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Kinetics of Ligand Exchange Reaction of Cu(II)–Poly(vinyl alcohol) Complex with Ethylenediamine-*N,N,N′,N′*-tetraacetic Acid

Tsuneo SUZUKI,** Hirofusa SHIRAI,* Fukashi SHIMIZU,*
and Nobumasa HOJO***

Faculty of Textile Science and Technology,
Shinshu University, Ueda 386, Japan

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ABSTRACT: The kinetics of the ligand exchange reaction of the Cu(II)–poly(vinyl alcohol) (PVA) complex with ethylenediamine-*N,N,N′,N′*-tetraacetic acid (edtaH_4) was studied by a stopped-flow method at pH 9.34—11.05, at $\mu=0.1$ (KNO_3) and at 25.0°C. The substitution reaction proceeds simultaneously through two different reaction paths. In one path, the reaction is initiated by the attack of H^+ on the bond between Cu(II) ion and dissociated $-O^-$ of PVA to form unstable Cu(II)–H-PVA. In the other path, solvolysis by water as a nucleophilic reagent proceeds. The rate law is written as $-d[\text{Cu(II)–PVA}]/dt=k[\text{Cu(II)–PVA}]/[\text{PVA}]$ where $k=k_1+k_2'[H^+]$, $k_1=3.62\times10^{-3}\ \text{M s}^{-1}$ and $k_2'=2.83\times10^{7}\ \text{s}^{-1}$ respectively. The rates were found to be independent of the edta anion concentration. A possible mechanism for the substitution reaction is discussed.

KEY WORDS Ligand Exchange Reaction / Cu(II)–Poly(vinyl alcohol) Complex / Ethylenediamine-*N,N,N′,N′*-tetraacetic Acid / Stopped-Flow Method /

In a previous series of papers, a study was made of the complex formation of several metal ions with polymeric ligands such as poly(vinyl alcohol), the coordination structure, conformation change of polymeric chain and the chemical functions of the metal–polymer complexes.[1–5]

Much research has been carried out on the kinetics and mechanisms of the ligand exchanges of metal complexes between other low molecular weight ligands.[6–8] However, there are little similar kinetic data available on metal–polymer complexes.[9] The kinetics and mechanisms of the ligand exchange reactions of metal–polymer complexes with other monomeric or polymeric ligands seem of interest in view of the model reactions for the metal transport *in vivo* and the basis of mechanochemical reactions by ligand exchange reactions as well as the incorporation of metal ions into chelate resins.[10,11]

We studied the kinetics and mechanisms of the exchange reactions of metal–polymer complexes with other ligands (ligand exchange reaction) or metal ions (metal exchange reaction). The present paper concerns ligand exchange kinetics between Cu(II)–poly(vinyl alcohol) (PVA) complexes and ethylenediamine-*N,N,N′,N′*-tetraacetic acid (edtaH_4) in aqueous solution.

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 weights according to the fractional precipitation given by Matsumoto[12]; each fraction was completely hydrolyzed by alkali in methanol.[4] The concentration of PVA ($\bar{P}_n=1400$) used in these experiments was 0.16 mol dm^{-3}. Reagent grade Na_2edtaH_2 was obtained from Wako Pure Chemical Ind. and purified by recrystallization

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* To whom correspondence should be addressed.

** Present address: *Nagano-ken Junior College, 49–7, Miwa 8-chome, Nagano 380, Japan.*

*** Present address: *Shinshu University, Matsumoto, Nagano 390, Japan.*

four times from methanol–water. Na_eedtaH_2 dried in air at 80°C was dissolved in 0.2 mol dm^{-3} KNO_3 aqueous solution. The concentration of a stock solution of Na_2edtaH_2 was 2×10^{-2} mol dm^{-3}. Cu(II) ion solutions were prepared from a stock solution of $Cu(NO_3)_2 \cdot 3H_2O$ standardized by an atomic absorption spectrophotometer (Hitachi 207 type). Cu(II)–PVA complex solutions were prepared as follows. An aqueous solution of Cu(II) ion was added to the PVA solution, and the pH of the mixed solution was adjusted to the desired pH value with KOH. The ionic strengths of the Cu(II)-complex solutions were maintained at 0.1 mol dm^{-3} with KNO_3. 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 obtained from commercial sources and used without further purification.

Method

Electronic spectra were measured on a Shimadzu UV-200 spectrophotometer. The reactions were carried out in a stopped-flow apparatus of Union Giken RA-401 (dead time = 1 ms) or a Shimadzu UV-200 spectrophotometer. The pH measurements were carried out with a Hitachi-Horiba F7-SS pH meter. In most cases, the kinetic measurements were made as follows. One solution containing $\sim 1.6 \times 10^{-1}$ mol dm^{-3} PVA and 8×10^{-6} mol dm^{-3} Cu^{2+} ion was brought to the starting pH. Ionic strength was maintained at 0.10 mol dm^{-3} with KNO_3. A second solution of Na_2edtaH_2 and KNO_3 (concentration necessary to bring the ionic strength 8×10^{-3} to 0.1 mol dm^{-3}) was brought to the same pH. These solutions were mixed in the ratio of 1 : 1 in a 1 cm cell inserted into a stopped-flow spectrophotometer. The optical density range of 0 to 0.35 at 360 nm was used for the absorption measurements. 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 and were the average from at least five runs.

RESULTS AND DISCUSSION

Kinetic Results

Cu(II)–poly(vinyl alcohol) (PVA) complex imparts a green color to aqueous solution above pH 7.3. The 640 nm, 260 nm peaks and an absorption shoulder at about 360 nm in the electronic spectra of the solution correspond to the formation of complexes of PVA with Cu(II) ion.[4] When a solution containing edta anions is added to a solution of the Cu(II)–PVA complex, the color of solution changes from green to light blue. This suggest that the ligand exchange reaction between the Cu(II)–PVA complex and edta anion occurs under the experimental condition and is much favored to the right so that the reaction goes to completion; the reverse reaction can be neglected in the kinetic study. The overall ligand substitution may be described as

$$\text{Cu(II)–PVA} + \text{edta} \rightarrow \text{Cu(II)–edta} + \text{PVA} \quad (1)$$

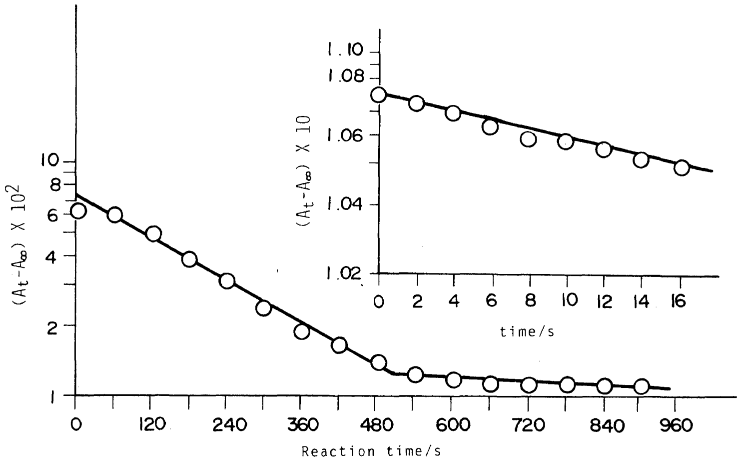


Figure 1. Semilog plot of $(A_t - A_\infty)$ as a function of time for the reaction of Cu(II)–PVA complex with edta anion in aqueous solution at pH 10.5, $\mu = 0.1$ (KNO_3) and at 25°C: [Cu(II)–PVA] $= 4 \times 10^{-4}$ mol dm^{-3}; [EDTA] $= 4 \times 10^{-3}$ mol dm^{-3}; $T_{Cu^{2+}}/T_{HL} = 0.05$; $\bar{P}_n$ of PVA = 1400.

where edta refers to ethylenediamine-*N,N,N′,N′*-tetraacetic acid anion species. The decomposition of the Cu(II)–PVA complex by edta anion can be detected by the disappearance of the absorption shoulder at about 360 nm. The reaction rates produced by mixing Cu(II)–PVA complexes with a large excess of edta anions were followed by monitoring the disappearance of absorption at 400 nm. Too fast to be measured by conventional means, the rates of this reaction were measured by stopped-flow techniques.

Plots of $\log(A_t - A_\infty)$ as a function of time were obtained using an approximate value (infinite value for the reaction) for A_∞; t is the time after the beginning of the reaction; A_t and A_∞ are the absorbances of the reaction system at $t=t$, and ∞, respectively. A typical run is shown in Figure 1. In general, straight lines were obtained for the reaction. All plots obtained in these experiments showed, as expected, that the reactions in the presence of a large excess of edta anions and under buffered conditions (0.1 mol dm^{-3} KNO_3) were of the pseudo-first order. Thus, the reaction of Cu(II)–PVA complex with a large excess of edta anion is

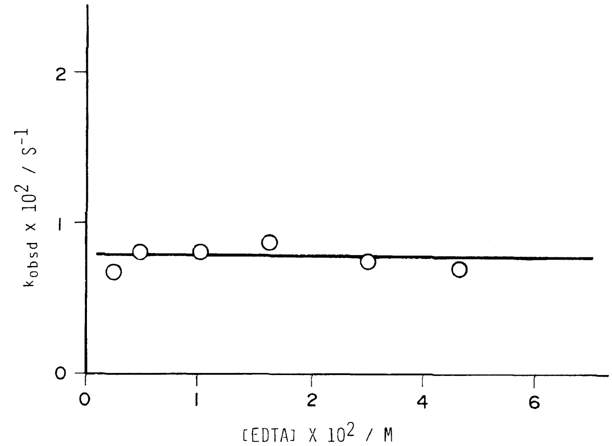


Figure 2. k_{obsd} as a function of edta anion concentration: [Cu(II)–PVA] = 1.6×10^{-3} mol dm^{-3}; [PVA] = 3.2×10^{-2} mol dm^{-3}; pH 10.5; $T_{Cu^{2+}}/T_{HL} = 0.05$; $\mu = 0.1$ (KNO_3), 25°C.

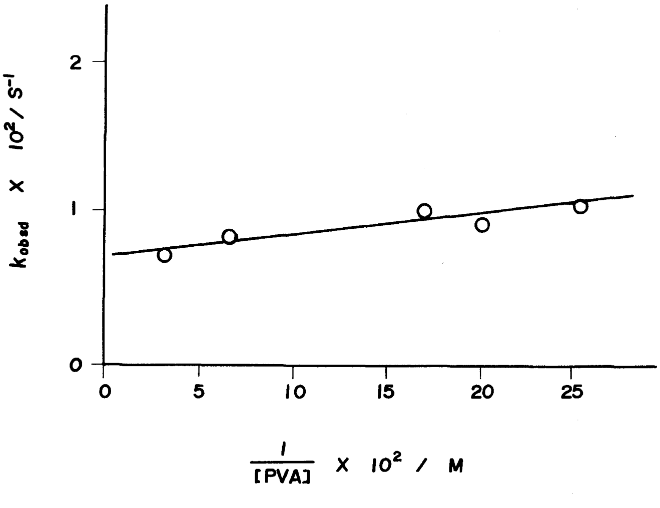


Figure 3. k_{obsd} as a function of PVA concentration for the ligand exchange reaction: [EDTA] = 4×10^{-3} mol dm^{-3}; pH = 10.5; $\mu = 0.1$ (KNO_3), 25°C.

expressed as:

$$-\frac{\mathrm{d[Cu(II)\text{–}PVA]}}{\mathrm{d}t}=k_{\mathrm{obsd}}\mathrm{[Cu(II)\text{–}PVA]} \tag{2}$$

where k_{obsd} is the conditional rate constant.

The dependence of k_{obsd} on the initial concentration of edta anions was studied at a constant concentration of Cu(II)–PVA and at pH 10.5. The value of k_{obsd} was plotted against the initial concentration of edta anions in Figure 2. The reaction order with respect to the initial concentration of edta anions was found to be zero. Next, the ligand exchange reaction between Cu(II)–PVA complex and edta anion was carried out at pH 10.5 and at 25°C. In these experiments, the Cu(II)–PVA complexes were prepared keeping the concentration of Cu(II) ions constant and varying the ratio of the total concentration of Cu(II) ions to the concentration of ligand ($T_{\mathrm{Cu^{2+}}}/T_{\mathrm{HL}}$). The results are shown in Figure 3. The figure shows k_{obsd} to be inversely proportional to the concentration of PVA. From these findings, the rate of the ligand exchange reaction is expressed as:

$$-\frac{\mathrm{d[Cu(II)\text{–}PVA]}}{\mathrm{d}t}=k_{\mathrm{O(H)}}\frac{\mathrm{[Cu(II)\text{–}PVA]}}{\mathrm{[PVA]}} \tag{3}$$

where $k_{\mathrm{O(H)}}$ refers to the conditional rate constant involving the concentration term of hydrogen ions.

Finally, the ligand exchange reaction was carried out at 25°C, varying the pH in the range 9.34—11.05, and keeping Cu(II)–PVA and edta anion concentrations constant. Figure 4 shows $k_{\mathrm{O(H)}}$ plotted against the initial hydrogen ion concentration. It is evident from Figure 4 that $k_{\mathrm{O(H)}}$ is linearly related to the hydrogen ion concentration. Thus, we obtain the following rate expression[13,14]:

$$-\frac{\mathrm{d[Cu(II)\text{–}PVA]}}{\mathrm{d}t}=k_1\frac{\mathrm{[Cu(II)\text{–}PVA]}}{\mathrm{[PVA]}}+k_2'\frac{\mathrm{[H^+][Cu(II)\text{–}PVA]}}{\mathrm{[PVA]}} \tag{4}$$

From the intercept and slope in Figure 4, k_1 and k_2' may be obtained: $k_1=3.62\times10^{-3}\ \mathrm{M\,s^{-1}}$ and $k_2'=2.38\times10^{7}\ \mathrm{s^{-1}}$.

Mechanism of Ligand Exchange Reaction

We have already reported that the complex formation of PVA with Cu(II) ion is expressed by the following two successive steps[3]:

$$\mathrm{Cu^{2+}+HL}\ \underset{K^{-\mathrm{H}}_{\mathrm{Cu(II)\text{–}L}}}{\rightleftharpoons}\ \mathrm{Cu(II)\text{–}L+H^+} \tag{5}$$

$$\mathrm{Cu(II)\text{–}L+HL}\ \underset{K^{-\mathrm{H}}_{\mathrm{Cu(II)\text{–}L_2}}}{\rightleftharpoons}\ \mathrm{Cu(II)\text{–}L_2+H^+} \tag{6}$$

where HL refers to two monomeric units of PVA. The rate law of the ligand exchange reaction between Cu(II)–PVA complex and edta anion as in eq 4 is consistent with the following mechanism.

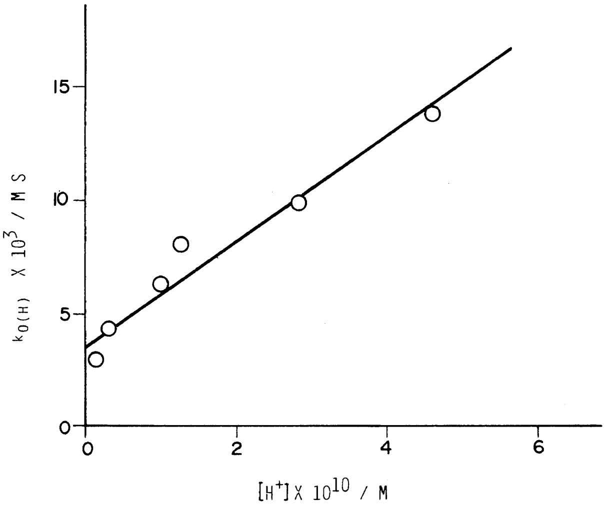
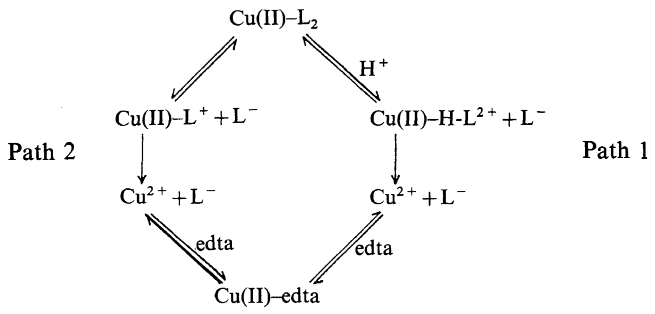


Figure 4. $k_{\mathrm{O(H)}}$ as a function of hydrogen ion concentration for the ligand exchange reaction: [Cu(II)–PVA]$=4\times10^{-4}$ mol dm^{-3}; [EDTA]$=4\times10^{-3}$ mol dm^{-3}; $T_{\mathrm{Cu^{2+}}}/T_{\mathrm{HL}}=0.05$; $\mu=0.1$ (KNO$_3$), 25°C.



Under the experimental conditions, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid is given in the form of edtaH^{3-} (37%) and edta^{4-} (63%) (pK_{a4} = 10.26).[15] In Path 1 of the mechanism, a proton from edtaH^{3-} first attacks the bond between the Cu(II) ion and dissociated $-\mathrm{O}^-$ of PVA to form unstable Cu(II)–H-PVA. Once protonated, the Cu(II)–PVA complex becomes unstable and PVA is partially dissociated from the complex. It hardly seems possible that edta^{4-} attacks the free site of partially dissociated Cu(II)–H-PVA to form a ternary complex edta–Cu(II)–H-PVA. The dissociation of PVA from the Cu(II)–H-PVA complex should be the rate-determining step, and then free Cu(II) ions are taken up by edta^{4-}. This dissociative process is supported by the experimental evidence that the rate of the reaction is independent of the concentration term of edta anions. The mechanism of this reaction belongs to the D-mechanism proposed by Langford.[16] The fact that the rate of the ligand exchange reaction is dependent on the concentration of $[\mathrm{PVA}]^{-1.0}$ indicates the participation of PVA in the step prior to the rate-determining step. On the other hand, Path 2 of the mechanism is solvolysis by water as a nucleophilic reagent. But it seems reasonable to consider that the contribution of this path to the reaction rate is smaller than the proton-assisted path because of the stability of the Cu(II)–L$_2$ complex under the experimental conditions.

The second term of eq 4 shows the participation of the protonated complex Cu(II)–H-PVA. Thus, substituting the successive stability constant of Cu(II)–PVA complex shown in eq 6, we have

$$-\frac{d[\mathrm{Cu(II)\text{–}PVA}]}{dt} = k_1 \frac{[\mathrm{Cu(II)\text{–}PVA}]}{[\mathrm{PVA}]} + k_2' K^{-\mathrm{H}}_{\mathrm{Cu(II)-PVA}} \frac{[\mathrm{Cu(II)\text{–}H\text{-}PVA}]}{[\mathrm{PVA}]} \tag{7}$$

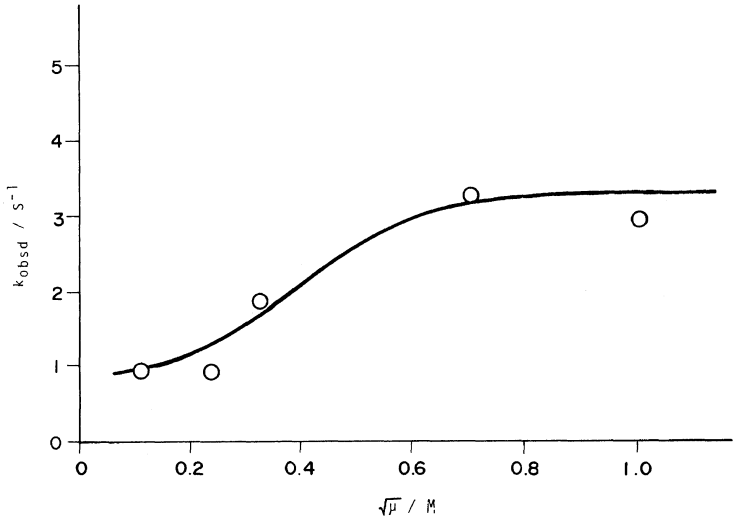


Figure 5. Effect of ionic strength on the rate constants for the ligand exchange reaction; [Cu(II)–PVA] = 4×10^{-4} mol dm^{-3}; [EDTA] = 3×10^{-3} mol dm^{-3}; $T_{\mathrm{Cu^{2+}}}/T_{\mathrm{HL}} = 0.05$; pH = 10.5, 25°C.

$$=k_1\frac{[\mathrm{Cu(II)}\text{–}\mathrm{PVA}]}{[\mathrm{PVA}]}+k_2\frac{[\mathrm{Cu(II)}\text{–}\mathrm{H\text{-}PVA}]}{[\mathrm{PVA}]} \qquad (8)$$

Therefore, $k_2=k_2'K^{-\mathrm{H}}_{\mathrm{Cu(II)-PVA}}=3.68\times10^4\ \mathrm{Ms}^{-1}$.

The ligand exchange reactions between Cu(II)–PVA and edta anion varying the concentration of neutral salt were carried out at pH 10.5 and at 25°C. Figure 5 shows k_{obsd} plotted against the ionic strength, μ. The value increased with increasing concentration of KNO_3 in the reaction media. This fact was attributed to an electrostatic repulsion between the partly negative charged PVA chain (pK_a of PVA = 10.64)[2] bonded to Cu(II) ion and also negative charged edta^{4-} ion. Namely, owing to addition of neutral salt the attack of edta^{4-} to Cu(II) ion is facilitated more by the relaxation of the electrostatic repulsion. At higher concentrations of potassium nitrate, the ligand exchange path may approach the associative path as was proposed for the ligand exchange reaction between the low molecular weight ligand complex with polyamine.[17]

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