Kinetics of ligand exchange reaction of Cu(II)–ammine complex with poly(vinyl alcohol) in aqueous solution

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The kinetics of the ligand exchange reaction of the Cu(II)–ammine complex with poly(vinyl alcohol) (PVA) has been studied by a stopped-flow method at pH 9–10, at μ=0.1 (NH_4Cl) and at 25°C. The reaction is initiated by the formation of unstable $[Cu(NH_3)_3]^{2+}$ by the attack of H^+ on Cu(II)–ammine complex, and proceeds through the mixed complex $\{[Cu(NH_3)_3(O\text{–}PVA)]^{2+}\}$. This step may be rate-determining, followed by a rapid reaction. Finally, the Cu(II) ion is taken up by PVA. The rate is given by $d[Cu(II)\text{–}PVA]/dt = k[H^+]\{[Cu(NH_3)_4]^{2+}\}[PVA]/[NH_4Cl]$, where $k = k_1 + k'_2[H^+]$, $k_1 = 4.25 \times 10\ s^{-1}$ and $k'_2 = 5.20 \times 10^{11}\ l\ mol^{-1}\ s^{-1}$.

Keywords Kinetics; ligand exchange reaction; Copper(II)–ammine complex; poly(vinyl alcohol); stopped flow; Copper(II)–poly(vinyl alcohol) complex; metal–polymer complex

INTRODUCTION

In a previous series of papers, we have studied the complex formation of several transition metal ions with polymeric ligands such as poly(vinyl alcohol)[1,2], the coordination structure[3], the conformation changes of the polymeric chain by the coordination of metal ions to the polymeric ligands[2] and the chemical functions of the metal–polymer complexes obtained[4,5]. Previously, we reported on complex formation of Cu(II) with PVA, discussed thermodynamically, and showed a 'polymeric effect' in the formation of metal-polymer complex[6,7]. Many works have been devoted to the thermodynamic consideration of complex formation between polymeric ligands and metal ions[8]. However, there are few kinetic data available on the formation of metal–polymer complexes.

We have studied the kinetics and mechanism for the exchange reactions of low molecular weight metal complexes with polymeric ligands; these seem of interest in view of the model reactions for metal transport *in vivo*[9].

As a first study, the ligand exchange reaction of Cu(II)–ammine complex with PVA was carried out in aqueous solution under various conditions including variation of the pH in the reaction media and variation of the concentration of the reaction species. The mechanism in the ligand exchange reaction was discussed from the results obtained.

EXPERIMENTAL

Materials

PVA (NM-14), a product of Nippon Synthetic Chemical Industry Co. Ltd., was used. The PVA was separated into several fractions of different average molecular weight according to the method given by Matsumoto[10], and each fraction was completely hydrolysed by alkali in methanol[11]. The concentration of the stock solution of PVA was 0.16 mol l^{-1}. Cu(II)–ammine complex solutions[11] were prepared as follows: a solution of 0.25 mol l^{-1} of NH_4OH aqueous solution was added dropwise with stirring to an aqueous solution containing 4×10^{-4} mol l^{-1} $CuCl_2$ and the pH of the mixed solution was adjusted to the desired pH value with NH_4OH. The ionic strength of the solution was maintained at 0.1 mol l^{-1} with NH_4Cl. A violet-blue aqueous solution of the Cu(II)–ammine complex $\{[Cu(NH_3)_4]Cl_2\}$ was obtained. The complex solutions thus obtained were kept at 25°C for 24 h before each experiment. The other reagents used here were of analytical grade from commercial origin and were used without further purification.

Measurements

The reactions were carried out in a Union Giken RA-401 stopped-flow apparatus or in a Shimazu UV-200 spectrophotometer. pH measurements were carried out with a Hitachi–Horiba F7-SS pH meter. Kinetic measurements were generally made as follows. One solution containing 8×10^{-3} mol l^{-1} PVA was brought to the starting pH with an NH_4OH–NH_4Cl buffer solution. A second solution containing 4×10^{-4} mol l^{-1} Cu(II)–ammine complex and NH_4Cl was brought to the same pH. The ionic strengths of these solutions were maintained at 0.1 mol l^{-1} with NH_4Cl. These solutions were mixed in the ratio 1:1 (v/v) in a 1 cm cell of the stopped-flow spectrophotometer. The 0 to 0.1 optical density range at 400 nm was used in the spectrophotometer. A National VP-526A storage oscilloscope equipped with a Polaroid camera was used to record the data. All rates were measured at 25° ±0.1°C.

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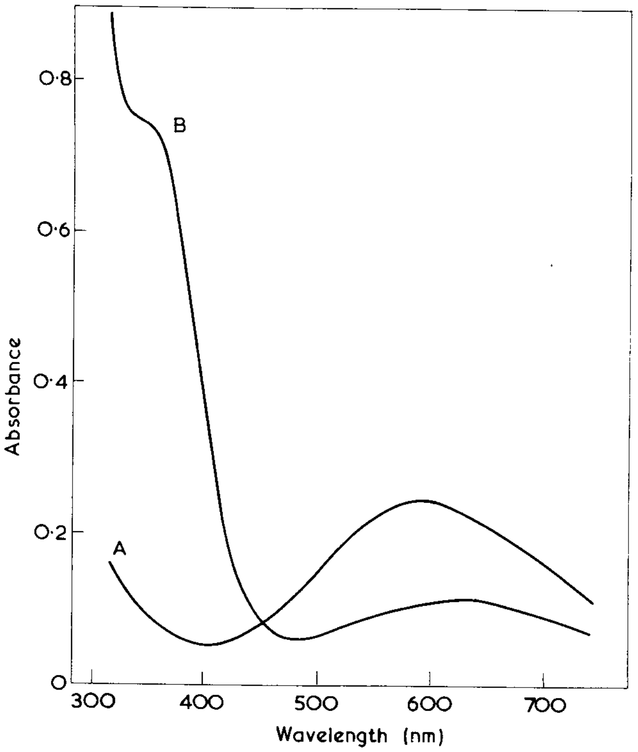


Figure 1 Change in electronic spectra observed (A) before and (B) after the reaction between $[Cu(NH_3)_4]^{2+}$ ion and PVA: $[Cu(NH_3)_4]^{2+}$, 4×10^{-4} mol l^{-1}; [PVA], 8×10^{-3} mol l^{-1}; pH 9.50; $\mu = 0.1$ (NH_4Cl); at 25°C

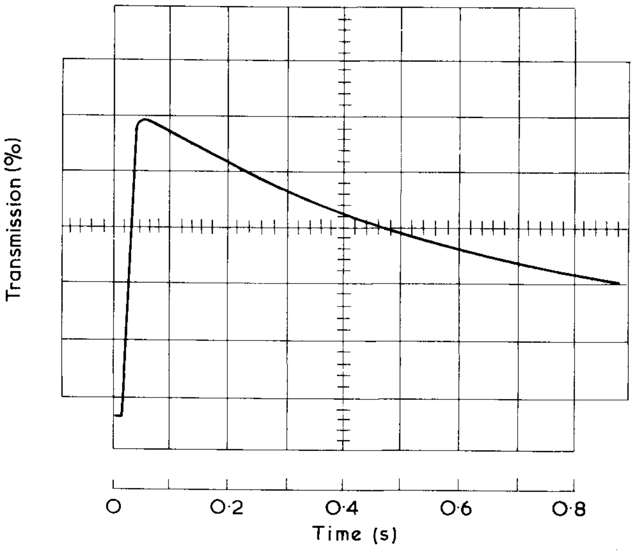


Figure 2 Change in D_{400} for the reaction of $[Cu(NH_3)_4]^{2+}$ with PVA at pH 9.40; $[Cu(NH_3)_4]^{2+}$, 4×10^{-4} mol l^{-1}; [PVA], 8×10^{-3} mol l^{-1}; $\mu = 0.1$ (NH_4Cl); 25°C; 0.1 s cm^{-1}

RESULTS AND DISCUSSION

Spectral results

When the solution containing Cu(II)–ammine complex is added to a solution containing PVA at pH 9.5 and at 25°C, the colour changes from violet-blue to green. The changes in electronic spectra observed before and after the reaction are shown in *Figure 1* as an example. The formation of a complex of PVA with Cu(II) ion was confirmed by the appearance of peaks at 640 as well as at 260 nm, and an absorption shoulder at about 360 nm.[2] As shown in this figure, the formation of Cu(II)–PVA complex can be detected by the appearance of an absorption shoulder at ~360 nm and a peak at 640 nm after the reaction. This suggests that ligand exchange between Cu(II)–ammine complex and PVA is occurring by mixing the solutions. We can observe the time course of the exchange reaction by detecting the remarkable absorption increase at 400 nm.

Kinetic results

The rates of reactions produced by mixing Cu(II)–ammine complexes with a large excess of PVA were followed by monitoring the appearance of the absorption at 400 nm. The stopped-flow oscilloscope traces displayed in *Figure 2* show the decrease of transmitted light intensity as the reaction proceeds. A plot of $\log(A_\infty - A_t)$ as a function of time was obtained using an approximate value for A_∞. A typical run is shown in *Figure 3* and appropriate plots in *Figure 4*.

In general, straight lines were obtained for the reactions. All plots obtained in these experiments showed, as expected, that the reactions in the presence of an excess of PVA and buffered conditions were pseudo-first order.

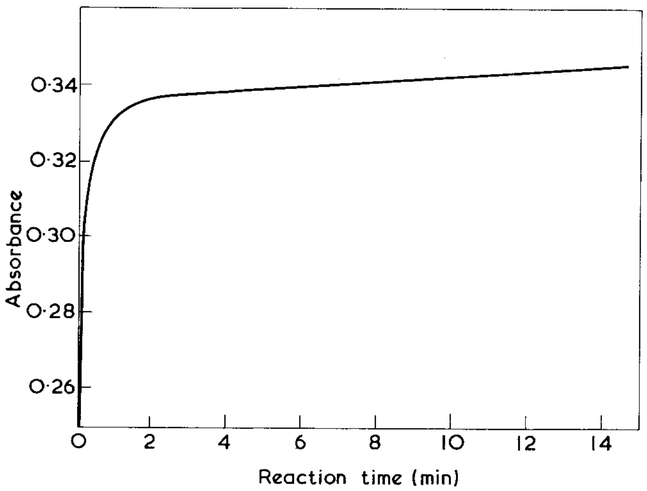


Figure 3 Change in D_{400} for the typical ligand exchange reaction of $[Cu(NH_3)_4]^{2+}$ with PVA: $[Cu(NH_3)_4]^{2+}$, 4×10^{-4} mol l^{-1}; [PVA], 8×10^{-3} mol l^{-1}; pH 9.50; $\mu = 0.1$ (NH_4Cl); 25°C

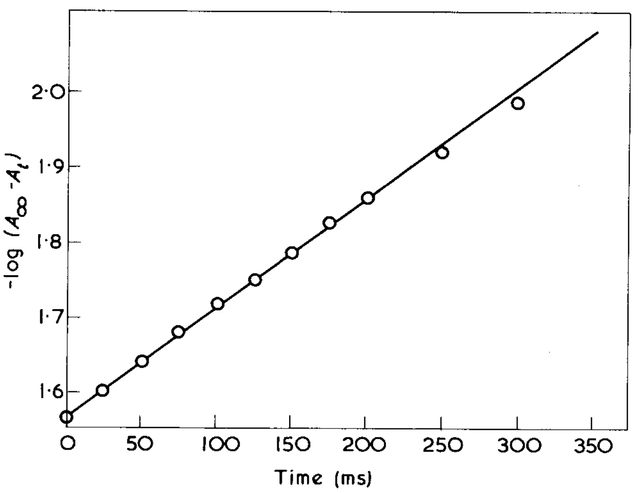


Figure 4 Semilog plots of log $(A_\infty - A_t)$ as a function of time for the reactions shown in *Figure 3*

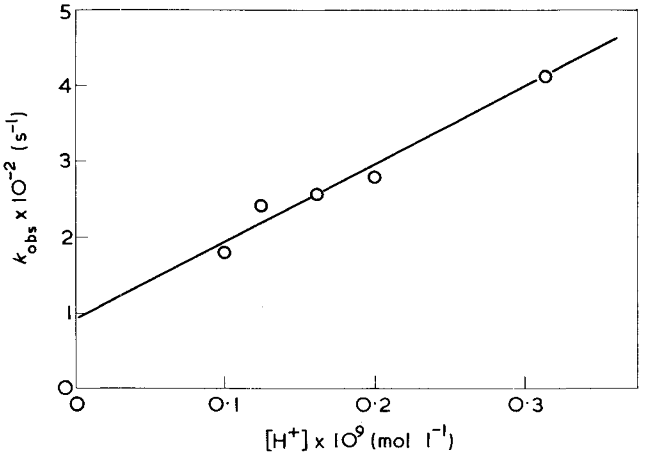


Figure 5 k_{obs} as a function of hydrogen ion concentration: $[Cu(NH_3)_4]^{2+}$, 4 x 10^{-4} mol l^{-1}; [PVA], 8 x 10^{-3} mol l^{-1}; $\mu = 0.1$ (NH_4Cl); 25°C

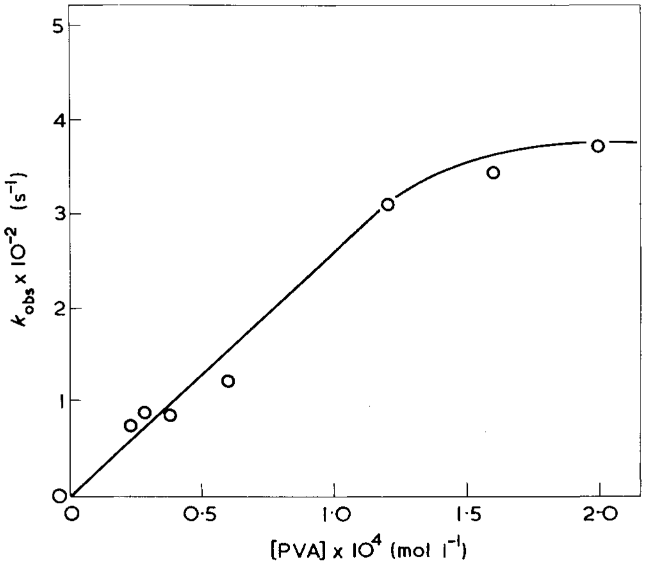


Figure 6 Effect of PVA concentration on the reaction of $[Cu(NH_3)_4]^{2+}$ with PVA: $[Cu(NH_3)_4]^{2+}$, 4 x 10^{-4} mol l^{-1}; pH 9.50; $\mu = 0.1$ (NH_4Cl); 25°C

From these findings, the reaction of Cu(II)–ammine complex with excess PVA followed the rate expression:

$$\frac{d[Cu(II)\text{–}PVA]}{dt} = k_{obs}\{[Cu(NH_3)_4]^{2+}\} \qquad (1)$$

The ligand exchange reactions were carried out at 25°C and $\mu = 0.1$ (NH_4Cl), varying the pH in the range pH 9.0–10.0 and keeping the concentrations of Cu(II)–ammine complex and PVA constant. *Figure 5* shows k_{obs} plotted against the initial concentration of hydrogen ion. From the figure it was found that k_{obs} is proportional to $[H^+]^{1.0}$. Thus the reactions exhibit specific acid catalysis.

In another series of runs, the dependence of k_{obs} on the initial concentration of PVA was studied at constant concentration of Cu(II)–ammine complex, at pH 9.5, at $\mu = 0.1$ (NH_4Cl) and at 25°C (*Figure 6*). From *Figure 6* it was found that the rate of the exchange reaction was proportional to the PVA concentration under the condition that the value was below 1.5×10^{-4} mol l^{-1}; on the other hand, above this the rate was not proportional to the PVA concentration and was approximately constant.

Finally, the ligand exchange reactions were carried out at 25°C and pH 9.5, varying the concentration of NH_4Cl, and keeping the concentrations of Cu(II)–ammine complex as well as PVA constant. The dependence of k_{obs} on the initial concentration of NH_4Cl is shown in *Figure 7*. From the results in *Figure 7* it was found that k_{obs} is inversely proportional to $[NH_4Cl]^{1.0}$.

From these findings, the rate of the substitution reaction is proportional to $\{[Cu(NH_3)_4]^{2+}\}$, as well as [PVA], and varies inversely with respect to [NH_4Cl]. Therefore, the rate is given by

$$\frac{d[Cu(II)\text{–}PVA]}{dt} = k\frac{[H^+]\{[Cu(NH_3)_4]^{2+}\}[PVA]}{[NH_4Cl]} \qquad (2)$$

$$= k_{0(H)}\frac{\{[Cu(NH_3)_4]^{2+}\}[PVA]}{[NH_4Cl]} \qquad (3)$$

$$= k_1\frac{\{[Cu(NH_3)_4]^{2+}\}[PVA]}{[NH_4Cl]}$$

$$= k_1\frac{\{[Cu(NH_3)_3\text{---}(NH_3\cdots\cdots H^+)]^{3+}\}[PVA]}{[NH_4Cl]} \qquad (4)$$

$$= k_1\frac{\{[Cu(NH_3)_4]^{2+}\}[PVA]}{[NH_4Cl]} + k_2'\frac{\{[Cu(NH_3)_3\text{---}(NH_4^+)]^{2+}\}[PVA]}{[NH_4Cl]} \qquad (5)$$

$$= (k_1 + k_2'[H^+])\frac{\{[Cu(NH_3)_4]^{2+}\}[PVA]}{[NH_4Cl]} \qquad (6)$$

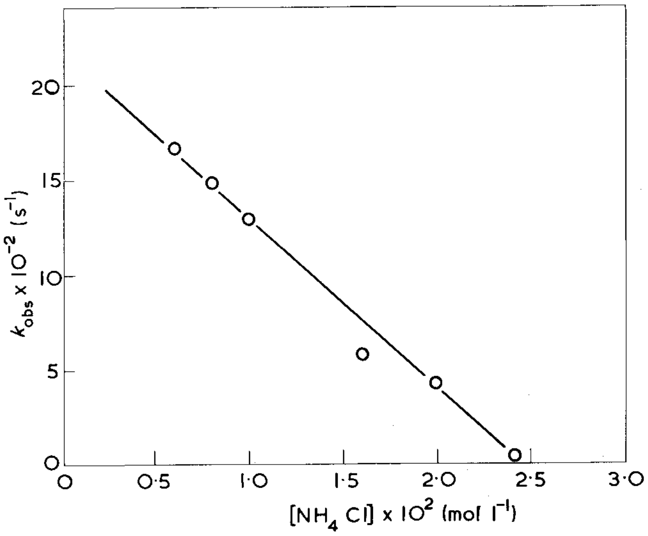


Figure 7 Effect of NH_4Cl concentration on the reaction of $[Cu(NH_3)_4]^{2+}$ with PVA: $[Cu(NH_3)_4]$, 4 x 10^{-4} mol l^{-1}; [PVA], 8 x 10^{-3} mol l^{-1}; pH 9.50; 25°C

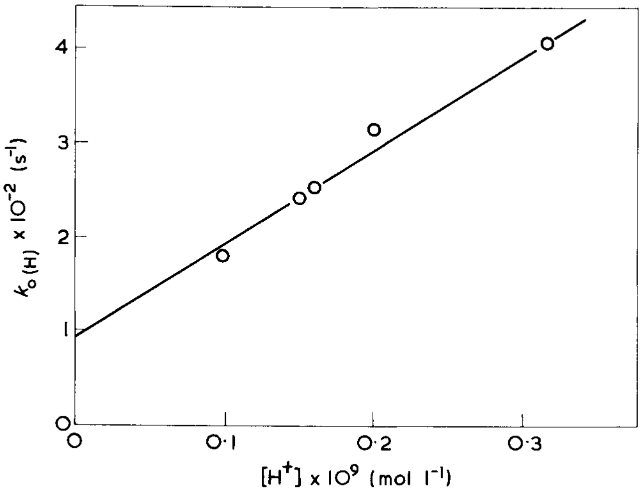
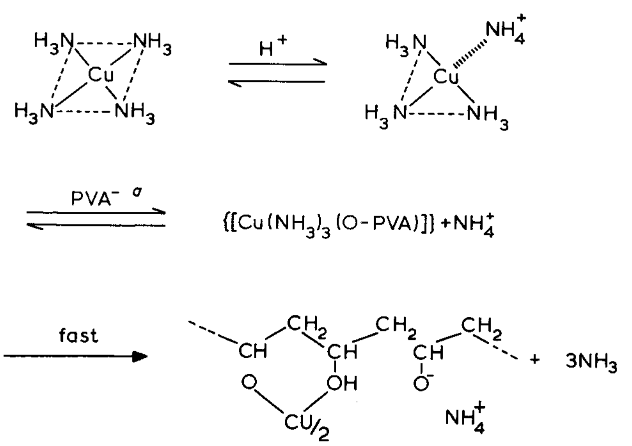


Figure 8 $k_{0(H)}$ as a function of hydrogen ion concentration obtained from *Figure 5*



^{a} pK_a of poly(vinyl alcohol) is 10.65 at 25°C and at μ = 0.1 (KCl)[6]

Figure 9 Schematic representation of the reaction of $[Cu(NH_3)_4]^{2+}$ complex with poly(vinyl alcohol) in aqueous solution

where

$$k_{0(H)} = k_1 + k_2'[H^+] = k_{obs}\frac{[NH_4Cl]}{[PVA]} \qquad (7)$$

In *Figure 8*, the values of $k_{0(H)}$ determined at various pHs and concentrations of $[Cu(NH_3)_4]^{2+}$ complex and of PVA are plotted against the hydrogen ion concentration. It is evident from the figure that $k_{0(H)}$ is linearly related to hydrogen ion concentration. From the slope of the graph in *Figure 8*, $k_2' = 5.20 \times 10^{11}$ l mol^{-1} s^{-1} for the dissociation of the Cu(II)–ammine complexes at pH 9.0–10.0 and 25°C.

The plots give zero intercept. The presence of a small positive intercept may reflect an $[H^+]$ term. From this intercept, $k_1 = 4.25 \times 10$ s^{-1}, and combining and rearranging equations (4) and (5), we obtain

$$k_2 = \frac{\{[Cu(NH_3)_3(NH_4^+)]^{3+}\}}{[H^+]\{[Cu(NH_3)_4]^{2+}\}} = K^{H+}_{Cu(NH_3)_4} \qquad (8)$$

$$k_2 = \frac{k_2'}{K^{H^+}_{Cu(NH_3)_4}} \qquad (9)$$

where $K^{H^+}_{Cu(NH_3)_4}$ is the successive acid hydrolysis constant[12]. Therefore, $k_2 = 5.20 \times 10^5$ l mol^{-1} s^{-1}.

Mechanism of the ligand exchange reaction

In the substitution of Cu(II)–ammine complex with PVA, a proton first attacks the $[Cu(NH_3)_4]^{2+}$ complex and the resulting NH_4^+ is released from $[Cu(NH_3)_4]^{2+}$. Once the NH_4^+ is released, the Cu(II)–ammine complex becomes unstable, and the $[Cu(NH_3)_3]^{2+}$ is attacked by PVA. A mixed complex $[Cu(NH_3)_3(O\text{–}PVA)]^+$ may be formed. This step may be rate-determining, followed by a rapid reaction, and Cu(II) ion is taken up by PVA. OH groups in PVA dissociate into O$^-$ ions in more alkaline solution[2]: pK_a = 10.67, μ = 0.1 (KNO$_3$), 25°C. Therefore, NH_4^+ released from $[Cu(NH_3)_4]^{2+}$ may be trapped by partially dissociated PVA anions. These steps can be described as in *Figure 9*.

After this ligand exchange reaction, NH_4^+, Cl$^-$ and free NH$_3$ were removed by dialysis from the reaction mixture. From the solutions thus obtained, Cu(II)–PVA film was prepared by casting on polyethylene film in dust-free air at 30°C. The film was dried under vacuum for several days. Elemental analysis of the film was carried out. From the result, the N content of Cu(II)–PVA film is found to be zero. The infra-red and electronic spectra of the film were identical with those of Cu(II)–PVA complexes in a previous series of papers[11,13]. Therefore, it was found that the coordination of NH$_3$ to Cu(II) atom in Cu(II)–PVA may not occur.

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