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Preparation and Complexation Properties of Chelating Resin Containing Lysine-N^α,N^α-Diacetic Acid

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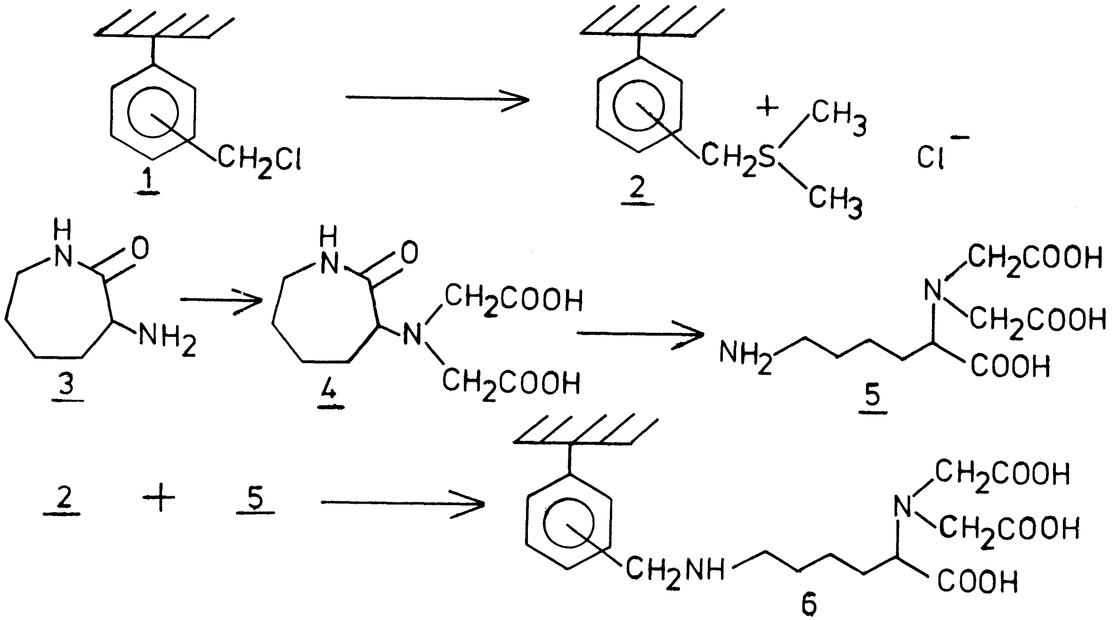
Lysine derivative consisting of amine-*N*,*N*,*N*-triacetic acid and spacer moiety has been immobilized onto cross-linked polystyrene beads by one-step reaction. The metal ion exchange property and selectivity of the newly prepared resin for some trivalent and divalent metal ions have been studied.

The essential requirements to be considered for the synthesis of a chelating polymer resin are the stable complexation and high selectivity toward certain metal ions.$^{1)}$ Since the stability of a metal complex increases with the number of chelating ring,$^{2)}$ it is desirable to immobilize a ligand of the higher dentate number. Attempts have been performed to prepare the chelating resins functionalized with multidentate complexane-type ligand capable of forming a stable 1 : 1 complex with various metal ions.$^{3-6)}$ However, the modification of a polymer matrix$^{1)}$ with such multidentate ligands generally requires a series of reactions which inevitably give a mixture of the structurally ambiguous functional group.$^{7)}$ Therefore it is preferable to fix the ligand unit onto polymer matrix by one step reaction to attain a uniform structure of the ligand. In addition, the ligating group should be sufficiently remote from polymer matrix so that it can behave in a similar manner to that of the ligand in a monomeric system.

We have synthesized a lysine-N^α,N^α-diacetic acid derivative (5) by the chemical modification of α-amino-ε-caprolactam (3). This ligand has been introduced onto cross-linked polymer beads by the reaction with dimethylsulfonated polystyrene$^{8)}$ (2). Thus, a chelating resin (6) having a functional group analogous to nitrirotriacetic acid has been obtained by one step reaction (Scheme 1). The ligating group locates spatially remote from the bulky polymer matrix due to the presence of a spacer arm. This paper describes the preparation and the complexation properties of the present chelating resin.



Scheme 1.

A 50 g of chloromethylated styrene-10%-divinylbenzene copolymer beads (1) (macroreticular type; surface area, 7.3 m^2 g^{-1}; mean pore diameter, 720 Å; Cl, 17.1%; 32-60 mesh) was converted into the dimethylsulfonium salt 2 by treatment of the beads with dimethylsulfide.[8] The resulting resin (S, 10.8%) was used as the starting polymer resin.

α-Amino-ε-caprolactam 3 (51 g, 0.4 mol) was carboxymethylated with sodium chloroacetate in alkaline aqueous solution. After the reaction, the pH of the solution was adjusted to 1.8. Upon standing at room temperature, crystals of α-amino-ε-caprolactam-N^{α},N^{α}-diacetic acid (4) (83 g, 0.34 mol) were obtained in 73% yield. This compound 4 (61 g, 0.25 mol) was hydrolyzed by refluxing the crystals with 300 cm^3 of 6 M (M=mol dm^{-3}) potassium hydroxide. After the reaction, the solution was acidified to pH 1.8 with 70% perchloric acid. A precipitate of potassium perchlorate was filtered off, and crystals of lysine-N^{α},N^{α}-diacetic acid 5 (58 g, 0.18 mol) were obtained in 73% yield from the concentrated filtrate. Elemental analysis and ^{13}C-NMR spectrum of these reaction products showed that the desired reaction had taken place.[9] The pH of the aqueous solution (300 cm^3)

containing 0.15 mol 5 (47.4 g) was adjusted to 12 with sodium hydroxide. To this solution was added dimethylsulfonated polystyrene resin 2 (180 cm^3) and the mixture was stirred at 85 °C for 24 h, keeping the pH in the range of 10-12 with 1 M sodium hydroxide solution. The resin 6 thus obtained was filtered off, washed with 2 M hydrochloric acid and then water, and dried. Yield, 62.4 g. The nitrogen analysis of the resin 6 (2.8%) indicates that the resin contains 1.0 mmol of the ligand per gram resin. Iminodiacetic acid (IDA) was immobilized onto polystyrene beads in a similar manner as given above (N : 3.22%, ligand content : 2.3 mmol g^{-1})

The resin (Na-form) gave intense IR absorption band at around 1630 cm^{-1} due to (C=O) stretching vibration of carboxylate group. Absence of the absorption bands higher than 1700 cm^{-1} indicates that ester carbonyls are not involved in the obtained resin. Therefore the lysine-N^{α},N^{α}-diacetic acid 5 appears to be introduced into the polymer matrix specifically through its ε-amino group.

The present resin readily adsorbs various kinds of metal ions from an acidic aqueous solution. The maximum exchange capacities of the resin for several metal ions are *ca.* 0.9-1.0 mmol g^{-1}. These values are comparable to the estimated ligand content. The distribution coefficients (Kd) (Kd=amount of metal ion adsorbed on one gram of the resin / amount of the metal ion remaining in 1 cm^3 of the solution) of the present resin for various metal ions were examined as a function of pH (Fig. 1). The selectivity sequence of the resin for several metal ions is appeared to be ; Ga(III)>In(III)>Cu(II)>Al(III)>Eu(III)>Ni(II)>Zn(II)>Co(II). This order agrees with that of the formation constants of nitrilotriacetic acid complexes.10) The linear slopes of the present resin for the trivalent and divalent metal ions are close to 3.0 and 2.0, respectively. These results indicate that three and two protons are liberated from the present resin upon complexation with these metal ions. Thus the ligating group of this resin presumed to form 1 : 1 complexes with the metal ions given in Fig. 1. The distribution coefficients of the chelating resin having iminodiacetic acid (IDA) has been also examined (Fig. 2). The log Kd vs. pH plots of the present resin always appear in relatively lower pH region than those of the IDA resin irrespective of the metal ions examined. In other words, the present resin can retain metal ions much firmly than the IDA resin due to the increased number of ligating atom.

Chromatgraphic separation of metal ions using the present chelating resin is under investigation.

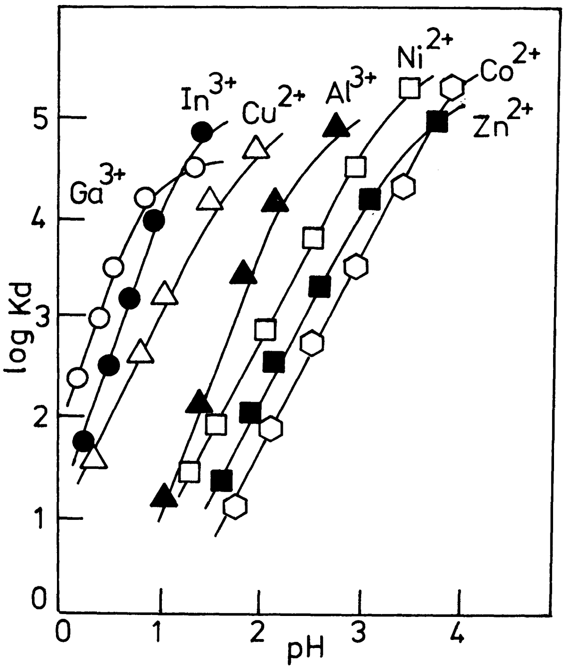


Fig. 1. Log Kd of the resin 6 for some metal ions as a function of pH.

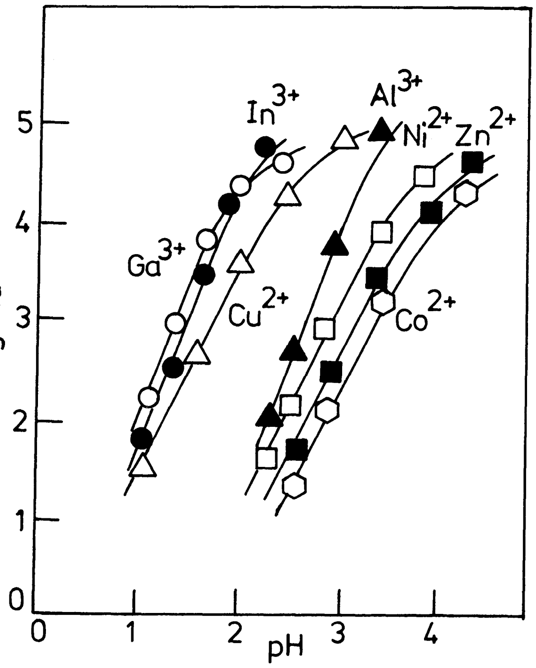


Fig. 2. Log Kd of the IDA resin for some metal ions as a function of pH.

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9) **4** Anal. Found : C, 48.80; H, 6.61; N, 11.47%. Calcd for $C_{10}H_{16}N_2O_5$; C, 49.17; H, 6.60; N, 11.47%. ^{13}C-NMR (D_2O + NaOD, 300 MHz, internal DSS) δ 183.0, 182.3, 65.8, 58.8, 44.1, 30.5, 30.2, 27.9.
   5 Anal. Found : C, 37.85; H, 7.63; N, 8.85%. Calcd for $C_{10}H_{18}N_2O_6$-$3H_2O$: C, 37.95; H, 7.60; H, 8.85%. ^{13}C-NMR (D_2O+NaOD, 300 MHz, internal DSS) δ 184.1, 182.7, 71.8, 59.6, 42.9, 34.5, 31.6, 26.2.
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