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 (M2+): Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ were investigated. The polymer changed color from orange yellow to blue or to red violet with its chelation to Cu²⁺ or to Ni²⁺, respectively. The maximum capacity of the polymer for Cu²⁺ 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 Zn²⁺ and Cu²⁺, respectively. The capacity of the polymer for M²⁺ hardly varied with the presence of alkali or alkaline earth metal ions. The elimination of metals from the polymer-M²⁺ chelates was achieved with 4 mol/1 HCl or 4 mol/1 H₂SO₄ solution.

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

In previous reports¹,², 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 (M²⁺): Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺ were investigated.¹ The color changes of the polymer bearing 2-(3-triazolylazo)phenol moiety in the formation of the polymer-M²⁺ chelate were remarkable, but the color of the polymer containing 4-(3-triazolylazo)phenol group did not appear to change remarkably with the M²⁺ chelate formation, except for its chelation with Cu²⁺. The magnitude of decrease in the capacity of the polymer containing 4-(3-triazolylazo)phenol group for M²⁺ 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-M²⁺ 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 moiety, 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 M²⁺ 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 reported³-⁴, 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-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 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 (CH₃CO₂H/CH₃CO₂Na, 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. The properties of the synthesized p-vinylphenol were presented in the previous report.

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 with 79.98% moisture content: yield 2.1 g (59%); IR (KBr) 1650 cm⁻¹ (νC=C(diazole ring)), 1220 (δOH), 1095 (δNH(diazole ring)), 900 (δCH(diazole ring)), 820 (δCH3); UV (methanol) λmax 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% diazolylazo-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 diazolylazo-phenol derivatives, 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 was 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 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 : diazolylazo-phenol 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...
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 group, 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 KNO₃ (or CaCl₂) 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 Mg(NO₃)₂ affected the 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, Zn^{2+} was quantitatively eluted from the polymer with 1 mol/l HCl solution, but 4 mol/l H₂SO₄ 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 H₂SO₄ solution (ca. 197 times equivalent of adsorbed Cu^{2+}) and 1 mol/l HCl solution (ca. 38 times that of adsorbed M^{2+}).
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 Cu$^{2+}$ 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 NH$_3$ in the plating process solution, as was shown in the previous reports. 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 Cu$^{2+}$ was achieved in the buffered solution (pH 5.80).

### Table 2 Adsorption of heavy metal ions in plating-process solutions by the chelating polymer at 23°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Metal ion</th>
<th>Initial concn. of metal/mol l$^{-1}$</th>
<th>Remaining concn. of metal/mol l$^{-1}$</th>
<th>Capacity/meq g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.90</td>
<td>Ni$^{2+}$</td>
<td>9.09×10$^{-3}$</td>
<td>8.75×10$^{-3}$</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>5.98</td>
<td>Ni$^{2+}$</td>
<td>9.09×10$^{-3}$</td>
<td>8.15×10$^{-3}$</td>
<td>0.47</td>
</tr>
<tr>
<td>B</td>
<td>7.43</td>
<td>Cu$^{2+}$</td>
<td>9.07×10$^{-3}$</td>
<td>8.25×10$^{-3}$</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>6.45</td>
<td>Cu$^{2+}$</td>
<td>9.07×10$^{-3}$</td>
<td>8.05×10$^{-3}$</td>
<td>0.51</td>
</tr>
<tr>
<td>C</td>
<td>5.80</td>
<td>Cu$^{2+}$</td>
<td>4.46×10$^{-3}$</td>
<td>2.90×10$^{-3}$</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn$^{2+}$</td>
<td>2.18×10$^{-3}$</td>
<td>2.18×10$^{-3}$</td>
<td>0</td>
</tr>
</tbody>
</table>

a. pH was controlled with 0.2 M acetate buffer.

### References


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