Kinetics of ligand exchange reaction of $Cu(OH)_2$–poly(vinyl alcohol) complex with potassium cyanide

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The kinetics of the ligand exchange reaction between the green complex of $Cu(OH)_2$ included in poly(vinyl alcohol) (PVA) and potassium cyanide (CN^-) was studied by a stopped-flow method at pH 11.6–12.60, at ionic strength $\mu = 0.1$ (KCl) and at 25°C. The $Cu(OH)_2$ is believed to be of type $Cu_n(OH)^{2+}_{2n-2}$. Therefore the polynuclear complex of the $Cu_n(OH)^{2+}_{2n-2}$ included in helical PVA chains can be expressed as PVA–$Cu_n(OH)^{2+}_{2n-2}$. The rate law, written as:

$$r = -\frac{d[\text{PVA-}Cu_n(OH)^{2+}_{2n-2}]}{dt}$$

can be explained by four different reaction paths. In paths 1 and 2, the reactions are initiated by attack of H^+ on the polynuclear copper complex $Cu_n(OH)^{2+}_{2n-2}$ included inside the PVA helical chains. In path 1, the intermediate, $Cu_n(OH)^{3+}_{2n-3}$ is formed in the bulk water. However, in path 2, the intermediate, PVA–$Cu_n(OH)^{3+}_{2n-2}(H_2O)$, is formed inside the PVA helix. In the highly alkaline region, paths 3 and 4 involve the ligand substitution reaction. In path 3, the $Cu_n(OH)^{2+}_{2n-2}$ is believed to be released from PVA helical chain and combines with CN^- in the exterior bulk water. In path 4, the rate-determining step is the bimolecular ligand exchange reaction between PVA–$Cu_n(OH)^{2+}_{2n-2}$ and CN^-. A possible mechanism for the substitution reaction is discussed.

(Keywords: kinetics; ligands; complexes)

INTRODUCTION

An aqueous solution of Cu^{2+} ion and poly(vinyl alcohol) (PVA) shows a green complex at pH > 6. It has been believed to date that the complex has a chelate type structure[1,2]. However, the experimental results of electron spin resonance and proton relaxation rate measurement cannot be explained by the chelate type structure of the green complex[3,4]. In accordance with magnetic susceptibility measurement, Yokoi *et al.*[3,5] showed that the effective moment, μ_{eff}, determined for aqueous PVA–Cu^{2+} solution was 1.33 μ_B at pH 7.0 or 1.47 μ_B at pH 9.0. The result indicates the formation of a polynuclear Cu^{2+} complex with a strong antiferromagnetic interaction at pH > 6. This polynuclear complex $Cu(OH)_2$ is believed to be of the type $[Cu_n(OH)^{2+}_{2n-2}]$. Furthermore, the invariance of the proton spin-lattice relaxation rate of H_2O with increase of Cu^{2+} ion concentration in aqueous PVA–Cu^{2+} solution at pH 12.5 suggests that all the Cu^{2+} ions, in the form of cupric hydroxide, are surrounded by helical PVA chains with their hydrophobic backbones facing towards the complex and the hydrophilic OH groups facing towards the bulk water[3,4].

The polynuclear copper of $Cu_n(OH)^{2+}_{2n-2}$ included in PVA chains can be expressed as PVA–$Cu_n(OH)^{2+}_{2n-2}$. This inclusion type structure of PVA–$Cu_n(OH)^{2+}_{2n-2}$ complex is sometimes called a 'cluster model' (or clathrate type) structure[6]. According to the cluster model, the PVA chain plays a role in the prevention of cupric hydroxide clusters from aggregations.

At pH > 6 the green solution shows three absorption bands at 260, 370 and 630 ± 10 nm. It is widely accepted that the 630 ± 10 nm band is due to the *d*–*d* transition and the 260 nm band is due to charge transfer[7]. The absorption band at 370 nm may be due to the $p_\pi(O) \rightarrow d_{x^2-y^2}(Cu)$ charge transfer transitions[3], where $p_\pi(O)$ denotes the p_π orbital on bridging OH group in $Cu_n(OH)^{2+}_{2n-2}$. The decomposition of the PVA–$Cu_n(OH)^{2+}_{2n-2}$ complex by the cyanide anion can be detected by the disappearance of the absorption shoulder band at about 370 nm, indicating that the cyanide breaks the Cu–OH bond of $Cu_n(OH)^{2+}_{2n-2}$ included in the PVA chain.

Studies of the kinetics and mechanisms of the exchange reactions of Cu^{2+}–PVA complexes with ethylene diamine tetra-acetic acid (EDTA) have been reported by Suzuki *et al.*[8]. They presumed that the Cu^{2+}–PVA complex had a chelate type structure[1,2,8]. In the present

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paper, however, the cluster model structure for the green complex is adapted to the investigation of the ligand exchange kinetics between PVA–$Cu_n(OH)^{2+}_{2n-2}$ complex and potassium cyanide in aqueous solution.

EXPERIMENTAL

Chemicals

Hydrolysed (98.9%) PVA with weight-average molecular weight M_w = 27 000 and number-average molecular weight M_n = 14 000 was purchased from Aldrich Chemical Company. The triad tacticity of PVA with *mm* 22%, *mr* 50% and *rr* 28% was derived from the methine carbon peak in ^{13}C measurements on a Bruker AM-400 NMR spectrometer[4]. The concentration of PVA was expressed in terms of the monomer residues. All other reagents were of analytical grade and were used without further purification.

Cu^{2+} ion solutions were prepared from a stock solution of $CuCl_2 \cdot 2H_2O$. PVA–$Cu_n(OH)^{2+}_{2n-2}$ complex solutions were prepared as follows. An aqueous solution of Cu^{2+} ion was added to the PVA solution, and the pH of the mixed solution was adjusted to the desired pH value with KOH solution. The ionic strengths of the PVA $Cu_n(OH)^{2+}_{2n-2}$ were maintained at 0.1 M with KCl. The complex solutions thus obtained were equilibrated at 25°C for 1 day before each experiment.

Method

U.v.-visible spectra were measured on a Hitachi U3210 spectrophotometer. The reactions were carried out in a stopped-flow apparatus of Union GA 401 spectrophotometer. The pH measurements were carried out with a Suntex SP-5A pH meter. In most cases, the kinetic measurements were made as follows. One solution containing ~0.02 M PVA and ~4 × 10^{-3} M Cu^{2+} ion was brought to the starting pH. Ionic strength was maintained at 0.1 M with KCl. A second solution of KCN, with KCl added to bring the ionic strength to 0.1 M, was brought to the same pH. These solutions were mixed in the ratio 1:1 (v/v) in a 1 cm cell of the stopped-flow spectrophotometer. An optical density range of 0 0.1 at 370 nm was used for the absorption measurements. All rates were measured at 25.0 ± 1.0°C and were averaged over six runs.

RESULTS AND DISCUSSION

Kinetic results

When excess cyanide solution is added to a solution of the PVA $Cu_n(OH)^{2+}_{2n-2}$, the green solution discolours. This suggests that the exchange of the hydroxy in the PVA -$Cu_n(OH)^{2+}_{2n-2}$ complex with cyanide anion occurs under these experimental conditions and the reaction goes nearly to completion so that the reverse reaction can be neglected in the kinetic study. The overall ligand substitution in the presence of H^+ may be described as:

$$\mathrm{PVA\text{-}Cu_n(OH)^{2+}_{2n-2} + 4CN^- + 2H^+ \rightarrow PVA + Cu(CN)_3^{2-} + \tfrac{1}{2}(CN)_2 + Cu_{n-1}(OH)^{2+}_{2n-4} + 2H_2O} \quad (1)$$

and in the highly alkaline region, it may be depicted as:

$$\mathrm{PVA\text{-}Cu_n(OH)^{2+}_{2n-2} + 4CN^- \rightarrow PVA + Cu(CN)_3^{2-} + \tfrac{1}{2}(CN)_2 + OH^- + Cu_{n-1}(OH)^{+}_{2n-3}} \quad (2)$$

The reaction rates in mixing PVA-$Cu_n(OH)^{2+}_{2n-2}$ complexes with a large excess of cyanide anions may be followed by monitoring the disappearance of absorption at 370 nm. The rates were too fast to be measured by conventional means and were therefore measured by the stopped-flow technique. Plots of $\ln(A_t - A_\infty)$ as a function of reaction time, t, were obtained by using an extrapolated value (infinite value for the reaction) for A_∞. A_t and A_∞ are the absorbance of the reaction system at times t, and infinity, respectively. A typical run is shown in *Figure 1*. In semi-log plots a straight line was generally obtained, as depicted in *Figure 2*. All plots obtained in these experiments showed, as expected, that the reaction in the presence of a large excess of cyanide anions was of pseudo-first order. Thus, the reaction of

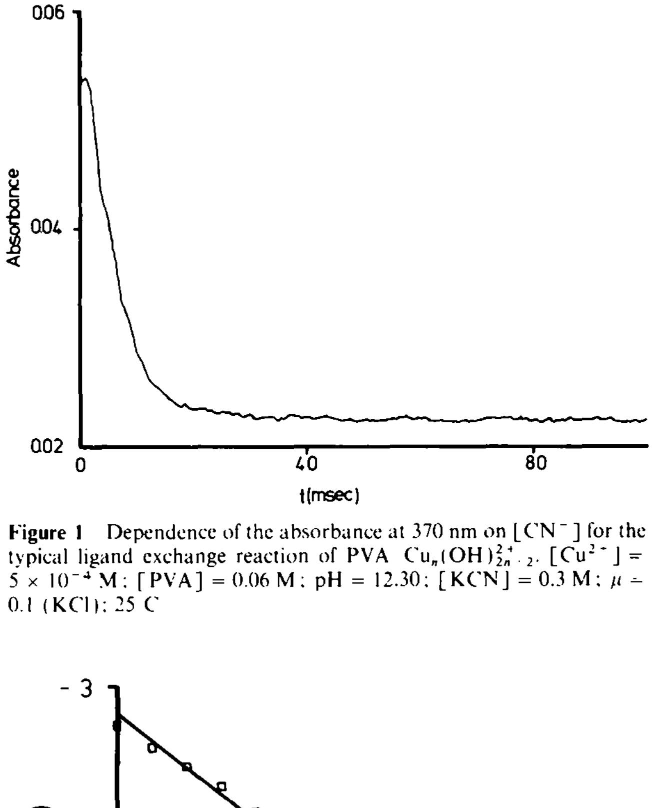

Figure 1 Dependence of the absorbance at 370 nm on $[CN^-]$ for the typical ligand exchange reaction of PVA $Cu_n(OH)^{2+}_{2n-2}$. $[Cu^{2+}]$ = 5 × 10^{-4} M; [PVA] = 0.06 M; pH = 12.30; [KCN] = 0.3 M; μ = 0.1 (KCl); 25°C

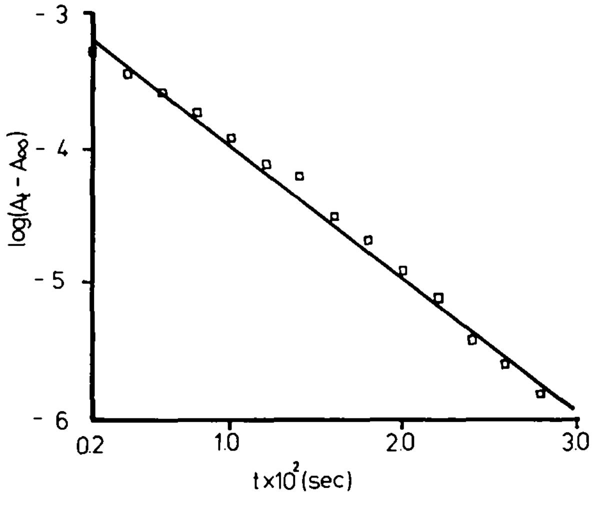

Figure 2 Semi-log plots of $\log(A_t - A_\infty)$ as a function of time for the reaction shown in *Figure 1*

PVA $Cu_n(OH)_{2n-2}^{2+}$ complex with a large excess of cyanide anion is expressed as:

$$r = \frac{d[\mathrm{PVA\ Cu}_n(\mathrm{OH})_{2n-2}^{2+}]}{dt} = k_{\mathrm{obs}}[\mathrm{PVA\ Cu}_n(\mathrm{OH})_{2n-2}^{2+}] \quad (3)$$

where k_{obs} is the pseudo-first order rate constant.

The dependence of k_{obs} on the initial concentration of cyanide anion was studied at a constant concentration of PVA $Cu_n(OH)_{2n-2}^{2+}$ and at pH 11.90. The plot of k_{obs} against the initial concentration of cyanide anions for different PVA concentration is shown in *Figure 3*, from which it was found that k_{obs} is proportional to $[CN^-]$ with the slope k_1. If $[CN^-] \gg [Cu^{2+}]$, equation (3) can be rewritten as:

$$r = -\frac{d[\mathrm{PVA\ Cu}_n(\mathrm{OH})_{2n-2}^{2+}]}{dt} = k_1[\mathrm{CN}^-][\mathrm{PVA\ Cu}_n(\mathrm{OH})_{2n-2}^{2+}] \quad (4)$$

With the help of data in *Figure 3*, it is shown in *Figure 4* that within the experimental error, k_1 is inversely proportional to the concentration of PVA. The result may be expressed by:

$$k_1 = \frac{k_2}{[\mathrm{PVA}]} + k_3 \quad (5)$$

Substituting equation (5) into equation (4), the rate of ligand exchange reaction is expressed as:

$$r = k_2\frac{[\mathrm{CN}^-][\mathrm{PVA\ Cu}_n(\mathrm{OH})_{2n-2}^{2+}]}{[\mathrm{PVA}]} + k_3[\mathrm{CN}^-][\mathrm{PVA\ Cu}_n(\mathrm{OH})_{2n-2}^{2+}] \quad (6)$$

Finally, the ligand exchange reactions were measured at 25°C with pH in the range 11.6–12.6. *Figures 5* and *6* show plots of the k_2 and k_3 against the initial hydrogen ion concentration, respectively. From *Figures 5* and *6*,

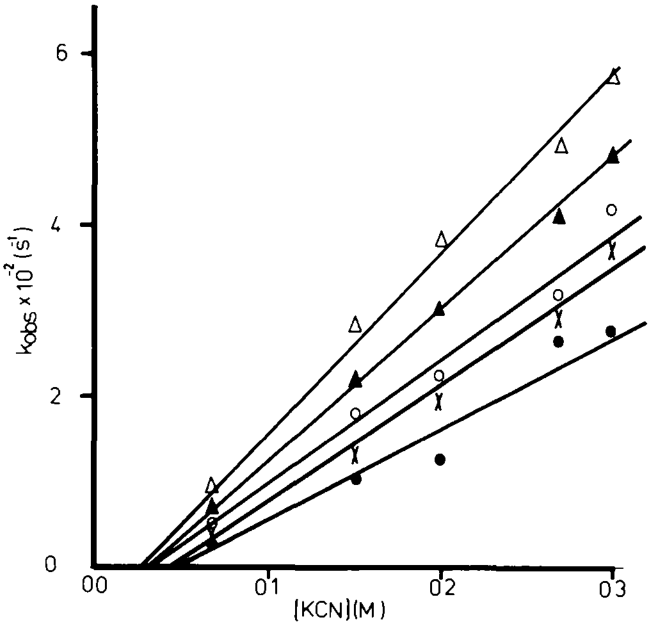

Figure 3 Plot of k_{obs} *versus* cyanide anion concentration. $[Cu^{2+}] = 5 \times 10^{-4}$ M; [PVA] = 0.01 M (△), 0.02 M (▲), 0.03 M (○), 0.04 M (×), 0.06 M (●); pH = 11.90; $\mu = 0.1$ (KCl); 25°C

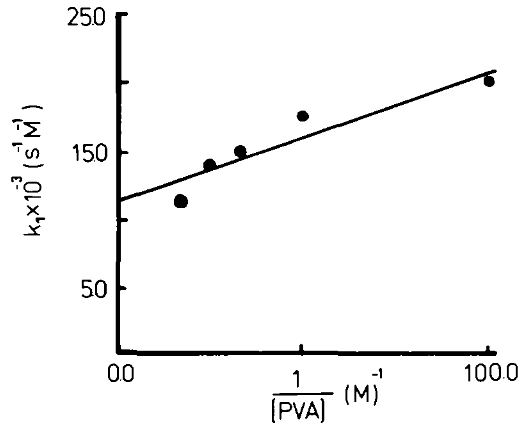

Figure 4 Plot of k_1 *versus* reciprocal of PVA concentration for the ligand exchange reaction obtained from data given in *Figure 3*. $[Cu^{2+}] = 5 \times 10^{-4}$ M; pH = 11.90; $\mu = 0.1$ (KCl); 25°C

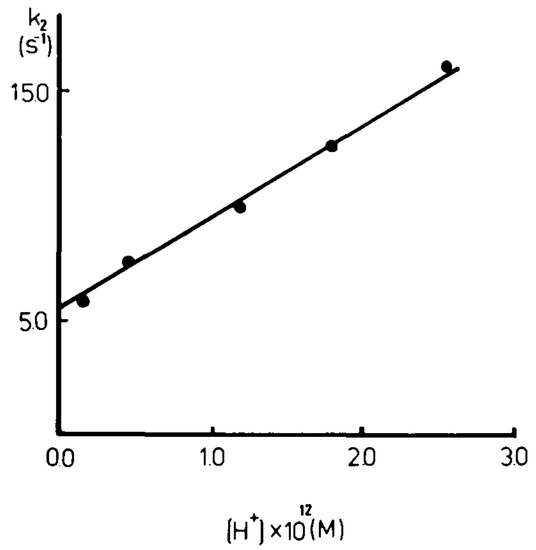

Figure 5 Plot of k_2 *versus* hydrogen ion concentration for the ligand exchange reaction. $[\mathrm{PVA\ Cu}_n(\mathrm{OH})_{2n-2}^{2+}] = 5 \times 10^{-4}$ M; $[Cu^{2+}] = 5 \times 10^{-4}$ M; $\mu = 0.1$ (KCl); 25°C

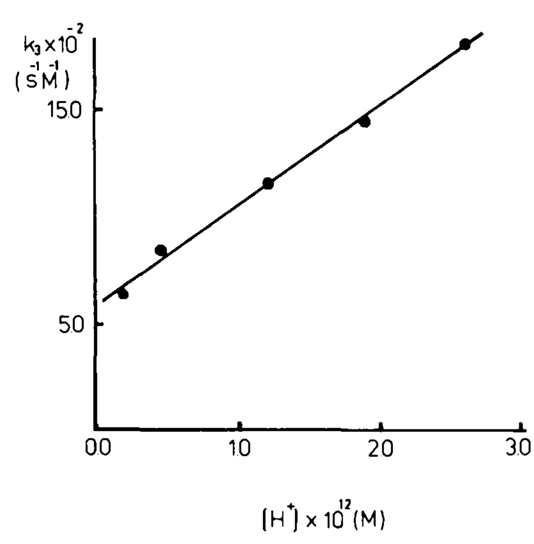

Figure 6 Plot of k_3 as a function of hydrogen ion concentration for the ligand exchange reaction. $[\mathrm{PVA{-}Cu}_n(\mathrm{OH})_{2n-2}^{2+}] = 5 \times 10^{-4}$ M; $[Cu^{2+}] = 5 \times 10^{-4}$ M; $\mu = 0.1$ (KCl); 25°C

it is evident that k_2 and k_3 are linearly related to the hydrogen ion concentration. They can be expressed by equations (7) and (8), respectively:

$$k_2 = 3.78 \times 10^{12}[H^+] + 5.04 \qquad (7)$$

$$k_3 = 5.17 \times 10^{14}[H^+] + 482 \qquad (8)$$

Substituting equations (7) and (8) into equation (6), we obtain the following rate expression:

$$\begin{aligned} r &= -\frac{d[PVA\text{-}Cu_n(OH)^{2+}_{2n-2}]}{dt} \\ &= 3.78 \times 10^{12}\frac{[H^+][CN^-][PVA\text{-}Cu_n(OH)^{2+}_{2n-2}]}{[PVA]} && \text{(path 1)} \\ &\quad + 5.17 \times 10^{14}[H^+] \\ &\quad \times [CN^-][PVA\text{-}Cu_n(OH)^{2+}_{2n-2}] && \text{(path 2)} \\ &\quad + 5.04\frac{[CN^-][PVA\text{-}Cu_n(OH)^{2+}_{2n-2}]}{[PVA]} && \text{(path 3)} \\ &\quad + 482[CN^-][PVA\text{-}Cu_n(OH)^{2+}_{2n-2}] && \text{(path 4)} \end{aligned} \qquad (9)$$

Mechanism of the ligand exchange reaction

The rate law of the ligand exchange reaction between PVA–$Cu_n(OH)^{2+}_{2n-2}$ complex and cyanide anion, as given in equation (9), may be described by the following mechanisms with four paths.

For paths 1 and 2, the reactions are initiated by the attack of H^+ on the polynuclear copper complex $Cu_n(OH)^{2+}_{2n-2}$ included inside the PVA chain.

Path 1. The rate law of path 1 is:

$$r = 3.78 \times 10^{12}\frac{[H^+][CN^-][PVA\text{-}Cu_n(OH)^{2+}_{2n-2}]}{[PVA]} \qquad (10)$$

The proposed mechanism is as follows:

$$PVA\text{-}Cu_n(OH)^{2+}_{2n-2} + H^+ \overset{K_1}{\rightleftarrows} PVA + Cu_n(OH)^{3+}_{2n-3} + H_2O \qquad \text{(equilibrium)}$$

$$Cu_n(OH)^{3+}_{2n-3} + CN^- \xrightarrow{k_1} CuCN^+ + Cu_{n-1}(OH)^{2+}_{2n-4} + OH^- \qquad \text{(RDS)}$$

$$\left.\begin{aligned} CuCN^+ + CN^- &\rightleftarrows Cu(CN)_2 \\ Cu(CN)_2 + CN^- &\rightleftarrows Cu(CN)_3^- \\ Cu(CN)_3^- + CN^- &\rightleftarrows Cu(CN)_4^{2-} \\ Cu(CN)_4^{2-} &\rightarrow Cu(CN)_3^{2-} + \tfrac{1}{2}(CN)_2 \end{aligned}\right\} \qquad (10a)$$

where K_1 is the equilibrium constant of step 1 and k_1 is the rate constant of the rate-determining step (RDS) and $k_1K_1/[H_2O] = 3.78 \times 10^{12}\ s^{-1}\ M^{-1}$.

Once protonated, the unstable intermediate $Cu_n(OH)^{3+}_{2n-3}$ escapes from the PVA chain to the bulk water and subsequently they are taken up by CN^- to form $CuCN^+$. This step is considered to be the rate-determining step. After several post-equilibrium steps, $Cu(CN)_4^{2-}$ is formed. Finally, the intermediate $Cu(CN)_4^{2-}$ complex undergoes a redox reaction[9] to form $Cu(CN)_3^{2-}$. The evidence of $Cu(CN)_3^{2-}$ will be explained in the following section.

Path 2. The rate law of path 2 is:

$$r = 5.17 \times 10^{14}[H^+][CN^-][PVA\text{-}Cu_n(OH)^{2+}_{2n-2}] \qquad (11)$$

The proposed mechanism is as follows:

$$PVA\text{-}Cu_n(OH)^{2+}_{2n-2} + H^+ \overset{K_2}{\rightleftarrows} PVA\text{-}Cu_n(OH)^{3+}_{2n-3}(H_2O) \qquad \text{(equilibrium)}$$

$$PVA\text{-}Cu_n(OH)^{3+}_{2n-3}(H_2O) + CN^- \xrightarrow{k_2} PVA + CuCN^+ + Cu_{n-1}(OH)^{2+}_{2n-4} + OH^- + H_2O \qquad \text{(RDS)}$$

The next reaction steps are as given in equation (10a).

In the above equations, K_2 is the equilibrium constant of step 1, k_2 is the rate constant for the rate-determining step and $k_2K_2 = 5.17 \times 10^{14}\ s^{-1}\ M^{-2}$.

After protonation, the intermediate, PVA–$Cu_n(OH)^{3+}_{2n-3}(H_2O)$, is formed inside the PVA chain. Then the CN^- diffuses into the PVA chain and attacks the Cu–OH bond of $Cu_n(OH)^{3+}_{2n-3}$ resulting in the formation of intermediate $CuCN^+$. This step is considered to be the rate-determining step. The final product is still $Cu(CN)_3^{2-}$.

Path 3. The rate law of path 3 is:

$$r = 5.04\frac{[CN^-][PVA\text{-}Cu_n(OH)^{2+}_{2n-2}]}{[PVA]} \qquad (12)$$

The proposed mechanism is as follows:

$$PVA\text{-}Cu_n(OH)^{2+}_{2n-2} \overset{K_3}{\rightleftarrows} PVA + Cu_n(OH)^{2+}_{2n-2} \qquad \text{(equilibrium)}$$

$$Cu_n(OH)^{2+}_{2n-2} + CN^- \xrightarrow{k_3} CuCN^+ + Cu_{n-1}(OH)^{1+}_{2n-3} + OH^- \qquad \text{(RDS)}$$

The next reaction steps are as given in equation (10a).

In the above equations, K_3 is the equilibrium constant of step 1, k_3 is the rate constant for the rate-determining step and $k_3K_3 = 5.04\ s^{-1}$.

In this path, the $Cu_n(OH)^{2+}_{2n-2}$ released from PVA chain combines with CN^- in the bulk water to form $CuCN^+$. The final product is $Cu(CN)_3^{2-}$.

Path 4. The rate law of path 4 is:

$$r = 482[CN^-][PVA\text{-}Cu_n(OH)^{2+}_{2n-2}] \qquad (13)$$

The proposed mechanism is as follows:

$$PVA\text{-}Cu_n(OH)^{2+}_{2n-2} + CN^- \xrightarrow{k_4} PVA + CuCN^+ + Cu_{n-1}(OH)^{1+}_{2n-3} + OH^- \qquad \text{(RDS)}$$

The next reaction steps are as given in equation (10a). In the above equations, k_4 is the rate constant for the rate-determining step and $k_4 = 482\ s^{-1}\ M^{-1}$. The formation of intermediate, $CuCN^+$, through the bimolecular ligand exchange reaction between PVA–$Cu_n(OH)^{2+}_{2n-2}$ and CN^- is the rate-determining step. The final product is $Cu(CN)_3^{2-}$.

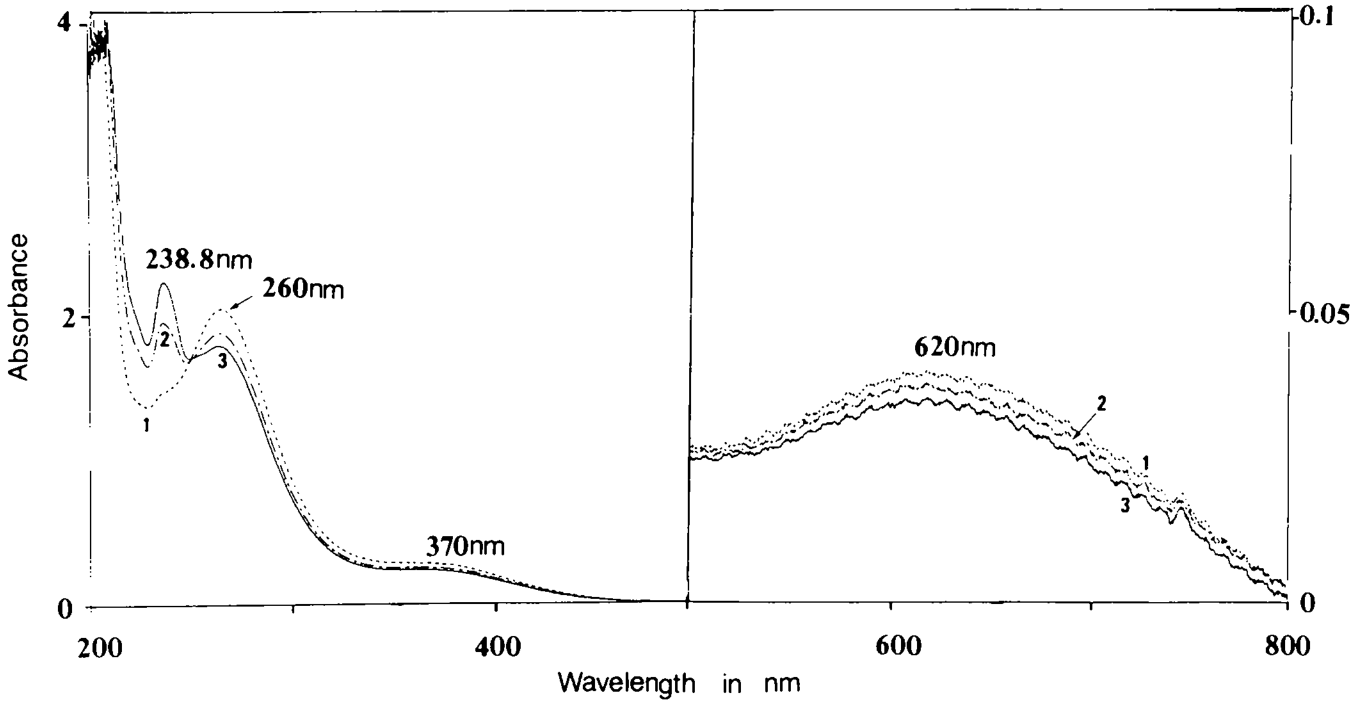

Figure 7 Absorption spectra for the reaction of PVA–$\mathrm{Cu}_n(\mathrm{OH})^{2+}_{2n-2}$ with CN^- anion in aqueous solution as a function of [KCN], at pH = 12.0, $\mu = 0.1$ (KCl) and at 25°C. [PVA] = 3.13×10^{-2} M; [Cu^{2+}] = 6.25×10^{-4} M; Curve 1, [KCN] = 6.25×10^{-5} M; curve 2 [KCN] = 2.5×10^{-4} M; curve 3, [KCN] = 3.75×10^{-4} M. The ordinate at the right hand side is the absorbance scale for the peak at 620 nm

In the absence of PVA, the u.v.-visible spectrum of the aqueous solution of freshly prepared $\mathrm{Cu}_n(\mathrm{OH})^{2+}_{2n-2}$ (or $\mathrm{Cu(OH)_2}$) dissolved in an excess of CN^- shows an absorption peak at 238 nm which is believed[10] to be the charge transfer band of $\mathrm{Cu(CN)}_3^{2-}$. The increases in the concentrations of either the cyanide or PVA–$\mathrm{Cu}_n(\mathrm{OH})^{2+}_{2n-2}$ result in an increase in absorption intensity at 238 nm and a decrease in absorbances at 260, 370 and 620 nm. The effects reflect that the excess of CN^- destroys the Cu–OH band of PVA–$\mathrm{Cu}_n(\mathrm{OH})^{2+}_{2n-2}$ complex and subsequently forms $\mathrm{Cu(CN)}_3^{2-}$. These results support the evidence for step 2 (RDS) of path 3.

The absorption spectrum for the increase in concentration of the cyanide in PVA–$\mathrm{Cu}_n(\mathrm{OH})^{2+}_{2n-2}$ solution at pH 12.0 is shown in *Figure* 7. In this figure, the diminution in 620 nm has been measured with a different absorption scale in comparison with that in 260 and 370 nm. Furthermore, the absorption intensity is invoked with the help of the slope ratio method to deduce the composition of product for the reaction between PVA–$\mathrm{Cu}_n(\mathrm{OH})^{2+}_{2n-2}$ and CN^-. The combining ratio between CN and Cu is found to be 2.7. Thus the final product may be inferred as $\mathrm{Cu(CN)}_3^{2-}$.

CONCLUSIONS

The kinetics of the ligand exchange reaction of the green PVA–$\mathrm{Cu}_n(\mathrm{OH})^{2+}_{2n-2}$ complex with CN^- has been studied by a stopped-flow method at pH 11.6–12.6, $\mu = 0.1$ (KCl) and 25°C. The substitution reaction proceeds simultaneously through four different reaction paths. The cluster model structure of the green PVA–$\mathrm{Cu}_n(\mathrm{OH})^{2+}_{2n-2}$ complex is used to interpret these four paths. The $\mathrm{Cu(CN)}_3^{2-}$ is inferred as the final product of the ligand substitution reaction.

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REFERENCES

1 Kuhn, W. and Toth, I. *Z. Naturforsch.* 1963, **18A**, 112
2 Hojo, N. and Shirai, H. *Nippon Kagaku Kaishi* 1972, 1316
3 Yokoi, H., Kawata, S. and Iwaizumi, M. *J. Am. Chem. Soc.* 1986, **108**, 3358
4 Chen, J. H. and Hwang, L. P. *J. Chinese Chem. Soc.* 1988, **35**, 273
5 Yokoi, H., Kawai, S., Kadowaki, A. and Ikoma, S. *Nippon Kagaku Kaishi* 1989, 872
6 Narisawa, M., Ono, K. and Murakami, K. *Polymer* 1989, **30**, 1540
7 Sumita, O., Fukuda, A. and Kuze, E. *J. Polym. Sci., Polym. Phys. Edn* 1978, **16**, 1801
8 Suzuki, T., Shirai, H., Shimizu, F. and Hojo, N. *Polym. J.* 1983, **15**, 409
9 Monsted, O. and Bjerrum, J. *Acta Chem. Scand.* 1967, **21**, 1116
10 Baxendale, J. H. and Westcott, D. T. *J. Chem. Soc.* 1959, 2347