

# Kinetics of Metal Exchange Reaction of Cu(II)-poly(vinyl alcohol) Complex with Ca(II)-ethylenediamine-N, N, N', N'-tetraacetic Acid in Aqueous Solution

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(Received October 4, 1982)

## SUMMARY

The kinetics of metal exchange reaction between Cu(II)-poly(vinyl alcohol) (PVA) complex and Ca(II)-ethylenediamine-N, N, N', N'-tetraacetic acid (Ca(II)-EDTA) have been studied by the mixing both solutions in a spectrophotometer at pH 9.7-11.0, at  $\mu=0.10(\text{KNO}_3)$  and at 25°C. The reaction is initiated by the formation of unstable Cu(II)-H-PVA by the attack of  $\text{H}^+$  to Cu(II)-PVA, and the both ligand exchange and the metal exchange step occur, the latter may be rate-determining.

$-d[\text{Cu(II)-PVA}]/dt = k[\text{Cu(II)-PVA}][\text{H}^+][\text{PVA}]/[\text{Ca(II)-EDTA}]$ , where  $k = k_1 + k_2'[\text{H}^+]$ ,  $k_1 = 3.85 \times 10^{-2} \text{ sec}^{-1}$ ,  $k_2 = k_2' \cdot K_{\text{Cu(II)-H-PVA}}^{\text{H}} = 9.59 \times 10^5 \text{ l mol}^{-1} \text{ sec}^{-1}$ .

## INTRODUCTION

The kinetics and mechanisms of exchange reaction of metal-polymer complexes seem of interest in view of the model reactions for the metal transport *in vivo*. In a previous series of papers, we have investigated on the kinetics of ligand exchange reactions between Cu(II)-poly(vinyl alcohol) (PVA) complex and ethylenediamine-N, N, N', N'-tetraacetic acid, and between Cu(II)-ammine complex and PVA in aqueous solution<sup>1-2</sup>). And we have reported on the kinetics of metal exchange reaction between Cu(II)-PVA complex and Zn(II)-EDTA in aqueous solution<sup>3</sup>). It is possible to classify the exchange reactions of metal-polymer complexes into five types<sup>3</sup>). In the metal exchange reaction between Cu(II)-PVA and Zn(II)-EDTA, the both ligand exchange (between metal-polymer complex and low molecular weight ligand) and the metal exchange (between metal-polymer complex and low molecular weight metal complexes) are cooperative events. The present paper concerns with the metal-exchange kinetics between Cu(II)-PVA complex and Ca(II)-edta anion 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 weight according to the method given by Matsumoto<sup>4)</sup>, and each fraction was completely hydrolyzed by alkali in methanol<sup>5)</sup>. The concentration of PVA used in these experiments was 0.08 mol/l. Ca(II)-edta anion obtained from Wako Pure Chemical Ind. was purified by recrystallization three times from methanol water and dried in air at 80°C. The concentration of a stock solution of Ca(II)-edta anion (0.16 mol/l) was standardized by an atomic absorption spectrophotometer (Hitachi-207 type). An aqueous solution of Cu(II) ion was added to the PVA solution, and the pH of mixed solution was adjusted to the desired pH value with KOH<sup>3)</sup>. The ionic strengths of Cu(II)-PVA and Ca(II)-edta anion were maintained at 0.1 mol/l with KNO<sub>3</sub>. The Cu(II)-PVA complex solutions were kept at 25°C for 24 hr before each experiment. Other reagents used here were of analytical grade from commercial origin and used without further purification.

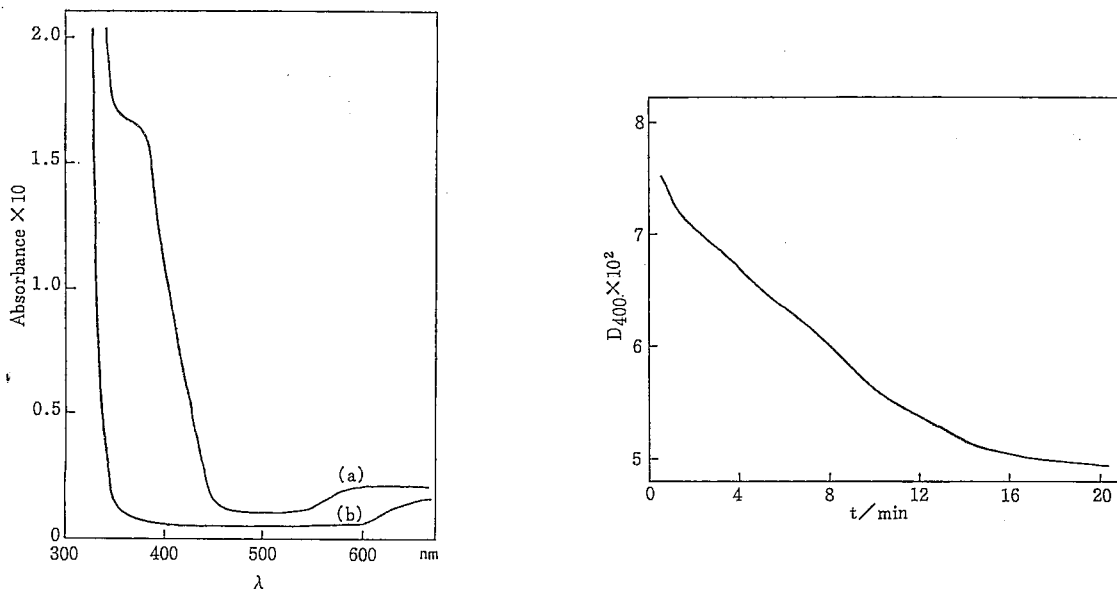
*Method*

Electronic spectra were measured on a Shimadzu UV-200 spectrophotometer. The reactions were carried out in a UV spectrometer. pH measurements were carried out with a Hitachi-Horiba F7-ss pH meter. Kinetic measurements were generally made as follows; one solution containing  $\sim 4 \times 10^{-4}$  mol/l Cu(II)-PVA, (the ratio of Cu(II) ion to OH group in PVA,  $T_{Cu^{2+}}/T_{HL} = 0.05$ ) was brought to the starting pH with 0.1N KOH solution. A second solution containing  $2 \times 10^{-2}$  mol/l Ca(II)-edta anion was brought to the same pH. Ionic strengths of these solutions were maintained at 0.1 mol/l with KNO<sub>3</sub>. These solutions were mixed in the ratio of 1:1 (v/v) in a 1 cm cell of UVspectrophotometer. 0 to 0.1 optical density range at 400 nm were used in the spectrophotometer. All rate were measured at  $25 \pm 0.1^\circ\text{C}$ .

## RESULTS AND DISCUSSION

*Spectral Results*

When a Cu(II)-PVA solution is added to a solution containing Ca(II)-edta anion complex, the colour of solution change from green to light blue. A change in electronic spectra observed before and after the reaction is shown in Figure 1 as an example. The formation of complex of PVA with Cu(II) ion was confirmed by the appearance of peaks at 640 nm as well as 260 nm, and an absorption shoulder at about 360 nm<sup>2)</sup>. As shown in this figure, the remarkable absorption for Cu(II)-PVA complex decay at about 360 nm and at 640 nm. This fact suggests that the metal exchange between Cu(II)-PVA and Ca(II)-edta anion is occurred by the mixing both solutions. We can observe the time-course of metal exchange reaction by detecting the remarkable decrease at 400 nm.



**Figure 1** Electronic spectra for the reaction of Cu(II)-PVA complex with Ca(II)-edta anion before (a) and after (b) the reaction in aqueous solution at pH 10.5 as well as at 25°C;  $T_{\text{Cu}^{2+}}/T_{\text{HL}}=0.05$ ,  $[\text{Cu(II)-PVA}]=4 \times 10^{-4}$  mol/l,  $[\text{Ca(II)-EDTA}]=2 \times 10^{-2}$  mol/l,  $\mu=0.1(\text{KNO}_3)$

**Figure 2** Change in  $D_{400}$  for the reaction of Cu(II)-PVA complex with Ca(II)-EDTA in aqueous solution at pH 10.5 and at 25°C;  $[\text{Cu(II)-PVA}]=4 \times 10^{-4}$  mol/l,  $[\text{Ca(II)-EDTA}]=2 \times 10^{-2}$  mol/l,  $T_{\text{Cu}^{2+}}/T_{\text{HL}}=0.05$ ,  $\bar{P}_n=1250$ ,  $\mu=0.1(\text{KNO}_3)$

### Kinetic Results

The rates of reactions produced by mixing Cu(II)-PVA complex with Ca(II)-edta anion were followed by monitoring the disappearance of the absorption at 400 nm. Figure 2 shows the decrease on transmitted light intensity as the reaction proceeds.

Plots of  $\log(A_t - A_\infty)$  as a function of time were obtained using an approximate value for  $A_\infty$ . Appropriate plots obtained from a typical run (Fig. 2) are shown in Figure 3.

In general, straight lines were obtained for the reactions. All plots obtained in thus experiments showed, as expected, that the reactions in the presence of an excess of Ca(II)-edta anion and under buffered conditions were pseudo-first order. From these findings, the reaction of Cu(II)-PVA complex with excess Ca(II)-edta anion followed the rate expression;

$$-\frac{d[\text{Cu(II)-PVA}]}{dt} = k_{\text{obsd}}[\text{Cu(II)-PVA}] \quad (1)$$

The metal exchange reactions were carried out at 25°C and at  $\mu=0.1$  ( $\text{KNO}_3$ ), varying the pH 9.7-11.0 and keeping the concentration of Cu(II)-PVA and Ca(II)-edta anion. Figure 4 shows the  $k_{\text{obsd}}$  plotted against the initial concentration of hydrogen ion.

From the figure, it was found that  $k_{\text{obsd}}$  was proportional to  $[\text{H}^+]^{+0}$ . Thus the reaction exhibits specific acid catalysis. In another series of runs, the dependence of  $k_{\text{obsd}}$  on the initial concentration of PVA was studied at constant concentration of Ca(II)-edta anion

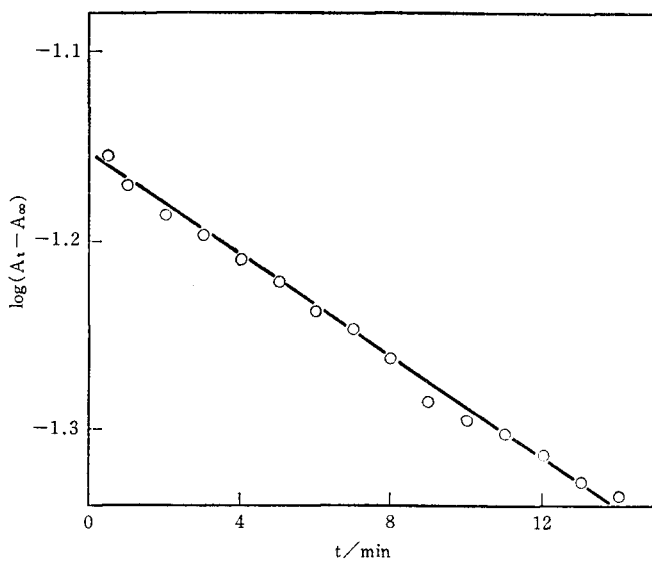


Figure 3 (A<sub>t</sub>-A<sub>∞</sub>) relation obtained from Fig. 2

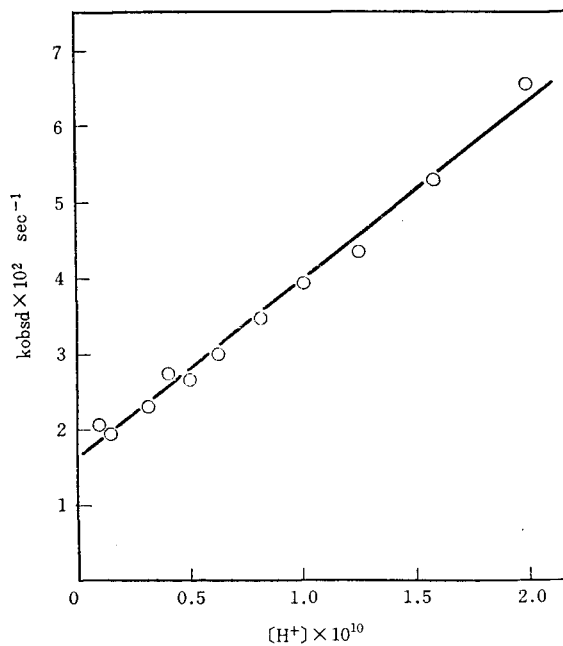
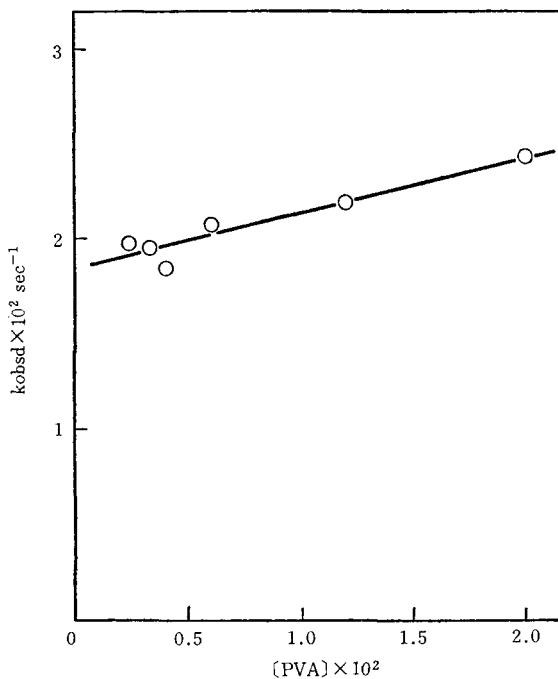
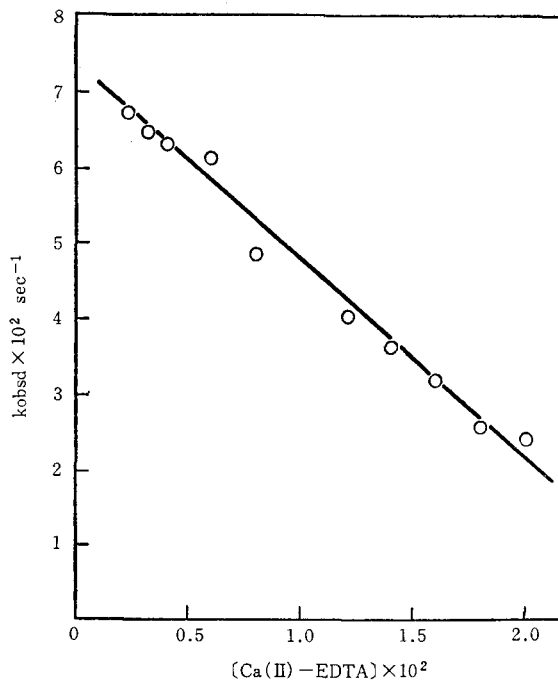


Figure 4  $k_{\text{obsd}}$  as a function of hydrogen concentration;  $[\text{Cu(II)-PVA}] = 4 \times 10^{-4} \text{ mol/l}$ ,  
 $[\text{Ca(II)-EDTA}] = 2 \times 10^{-2} \text{ mol/l}$ ,  $T_{\text{Cu}^{2+}}/T_{\text{HL}} = 0.05$ ,  $25^\circ\text{C}$ ,  $\mu = 0.1(\text{KNO}_3)$

as well as  $\text{Cu(II)}$  ion concentration, at pH 10.5,  $\mu=0.1(\text{KNO}_3)$ , and at  $25^\circ\text{C}$  (Figure 5).



**Figure 5**  $k_{\text{obsd}}$  as a function of PVA concentration;  $[\text{Cu}^{2+}] = 4 \times 10^{-4} \text{ mol/l}$ ,  $[\text{Ca(II)-EDTA}] = 2 \times 10^{-2} \text{ mol/l}$ , pH 10.5,  $\mu=0.1(\text{KNO}_3)$ ,  $25^\circ\text{C}$



**Figure 6**  $k_{\text{obsd}}$  as a function of Ca(II)-edta anion concentration;  $[\text{Cu(II)-PVA}] = 4 \times 10^{-4} \text{ mol/l}$ , pH 10.5,  $T_{\text{Cu}^{2+}}/T_{\text{HL}} = 0.05$ ,  $\mu=0.1(\text{KNO}_3)$ ,  $25^\circ\text{C}$

From Figure 5, it was found that the rate of exchange reaction was also proportional to  $[PVA]^{1.0}$ .

Finally the metal exchange reactions were carried out at 25°C, pH 10.5 and at  $\mu=0.1$  ( $KNO_3$ ), varying the concentration of Ca(II)-edta anion, and keeping the concentration of Cu(II)-PVA complex as shown in Figure 6.

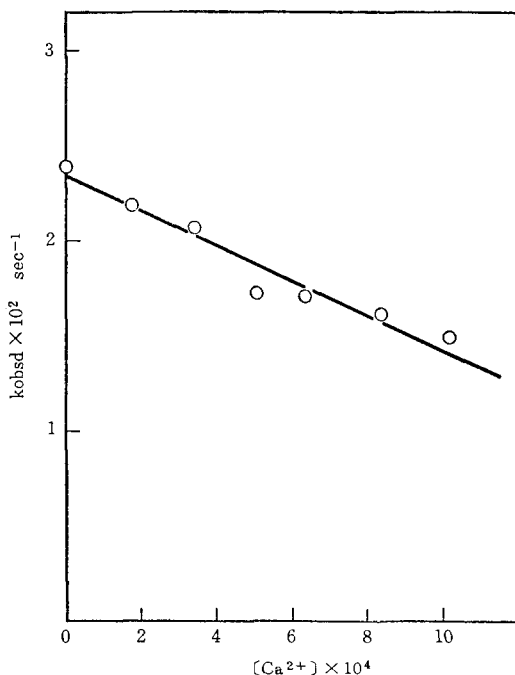
From the results of Figure 6,  $k_{obsd}$  is inversely proportional to first order with respect to Ca(II)-edta anion. Because the exchange reaction can not occur without Ca(II)-edta anion, the formation of  $Ca(OH)_2$  at higher pH seems to have any influence for the exchange reaction.



at higher pH



Figure 7 shows the dependence of  $k_{obsd}$  on the concentration of added  $Ca(OH)_2$ , at pH 10.5,  $\mu=0.1(KNO_3)$ , and at 25°C.



**Figure 7**  $k_{obsd}$  as a function of added  $Ca^{2+}$  ion concentration;  $[Cu(II)-PVA]=4 \times 10^{-4}$  mol/l,  $[Ca(II)-EDTA]=2 \times 10^{-2}$  mol/l, pH 10.5,  $\mu=0.1(KNO_3)$ , 25°C

As expected, the rate of exchange reaction is proportional to  $[Ca(OH)_2]^{-1}$ .

On the other hand, the rate of exchange reaction was accelerated by the addition of free EDTA anion. This fact suggests the ligand exchange reaction by edta anion formed in EQ. (2) takes place in this reaction.

By which mentioned above, the rate law of this reaction is given by

## Kinetics of Metal Exchange Reaction

$$-\frac{d[\text{Cu(II)-PVA}]}{dt} = k \frac{[\text{Cu(II)-PVA}][\text{H}^+][\text{PVA}]}{[\text{Ca(II)-EDTA}]} \quad (4)$$

$$= k_{o(H)} \frac{[\text{Cu(II)-PVA}][\text{PVA}]}{[\text{Ca(II)-EDTA}]} \quad (5)$$

$$= k_1 \frac{[\text{Cu(II)-PVA}][\text{PVA}]}{[\text{Ca(II)-EDTA}]} + k_2 \frac{[\text{Cu(II)-H-PVA}][\text{PVA}]}{[\text{Ca(II)-EDTA}]} \quad (6)$$

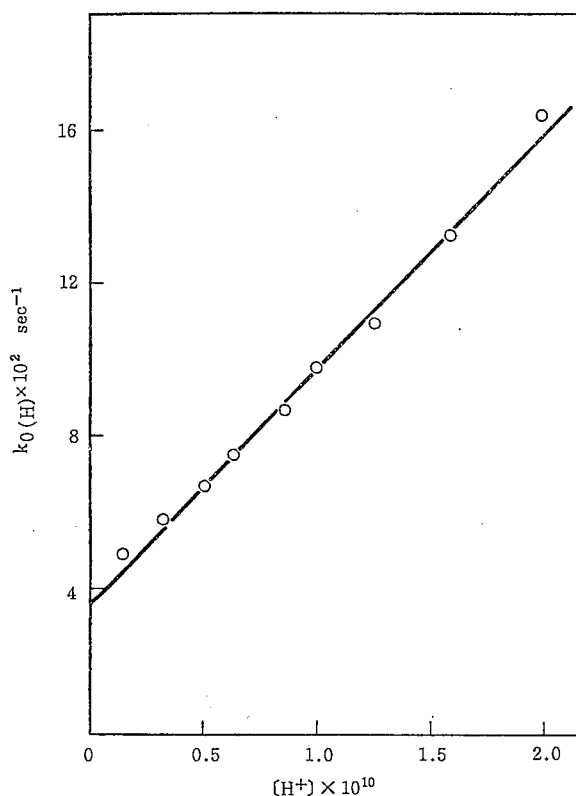
$$= k_1 \frac{[\text{Cu(II)-PVA}][\text{PVA}]}{[\text{Ca(II)-EDTA}]} + k'_2 \frac{[\text{Cu(II)-PVA}][\text{PVA}][\text{H}^+]}{[\text{Ca(II)-EDTA}]} \quad (7)$$

$$= (k_1 + k'_2[\text{H}^+]) \frac{[\text{Cu(II)-PVA}][\text{PVA}]}{[\text{Ca(II)-EDTA}]} \quad (8)$$

where,  $k_{o(H)} = k_1 + k'_2[\text{H}^+]$  (9)

$$= k_{\text{obsd}} \frac{[\text{Ca(II)-EDTA}]}{[\text{PVA}]} \quad (10)$$

In Figure 8, the values of  $k_{o(H)}$  determined at various pHs are plotted against the hydrogen ion concentration. It is evident that  $k_{o(H)}$  is linearly related hydrogen ion concentration. From the slope of the graph in Fig. 8,  $k'_2 = 6.23 \times 10^3 \text{ l mol}^{-1} \text{ sec}^{-1}$ , and from the intercept of that,  $k_1 = 3.85 \times 10^{-2} \text{ sec}^{-1}$  at  $\mu = 0.1 (\text{KNO}_3)$  and at  $25^\circ\text{C}$ .



**Figure 8**  $k_{o(H)}$  as a function of hydrogen ion concentration ;  $[\text{Cu(II)-PVA}] = 4 \times 10^{-4} \text{ mol/l}$ ,  $[\text{Ca(II)-EDTA}] = 2 \times 10^{-2} \text{ mol/l}$ ,  $T_{\text{Cu}^{2+}}/T_{\text{HL}} = 0.05$ , pH 10.5,  $\mu = 0.1 (\text{KNO}_3)$ ,  $25^\circ\text{C}$

From EQ. (6) and EQ. (7), we obtain

$$k_2[\text{Cu(II)-H-PVA}] = k'_2[\text{Cu(II)-PVA}] [\text{H}^+] \quad (11)$$

$$\frac{k_2}{k'_2} = \frac{[\text{Cu(II)-PVA}] [\text{H}^+]}{[\text{Cu(II)-H-PVA}]} = K_{\text{Cu(II)-H-PVA}}^{-\text{H}} = 10^{-2.81} \text{ s} \quad (12)$$

$$\begin{aligned} k_2 &= k'_2 \cdot K_{\text{Cu(II)-H-PVA}}^{-\text{H}} \\ &= 9.59 \times 10^5 \text{ l mol}^{-1} \text{ sec}^{-1}. \end{aligned}$$

#### Mechanism of Exchange Reaction

In the substitution of Cu(II)-PVA complex with Ca(II)-edta anion, first, a proton attacks to the Cu(II)-PVA to form the intermediate Cu(II)-H-PVA, and the reaction initiates. Once protonated, Cu(II)-PVA complex becomes to be unstable, and is attacked by EDTA<sup>4-</sup> formed in EQ. (2) equilibrium.

This step is the ligand exchange reaction such as the mechanism proposed to the reaction between Co(II)-EDTA and PAR<sup>6)</sup>. Namely the role of this proton is to enter into the unstable site of the complex and prevent the recombination of the multidentate ligand, as well as to promote the dissociation electrostatically.



On the other hand, free Ca<sup>2+</sup> ion attacks to the Cu(II)-PVA complex to form the binuclear intermediate Cu(II)-PVA-Ca<sup>2+</sup>, and Cu<sup>2+</sup> ion is released from this intermediate. This step is the metal exchange reaction.

In case of the metal exchange reaction of low molecular ligand complex<sup>7, 8)</sup>, such as between Ni(II)-EDTA and Zn<sup>2+</sup><sup>9)</sup>, the step of Ni<sup>2+</sup> elimination from the binuclear intermediate is rate-determining.

The protonation of Cu(II)-PVA complex is very rapid, but the binuclear intermediate is not protonated, so the addition of Ca<sup>2+</sup> to Cu(II)-PVA serves to slow down the rate of exchange reaction.

This Cu<sup>2+</sup> elimination from the intermediate is rate-determining, and the metal exchange step is a dominant factor of the rate.

Eliminated Cu<sup>2+</sup> is caught by free edta<sup>4-</sup> anion.

#### ACKNOWLEDGEMENT

The author would like to thank Dr. Hirofusa Shirai of Department of Functional Polymer Science, Shinsyu University for helpful discussions and Miss Kyoko Negishi for assistance in this study.



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