

Interaction and structure of PVA–Cu(II) complex: 1. Binding of a hydrophobic dye toward PVA–Cu(II) complex

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(Received 19 September 1988; revised 7 October 1988; accepted 13 October 1988)

The interaction between PVA–Cu(II) complex and a hydrophobic dye, *p*-aminoazobenzene, was investigated by means of absorption spectrometry. The binding behaviour of the dye could be analysed on the basis of the method proposed by Klotz *et al.*¹. A structure model of the complex which was termed 'cluster model' was found to be consistent with the following experimental results: the binding affinity of the dye appeared only when the complex is formed, and the degree of binding is principally determined by the concentration of cupric ion.

(Keywords: PVA–Cu(II) complex; cupric hydroxide cluster; dye binding; hydrophobic interaction)

INTRODUCTION

Polyvinyl alcohol (PVA) forms a green complex with Cu(II) ions in aqueous solution in the vicinity of pH 6 (ref. 2). It has been believed that the complex has a chelate type structure as shown in *Figure 1a*^{3,4}. However, the structure is doubtful from the experimental results of electron spin resonance (e.s.r.)⁵ and pH titration⁶. The pH titration study suggests that the adsorption of Cu ions on a PVA chain proceeds in a cooperative manner.

In order to explain the cooperative nature of the complex formation, we proposed a new model called a 'cluster model' (*Figure 1b*). This model is consistent with the disappearance of the e.s.r. signal of the hydrated Cu ion in the vicinity of pH 6. According to this model, the PVA chain plays a role in the protection of the cupric hydroxide clusters formed by the hydrolysis of Cu ions, and prevents them from aggregation. An important feature of PVA–Cu(II) complex is the effect of catalysing ester hydrolysis reaction⁷. The dependence of the aliphatic chain length on the rate of the ester hydrolysis indicates that the complex has some hydrophobic character, even though both PVA and cupric ion are hydrophilic by nature. This unique character of the complex has motivated us to investigate the interaction between the complex and hydrophobic small molecules in detail.

In this report, we wish to provide a quantitative estimation of the ability of the complex to bind a hydrophobic dye. The effect of the concentrations of PVA and cupric ion on the dye binding will offer further evidence of the validity of the proposed structure model.

EXPERIMENTAL

Commercial PVA from Tokyo Kasei with a degree of saponification of 99% (PVA-99) and 80% (PVA-80) was

used. The degree of polymerization, P_n , for PVA-99 and PVA-80 was 1750 and 2000, respectively. Except where indicated, PVA denotes the PVA-99. Cupric nitrate and a hydrophobic dye, *p*-aminoazobenzene, were obtained from Wako Chemicals and used without further purification. The concentrations of cupric nitrate and *p*-aminoazobenzene were determined by a chelate titration and by using the absorption intensity at 375 nm⁸. The PVA–Cu(II) complex was formed by the neutralization of an aqueous mixture of PVA and cupric nitrate with a potassium hydroxide solution.

The binding of the dye on the complex was studied by means of absorption spectrometry. A Shimadzu UV-240 spectrophotometer equipped with an optional program/interface unit OPI-2 was used to obtain differential absorption spectra. Measurements were carried out at $25 \pm 0.1^\circ\text{C}$. The pH of the solution was maintained at around 8 by using a buffer. Above this the binding affinity of the dye was virtually constant.

The absorption spectra of the dye in a PVA–Cu(II) complex solution were recorded with reference to the complex solution without dye. The differential absorption spectra were numerically calculated as the difference between the absorption spectra and the spectrum of pure dye solution.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of *p*-aminoazobenzene. The spectrum of the dye in aqueous PVA solution at pH 8 and that in the aqueous mixture of PVA and hydrated copper ion were virtually the same as the spectrum of the aqueous dye solution and showed absorption maximum in the vicinity of 375 nm. It was also confirmed from the analysis of supernatant solution that the dye cannot be bound on the cupric hydroxide gel which is formed above pH 6 in the absence of PVA. Only when the green complex was formed, was a spectral

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0032-3861/89/081540-06\$03.00

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change observed and the absorption maximum shifted to a longer wavelength. This reveals that the dye can be bound on the complex, although it has no binding ability toward PVA or Cu ions alone.

The absorption and difference absorption spectra are shown in Figure 3a and b as a function of the concentration of the complex, with the $[PVA]/[Cu]$ ratio held constant. The absorption maximum at 375 nm observed in aqueous solution shifted to a longer wavelength with increasing concentration of the complex and an isosbestic point appeared at 387 nm. These results show that the complex has well-defined sites for dye binding which have a hydrophobic character. The addition of the dye had no effect on the absorption spectrum of the green complex.

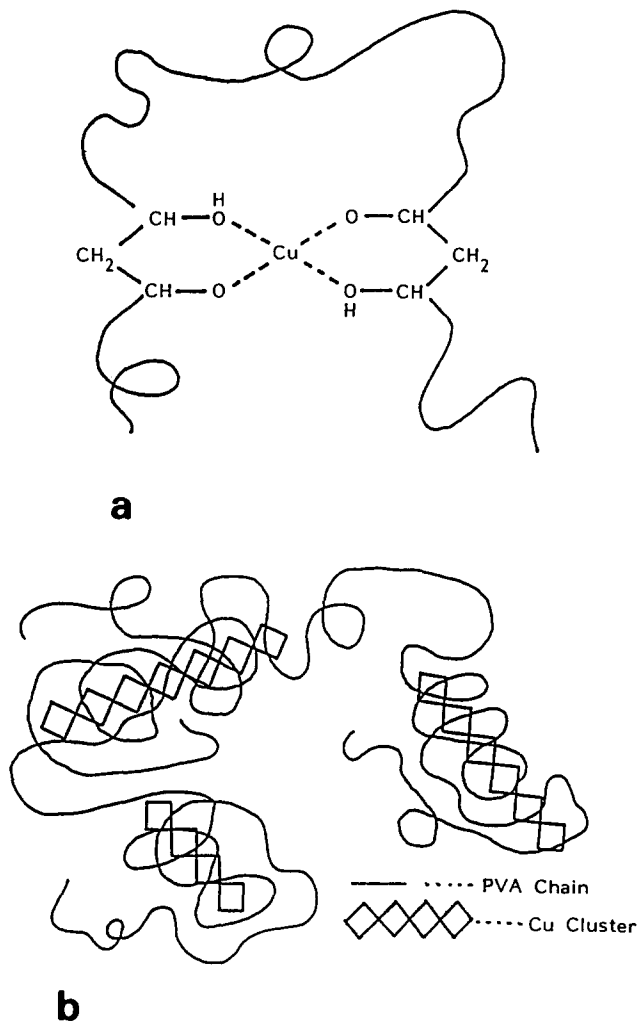


Figure 1 (a) Chelate-type structure model for PVA-Cu(II) complex. (b) Cluster model for PVA-Cu(II) complex

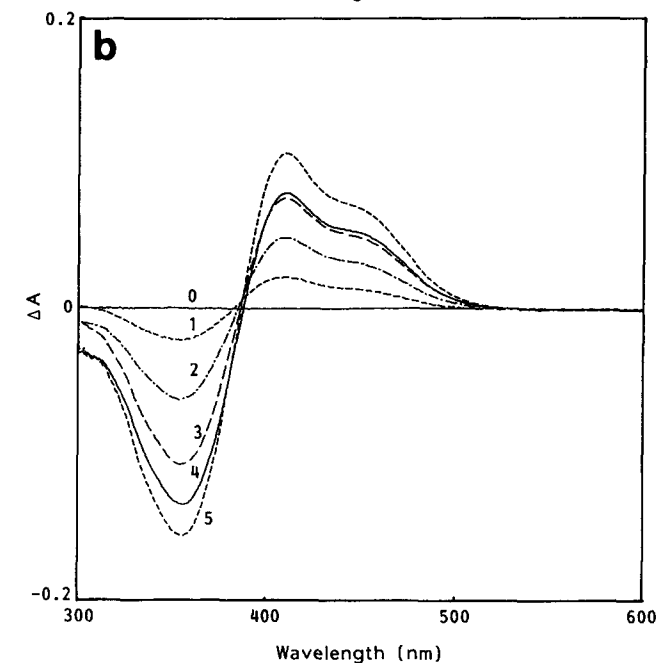
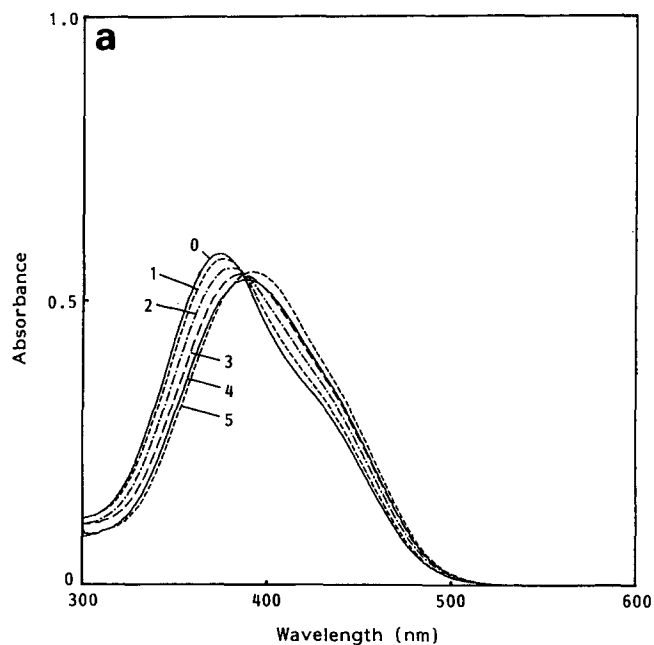


Figure 3 The absorption (a) and difference absorption (b) spectra of *p*-aminoazobenzene as a function of the copper ion concentration of the complex. —, Concentration of the copper ion. Curve 0, 0; curve 1, 0.24; curve 2, 0.72; curve 3, 1.43; curve 4, 1.91; curve 5, 2.86 ($\times 10^{-3} \text{ mol dm}^{-3}$). (Dye) = $2.71 \times 10^{-5} \text{ mol dm}^{-3}$. (PVA)/(Cu) = 37.4. PVA-99 was used

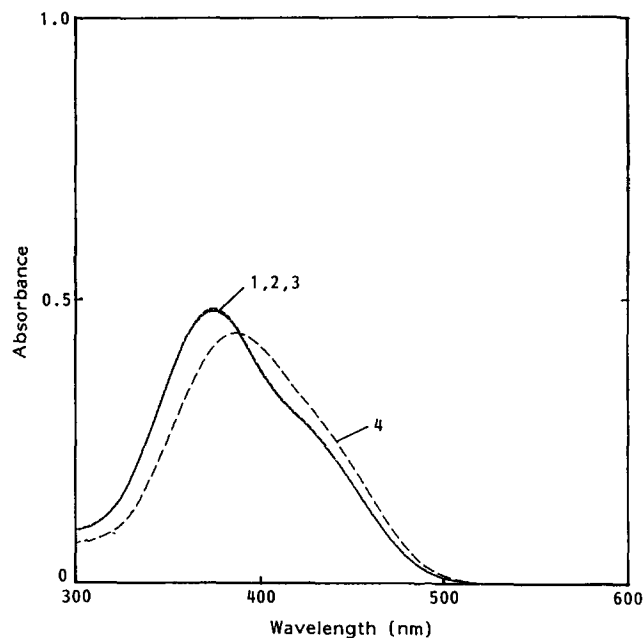


Figure 2 The absorption spectra of *p*-aminoazobenzene in curve 1, water ($\text{pH} \approx 8.5$); curve 2, aqueous PVA solution ((PVA) = $1.80 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{pH} \approx 8.5$); curve 3, aqueous mixture of PVA and Cu ion ((PVA) = $1.80 \times 10^{-2} \text{ mol dm}^{-3}$, (Cu) = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} \approx 4$); curve 4, solution of PVA-Cu(II) complex ((PVA) = $1.80 \times 10^{-2} \text{ mol dm}^{-3}$, (Cu) = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{pH} \approx 8.5$). (Dye) = $2.31 \times 10^{-5} \text{ mol dm}^{-3}$. PVA-99 was used

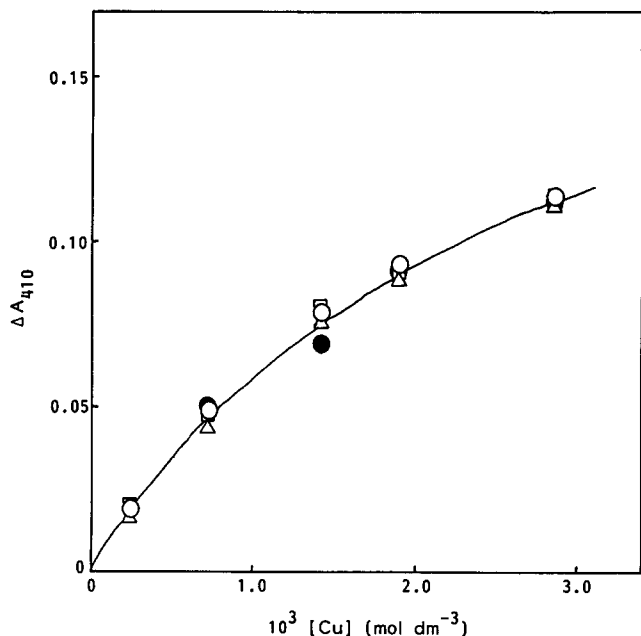
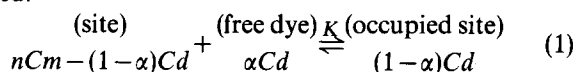


Figure 4 The plots of differential absorbance ΔA_{410} against the copper ion concentration: (PVA)/(Cu) ratios are (○), 7.47; (△), 14.9; (□) 28.0; (●), 37.4. (Dye) = 2.78×10^{-5} mol dm $^{-3}$. PVA-99 was used

Because there is an isosbestic point in the spectra, the intensity of the difference spectra (ΔA) may be proportional to the quantity of bound dye. In the following analysis, we used the differential absorbance at 410 nm (ΔA_{410}) because the intensity of the differential absorbance had a maximum value at this wavelength. Figure 4 shows the plots of differential absorbance ΔA_{410} against the copper ion concentration for four types of the complex whose PVA/Cu ratios are different from each other. It is evident from the figure that the four curves fall on a universal curve, indicating that the quantity of the bound dye is not determined by the concentration of PVA but by that of copper ion. This is in sharp contrast to the dye binding on a hydrophobic polymer, where the degree of binding is dependent on the concentration of the polymer. The result gives further evidence that the chelate model (Figure 1a) is incorrect, and that the formation of the copper cluster is possible.

The complex solution was completely purified by dialysis, so as to check the chemical composition of the complex. From the elemental analysis of the freeze-dried sample, the composition of the copper cluster was determined by subtracting the contribution of PVA from the total composition of the complex. The composition of the cluster was the same as that of cupric hydroxide. Hence it is probable that the dye is bound on the surface of the copper hydroxide cluster, and is stabilized by the PVA chain.

In order to analyse the binding behaviour of the dye to the complex, equilibrium between the binding site on the copper cluster and the free *p*-aminoazobenzene was assumed. In this equilibrium, the interaction between bound dyes was not taken into account. It should be noted that all the copper atoms are incorporated in the cluster in the vicinity of pH 8, and that there are no free copper ions in the solution. The analysis of the dye binding to a polymer proposed by Klotz¹ was formally applied.



where, n , the number of sites per copper ion, Cm , the concentration of copper ion, Cd , the concentration of *p*-aminoazobenzene, and α , the fraction of free dye. Then the equilibrium constant, K , is represented by

$$K = \frac{1 - \alpha}{[n\text{Cm} - (1 - \alpha)\text{Cd}]\alpha} \quad (2)$$

α is related to ΔA_{410} by

$$1 - \alpha = \Delta A_{410}/LA \quad (3)$$

where LA is the asymptotic value of ΔA_{410} when all the dye molecules are bound on the complex. From equations (2) and (3),

$$K = \frac{\Delta A_{410}/LA}{(n\text{Cm} - \text{Cd}\Delta A_{410}/LA)(1 - \Delta A_{410}/LA)} \quad (4)$$

By solving equation (4), we obtain an expression for ΔA_{410}

$$\Delta A_{410} = (LA/\text{Cd})[(n\text{Cm} + \text{Cd} + 1/K) - ((n\text{Cm} + \text{Cd} + 1/K)^2 - 4n\text{Cm}\text{Cd})^{1/2}]/2 \quad (5)$$

It should be noted that there are only three unknown parameters, n , K and LA in equation (5). These parameters can be determined by simulating the experimental ΔA_{410} vs. Cm curves using a non-linear least squares fitting program.

The parameters determined are summarized in Table 1 as the function of the dye concentration and the PVA/Cu ratio of the complex. Here $1/n$ denotes the number of copper atoms per binding site. As shown in Table 1, $1/n$ and LA were virtually independent of the PVA/Cu ratio under a constant concentration of dye. It is evident that K is independent of the PVA/Cu ratio.

As has been pointed out by Klotz¹, the value nK may be regarded as the equilibrium constant corresponding to one copper atom. Figure 5 shows the plot of nK against the PVA/Cu ratio. As would be expected, nK is almost independent of the PVA/Cu ratio. However it tends to decrease with increasing dye concentration.

The above results suggest that the dye molecules are bound on the hydrophobic sites near the surface of the cluster. These sites would be stabilized by adsorbed PVA molecules. In order to alter the hydrophobic

Table 1 Determined parameters of n , K and LA . PVA-99 was used

(PVA)/(Cu)	LA	$1/n$	K (mol $^{-1}$ dm 3)
(A) (Dye) = 2.78×10^{-5} mol dm $^{-3}$			
7.47	0.197	10.5	5.33×10^3
14.9	0.215	12.0	4.84×10^3
28.0	0.196	10.8	5.50×10^3
37.4	0.204	11.5	5.17×10^3
Average	0.203	11.2	
(B) (Dye) = 1.10×10^{-5} mol dm $^{-3}$			
7.47	7.63×10^{-2}	8.17	5.43×10^3
14.9	7.19×10^{-2}	8.31	6.42×10^3
28.0	7.53×10^{-2}	8.10	5.21×10^3
37.4	7.49×10^{-2}	7.90	5.50×10^3
Average	7.46×10^{-2}	8.12	

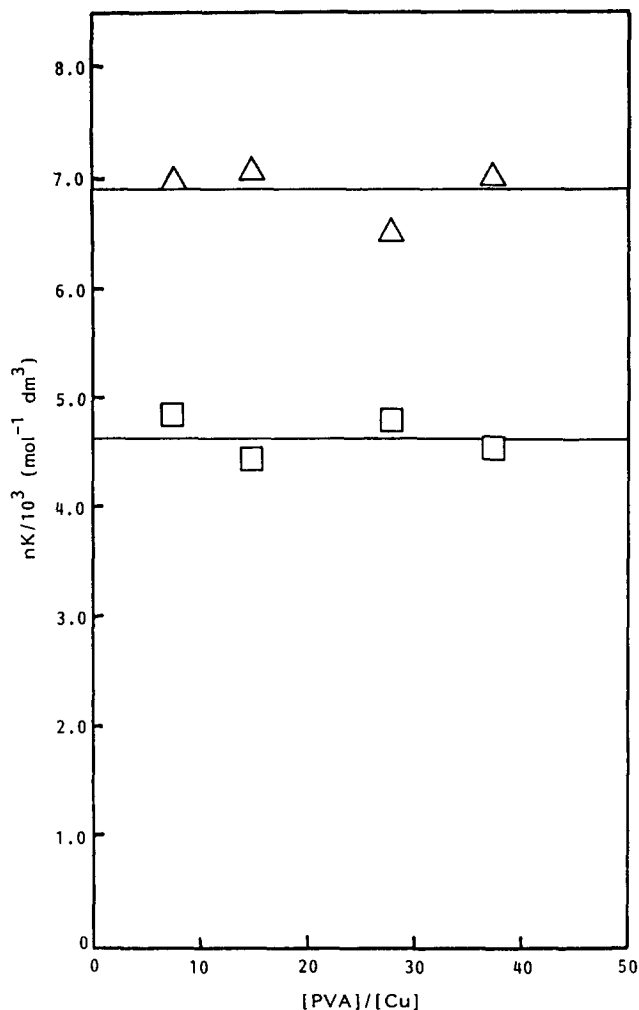


Figure 5 The plots of nK against (PVA)/(Cu) ratio. —, Concentration of the dye. (Δ), $1.10 \times 10^{-5} \text{ mol dm}^{-3}$; (\square), $2.78 \times 10^{-5} \text{ mol dm}^{-3}$. PVA-99 was used

environment, we used PVA with a low degree of saponification.

The complex of commercial 80% saponified PVA (PVA-80) with cupric ion was prepared, and the dye binding behaviour was analysed in a similar manner as before. The absorption and difference absorption spectra of the dye are shown in *Figure 6a* and *b*. Similarly to the case of the complex of PVA-99, absorption maximum shifted to a longer wavelength with increasing concentration of the complex. An isosbestic point appeared at 385 nm.

The differential absorbance ΔA_{410} was plotted against copper ion concentration (*Figure 7*). The figure reveals that ΔA_{410} is larger than in the case of the complex from PVA-99. It should be noted that the binding curve is affected by the PVA/Cu ratio. The binding affinity of the dye seems to increase with increasing PVA concentration under a constant concentration of copper ion.

Binding parameters for the complex obtained from PVA-80 are summarized in *Table 2*, and a binding parameter nK is plotted as a function of PVA/Cu ratio in *Figure 8*. It must be emphasized that the binding constants for PVA-80 are about three times as large as those for PVA-99. Moreover, in contrast to PVA-99, nK is no longer independent of PVA/Cu ratio. nK seems to increase with increasing PVA concentration, and then to approach a constant value. These observations suggest

that the dye is bound not only on the surface of the cluster but also on the polymer chain itself, because PVA-80 bears hydrophobic polyvinyl acetate blocks.

A question arises as to whether the dye binding is due to the hydrophobic interaction or to other interactions, for example the hydrogen bonding. The answer to this question is not conclusive at present, but it was found that the PVA-Cu(II) complex has an influence upon the solubility or the absorption spectrum of several hydrophobic molecules. For example, the complex solubilizes pyrene carboxyaldehyde, which is insoluble in water, and shifts the absorption maximum of anilinoanthalene. These results suggest that the interaction between the complex and *p*-aminoazobenzene

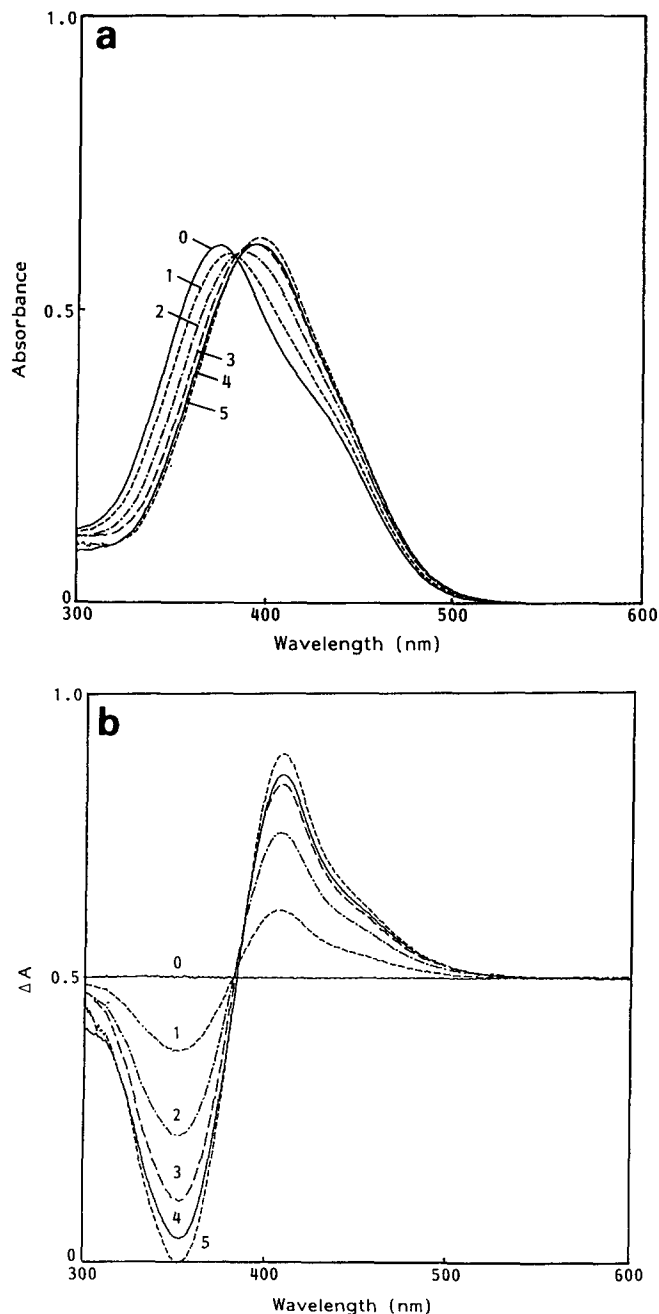


Figure 6 The absorption (a) and difference absorption (b) spectra of *p*-aminoazobenzene as a function of the copper ion concentration of the complex. —, Concentration of the complex. Curve 0, 0; curve 1, 0.24; curve 2, 0.72; curve 3, 1.43; curve 4, 1.91; curve 5, 2.86 ($\times 10^{-3} \text{ mol dm}^{-3}$). (Dye) = $2.98 \times 10^{-5} \text{ mol dm}^{-3}$. (PVA)/(Cu) = 7.27. PVA-80 was used

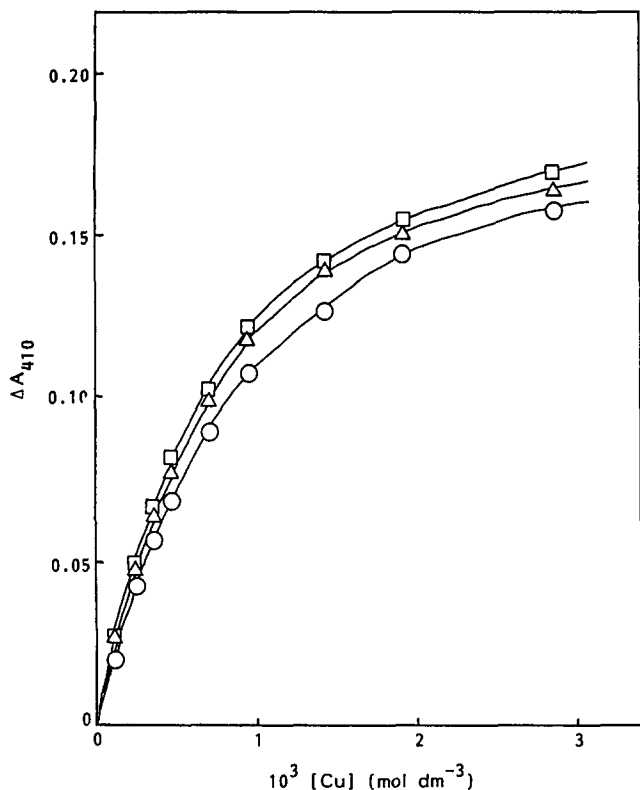


Figure 7 The plots of differential absorbance ΔA_{410} against the copper ion concentration. (PVA)/(Cu) ratios are (○), 7.27; (△), 14.5; (□), 21.8 and 29.1. (Dye) = $2.98 \times 10^{-5} \text{ mol dm}^{-3}$. PVA-80 was used

Table 2 Determined parameters of n , K and LA . PVA-80 was used

(PVA)/(Cu)	LA	$1/n$	$K \text{ (mol}^{-1} \text{ dm}^3)$
(A) (Dye) = $2.98 \times 10^{-5} \text{ mol dm}^{-3}$			
7.27	0.204	9.51	1.30×10^4
14.5	0.204	9.15	1.55×10^4
21.8	0.208	9.11	1.60×10^4
29.1	0.211	5.94	9.12×10^3
Average	0.207	8.43	
(B) (Dye) = $1.19 \times 10^{-5} \text{ mol dm}^{-3}$			
7.27	9.51×10^{-2}	10.3	1.51×10^4
14.5	8.95×10^{-2}	8.96	1.72×10^4
21.8	8.93×10^{-2}	8.32	1.71×10^4
29.1	9.16×10^{-2}	9.17	1.81×10^4
Average	9.14×10^{-2}	9.17	
(C) (Dye) = $6.57 \times 10^{-6} \text{ mol dm}^{-3}$			
7.77	4.94×10^{-2}	13.8	2.52×10^4
14.5	4.93×10^{-2}	12.5	2.73×10^4
21.8	4.92×10^{-2}	12.2	2.90×10^4
38.9	4.71×10^{-2}	11.7	3.17×10^4
Average	4.88×10^{-2}	12.5	

is not a specific one, but is the commonly observed effect for hydrophobic molecules.

In order to explain the experimental results on the binding affinity of the dye and the complex, a schematic picture of binding is proposed as shown in Figure 9. In this model, the copper cluster indicates a hydrolysed oligated complex having the same chemical composition as the cupric hydroxide. The clusters are protected by PVA chains so as not to aggregate with each other. Such effect is also to be expected for other water soluble polymers, such as poly(vinylpyrrolidone) or poly(acrylamide). In

fact, it was reported that these polymers could solubilize the copper hydroxide, although the effect was weaker than PVA⁹. However, the enhancement of the dye binding with the complex formation was not observed for these polymers.

Thus the dye binding to the PVA-Cu(II) complex is associated with the specific structure of the complex. It seems likely that the hydrophobic methylene groups of PVA direct to the surface of the cluster, since the cupric hydroxide is regarded as a kind of lyophilic colloid. As a result, a hydrophobic domain is formed on the surface of the cluster, which is responsible for the dye binding.

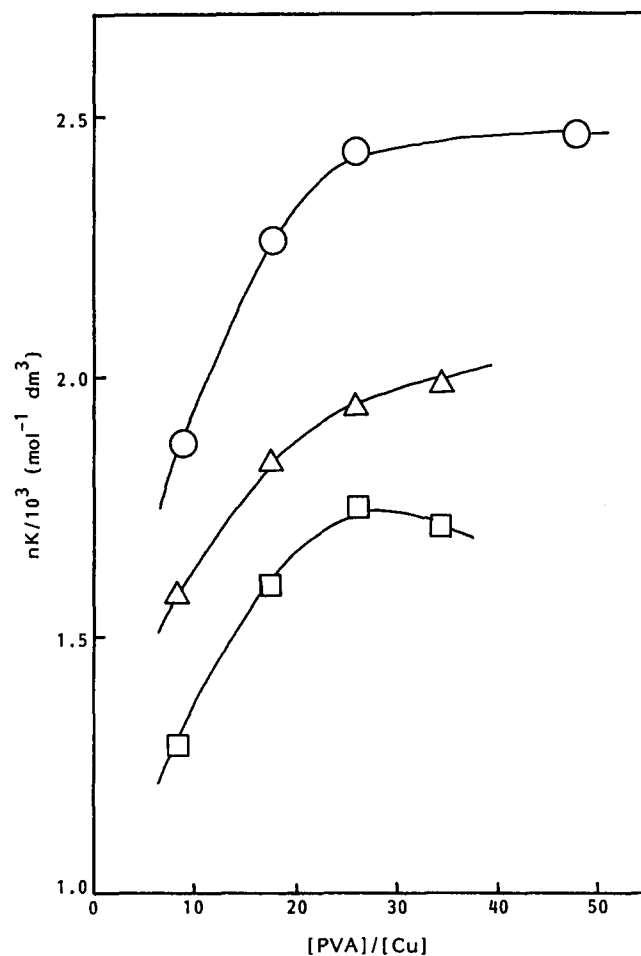


Figure 8 The plots of nK against (PVA)/(Cu) ratios. —, Concentration of the dye. (○), $6.57 \times 10^{-6} \text{ mol dm}^{-3}$; (△), $1.19 \times 10^{-5} \text{ mol dm}^{-3}$; (□) $2.98 \times 10^{-5} \text{ mol dm}^{-3}$. PVA-80 was used

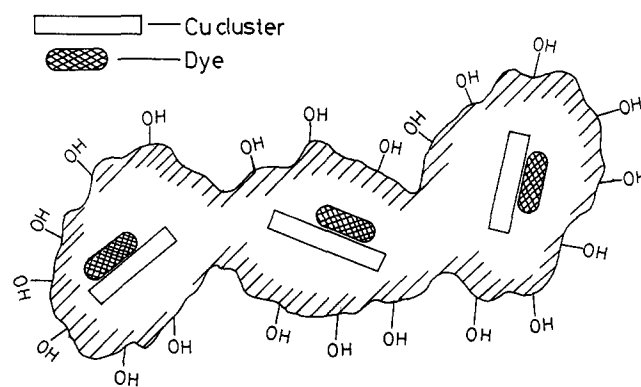


Figure 9 Schematic representation of dye binding on a hydrophobic site in the PVA-Cu(II) complex

According to this model, the number of binding sites should be proportional to the number of clusters, if the clusters have a constant surface area.

Several pieces of evidence to support this speculation are found in the above results. First, the model can explain the fact that the binding affinity appears only after the complex is formed. Second, the model is consistent with the fact that the degree of binding is principally determined by the concentration of copper ion. Moreover, the enhancement of binding affinity of PVA-80 can be easily understood because the hydrophobic domain on the cluster is more stabilized if the more hydrophobic polymer chains are used.

CONCLUSIONS

The unique properties of the complex are mainly associated with the peculiar structure and size of colloidal cupric hydroxide particles. The polymer chain plays a

role in dispersing the particle probably by the steric repulsive force. A more quantitative estimation of the thermodynamics of the dye binding will be presented in a subsequent paper.

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