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Complex Formation of Crosslinked Poly(4-vinylpyridine) Resins with Copper(II)

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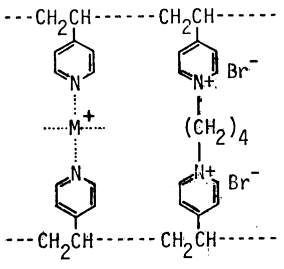
Poly(4-vinylpyridine) was crosslinked with 1,4-dibromobutane. The obtained resin(DBQP) formed a stable complex with Cu^{2+}, and the adsorption capacity of DBQP varied with the degree of crosslinking. The complex formation of DBQP with Cu^{2+} was studied by examining the adsorption equilibrium and the spectroscopic measurement. The resin complex seems to be formed *via* no step-by-step mechanism, and the stability constant was appreciably large in comparison with those of non-crosslinked polymers and of a monomeric analogue. In the highly crosslinked resins, the ligand-field is relatively weak and the stability of the Cu^{2+} complex is decreased.

Poly(4-vinylpyridine) (PVP) forms a stable intrapolymer chelate with copper ions, in which the PVP-chain is markedly contracted.[1-3] Thus, if one makes the PVP-ligand crosslinked and the polymer chain is previously contracted, it is expected that the obtained PVP resin will form the stable complex with Cu^{2+}.

In the present paper, PVP was crosslinked with 1,4-dibromobutane to yield the insoluble PVP resin-(DBQP, **I**), of which free and unquaternized pyridine groups were utilized to coordinate with a metal ion.



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The complex formation of this DBQP resin with Cu^{2+} was studied by the adsorption equilibrium and the spectroscopic measurement. The effects of the crosslinking on the stability and structure of the resin complex were discussed.

Experimental

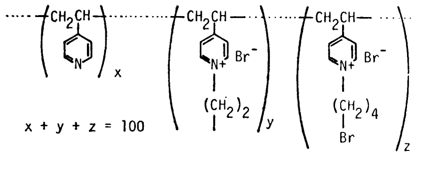
Materials. PVP was prepared by radical polymerization of 4-vinylpyridine, and was purified twice by reprecipitation. The average degree of polymerization of PVP used in this experiment was 122 as measured by vapor pressure osmometry. Analytical grade reagents of 1,4-dibromobutane, pyridine (Py), and copper(II) chloride were used. All solutions were prepared with deionized water.

Preparation of DBQP Resins. The crosslinking reagent, 1,4-dibromobutane, of prescribed concentration [0.025 M (DBQP(1)), 0.1 M (DBQP(2)), 0.3 M(DBQP(3)), or 0.5 M (DBQP (4))] was added to the methanol solution of PVP (1 M). The mixture was vigorously stirred at 65 °C for 5 days. The resin was filtered off, washed with methanol repeatedly, and dried *in vacuo*. The dried resin was ground and the portion of 100—150 mesh size was used in all the experiments presented. The elemental analyses of the resins are shown in Table 1. The total Br content was determined by the Volhard method and the free Br ion in the resin was titrated after the resin was soaked into water. The percentages of crosslinking and of quaternization were calculated by using the C/N ratio, the free Br ion, and the total Br content. The percentage of quaternization was also deduced from the ratio of absorption at 1600 cm^{-1} (due to pyridine group) to the absorption at 1640 cm^{-1} (due to quaternized pyridine group) of IR spectra, and this value was nearly equal to the value which was determined

Table 1. Elemental analyses of PVP with 1,4-dibromobutane

Resin	Found(Calcd)				Cross-linking %[a]	Quater-nization %[b]	Quater-nization %[c]
	C%	N%	Br ion %	Br total %			
DBQP (1)	75.7 (75.5)	12.3 (12.3)	5.77 (5.76)	5.78 (5.76)	4.1	8.2	10
DBQP (2)	68.7 (68.6)	10.6 (10.7)	14.6 (14.7)	14.6 (14.7)	12	24	22
DBQP (3)	60.3 (59.9)	8.65 (8.69)	25.3 (25.3)	26.0 (25.8)	25	51	53
DBQP (4)	57.9 (57.1)	8.02 (8.04)	29.0 (29.0)	29.6 (29.4)	31	63	68

a) Percentage of bridged dibromobutane per pyridine groups of PVP=$y/2$(If all pyridine groups of PVP are crosslinked by dibromobutane, crosslinking % is 50). b) Percentage of quaternized pyridine groups per pyridine groups of PVP=$(y+z)$. c) Percentage of quaternized pyridine groups per pyridine groups of PVP determined by IR spectra.



by the elemental analyses (Table 1). The z term given in the footnote of Table 1 was extremely small, and almost all 1,4-dibromobutane molecules built bridges between two vinylpyridine groups.

Partially-quaternized PVP (QPVP) was prepared by quaternization of PVP with ethylbromide, and the percentage of quaternization was 45.

Adsorption of Cu^{2+} on the DBQP Resin. A batch type equilibration procedure was used to determine the Cu^{2+} uptaken from solution by the resin. The pH value of the system was kept constant by a 0.1 M CH_3COOH-CH_3COONa buffer. The two phases were shaken on a mechanical shaker at room temperature for 5 h. After shaking, the two phases were separated, and the supernatant solution was then analyzed for Cu^{2+} using atomic absorption spectrophotometry (JEOL JAA-7000). The amount of Cu^{2+} in the supernatant subtracted from the amount initially added gave the amount of Cu^{2+} adsorbed on the resin. Cu^{2+} adsorbed on QPVP and PVP were determined by dialysis equilibrium.

Measurements. The visible absorption spectra of the Cu^{2+} complexes of the fine powdered DBQP resin were measured in a Nujol mull or in suspension with a high sensitive spectrophotometer (Union Giken SM-401).

The apparent dissociation rate constant of Cu^{2+} from the Cu^{2+}-resin complex was determined as follows; the Cu^{2+}-resin complex was soaked into 0.1 M EDTA solution, and the increase in the spectra of the Cu^{2+}-EDTA (λ_{max}: 745 nm) formed in the supernatant solution was continuously measured.

Magnetic susceptibility measurements were carried out by Gouy method.

Results and Discussion

When the DBQP resin is added to the Cu^{2+} aqueous solution, the Cu^{2+}-resin complex is easily formed. As seen in Fig. 1, the adsorption equilibrium was attained within 1 h. It was shown in Figs. 1 and 2 that the adsorption of Cu^{2+} on the DBQP resins varied with the degree of crosslinking. Here the concentration of the unquaternized pyridine groups in the resin was kept constant for each resin. The adsorption capacity of Cu^{2+}, *i.e.*, the value of ordinate in Fig. 2 was changed with the degree of crosslinking. The effect of the crosslinking on the Cu^{2+}-resin complexes were studied from the complex formation equilibrium and the structure of the Cu^{2+} complex.

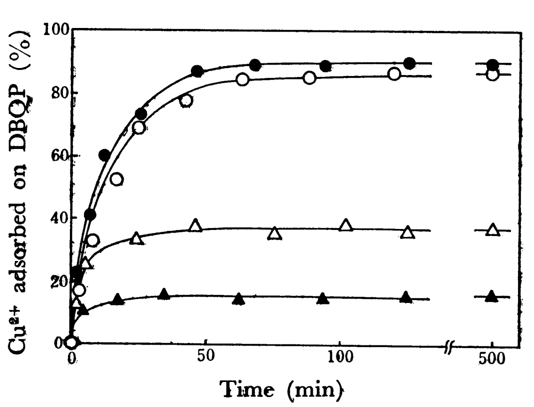


Fig. 1. Complexation between DBQP and Cu^{2+}. [Cu]=0.001 M, [$\overline{N}$]/[Cu]=10, μ=0.1, pH 5.5, ○: DBQP(1), ●: DBQP(2), △: DBQP(3), ▲: DBQP(4), where $\overline{N}$ is the unquaternized and coordinable vinylpyridine group in the resin. DBQP(1)—(4) are shown in Table 1.

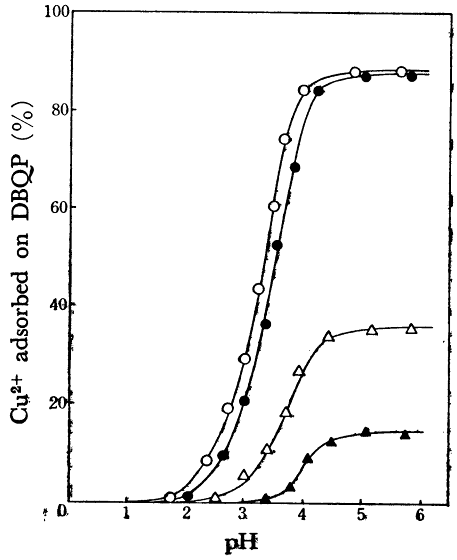


Fig. 2. Effect of crosslinking on Cu^{2+} adsorption. [$\overline{N}$]=0.01 M, [$\overline{N}$]/[Cu]=4, μ=0.1, ○: DBQP(1), ●: DBQP(2), △: DBQP(3), ▲: DBQP(4).

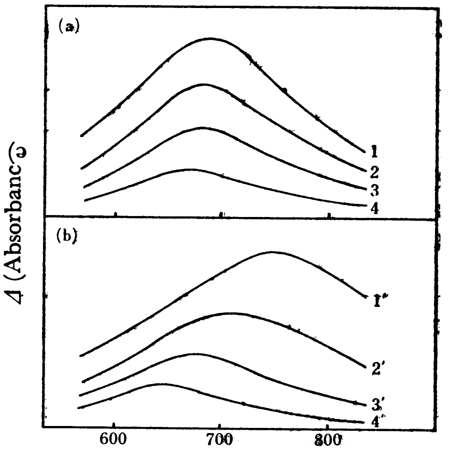


Fig. 3. Visible spectra of Cu^{2+}-DBQP(a) and Cu^{2+}-Py complexes(b). [$\overline{N}$]=[Py]=0.05 M, μ=0.1, pH 5.5, [$\overline{N}$] or [Py]/[Cu]=1(1, 1'), 2.5(2, 2'), 5(3, 3'), 20(4), 100(4').

The visible spectra of the Cu^{2+} complexes with the resin and with Py were measured. As seen in Fig. 3(b), the absorption maximum of the Cu^{2+} complex shifted progressively to shorter wave length as the concentration of Cu^{2+} decreased. This suggests the stepwise formation of Cu^{2+}-Py complexes. On the contrary, the absorption maximum of the Cu^{2+} complex with the resin hardly shifted in Fig. 3 (a). It means that the complex formation between Cu^{2+} and the resin does not proceed *via* step-by-step mechanism and the composition of the Cu^{2+} complex in the resin remains constant throughout the experimental conditions.

The successive stepwise formation constants are represented in Eq. 1 and were calculated by Eq. 2 as follows:

$$\left.\begin{aligned} \mathrm{Cu} + \mathrm{L} &\xrightleftharpoons{\kappa_1} \mathrm{CuL_1} \\ \mathrm{CuL_1} + \mathrm{L} &\xrightleftharpoons{\kappa_2} \mathrm{CuL_2} \\ \mathrm{CuL_2} + \mathrm{L} &\xrightleftharpoons{\kappa_3} \mathrm{CuL_3} \\ \mathrm{CuL_3} + \mathrm{L} &\xrightleftharpoons{\kappa_4} \mathrm{CuL_4} \end{aligned}\right\} \quad (1)$$

$$\frac{[\mathrm{Cu}]_t}{[\mathrm{Cu}]} = 1 + \sum_{n=1}^{4} \left(\prod_{n=1}^{n} \kappa_n\right)[\mathrm{L}]^n \quad (2)$$

(L is a pyridine group in the resin and $[\mathrm{Cu}]_t$ is the total concentration of Cu)

The concentrations of Cu^{2+} in the supernatant were measured as changing the amount of the resin ($[\mathrm{Cu}]_t = 1 \times 10^{-5}$ M=const, $[\mathrm{L}] \gg [\mathrm{Cu}]_t$, $[\overline{\mathrm{N}}] = 2 \times 10^{-3}$—$5 \times 10^{-4}$ M).* As shown in Table 2, the constants increased from κ_1 to κ_4 in the resin system in contrast to the monomeric Py system. This result also supports that the composition of the Cu^{2+} complex is almost $\mathrm{CuL_4}$ where four pyridine groups in the resin coordinate to the Cu^{2+} ion, although the experimental conditions of Table 2 are not the same as the others.

Table 2. Stepwise formation constants (κ l/mol) of Cu^{2+}-DBQP complexes

Ligand	log κ_1	log κ_2	log κ_3	log κ_4
DBQP (1)	2.4	2.8	3.3	3.8
DBQP (2)	2.3	2.7	3.2	3.7
DBQP (3)	2.2	2.4	3.1	3.3
DBQP (4)	1.9	2.3	3.0	3.1
Py[2]	2.5	1.9	1.3	0.8

$[\mathrm{Cu}]_t = 1 \times 10^{-5}$ M, $[\overline{\mathrm{N}}] = 2 \times 10^{-3}$—$5 \times 10^{-4}$ M, $\mu = 0.10$, pH 5.5.

From the results, the above equations can be also represented by the following.

$$\mathrm{Cu} + \mathrm{L}' \xrightleftharpoons{K} \mathrm{CuL}' \quad (3)$$

(L′ is four pyridine groups in the resin)

The adsorption curves given in Fig. 4 appeared to be a Langmuir type and the stability constant K of the Cu^{2+} complex and the saturated adsorption amount of Cu^{2+} were evaluated by fitting Langmuir's Eq. 4;

$$\frac{c}{a} = \frac{1}{K \cdot A_s} + \frac{1}{A_s} c \quad (4)$$

where A_s is a constant value which corresponds to the saturated adsorption amount, c is the concentration of Cu^{2+}, K is the stability constant, and a is the quantity of adsorption. They are summarized in Table 3 with those of the Cu^{2+} complexes of Py, PVP, and QPVP.

The stability constant K of the Cu^{2+}–PVP complex was about forty times as large as that of the Cu^{2+}–Py complex. Furthermore, the K values in the Cu^{2+}–DBQP system were about one order of magnitude greater than in the non-crosslinked PVP system, which indicates that the DBQP resin uptakes Cu^{2+} from solution in a high efficiency. This phenomenon appears to be general with the polymer complex system,[2,3] and can be explained by the assumption that the concentration of ligand is higher in the polymer domain, especially in the domain for the crosslinked resin system. So that, once the metal ion is attached to one ligand group of the polymer chain, other ligands coordinate more readily.

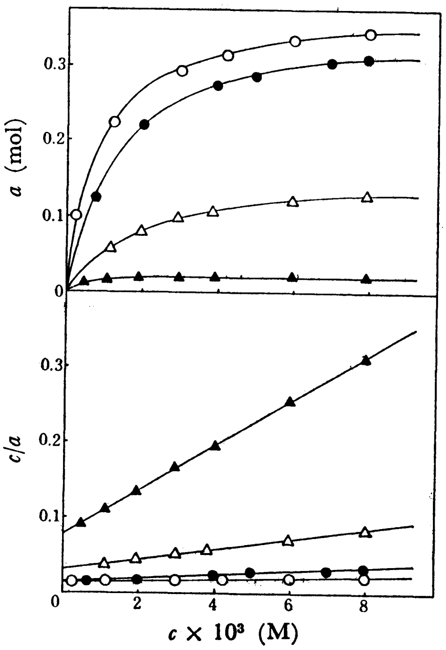


Fig. 4. Adsorption behavior of Cu^{2+} on DBQP resins. $[\overline{\mathrm{N}}] = 0.01$ M const., $\mu = 0.1$, pH 5.5, ○: DBQP(1), ●: DBQP(2), △: DBQP(3), ▲: DBQP(4), a is $[\mathrm{Cu}^{2+}]$ in solution(M), c is Cu^{2+} adsorbed on DBQP(mol).

Table 3. K and A_s of Cu^{2+} complexes

Ligand	K(l/mol)	A_s(mol/unit mol)
DBQP (1)	2810	0.32
DBQP (2)	2370	0.30
DBQP (3)	630	0.12
DBQP (4)	540	0.03
PVP	124	0.45
QPVP	97	0.48
Py[2]	3.2	—

$[\overline{\mathrm{N}}]$ in DBQP, QPVP=0.01 M, $\mu = 0.10$, pH 5.5.

K and A_s for DBQP decreased largely according to an increase in the number of the crosslinking points. This seems to be caused by the steric hindrance of the crosslinking agent and of the contracted polymer chain, and caused by the electrostatic repulsion among the coordinating Cu^{2+} and the pyridinium ions on the polymer chain as the K value of QPVP is smaller than that of PVP.

Apparent rate constant k_f' of the complex formation given in Eq. 5 was determined. The stability constant of Cu^{2+}–EDTA complex is moderately larger than that of Cu^{2+}–DBQP, and we estimated the apparent

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* Although the κ values in Table 2 are valid under the conditions given in the foothote in Table 2, they may not be adequate under the other conditions (*e. g.* in Fig. 1).

dissociation rate constant k_b' for the reaction in which

$$\mathrm{Cu^{2+}} + \mathrm{DBQP} \overset{k_f'}{\rightleftarrows} \mathrm{Cu^{2+}\text{-}DBQP} \quad (5)$$

$$\mathrm{Cu^{2+}\text{-}DBQP} + \mathrm{EDTA} \overset{k_b'}{\rightleftarrows} \mathrm{Cu^{2+}\text{-}EDTA} + \mathrm{DBQP} \quad (6)$$

EDTA took $\mathrm{Cu^{2+}}$ from the stable resin complex, as represented by Eq. 6. In Fig. 5, k_f' and k_b' were plotted against the degree of crosslinking. The k_b' value increased with the stability constant, *i.e.*, $\mathrm{Cu^{2+}}$ is more easily dissociated in the highly crosslinked resin, because of the instability of the complex.

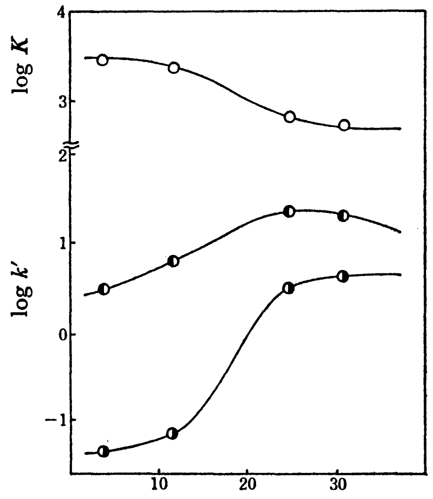

Fig. 5. Effect of crosslinking on k_f' and k_b'.
◐: k_f', ◑: k_b', ○: K value being in Table 3.

TABLE 4. D-d ABSORPTION MAXIMUM AND MAGNETIC SUSCEPTIBILITY OF $\mathrm{Cu^{2+}}$-DBQP COMPLEXES

Ligand	λ_{max}(nm)	Magnetic Moment (B.M.)
DBQP (1)	668	1.6
DBQP (2)	658	1.8
DBQP (3)	700 (broad)	1.6
DBQP (4)	700 (broad)	1.4
QPVP	692	1.7

a) [N] in DBQP=0.05 M, [N]/[Cu]=5, μ=0.1, pH 5.5. b) Gouy method: 20 °C, 7000 G.

The structure of $\mathrm{Cu^{2+}}$ complexes involving the resin was deduced from the measurements of visible spectra and magnetic susceptibility of the fine powdered resin complex (Table 4). The effective magnetic moments of the $\mathrm{Cu^{2+}}$–DBQP complexes were about 1.7 B. M. and approximately equal to the value for the mononuclear $\mathrm{Cu^{2+}}$ complex. The d-d absorption maxima for the highly crosslinked resins were located at longer wave length and this suggests the relatively weak ligand-field of the highly crosslinked resins.

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