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Metal complexing properties of water-soluble poly(*N*-maleyl glycine) studied by the liquid-phase polymer-based retention (LPR) technique

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SUMMARY

The separation of various metal ions by the water-soluble N-maleyl glycine polymer in conjunction with membrane filtration was investigated. The method is based on the retention of inorganic ions by this polymer in a membrane filtration cell and subsequent separation of low-molecular-weight species from the polymer complex formed. It is shown that poly(N-maleyl glycine) can bind several metal ions in aqueous solution at pH 3. At higher pH, the water-soluble polymer can be applied to the separation and preconcentration of many metal ions. In addition, the maximum capacity values of the homopolymer for copper(II) were investigated and compared in the presence of various metal ions at different pHs.

INTRODUCTION

Polymers as metal ion-complexing agents have been extensively studied (1-10). The formation of complexes with polymers has been widely used for concentration, separation and extraction of metal ions. When a metal ion is added to the solution of a polymeric ligand, a polymer-metal complex is rapidly formed. The binding of metal ions to polymers considerably improves their mechanical properties and thermostability. As has been reported previously (11,12), metal complexed polymers show the following features: a) the polymeric ligand is markedly contracted because intrapolymer chelation causes a very compact form of the complexed polymer, and b) the formation constants of a complexed polymer are larger than those of a complexed monomeric analogue which is caused by the enhancement of successive stepwise formation constants due to the effect of the polymer.

An efficient and selective separation of inorganic ions can be achieved by water-soluble polymeric reagents in combination with membrane filtration. This technique, called Liquid-Phase Polymer-Based Retention (LPR), is based on the separation of ions bound to water-soluble polymers with chelating groups (polychelatogens) from non-complexed ions (13-18).

In this paper, the complexing properties of a water-soluble polymer, poly(N-maleyl glycine), as polychelatogen towards nine metal ions are investigated in conjunction with membrane filtration. To this end, the metal ion binding studies have been conducted using the LPR technique.

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EXPERIMENTAL

Materials: Poly(N-maleyl glycine) (P-MG) $(C_6H_5NO_4)_n$ was synthesized in solution using 0.5 mol% of AIBN as the initiator (19) and had a molecular weight of 11,500 g mol^{-1}. Prior to interaction studies, the polymer was purified by membrane filtration using a membrane with exclusion limit of molecular weight of 10,000 g mol^{-1}. All salts were of analytical grade and used as received.

Equipment: A Perkin-Elmer 1100 Atomic Absorption Spectrometer was used for the determination of the metal ion concentrations in the filtrate and retentate. Viscosimetric measurements were performed with an Ostwald viscosimeter. The pH was determined with a Metrohm pH-meter E 512. For the LPR technique, a membrane filtration system was employed to test the coordinating properties of the polychelatogen P-MG (see Fig. 1). Details have been described previously (13, 14, 16).

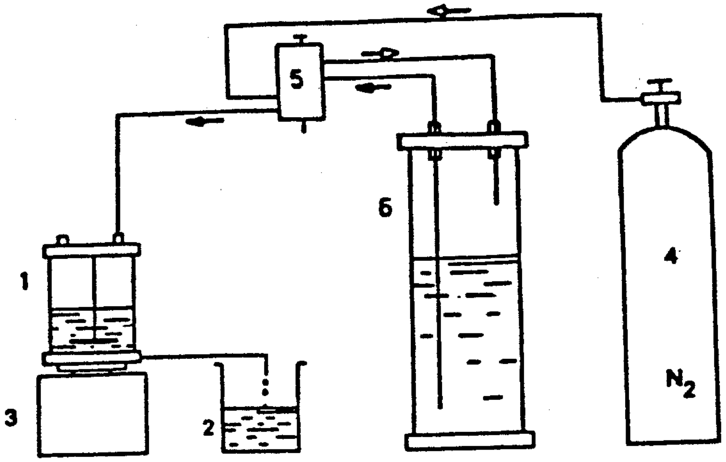

Figure 1. Instrumental arrangement for the LPR method (13, 14). **1** Filtration cell with solution of polymeric complex, **2** Membrane filtrate, **3** Magnetic stirrer, **4** Pressure trap, **5** Selector, and **6** Reservoir with metal salt solution.

Procedure: The polymer was dissolved in water and the solution adjusted to the corresponding pH by the addition of diluted nitric acid or sodium hydroxide. The aqueous solutions of polymer (2 wt%) and metal nitrates or chlorides were placed into the filtration cell. The total volume in the cell was kept constant at 20 ml. The reservoir contained water adjusted to the same pH as that of the cell solution. A membrane with an exclusion limit of 10,000 g mol^{-1} (Filtron NOVA 10 K or equivalent) was used. The system was pressurized (330 KPa), the cell solution was stirred for 5 min and then washed with the reservoir fluid at a flow rate of 4-6 ml min^{-1}. The filtration fractions (Z=1-10) were collected and the concentrations of metal ions in the filtrate and the retentate were determined by atomic absorption spectroscopy.

Capacity determination of copper(II): Protolysis was employed for the regeneration of P-MG. The P-MG solution was saturated with an aqueous copper(II) nitrate (10 wt%) to determine the binding capacity. Subsequently, it was washed by using the LPR technique. The P-MG-copper(II) complex was treated with concentrated nitric acid (100 mg ml^{-1}). The concentration of released copper(II) was analyzed by atomic absorption spectrometry.

RESULTS AND DISCUSSION

The complexation properties of P-MG were investigated by using the LPR technique.

The retention of metal ions in the cell solution by polymeric reagents can be calculated as follows:

$$R = C_r \cdot C_o^{-1} \cdot 100\ (\%)$$

where C_r is the metal ion concentration in the retentate (the cell solution after a filtrate volume of V_f has been passed) and C_o is the initial metal ion concentration in the cell (13,14,16).

Typical retention profiles of P-MG are shown in Fig. 2. Filtration factor Z was defined as the ratio of the volume of filtrate V_f, and the volume of cell solution V_o. In general, only slight complexation of P-MG took place with all metal ions studied at pH 3, except for Zn(II) and Sr(II). At pH 3, the retention values of Cd(II) , Co(II), Ni(II), Zn(II), and Sr(II) are 54.8; 54.8; 58.2; 59.4, and 20.8% respectively at Z = 10 (see Table 1).

Table 1. % Retention of nine metal ions by poly(N-maleyl glycine) at pH 3 and 5.

Metal Ion	(%) R pH 3	(%) R pH 5
Cr(III)	90.1	99.0
Fe(III)	91.4	99.8
Cd(II)	54.8	99.6
Co(II)	54.8	99.1
Cu(II)	91.6	97.9
Ni(II)	58.2	94.8
Pb(II)	94.4	90.1
Zn(II)	59.4	98.8
Sr(II)	20.8	100.0

All the other metal ions showed a strong dependence on the pH and on the filtration factor Z. For example, Zn(II) showed a retention value of 98.8% and Sr(II) of 100% at pH 5 for Z = 10 (see Table 1). At the same pH, complete retention was observed for Cu(II), Cd(II), Ni(II). At pH 5, the polymer P-MG retained 99.8% of Fe(III), 99.1% of Co(II) and 90.1% of Pb(II) at Z=10. The only representative investigated from the earth alkaline metals, Sr(II) retained 20.8% at pH 3 and 100% at pH 5.

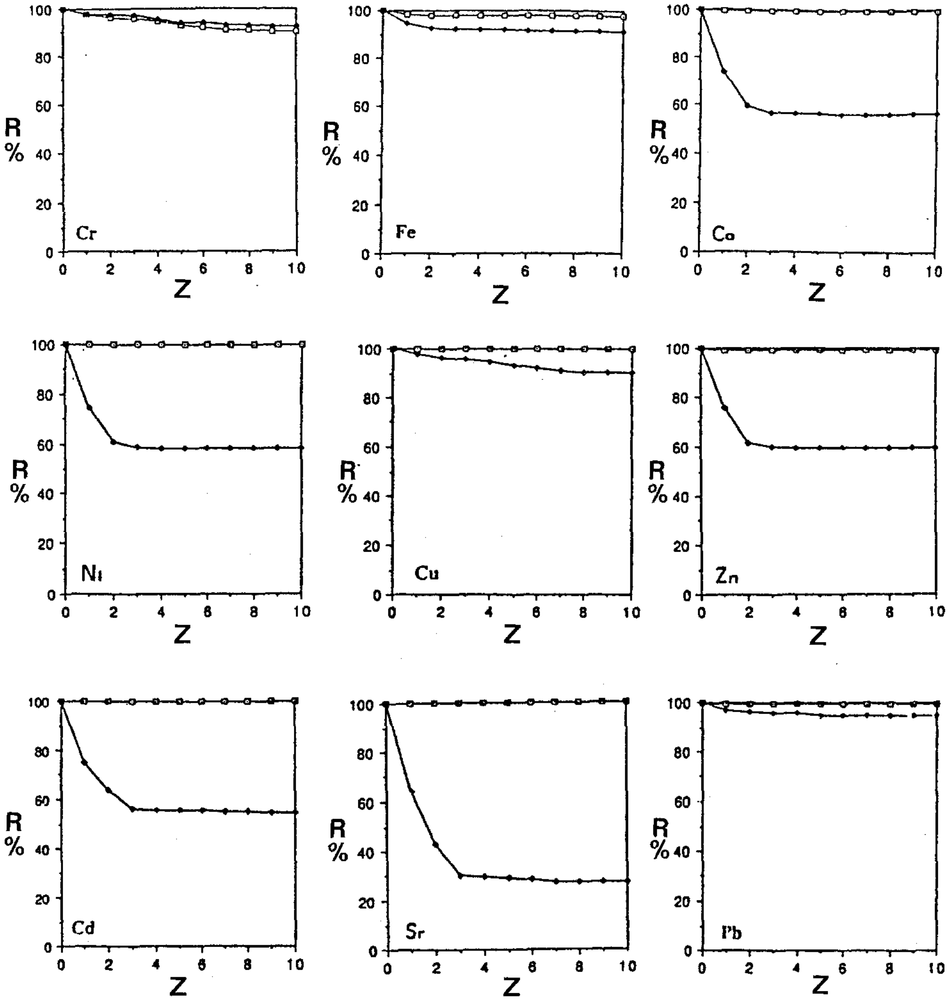

Figure 2. Retention profiles for different metal ions by an aqueous solution (2 wt %) of P-MG at pH 3 (-●-) and 5 (-o-).

The influence of the pH is illustrated in Fig. 2. This factor affects both the complexation and the flow rate through the membrane. In the presence of P-MG, the flow rate in the cell dropped at pH 3.

The intrinsic viscosity of aqueous solutions (0.1 M NaCl) of the polymer in the presence of the metal ions Cr(III), Fe(III), Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Zn(II), and Sr(II), (20 ppm each), were measured at pH 3 and pH 5 (see Table 2). The results show that the intrinsic viscosity of solutions depends on the pH. In both cases it increased in the presence of the metal ions.

According to the probable intramolecular complexation of the metal ions by the polymer, the corresponding parts of the polymer chains are arranged around the metal ions. This change in the conformation leads to an alteration of the viscosity (17,20).

At pH 5 the viscosity of the polymer is generally increased in the presence of the metal ions. This behavior can be attributed to a weakening of the intramolecular hydrogen bonding attraction of the chains, due to an increasing of the charges along the macromolecules during the complexation. Therefore, the intrinsic viscosity of the metal ions changes at pH 3 and 5.

Table 2. Intrinsic viscosity of poly(N-maleyl glycine) with nine metal ions at pH 3 and pH 5 (35°C, 0.1 M NaCl).

Polymer	Intrinsic viscosity $[\eta]$, (dl g^{-1})	
	pH 3	pH 5
P-MG	0.039	0.056
P-MG complex (nine metal ions)	0.217	0.231

The maximum binding capacity of the polychelatogen has been also investigated (see Table 3) for copper(II) ions. Accordingly, the P-MG binds 3.8-8.0 mmol metal per g polymer, depending on the pH.

Table 3. Maximum binding capacity of P-MG for Cu(II) at different pH.

pH	Maximum capacity	
	mg g^{-1}	mmol g^{-1}
1	240	3.8
3	365	5.8
5	512	8.0

CONCLUSIONS

The interaction behavior of aqueous solutions of poly(N-maleyl glycine) with nine metal ions was investigated at different pH values. At pH 5, most metal ions showed > 90% retention. At pH 3, the polymer interacted partially with nine metal ions but only Cr(III), Fe(III) and Cr(II) showed > 90% retention.

The intrinsic viscosity increased in the presence of metal ions at pH 5 and it depended also on the pH.

The maximum binding capacity of the P-MG with copper(II) ions depended on the pH with a maximum of 512 mg copper(II) per g polymer at pH 5.

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REFERENCES

1. E. Tsuchida, H. Nishide. *Adv. Polym. Sci.*, **24**, 2 (1977).
2. K.E. Geckeler, G. Lange, H. Eberhadt, E. Bayer. *Pure Appl. Chem.*, **52**, 1883 (1980).
3. M. Kaneko, E. Tsuchida. *J. Macromol. Sci. Rev.*, **16**, 397 (1984).
4. S.D. Alexandratos, D.L.W. Wilson, M.A. Strand, D.R. Quillen, A.J. Walder, W.J. McDowell. *Macromolecules*, **18**, 835 (1985).
5. D.C. Sherrington, P. Hodge. *Synthesis and Separations Using Functional Polymers*, Wiley, New York 1988, Chap. 10.
6. J.S. Parmar, C.G. Patel, D.K. Patel. *High Performance Polymers*, **3**, 89 (1991).
7. B.L. Rivas, K.E. Geckeler. *Adv. Polym. Sci.*, **102**, 171 (1992).
8. B.N. Kolarz, J. Jezienka, D. Bartowiak, A. Gontarczyk. *React. Polym.*, **53**, 23 (1994).
9. A. von Zelewsky, L. Barbosa, C.W. Schläpfer. *Coordination Chem. Rev.*, **123**, 229 (1994).
10. B.L. Rivas, H.A. Maturana, I.M. Peric, E. Pereira. *Bol. Soc. Chil. Quím.*, **39**, 211 (1994).
11. E. Tsuchida, H. Nishide, T. Nishiyama. *J. Polym. Sci. Polym. Symp.*, **47**, 35 (1974).
12. H. Nishikawa, E. Tsuchida. *J. Phys. Chem.*, **79**, 2072 (1975).
13. B. Ya Spivakov, K. Geckeler, E. Bayer. *Nature*, **315**, 313 (1985).
14. K.E. Geckeler, E. Bayer, B. Ya. Spivakov, V.M. Shkinev, G.A. Vorob'eva. *Anal. Chim. Acta*, **189**, 285 (1986).
15. K.E. Geckeler, V.M. Shkinev, B.Ya. Spivakov. *Angew. Makromol. Chem.*, **155**, 151 (1987).
16. K.E. Geckeler, V.M. Shkinev, B.Ya. Spivakov. *Sep. Purif. Methods*, **17**, 105 (1988).
17. K.E. Geckeler, B.L. Rivas, R. Zhou. *Angew. Makromol. Chem.*, **193**, 195 (1991).
18. K.E. Geckeler, R. Zhou, B.L. Rivas. *Angew. Makromol. Chem.*, **197**, 107 (1992).
19. G. del C. Pizarro, B.L. Rivas, K.E. Geckeler. *Bol. Soc. Chil. Quím.*, **41**, 181 (1996).
20. Ph. Teyssié, C. Decoene, M.T. Teyssié. *Makromol. Chem.*, **84**, 51 (1985).