approx 0$, AND pH 7.0

ΣPAA	ΣCu	R	τ^{-1}
10^{-3} M			s^{-1}
1.25	0.125	10	3.34
2.00	0.200	10	4.12
2.00	0.250	8	4.98
2.50	0.125	20	6.02
2.50	0.250	10	4.79
2.50	0.313	8	4.36
4.00	0.250	16	10.1
4.00	0.400	10	7.30
5.00	0.250	20	12.3
5.00	0.500	10	10.4

a) Solutions contain 1.0×10^{-5} M Bromocresol Purple as an indicator.

τ^{-1} observed in the higher pH-region.

Since the kinetic behavior of PAA varies so much with the pH, as has been described above, the kinetic experiments should be carried out at a constant pH for a quantitative analysis to be made. Thus, the concentration-jump experiments were carried out at pH 7.0 by varying the concentrations of both ΣPAA and ΣCu. The values of τ^{-1} thus obtained are listed in Table 1. The experimental data in Table 1 exhibit the following kinetic features: i) when the concentrations of the polymer (ΣPAA) and copper(II) (ΣCu) simultaneously increase under a constant mixing ratio R ($=\Sigma\text{PAA}/\Sigma\text{Cu}$), the τ^{-1} value increases; ii) the value of τ^{-1} increases with an increase in the polymer concentration at a constant copper(II) concentration, and iii) it decreases with an increase in the copper(II) concentration at a constant polymer concentration.

Below, we will perform a relaxation analysis of the kinetic data in Table 1. From Eq. 2, the rate equation is given by;

$$d[\text{Cu(L}_2)_2]/dt = k_2[\text{CuL}_2][\text{L}_2] - k_{-2}[\text{Cu(L}_2)_2], \tag{3}$$

where the square brackets denote the molar concentrations. By assuming that the carboxyl group, HL, the uncomplexed carboxylato group, L, and the coordinated ligand-unit are randomly distributed over a polymer chain, the concentration of the uncoordinated ligand-unit, L_2, may be expressed in terms of the concentration [L] multiplied by the probability for one definite L to find another L at its adjacent position on the polymer:[16]

$$[\text{L}_2] = \frac{[\text{L}]^2}{[\text{L}]+[\text{HL}]+[\text{CuL}_2]+2[\text{Cu(L}_2)_2]}. \tag{4}$$

The protolytic reactions of acid groups on PAA and of the pH-indicator reach equilibrium much faster than the metal–complex reactions, and they can be assumed to be in equilibrium at all times of the relaxation process. Thus, we may use the equilibrium relations:

$$K_a = ([\text{H}][\text{L}]/[\text{HL}])z^{n-1}, \tag{5}$$

$$K_{\text{In}} = [\text{H}][\text{In}]/[\text{HIn}], \tag{6}$$

where In denotes the anionic form of the indicator; K_a and K_{In} are the dissociation constant of HL and that of the indicator, respectively. The quantity z in Eq. 5 is the ratio of the populations of charged to uncharged groups on the polymer.[7] Taking into account the metal complexation, it is given by:

$$z = \{[\text{L}]+2[\text{Cu(L}_2)_2]\}/\{[\text{HL}]+2[\text{CuL}_2]+2[\text{Cu(L}_2)_2]\}. \tag{7}$$

For the relaxation treatment of Eq. 2, the coupling effect of Eq. 1 can be ruled out, since the potentiometric results indicate that the concentration of the free copper(II) ion is negligibly small in the final equilibrium solutions. Thus, we have the conservation relations:

$$\Sigma\text{Cu} = [\text{CuL}_2] + [\text{Cu(L}_2)_2], \tag{8}$$

$$\Sigma\text{PAA} = [\text{L}] + [\text{HL}] + 2[\text{CuL}_2] + 4[\text{Cu(L}_2)_2]. \tag{9}$$

By expanding Eq. 3 in the vicinity of the equilibrium concentrations and by using Eqs. 4—9 together with the electroneutrality condition, the relaxation time is found to be:

$$1/\tau = k_2 B,$$
$$B = [\text{CuL}_2]\left(\frac{[\text{L}_2]}{[\text{L}]}\right)\left(\frac{4}{1+\alpha} - \frac{[\text{L}_2]}{[\text{L}]}\right) + [\text{L}_2] + \frac{1}{K_2}, \tag{10}$$

where K_2 ($=k_2/k_{-2}$) is the equilibrium constant of Eq. 2 and where:

$$\alpha = \frac{[\text{H}]}{\gamma[\text{L}]+K_a z^{1-n}+(n-1)(1+z)\beta},$$
$$\beta = \frac{[\text{H}][\text{L}]}{[\text{L}]+2[\text{Cu(L}_2)_2]}, \tag{11}$$
$$\gamma = \frac{K_{\text{In}}+[\text{H}]}{K_{\text{In}}+[\text{H}]+[\text{In}]}.$$

The quantity α expresses the contributions from the rapid protolytic reactions to the relaxation time. However, under the present experimental conditions, the values of α were less than 3×10^{-3}, too small to be significant in Eq. 1.

The experimental data in Table 1 were fitted to Eq. 10 by optimizing the adjustable parameters, K_2 and k_2, so as to minimize the root-mean-square percentage deviation between the calculated and observed values of τ^{-1}. The calculations were carried out using an iterative computer routine. As is shown in Fig. 3, the calculated τ^{-1} values agree fairly well with the experimental values (the r.m.s. % deviation=9.5). The K_2, k_2, and k_{-2} values thus determined are shown in Table 2, together with the equilibrium parameters used.

In relation to the $\text{Cu(L}_2)_2$ formation through Eq. 2, the following two possibilities may be considered.[10,11] One is the $\text{Cu(L}_2)_2$ complex formation *via* the intrapolymer reaction; the reacting CuL_2 and L_2 units lie on the same polymer chain, and the complex formation proceeds by means of the bending of the polymer chain. The other is the inter-polymer complex formation; the reacting CuL_2 and L_2 units lie on different polymer chains, and the reaction occurs by the approach of the two polymer chains. In the present kinetic treatment, we assumed, as a first approximation, the random distribution of the reacting units (*i.e.*, CuL_2 and L_2) in solution; thus, we could not discriminate the contributions from the two types of com-

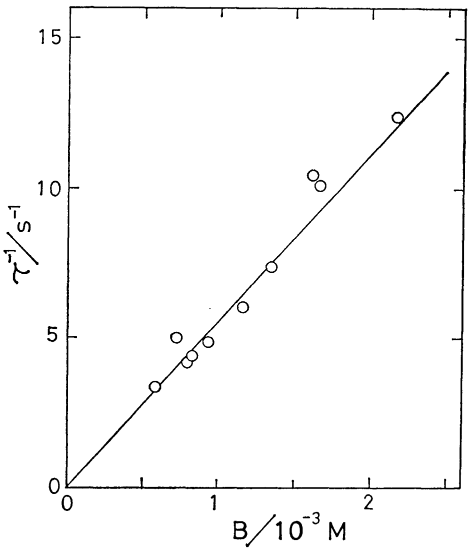

Fig. 3. τ^{-1} *vs.* B plot of the PAA–copper(II) system at 25 °C, $I\approx0$, and pH 7.0.
The straight line expresses the τ^{-1} value calculated by Eq. 10 using the parameters in Table 2.

TABLE 2. EQUILIBRIUM PARAMETERS USED AND KINETIC RESULTS OBTAINED FOR THE PAA–COPPER(II) SYSTEM AT 25 °C, $I\approx0$, AND pH 7.0

Formation constant of the $Cu(L_2)_2$ complex	$K_2=(7.9\pm3.3)\times10^3$ [a]
Dissociation parameters of carboxyl group on PAA	$pK_a=6.17$ [b] $n=2.0$ [b]
Dissociation constant of Bromocresol Purple	$pK_{In}=6.42$ [c]
Rate constants of the $Cu(L_2)_2$ complex formation	$k_2=(5.6\pm0.6)\times10^3$ M^{-1} s^{-1} [a] $k_{-2}=0.7\pm0.3$ s^{-1} [a]

a) This work. b) Ref. 7. c) Ref. 17.

plex formation. For a detailed treatment of the reaction mechanism, we need knowledge of the local distribution of the polymer sites in solution. Therefore, we must be satisfied at present with the determination of the overall rate constants, as given in Table 2.

The rate constant of the $Cu(L_2)_2$ formation (k_2 in Table 2) is by three to four orders of magnitude smaller than the formation-rate constant of CuL_2,[4] *i.e.*, $k_1=(0.93-1.7)\times10^8$ M^{-1} s^{-1}, and also than those of the copper(II) complexes of simple ligands.[12] The unusually small value of k_2 may reflect the electrostatic repulsion between the negatively charged polymer chains, which prohibits the approach of the reacting units in either intra- or the inter-polymer complex formation. Here, it may be worthwhile to consider the reactivity of the polymer from another point of view. According to the Eigen mechanism,[12] the rate constant of the metal-complex formation is described in terms of the association constant, K_0, of the ion-pair formation and the first-order rate constant, k_0, of the water release from the inner-coordination sphere of the metal. Thus, by applying this idea to the present case, we obtain: $k_2=K_0k_0$. An oxygen-17 NMR study of the hexaaquacopper(II) ion[18] gave the rate constant of water exchange as: $k_0=2\times10^8$ s^{-1} (at 25 °C). A comparison of this value with that of k_2 obtained in this study gives an estimate for K_0 of the extremely small value of 10^{-5}. This result also supports the strong hindrance of the approach of the reaction partners of CuL_2 and L_2.

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