

Chelating Polymer-Bearing 4-(3-Triazolylazo)phenol Moiety as the Functional Group

INTRODUCTION

The color of *ortho*-hydroxyazo compounds such as 1-(2-pyridylazo)-2-naphthol (PAN)¹ and 4-(2-thiazolylazo)resorcinol (TAR)² in chelation with some heavy metal ions is known, and application as metallochromic indicators for heavy metal ions were investigated. On the other hand, little is known about the chelation of *para*-hydroxyazo compounds with heavy metal ions. In the chelation with heavy metal ions, the difference in coloration between the two isomeric compounds containing hydroxyazo moieties (*ortho*-hydroxyazo or *para*-hydroxyazo structure) is based mainly on the presence or the absence of the donor oxygen atom. In *para*-hydroxyazo moieties, the oxygen atom of the hydroxyl group cannot be a chelating site because of steric hindrance, and the number of its chelating sites decreases compared with that of its corresponding isomeric compound containing the *ortho*-hydroxyazo moiety. The chelating polymer-bearing 4-(3-triazolylazo)phenol moiety was expected, therefore, to form somewhat less stable chelates with heavy metal ion compared with the case of the corresponding chelating polymer containing 2-(3-triazolylazo)-phenol moiety.³

The polymer-bearing 4-(3-triazolylazo)phenol moiety was synthesized, and the metal adsorption properties of it for 6 divalent heavy metal ions (M^{2+}); Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were investigated. The object of this paper is to examine the effect of the donor oxygen atom of the hydroxyl group on the metal adsorption ability of the chelating polymer-bearing triazolylazophenol moiety, and to investigate the application of the polymer for removal of heavy metals from plating process solutions.

EXPERIMENTAL

Measurement

¹H nuclear magnetic resonance (NMR) spectra were taken on a Hitachi 60 MHz R-24B high resolution spectrometer in acetone-d₆ at 35°C by employing TMS as an internal standard. Infrared absorption spectra were measured on a Nihon Bunko IRA-2 spectrometer. Ultraviolet absorption spectra were obtained using a Hitachi 323 spectrophotometer in methyl alcohol at room temperature. Elemental analysis was performed on a Yanaco MT-3 CHN Corder. A Hitachi 308 atomic absorption spectrometer and EDTA titrations were employed for determinations of metal concentrations.

Preparation of the Chelating Polymer

o-Vinylphenol was prepared by employing cumarin as a starting material in nearly the same way as the method reported in the literature.^{4,5}

Cumarin, 29.2 g, was refluxed for 2.5 h at 130°C with 120 mL ethanol and 27.2 g sodium ethylate, followed by addition of 200 mL water, and then ethanol was distilled off. The resulting solution was neutralized with HCl, and *o*-hydroxycinnamic acid was obtained as white crystalline needles: yield 26.7 g (81.5%); mp 210°C; ¹H NMR (acetone-d₆) δ 6.58 (d, J = 16.6, 1 H), ca. 6.86-7.66 (m, 4H), 8.02 (d, J = 16.6, 1 H), 9.22 (bs, 1 H); infrared (KBr) 1663 cm⁻¹ ($\nu_{C=O}$), 1617 ($\nu_{C=C}$), 1460 ($\nu_{C=C}$), 1427 ($\nu_{C=C}$), 1333 ($\nu_{C=O}$) 1220 (δ_{OH}); ultraviolet (methyl alcohol) λ_{max} 212.5 nm (1.52×10^4), 276 (1.72×10^4), 327 (9.45×10^3).

Anal. Calcd for C₉H₈O₃: C, 65.85; H, 4.91. Found: C, 66.45; H, 4.97.

o-Vinylphenol was prepared by the decarboxylation of 10 g *o*-hydroxycinnamic acid and 2 g Cu-powder at 230°C for 2.5 h: yield 5.4 g (73.8%); ¹H NMR (acetone-d₆) δ 5.16 (d, J = 11.6, 1 H), 5.73 (d, J = 18.1 H), ca. 6.64-7.51 (m, 5 H), 8.34 (s, 1 H); IR (KBr) 1623 cm⁻¹ ($\nu_{C=C}$), 1620 ($\nu_{C=C}$),

1487 ($\nu_{C=C}$), 1455 ($\nu_{C=C}$), 1345 (ν_{C-O}), 1230 (δ_{OH}), 998 ($\delta_{CH=CH}$), 913 ($\delta_{=CH_2}$); UV (methyl alcohol) λ_{max} 248 nm (ca. 8.4×10^3), 304 (ca. 3.4×10^3).

Anal. Calcd for C_8H_8O : C, 79.97; H, 6.71. Found: C, 78.13; H, 6.70.

The polymerization was carried out *in vacuo* by employing 100 mL of 50 w/v% *o*-vinylphenol methylethyl ketone solution and 6.5 g azobisisobutyronitrile for 6 h at 90°C. The obtained *o*-vinylphenol polymer was washed with a large amount of distilled water, filtered, and dried for 2 weeks at 50°C: yield 21.5 g (43 %); 1H NMR (acetone- d_6) ca. 6.82 (bs, 4 H); IR (KBr) 1603 cm^{-1} ($\nu_{C=C}$), 1490 ($\nu_{C=C}$), 1455 ($\nu_{C=C}$), 1350 (ν_{C-O}), 1230 (δ_{OH}); UV (methyl alcohol) λ_{max} 276.5 nm.

Anal. Calcd for $(C_8H_8O)_n$: C, 79.97; H, 6.71. Found: C, 78.47; H, 6.69.

The chelating polymer was prepared by the conventional diazotized coupling reaction of 4.9 g 3-amino-1,2,4-triazole with 7.0 g *o*-vinylphenol polymer. The obtained chelating polymer was used for experiment as a wet polymer of 85.74% moisture content: yield 10.2 g (81%).

Anal. Found for the chelating polymer: C, 57.28; H, 4.65; N, 23.24. This indicates an approximate composition of 58.3 mol% triazolylazo-vinylphenol.

RESULTS AND DISCUSSION

Metal Adsorption Ability of the Chelating Polymer

As was expected, color of this chelating polymer in the formation of the polymer- M^{2+} chelates were not remarkable except for chelation with Cu^{2+} . The color of the polymer changed from orange to green (λ_{max} 655 nm) by chelate formation with Cu^{2+} . The color change was reversible with metal ion elimination.

The effect of pH on the capacity of the chelating polymer for M^{2+} is shown (Fig. 1). The experiment was done with 50 mL of a metal ion solution (ca. 10^{-2} mol/L) and 1 g wet polymer in a similar manner as described in the previous report.³ If 4-(3-triazolylazo)-phenol moiety of the polymer forms a 1:1 chelate with M^{2+} , the maximum capacity for M^{2+} was expected to be 6.64 mEq/g according to elemental analysis. The observed maximum capacity of the polymer for M^{2+}

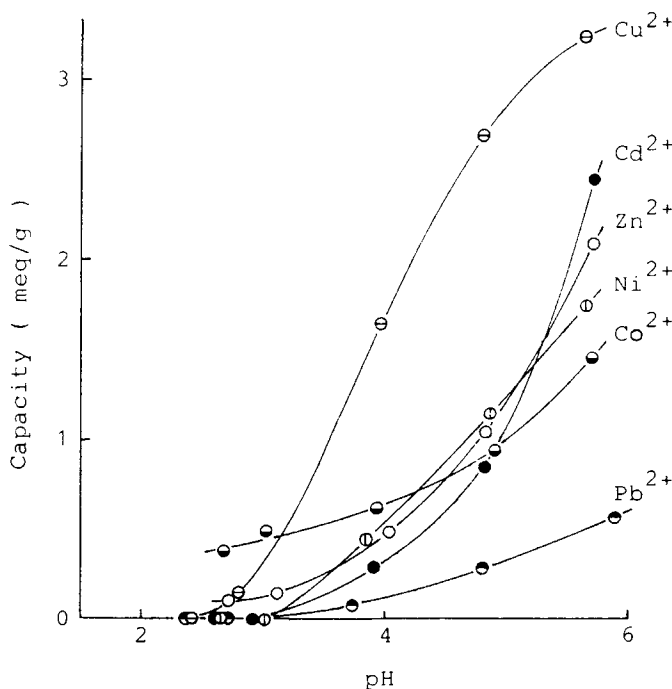


Fig. 1. Effect of pH on the capacity of the chelating polymer for heavy metal ions at 23°C. Shaking time: 6 h. Buffer solution: $CH_3CO_2H + CH_3CO_2Na = 0.2$ mol/L.

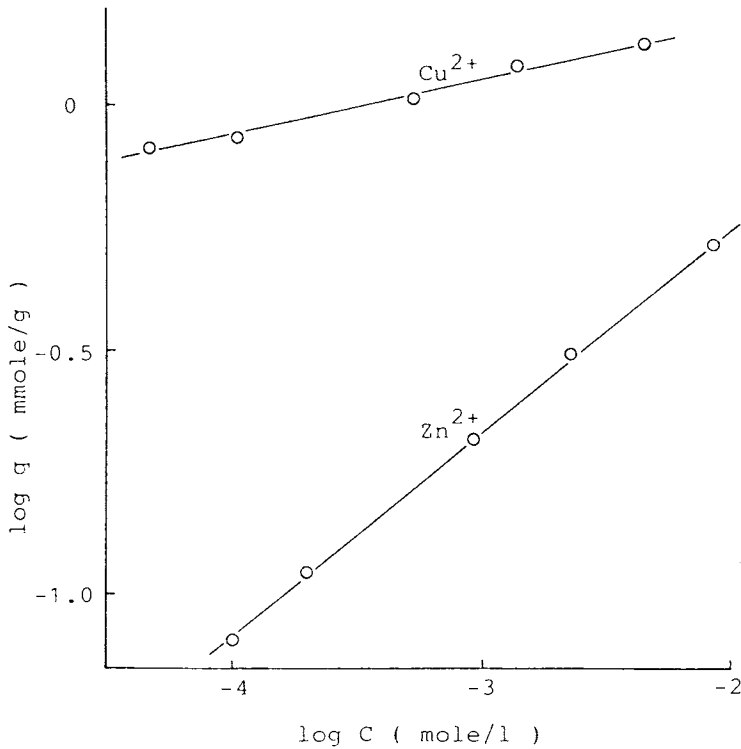


Fig. 2. Isotherm adsorption curves for the adsorption of Cu^{2+} and Zn^{2+} by the chelating polymer at 23°C . Shaking time: 6 h. pH: 5.0 ($\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{Na} = 0.2 \text{ mol/L}$).

TABLE I
Effect of Shaking Time and Alkali or Alkaline Earth Metal Ion
on the Capacity of the Polymer for M^{2+} at 23°C .

pH of solution: for adsorption of Cu^{2+} or (Zn^{2+})	Shaking time (min)	Concn. of KNO_3 or (CaCl_2) (%)	Metal adsorbed: Cu^{2+} or (Zn^{2+}), (mEq/g)
4.87(4.90)	15	—	2.02(0.65)
4.87(4.90)	30	—	2.16(0.74)
4.87(4.90)	60	—	2.30(0.82)
4.87(4.90)	120	—	2.40(0.91)
4.87(4.90)	240	—	2.58(0.99)
4.87(4.90)	360	—	2.69(1.02)
4.83	360	0.3	2.51
4.83	360	0.6	2.55
4.83	360	1.0	2.58
4.83	360	(0.3)	2.65
4.83	360	(0.6)	2.65
4.83	360	(1.0)	2.69

Buffer: $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{Na} = 0.2 \text{ mol/L}$.

was 3.24 mEq/g for adsorption of Cu^{2+} at pH 5.63. The achieved maximum capacity was about 50% of its expected value. In the metals investigated, Cu^{2+} was most strongly adsorbed by the polymer in the pH region of 3.0-5.7. In this experiment, the magnitude of drop in capacity of the polymer for M^{2+} with a lowering of pH was larger than that in capacity of the polymer bearing the 2-(3-triazolylazo)phenol moiety.³

The typical isotherm adsorption curves measured for the chelation of the polymer with M^{2+} are shown (Fig. 2). The $1/n$ values of the Freundlich equation evaluated for Cu^{2+} and Zn^{2+} adsorptions were 0.12 and 0.42, respectively. These metals were effectively adsorbed, but it can be said that the extent of variation of the affinity of the polymer for M^{2+} with metal ion is larger than that shown in the case of the polymer-bearing 2-(3-triazolylazo)phenol moiety.³

Effects of shaking time and the presence of alkali or alkaline earth metal ions on the capacity of the chelating polymer for M^{2+} were examined at 23°C (Table I). The time needed for perfect saturation of the capacity of the polymer for M^{2+} was about 4 h, and the degree of saturation after shaking for 30 min were 73 and 80% for the adsorption of Zn^{2+} and Cu^{2+} , respectively. The equilibration rates obtained in this experiment were smaller than those of the polymer bearing 2-(3-triazolylazo)phenol moiety.³ The capacity of the polymer for M^{2+} showed to be hardly variable with the presence of alkali or alkaline earth metal ion in water.

Elimination of Metal Ions from Polymer- M^{2+} Chelates.

The results are shown (Fig. 3). Similarly to the case of the polymer bearing 2-(3-triazolylazo)phenol moiety,³ Zn^{2+} and Ni^{2+} were perfectly eluted from the polymer with 1 mol/L HCl solution, but 4 mol/L H_2SO_4 solution was required to eliminate Cu^{2+} .

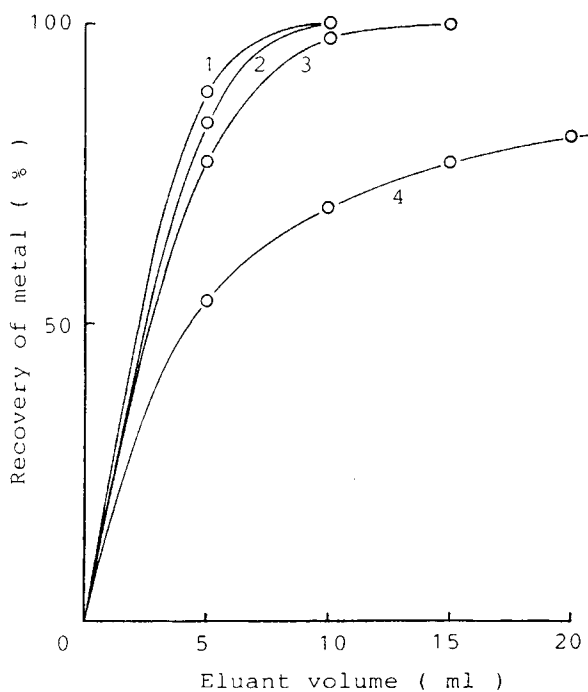


Fig. 3. Elimination of metal ions from the chelating polymer- M^{2+} chelates by mineral acids at 23°C. Initial amount of the adsorbed M^{2+} : Cu^{2+} , 2.01×10^{-4} mol; Ni^{2+} , 0.97×10^{-4} mol; Zn^{2+} , 1.49×10^{-4} mol. 1: Ni^{2+} chelate-1 mol/L HCl, 2: Zn^{2+} chelate-1 mol/L HCl, 3: Cu^{2+} chelate-1 mol/L H_2SO_4 , 4: Cu^{2+} chelate-1 mol/L HCl.

TABLE II
Adsorption of Heavy Metal Ions in Plating-Process Solutions by the Chelating Polymer at 23°C

Sample	pH	Metal ion	Initial concn. of metal (mol/L)	Remaining concn. of metal (mol/L)	Capacity (mEq/g)
A	3.85	Ni ²⁺	9.01×10^{-3}	8.41×10^{-3}	0.42
	5.68 ^a	Ni ²⁺	9.01×10^{-3}	7.51×10^{-3}	1.05
B	7.12	Cu ²⁺	9.25×10^{-3}	7.35×10^{-3}	1.33
	6.18 ^a	Cu ²⁺	9.25×10^{-3}	7.05×10^{-3}	1.54
C	5.52 ^a	Cu ²⁺	4.14×10^{-3}	1.64×10^{-3}	1.76
		Zn ²⁺	2.27×10^{-3}	2.11×10^{-3}	0.12

A: Solution of the electrolytic-plating process of Ni. B: Solution of the electrolytic-plating process of Cu. C: Solution of the chemical polishing process of Cu-Zn alloy. ^apH was controlled with acetate buffer ($\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{Na} = 0.2 \text{ mol/L}$).

Removal of Heavy Metal Ions from Plating Process Solutions

The chelating polymer was also applied to the adsorption of heavy metal ions from plating process solutions (Table II). In electrolytic copper-plating process solution, the capacity (1.54 mEq/g) of the polymer in the buffered solution (pH 6.18) was larger than that (1.33 mEq/g) in the initial solution (pH 7.12). When the solution of the chemical polishing process (copper-zinc alloy) was treated with this chelating polymer, the amount of Cu²⁺ removed by the polymer was larger than that of Zn²⁺.

From these results, it can be said that the chelating polymer bearing 4-(3-triazolylazo)phenol moiety is applicable to the removal of heavy metal from plating process solutions.

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Received April 14, 1987

Accepted July 16, 1987