Chelating Resins Containing 1,4,8,11-Tetraazacyclotetradecane-5,7-dione Based on Crosslinked Copolymer Beads of the Macroreticular Type

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Chelating resins containing a macrocyclic ligand, 1,4,8,11-tetraazacyclotetradecane-5,7-dione, were prepared by ligand reactions with two different crosslinked copolymer beads of the macroreticular type: chloromethylated styrene-divinylbenzene (RCS) and glycidyl methacrylate-divinylbenzene (RG) copolymers. Although both resins have nearly equal amounts of the fixed ligand, the RG-based resin (RGD) shows a much higher uptake of Cu(II) than does the RCS-based resin (RCSd). This indicates that the complexing ability of the fixed ligand is strongly influenced by copolymer matrices. A further detailed study of RGD revealed that the characteristics of RGD include high selectivity toward Cu(II) and a rapid elution rate of Cu(II) with an aqueous solution of strong acid. The usefulness of RGD in the separation of Cu(II) has been demonstrated by means of column operation.

Keywords Chelating resins, macrocyclic polyamine, macrocyclic dioxotetraaza ligand

During the last decade, coordination chemistry of the titled macrocyclic ligand, 1,4,8,11-tetraazacyclotetradecane-5,7-dione (dioxocyclam), has been widely studied by Kimura's group¹⁻¹² as well as by other researchers.¹³⁻²⁰ These intensive studies¹⁻²⁰ have clarified some novel properties of this ligand, including promising use in separation chemistry. Indeed, Kimura *et al.*⁸⁻¹⁰ have proposed highly selective extraction and the liquid membrane transport of Cu(II) based on the organic solutions of an alkylated derivative of dioxocyclam. Thus, a chelating resin containing dioxocyclam has become of interest, since separation processes based on chelating resins do not require the use of organic solvents, which sometimes cause serious environmental problems. In this connection, Kato²¹ and Tabushi *et al.*²² have described the preparation and properties of a condensation polymer obtained by the reaction of non-crosslinked chloromethylated polystyrene with dioxocyclam.²³ However, the practical meaning of this condensation polymer is not significant, because of difficulties in preparing spherical condensation products.

In this work, two types of chelating resins containing dioxocyclam were prepared by reactions of the ligand with chloromethylated styrene-divinylbenzene (RCS) and glycidyl methacrylate-divinylbenzene (RG) copolymer beads of the macroreticular type (Scheme); adsorption of Cu(II) with the resulting chelating resins was studied in order to evaluate which is a more suitable copolymer matrix for the fixation of dioxocyclam. Although nearly equal amounts of dioxocyclam were fixed in both copolymers, the RG-based chelating resin (RGD) more effectively took up Cu(II) than did the

RCS-based resin (RCSd). Because of the higher capacity of RGD for Cu(II), the behavior of RGD in the adsorption of some metal ions was studied in greater detail by means of batch-wise and column-mode approaches.

Experimental

Materials

Dioxocyclam was prepared according to a reported procedure²⁴ and identified by means of CHN analysis as well as proton NMR. Two kinds of spherical copolymer beads, RCS²⁵ and RG²⁶, were prepared according to reported procedures; their properties are summarized in Table 1. All of the other reagents were of reagent grade. Distilled and deionized water was used throughout.

Table 1 Properties of precursory copolymers

Symbol for copolymer ^a	Chlorine content (% wt)	Size of bead (mesh)	Specific surface area/m ² g ⁻¹
RCS ^b	20	42-80	64.4
RG ^c	—	32-60	46.8

a. Degree of crosslinking of each copolymer is 10 nominal mol% of divinylbenzene.

b. Chloromethylated styrene-divinylbenzene copolymer.

c. Glycidyl methacrylate-divinylbenzene copolymer.

Table 2 Selected conditions for fixation of the ligand and amounts of fixed ligand in resulting chelating resins

Symbol for chelating resin	Precursory copolymer	Weight ratio of reactants ^a	Temp./°C	Time/h	Amount of fixed ligand/mmol g ⁻¹
RCSD	RCS	1 : 1.5 : 4 : 1	150	6.5	1.3
RGD	RG	1 : 2 : 4.5 : 0	140	5	1.5 (1.5) ^b

a. Copolymer : ligand : ethanol : benzene. b. Value for regenerated resin.

Preparation of chelating resins

Chelating resins were prepared by heating the respective copolymer beads and organic solutions of the ligand in a stainless-steel autoclave. Preliminary preparation was conducted by changing the solvent, ligand concentration, temperature, and heating time in order to search for conditions that are suitable for fixing the ligand to both copolymers. Selected reaction conditions for each copolymer are given in Table 2. In the case of RCS, benzene was added to the reaction mixture for greatly swelling the RCS. The resulting chelating resins were washed with ethanol in a Soxhlet extractor for 24 h in order to remove any unreacted ligand. After air-drying, they were dried *in vacuo* at 40°C. Introducing the ligand into each copolymer was identified by means of the IR spectra (KBr disc) as well as elemental analysis. RCS shows absorption at 1260 cm⁻¹, which is assigned to chloromethyl groups. After the reaction, this band disappeared and new adsorption bands (assigned to amide groups) appeared at 1660 and 1540 cm⁻¹, indicating ligand fixation. After reaction of RG with the ligand, the adsorption bands of RG between 710 and 990 cm⁻¹ disappeared and new bands were observed at 1660 and 1540 cm⁻¹, showing an addition of the ligand to the epoxy group of RG. The amounts of

fixed ligand in the resulting resins were calculated in terms of their nitrogen contents; they are listed in Table 2.

Batch-wise adsorption of metal ions

Measured amounts of each resin and definite volumes of metal ion solutions of known concentrations were taken into tightly stoppered flasks. These flasks were shaken at 30°C by a thermostated mechanical shaker. At a pertinent interval, the flasks were taken out from the bath, and the aqueous phases were separated from the resins. Then, the concentrations of the metal ions in the aqueous phases were determined by means of ICP-AES or chelatometric titration against a standardized EDTA. From the decrease in the metal ions in the aqueous phases, the uptake of metal ions by the resins was calculated. The pH of the aqueous phases was adjusted with acetic acid and/or sodium acetate.

Regeneration of the resin

To a column packed with RGD, 1 M hydrochloric acid, water, 1 M sodium hydroxide, water and ethanol were fed in succession. After air-drying, the thus-regenerated resins were dried *in vacuo* at 40°C. The regenerated RGD was analyzed by means of X-ray

fluorescence analysis (XRF) (Seiko Denshi Kogyo SEA-2001 X-ray fluorometer). Elemental and IR spectroscopic analyses were also conducted.

Separation of Cu(II) by column operation

The RGD resin (1 g) was packed in a glass column (0.8 cm i.d., 10 cm long, bed volume 3.4 ml). After the column had been equilibrated with a buffer solution consisting of an equimolar mixture of acetic acid and sodium acetate (0.1 M of each), 250 ml of a sample solution containing metal ions (0.001 M of each) was fed into the column. The sample solution contained Cu(II), Ni(II), Mn(II) and Zn(II); its pH was maintained with the buffer solution. After the column was washed with 12 ml of the buffer, 1 M hydrochloric acid was fed into the column. The space velocity of all feeding solutions was maintained at 3.3–3.8 h⁻¹, and all column effluents were collected with a fraction collector. The volume of each fraction was 6 ml. The concentration of each metal ion in all fractions was determined by means of ICP-AES. All column operations were made under ambient conditions.

ESR spectra of Cu(II) adsorbed resins

Cu(II)-loaded resins were sealed in a glass capillary with ethanol, and their spectra measured using a JEOL Jes-Feax ESR spectrometer. The spectrum of a methanol solution of a Cu(II) complex of dioxocyclam was also measured. The measurements were carried out at both room temperature and liquid-nitrogen temperature (77 K).

Results and Discussion

Equilibrium capacity for the uptake of Cu(II) by chelating resins RGD and RCSD

The uptake of Cu(II) by RGD and RCSD was examined under various conditions in order to evaluate the effect of copolymers on the equilibrium adsorption capacities for Cu(II). Figure 1 illustratively shows the time course for the uptake of Cu(II) by RGD from

Fig. 1 Time course of the uptake of copper(II) by RGD. Resin, 0.1 g; aqueous phase, 30 ml of 0.0053 M CuSO₄ buffered with acetic acid (0.083 M) and sodium acetate (0.083 M); pH, 4.6; temperature, 30°C.

weakly acidic media. A shaking time of ca. 24–72 h was required for completely establishing adsorption equilibrium. However, ca. 90% of the equilibrium uptake was attained within 24 h. In adsorption experiments, a much prolonged shaking time (longer than 96 h) was adopted in order to ensure the establishment of an adsorption equilibrium.

Figure 2 shows the dependence of the equilibrium uptake on the initial concentrations of Cu(II) in the aqueous phases. Although the amounts of the fixed ligand are nearly equal between both resins RCSD and RGD (Table 2), RGD takes up much greater amounts of Cu(II) than does RCSD. Figure 3 compares the pH dependence of the equilibrium uptake of Cu(II) between RGD and RCSD. The uptake of Cu(II) by RGD remarkably increases with an increase in the pH, whereas

Fig. 2 Dependence of the uptake of copper(II) on the initial concentration of copper(II) in aqueous phases. Resin, 0.1 g; O, RGD; Δ, RCSD; ●, regenerated RGD; aqueous phase, 30 ml of CuSO₄ solutions buffered with acetic acid (0.083 M) and sodium acetate (0.083 M); pH, 4.6±0.1; temperature, 30°C.

Fig. 3 Dependence of the uptake of copper(II) on pH. Resin, 0.1 g; O, RGD; Δ, RCSD; ●, regenerated RGD; aqueous phase, 30 ml of 0.0053 M and 0.0043 M CuSO₄ for RGD and RCSD, respectively; pH was adjusted by changing molar ratio of acetic acid to sodium acetate under the relation [CH₃COOH]+[CH₃COONa]=0.166 M. Temperature, 30°C.

an increase in the uptake with RCSD is not so marked. These results clearly show that copolymer matrices or the mode of ligand fixation strongly influences the complexing ability of the fixed ligand, and that RG is more suitable for fixation of dioxocyclam than RCS. Thus, copolymer matrices significantly contribute to the overall performance of the resulting chelating resins. In other words, the selection of suitable copolymer matrices is very important in order to minimize changes in the complexing ability of the parent ligand by fixation.

The difference in adsorption ability for Cu(II), between RGD and RCSD, is qualitatively understandable by considering the mode of ligand fixation. RG fixes the ligand *via* rather longer, flexible spacer groups; also the fixed ligand in RGD is far from the polymer chains. On the other hand, RCS fixes the ligand *via* shorter spacer groups, and the ligand in RCSD comes to be located just near the bulky and rigid phenyl groups. Accordingly, it seems that the steric hindrance in the complexation of a fixed ligand is much greater in RCSD than in RGD. This may be the reason why RCSD can not effectively take up Cu(II), compared with the ability of RGD.

In order to clarify the structures of the coordination spheres around the central metal atom in the Cu(II) adsorbed resins, an ESR study of Cu(II)-loaded resins was conducted. Figure 4 shows the ESR spectra of Cu(II)-loaded resins. For the sake of comparison, the spectrum of a Cu(II) complex with dioxocyclam was also recorded. Even at room temperature, the Cu(II)-loaded RGD and RCSD gave anisotropic spectra; both spectra resemble that of the Cu(II)-dioxocyclam complex observed at 77 K. This means that Cu(II) is incorporated into the macrocycles of the fixed ligands in RGD and RCSD, as in the case of the non-fixed ligand.^{27,28} Thus, the structures of the coordination spheres around Cu(II) are not greatly different between RGD and RCSD once Cu(II) is taken up by the fixed ligands, even though

the complexing ability of the fixed ligands is strongly influenced by the copolymer matrices.

Metal-ion selectivity of RGD and the partition of Cu(II) between RGD and weakly acidic aqueous media

Since RGD has a higher capacity for Cu(II) than does RCSD, the selectivity of RGD toward four kinds of first-transition metal ions was examined at two different concentration levels of each metal ion; the amounts of each metal were larger or much smaller than those of the fixed ligand. The results are summarized in Table 3, indicating the high selectivity of RGD toward Cu(II). Since no metal ions, except for Cu(II), were adsorbed, even at higher concentration levels, a further detailed study concerning partition was limited to Cu(II). As shown in Fig. 5, the partition coefficient of Cu(II) increases markedly with an increase in the pH.

Kimura *et al.*¹⁻⁷ have clarified that the complexation of dioxocyclam with transition metal ions accompanies the dissociation of two amide protons, as follows:

The formation constant (K_M) is designated as

$$K_M = \frac{[MLH_{-2}][H^{+}]^2}{[M^{2+}][L]}$$

Table 3 Uptake and partition of divalent metal ions by RGD from a weakly acidic solution

Metal	Uptake from 0.0053 M solution ^a /mmol g ⁻¹	Partition from 0.0001 M solution ^b , %
Mn(II)	0.00	0.0
Ni(II)	0.00	0.0
Cu(II)	0.37	86.1
Zn(II)	0.00	0.0

Resin, 0.1 g; volume of aqueous phase, 30 ml.

a. pH 4.6 CH₃COOH 0.083 M, CH₃COONa 0.083 M.

b. pH 4.7 CH₃COOH 0.1 M, CH₃COONa 0.1 M.

Fig. 4 ESR spectra of (A) frozen (77 K) methanol solution of copper(II)-dioxocyclam, (B) copper(II) loaded RCSD (0.06 mmol/g), and (C) copper(II) loaded RGD (0.32 mmol/g). Spectra (B) and (C) were recorded at room temperature.

Fig. 5 Dependence of the distribution coefficient of copper(II) on pH. Resin, RGD 0.1 g; aqueous phase, 30 ml of 0.0001 M CuSO₄; pH of aqueous phase was adjusted by changing concentration of acetic acid from 0.4 M to 0.025 M but by fixing concentration of sodium acetate at 0.1 M.

Since the ligand has two secondary amino groups, the ratio of complexed metal to free metal is expressed as R

$$R = \frac{[MLH_2]}{[M]} = \frac{K_M[L]^F}{[H^+]^2(1 + K_1[H^+] + K_1K_2[H^+]^2)},$$

where K_1 and K_2 are protonation constants of the two basic sites of the ligand; $[L]^F$ is the concentration of the uncomplexed ligand. Since $\log K_1$ and $\log K_2$ are reported to be 9.57 and 5.97, respectively¹, R is inversely proportional to the third or fourth powers of the hydrogen ion concentration below pH 6. This argument gives a semi-quantitative explanation concerning the marked pH dependence of the distribution coefficient of Cu(II), even though real situations in a fixed ligand system are complicated. According to Kimura's reports^{1,4,6}, K_{Cu} is greater than K_{Ni} by *ca.* 6 orders of magnitude, indicating that dioxocyclam forms a complex with Cu(II) only in weakly acidic media among the tested ions. The selectivity of RGD observed in this work is also in semi-quantitatively agreement with that of dioxocyclam, suggesting that RG can fix dioxocyclam without any drastic change in the metal-ion selectivity.

Repeated use of resins after regeneration

Surprisingly, any Cu(II) adsorbed by RGD was rapidly eluted with 1 M hydrochloric acid, as described more quantitatively in the later section. As soon as the Cu(II)-adsorbed resin came into contact with 1 M hydrochloric acid, the purple color of the Cu(II)-adsorbed resins immediately disappeared and the color of the solution phase became blue. Under this connection, Hay *et al.*¹⁶ have reported that acid dissociation of the Cu(II) complex of dioxocyclam is quite rapid, and different from Cu(II) complexes of macrocyclic polyamines bearing no amide group. The rate constant for the acid catalyzed dissociation of the Cu(II)-dioxocyclam complex is *ca.* $10^7 \text{ M}^{-2} \text{ s}^{-1}$. Thus, the half-life of the complex at pH=0 is *ca.* $7 \times 10^{-6} \text{ s}$. This provides evidence for the extremely rapid rate of Cu(II) elution from RGD with 1 M hydrochloric acid.

The XRF of regenerated RGD showed that the elution of Cu(II) was complete. Further, no change in the IR spectra and ligand content (Table 2) was observed either before and after regeneration. As shown by the filled circles in Figs. 2 and 3, the regenerated resin also gave reproducible results for the adsorption of Cu(II).

Separation of Cu(II) by column operation

In order to demonstrate the usefulness of RGD for the separation of Cu(II), the adsorption of Cu(II) from an equimolar mixture of four kinds of divalent first-transition metals was conducted. Figures 6 and 7 illustratively show the results of breakthrough and elution experiments, respectively. The breakthrough curves in Fig. 6 indicate that only Cu(II) was adsorbed. The amount of adsorbed Cu(II) was 0.14–0.16 mmol/g. As judged from Fig. 7, the elution of Cu(II) with 1 M

Fig. 6 Breakthrough curves at pH 4.7. Resin, RGD 1 g (bed volume 3.4 ml); loading solution, equimolar mixture of metal ions; ○, copper(II) 0.99 mM; ●, nickel(II) 0.96 mM; △, zinc(II) 0.95 mM; ▲, manganese(II) 1.00 mM, space velocity 3.5 h^{-1} .

Fig. 7 Elution curves. Resin, RGD 1 g (bed volume 3.4 ml); eluting solution, 1.0 M HCl, space velocity 3.3 h^{-1} ; ○, copper(II); ●, nickel(II); △, zinc(II); ▲, manganese(II).

hydrochloric acid was extremely rapid. Until the second fraction, Cu(II) was quantitatively eluted. Since the space velocity and the volume of fraction were 3.3 h^{-1} and 6 ml, respectively, Cu(II) was completely eluted within 1 h. In the column effluent, no metal ion, except for Cu(II), was detected throughout.

After regeneration of the column, the adsorption and elution of Cu(II) were repeated. Almost the same results were obtained. Thus, the presented resin RGD is useful for purifying and concentrating Cu(II). A further detailed study on the separation of Cu(II) is in progress using the same columns reported here; no deterioration of the column was observed, even after several cyclic use of the column.

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