Chelating Polymer Bearing 2-(2-Diazolylazo)phenol Moiety for Adsorbent of Heavy Metal Ions

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Chelating polymer bearing 2-(2-diazolylazo)phenol moiety was synthesized and its metal adsorption properties for 6 divalent heavy metal ions (M^{2+}): Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} were investigated. The polymer changed color from orange yellow to blue or to red violet with its chelation to Cu^{2+} or to Ni^{2+} , respectively. The maximum capacity of the polymer for Cu^{2+} was found to be 1.35 meq/g in pH 5.71 solution. The degrees of saturation of the capacity of the polymer after shaking for 30 min were 71.3 and 83.6% for the adsorptions of Zn^{2+} and Cu^{2+} , respectively. The capacity of the polymer for M^{2+} hardly varied with the presence of alkali or alkaline earth metal ions. The elimination of metals from the polymer- M^{2+} chelates was achieved with 4 mol/l HCl or 4 mol/l H_2SO_4 solution.

Keywords Chelating polymer, 2-(2-diazolylazo)phenol moiety, metal adsorption ability, heavy metal ion

In previous reports^{1,2}, the chelating polymers bearing 2-(3-triazolylazo)phenol or 4-(3-triazolylazo)phenol moiety as a functional group were synthesized and the metal adsorption abilities of these polymers for 6 divalent heavy metal ions (M^{2+}): Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} were investigated. The color changes of the polymer bearing 2-(3-triazolylazo)phenol moiety in the formation of the polymer- M^{2+} chelate were remarkable, but the color of the polymer containing 4-(3-triazolylazo)phenol group did not appear to change remarkably with the M^{2+} chelate formation, except for its chelation with Cu^{2+} . The magnitude of decrease in the capacity of the polymer containing 4-(3-triazolylazo)phenol group for M^{2+} with lowering of pH was larger than that in the capacity of the polymer bearing 2-(3-triazolylazo)phenol moiety. From these experimental results, in the chelate formation of the polymer bearing triazolylazophenol moiety, which has nitrogen as the only hetero atom of azole ring (5 membered heteroaromatic ring), with transition metal ions, the effect of the donor oxygen atom of its phenol group was known. However, the function of the donor nitrogen atom of its azole ring on the polymer- M^{2+} chelate formation is still not elucidated. In order to reveal the metal adsorption ability of the polymer bearing azole ring as a component of its *ortho*-hydroxyazo-heteroaromatic group, the effect of variation in the number of nitrogen atoms of the azole ring, therefore, is an interesting subject for investigation.

In the present work, the polymer bearing 2-(2-diazolylazo)phenol moiety was newly prepared, and its metal adsorption properties for M^{2+} were investigated. The purpose of this paper is to examine the effect of the decrease of the number of nitrogen atoms of the azole ring on the metal adsorption ability of the chelating

polymer bearing *ortho*-hydroxyazo-heteroaromatic moiety as a functional group, and to investigate the application of this polymer for removal of heavy metals from plating process solutions. Some monomeric diazolylazophenol derivatives and their chelate forming abilities with transition metal ions have already been reported³⁻⁷, but little is known about the polymer bearing diazolylazophenol moiety.

Experimental

Measurement

Proton nuclear magnetic resonance (NMR) spectra were taken on a Hitachi 60 MHz R-24B high resolution spectrometer in acetone- d_6 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 methanol at room temperature. Elemental analysis was performed on a Yanaco MT-3 CHN Corder. A Hitachi 308 atomic absorption spectrophotometer and EDTA titration were employed for the determination of metal concentrations.

Reagents

Metal ion solutions were prepared by dissolving the reagent grade metal nitrate in distilled water. Acetate buffer solutions (CH_3CO_2H/CH_3CO_2Na , 0.2 M) were used to adjust pH values.

Preparation of the chelating polymer

p-Vinylphenol was prepared by employing *p*-hydroxybenzaldehyde as a starting material in nearly the same way

as the method reported previously.¹ The properties of the synthesized *p*-vinylphenol were presented in the previous report.¹

The chelating polymer was prepared by the conventional diazotized coupling reaction of 4.4 g of 2-amino-1,3-diazole with 2.0 g of *p*-vinylphenol polymer. The obtained chelating polymer was used for experiment as a wet polymer of 79.98% moisture content: yield 2.1 g (59%); IR (KBr) 1650 cm⁻¹ ($\nu_{C=C(\text{diazole ring})}$), 1220 (δ_{OH}), 1095 ($\delta_{NH(\text{diazole ring})}$), 900 ($\delta_{CH(\text{diazole ring})}$), 820 (δ_{CH}); UV (methanol) λ_{max} 280 nm, 370; Anal. Calcd. for (C₁₁H₁₀N₄O)_n: C, 61.67; H, 4.71; N, 26.15%. Found for the chelating polymer: C, 69.89; H, 6.15; N, 5.46%. This indicates an approximate composition of 12.9 mol% diazolyazo-vinylphenol. The polymer was soluble in organic solvents such as methanol and *N,N*-dimethylformamide.

Elimination of adsorbed M²⁺

The elimination of M²⁺ from its polymer chelate was carried out with a mineral acid solution in the following manner. The wet polymer, 1 g, was equilibrated with 50 ml of the buffered solution of M²⁺ (ca. 10⁻² mol/l), and its M²⁺ chelate was obtained from the solution by centrifugation. The chelate was washed with 10 ml distilled water, followed by treatment with a mineral acid solution.

Removal of heavy metals from plating process solutions

The applicability of the chelating polymer for removal of heavy metal ions from plating process solutions was examined. A mixture of 50 ml of the acetate buffer solution containing the metal and 1 g of wet polymer was equilibrated for 30 min, after which time the remaining concentration of metal was determined by using atomic absorption spectrometry.

Results and Discussion

Metal adsorption ability of the chelating polymer

In analogy with the case of monomeric diazolyazo-phenol derivatives³⁻⁷, this chelating polymer changed color with its chelation to heavy metal ions; such color changes were reversible with chelate deformation. The colors of this chelating polymer in chelate formation of the polymer-M²⁺ are shown in Table 1.

The effect of pH on the capacity of the chelating polymer for M²⁺ is shown in Fig. 1. A solution (50 ml) containing metal ions (ca. 10⁻² mol/l), the pH of which was controlled with 0.2 M acetate buffer, and 1 g of wet polymer were placed in a 300-ml flask. The mixture was shaken and equilibrated for 6 h at 23°C, after which time the chelate was excluded immediately by centrifugation. The metal ion concentration of the supernatant was determined by EDTA titration with Xylenol Orange (XO), 1-(2-pyridylazo)-2-naphthol (PAN) or mixture of Cu-EDTA and PAN (Cu-PAN) as a metal indicator. If 2-(2-diazolyazo)phenol moiety of the polymer forms a

Table 1 Color and absorption maxima of polymer-M²⁺ chelates

Metal ion	λ_{max}/nm	Color
—	450	orange yellow
Co ²⁺	620	orange red
Ni ²⁺	600	red violet
Cu ²⁺	650	blue
Zn ²⁺	625	red orange
Cd ²⁺	595	orange
Pb ²⁺	640	orange

Fig. 1 Effects of pH on the capacities of the chelating polymer for the heavy metal ions at 23°C. Shaking time, 6 h; buffer solution, CH₃CO₂H/CH₃CO₂Na, 0.2 M.

1 : 1 chelate with M²⁺, the maximum capacity for M²⁺ was expected to be 1.95 meq/g according to elemental analysis. The observed maximum capacity of the polymer for M²⁺ was 1.35 meq/g for adsorption of Cu²⁺ at pH 5.71. The achieved maximum capacity was about 69.2% of its expected value. Of the metals, Cu²⁺ was most strongly adsorbed by the polymer in the pH region of 3.0–5.7. The capacity of this chelating polymer for Cu²⁺ was shown to be twice, or a little more, that for the other metal ions. The result indicated the formation of a 1 : 1 chelate (metal : diazolyazophenol moiety of the polymer), but the other metal ions probably formed 1 : 2 chelates with it.

Typical isotherm adsorption curves measured for the chelating polymer with M²⁺ are shown in Fig. 2. The 1/*n* values of the Freundlich equation ($\log q = \log k + (1/n)\log C$) evaluated for Cu²⁺ and Zn²⁺ adsorptions by the polymer were 0.09 and 0.34, respectively. For metal adsorbing agents, 1/*n* value obtained from the Freundlich equation should be in the range of about 0.1–0.5 in order for the agent to be applied to practical use. These metals were shown to be effectively adsorbed by the

Fig. 2 Isotherm adsorption curves for the adsorptions of Cu^{2+} and Zn^{2+} by the chelating polymer at 23°C . Shaking time, 6 h; pH, 4.93 (Cu^{2+}) and 5.0 (Zn^{2+}).

Fig. 3 Effects of shaking time on the adsorptions of Cu^{2+} and Zn^{2+} by the chelating polymer at 23°C . pH, 4.97 (Cu^{2+}) and 4.99 (Zn^{2+}).

polymer.

The effect of shaking time on the capacity of the chelating polymer for M^{2+} was examined at 23°C (Fig. 3). The time needed for perfect saturation of the capacity of the polymer for M^{2+} was about 4 h. The degrees of saturation after shaking for 30 min were 71.3 and 83.6% for the adsorption of Zn^{2+} and Cu^{2+} , respectively. Compared with the equilibration rate of the chelating polymer bearing 2-(3-triazolylazo)phenol moiety as a functional group¹, the rate of the polymer bearing 2-(2-diazolylazo)phenol moiety was slow.

The effect of the presence of alkali or alkaline earth metal ions on the capacity of the chelating polymer for M^{2+} was examined. The relationship between the capacity of the polymer for Cu^{2+} and the amount of the coexisting KNO_3 (or CaCl_2) is shown in Fig. 4. The capacity of the polymer for the heavy metal ion varied little with the presence of these ions. Neither the coexistence of NaCl nor of $\text{Mg}(\text{NO}_3)_2$ affected the

Fig. 4 Effect of alkali or alkaline earth metal ion on the chelation of the polymer to Cu^{2+} at 23°C . Shaking time, 6 h; pH, 4.95.

Fig. 5 Elimination of metal ions from the polymer- M^{2+} chelates by mineral acids solutions at 23°C . Initial amount of the adsorbed M^{2+} : Cu^{2+} , 1.47×10^{-4} mol; Zn^{2+} , 0.80×10^{-4} mol. 1: Zn^{2+} chelate-1 mol/l HCl ; 2: Cu^{2+} chelate-4 mol/l H_2SO_4 ; 3: Cu^{2+} chelate-1 mol/l HCl .

capacity.

Elimination of metal ions from polymer- M^{2+} chelates

The results are shown in Fig. 5. Similarly to the cases of the polymers bearing triazolylazophenol moiety as functional group^{1,2}, Zn^{2+} was quantitatively eluted from the polymer with 1 mol/l HCl solution, but 4 mol/l H_2SO_4 solution was required to eliminate Cu^{2+} . A 90% removal of Cu^{2+} and of the other metal ions from the polymer- M^{2+} chelates, respectively, was achieved with 4 mol/l H_2SO_4 solution (ca. 197 times equivalent of adsorbed Cu^{2+}) and 1 mol/l HCl solution (ca. 38 times that of adsorbed M^{2+}).

Table 2 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 ⁻¹	Remaining conc. of metal/mol l ⁻¹	Capacity/meq g ⁻¹
A	3.90	Ni ²⁺	9.09×10 ⁻³	8.75×10 ⁻³	0.17
	5.98 ^a	Ni ²⁺	9.09×10 ⁻³	8.15×10 ⁻³	0.47
B	7.43	Cu ²⁺	9.07×10 ⁻³	8.25×10 ⁻³	0.41
	6.45 ^a	Cu ²⁺	9.07×10 ⁻³	8.05×10 ⁻³	0.51
C	5.80 ^a	Cu ²⁺	4.46×10 ⁻³	2.90×10 ⁻³	0.78
		Zn ²⁺	2.18×10 ⁻³	2.18×10 ⁻³	0

a. pH was controlled with 0.2 M acetate buffer.

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 2). In the electrolytic copper-plating process solutions, the capacity of the polymer for Cu²⁺ in the buffered solution (pH 6.45) was larger than that in the initial solution (pH 7.43). This may be due to the presence of NH₃ in the plating process solution, as was shown in the previous reports.¹⁻² In the case of the solution of the chemical polishing process of copper-zinc alloy, as was expected from the Irving-Williams order, the selective adsorption of Cu²⁺ was achieved in the buffered solution (pH 5.80).

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