

Synthesis and Properties of Hydrophilic Polymers. III. Ligand Effects of the Side Chains of Polyaziridines on Metal Complexation in Aqueous Solution

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SYNOPSIS

The metal-complexing properties of five different polyaziridines—poly[1-(2-aminoethyl)aziridine], poly(1-acetylaziridine), poly[1-(2-hydroxyethyl)aziridine], poly[1-(2-hydroxyethyl)aziridine-co-1-acetylaziridine], and poly[1-(2-aminoethyl)aziridine] oxine—were investigated in an aqueous solution with regard to the side-chain effects using membrane filtration. The results are discussed and compared with the stability constants of metal complexation of the corresponding functional moieties. Poly[1-(2-aminoethyl)aziridine], a poly(aziridine) with neutral nitrogen donors in the side chains, showed similar complexing properties to those of ammonia. The only exceptions are Fe(III) and Cr(III), which cannot form complexes with ammonia but can be retained in the membrane filtration process due to the formation of Fe(III)-colloidal species and hydroxides. The complexing properties of polyaziridines containing hydroxyl groups in the side chains (i.e., poly[1-(2-hydroxyethyl)aziridine] and poly[1-(2-hydroxyethyl)aziridine-co-1-acetylaziridine]) can be explained and described by the formation constants with the corresponding hydroxides. The introduction of a carbonyl moiety in the polyaziridine side chain, e.g., polyacetylaziridine, reduces the complexing ability for metal ions because the carbonyl group cannot form complexes with the metal ions investigated. Poly[1-(2-aminoethyl)aziridine]oxine showed the strongest complexing ability in the series of metal ions due to the strong complexing ligand 8-hydroxy quinoline attached to the polymer backbone. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Metal complexation with functional polymers has been a subject not only of theoretical interest but also of extensive practical applications. A variety of functionalized polymers are widely used as complexing reagents for metal complexation and metal separation.¹⁻³ Many technical applications, e.g., for coatings, flocculation, in paper and textile industries, and as adhesives, require water-solubility of the polymers. To date, a limited number of soluble polymers have been used as polymeric reagents suitable for technical use. These include hydrophilic polymers, which are commercially

produced in large quantities such as branched polyethyleneimine.^{4,5}

The data on the complexing properties of the low molecular weight analogs of poly[1-(2-aminoethyl)aziridine] show that they are able to form stable complexes with many metal ions and the stability of these metal chelates is strongly dependent on the structure of the amine moiety.⁶ Because poly[1-(2-aminoethyl)aziridine] contains three different types of amine groups, the complexation behavior is correspondingly versatile and intricate. Therefore, poly[1-(2-aminoethyl)aziridine] has been used as a polymeric reagent to enrich and to separate inorganic ions in the homogeneous phase in combination with membrane filtration.^{5,7-11}

The technique developed was called liquid phase polymer-based retention (LPR) and has found many

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applications.^{10,12-15} Very recently, it was approved by an IUPAC commission.¹⁶ According to the elution profiles obtained using this method, which were measured for each metal at different pH, it is evident that poly[1-(2-aminoethyl)aziridine] is an effective polymeric complexing agent suitable for the enrichment and separation of metals in aqueous solutions.¹⁰ In addition, it can also be used for the separation and preconcentration of elements from diluted solutions.^{9,10} Polyaziridines represent an interesting class of functional polymers for metal complexation.¹⁷⁻¹⁹ A few poly[1-(2-aminoethyl)aziridine] derivatives with different side chains were investigated in aqueous solution.^{7,9,12,20-25} The influence of some polymer backbones on metal complexation was investigated in a study previously.²¹ The results indicate that the metal-complexing ability of these polymers is affected by the ligands in the side chains of the polymers.

In this study, the structural relationship between the ligand types of the side chains of five hydrophilic polyaziridines—poly[1-(2-aminoethyl)aziridine], poly[1-(2-hydroxyethyl)aziridine], poly(1-acetylaziridine), poly[1-(2-hydroxyethyl)aziridine-co-1-acetylaziridine], and poly[1-(2-aminoethyl)aziridine]oxine—and their metal-complexing ability was investigated.

EXPERIMENTAL

Materials and Methods

Solvents, acetonitrile, *N,N*-dimethylformamide, dichloromethane, toluene, and diethyl ether were purified according to the literature.²⁶ The aziridine monomers (Aldrich) were purified by distillation under nitrogen.

Poly[1-(2-aminoethyl)aziridine],⁵ i.e., branched polyethyleneimine (BPEI), was a commercial product ($M_r = 35,000 \text{ g mol}^{-1}$; BASF, Germany) and poly[1-(2-aminoethyl)aziridine]oxine (POX) was prepared by polymer-analogous modification of BPEI as reported earlier.^{7,20} All polymers in this study were membrane-filtrated prior to use. All salts were of analytical grade and used as received.

Polymerization Procedure

Polymerizations were carried out in glass flasks provided with lateral stopcocks. The monomer, initiator, and solvent were introduced in a current of nitrogen. The reaction tubes were placed in a thermostat at the defined temperature. The polymers

were isolated by pouring the reaction mixtures into an excess of diethyl ether and subsequent decantation. For the purification of the polymers, they were dissolved in methanol, precipitated twice in diethyl ether, and then dried under vacuum.

Poly(1-acetylaziridine) (PAAZ) was synthesized in solution (acetonitrile, 0.1 mol % BF_3 -etherate, 70°C, 24 h) from 2-methyl-2-oxazoline; poly[1-(2-hydroxyethyl)aziridine] (PHEA), from 1-(2-hydroxyethyl)aziridine (1 mol % BF_3 -etherate, acetonitrile, 45°C; and poly[1-(2-hydroxyethyl)aziridine-co-1-acetylaziridine] (HEA-AAZ), from 2-methyl-2-oxazoline and 1-(2-hydroxyethyl)aziridine.

PAAZ. Yield: 100%. Anal: Calcd for $(\text{C}_4\text{H}_7\text{NO})_n$: C, 56.4%; H, 8.23%; N, 16.23%. Found: C, 56.71%; H, 8.31%; N, 16.38%. $^1\text{H-NMR}$ (D_2O): 2.1 (— CH_3); 2.1 (— CH_3); 2.70 (— CH_2N); 3.70 (— CH_2OH).

PHEA. Yield: 79%. $[\eta] = 0.222 \text{ dL g}^{-1}$. Anal: Calcd for $(\text{C}_4\text{H}_9\text{NO})_n$: C, 55.10%; H, 10.43%; N, 16.06%. Found: C, 55.10%; H, 10.33%; N, 16.07%. $^1\text{H-NMR}$ (D_2O): 2.80 (— CH_2N); 3.82 (— CH_2O).

HEA-AAZ. Yield: 60%. Anal: Calcd for $(\text{C}_4\text{H}_9\text{NO})_{0.81}(\text{C}_4\text{H}_7\text{NO})_{0.19}$: C, 55.41%; H, 10.01%; N, 16.38%. Found: C, 55.41%; H, 8.23%; N, 16.23%. $^1\text{H-NMR}$ (D_2O): 1.98 (— CH_3); 2.70 (— CH_2N); 3.70 (— CH_2OH).

Procedure

Membrane filtration was performed using a system as described previously in detail.^{7,9,27} The membrane filtration unit consisted of a membrane filtration cell containing the polymer solution, to which the solution of metal ions was added under stirring. For the interaction studies' separation procedure, the washing solution was passed into the cell from the reservoir.

For the determination of the complex binding ability, a 2% (w/w) aqueous solution of each polymer was prepared and adjusted to the defined pH by addition of nitric acid or sodium hydroxide, correspondingly. The solutions of the polymer and the metal nitrates or chlorides (20 mg L^{-1}) were then placed into the filtration cell. The total volume of the solution in the cell was kept constant at 20 mL. The reservoir contained demineralized water at a pH adjusted to the same value as in the cell solution.

The system was pressurized with nitrogen gas and kept constant at 300 kPa during membrane filtration. Membranes with a nominal molecular weight exclusion rate of 1000 g mol^{-1} (Amicon UM-1 or equivalent) were used. The permeate fractions were continuously collected and the concentrations of

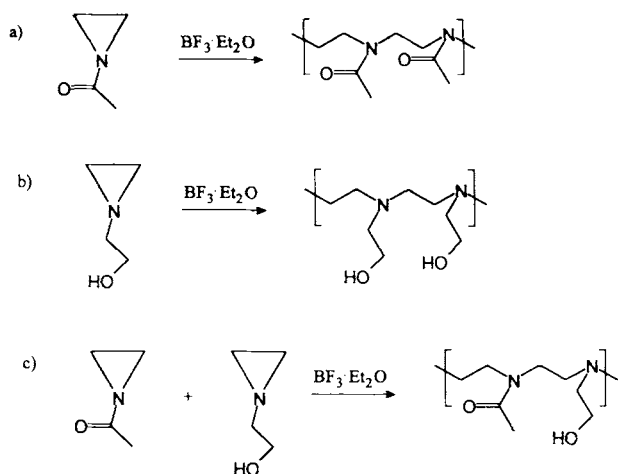


Figure 1 Synthetic scheme of the polyaziridine derivatives: (a) poly(1-acetylaziridine) (PAAZ); (b) poly[(2-hydroxyethyl)aziridine] (PHEA); (c) poly[(2-hydroxyethyl)aziridine-co-1-acetylaziridine] (HEA-AAZ).

metal ions in the permeate and the retentate were determined by atomic absorption spectrometry (Perkin-Elmer 1100, Überlingen, Germany). All measurements were carried out at room temperature (22°C).

RESULTS AND DISCUSSION

Synthesis

To assess and to understand the effects of functional groups in polymers on metal complexation, five hydrophilic water-soluble poly-aziridines with different functional moieties pendant to the backbone, i.e., poly[1-(2-hydroxyethyl)aziridine] (PHEA), poly(1-acetylaziridine) (PAAZ), poly[1-(2-hydroxyethyl)aziridine-co-1-acetylaziridine] (HEA-AAZ), poly[1-(2-aminoethyl)aziridine] (BPEI),⁵ and poly[1-(2-aminoethyl)aziridine]oxine (POX),^{7,20} were selected to study the complexing behavior for different metal ions. They were synthesized by homo- or copolymerization in solution using BF_3 -etherate as the initiator.²⁸⁻³⁰ The scheme of synthesis is presented in Figure 1.

LPR Method

The principle of the interaction studies and the metal-complexation process based on membrane filtration is schematically shown in Figure 2. The process employed, termed liquid-phase polymer-based retention (LPR), was designed to separate low molecular weight species. Thus, metal ions can in-

teract with a polymeric ligand and, consequently, be separated. For example, noncomplexed metal ions are passed through the membrane due to their small molecular size into the permeate. In contrast, the polymeric species, precursor polymer, and polymer complexes, with a substantial larger size than the membrane pores, are retained in the cell solution. The scheme of the experimental arrangement of the membrane filtration system for the complexation studies is depicted in Figure 3.

Metal Ion Complexation

The complexing behavior in this study was documented as retention profiles, which are plots of the retention R vs. the filtration factor Z , which is defined as the ratio of the volume of permeate V_p and the volume of cell solution V_0 (i.e., retentate volume). The retention of metal ions by a polymeric reagent in solution can be calculated as follows^{9,10}:

$$R = C_r \cdot C_0^{-1} (100\%)$$

where C_r is the metal concentration in the retentate (the cell solution after a filtrate volume of V_p has been passed) and C_0 is the initial metal ion concentration in the cell.

As a typical example, the retention R of Ni(II) ions by a 2 wt % aqueous solution of HEA-AAZ at different pH in the presence of 0.15M sodium nitrate as a function of the filtration factor Z is shown in Figure 4. The retention values by the polyaziridines investigated at different pH with a constant filtration factor ($Z = 10$) are listed in Table I. The complexing behavior of the polymers was investigated with nine different metal ions (Cr(III), Fe(III),

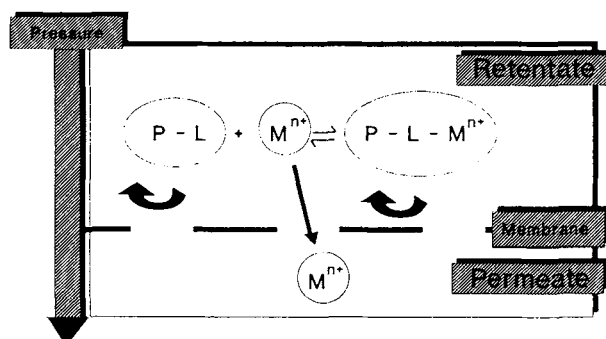


Figure 2 Principle of the membrane permeation process used for the complexation studies. P-L, poly(aziridine) with pendant ligand L in the side chain; M^{n+} , metal ion; P-L- M^{n+} , polymer metal ion complex (explanation, see text).

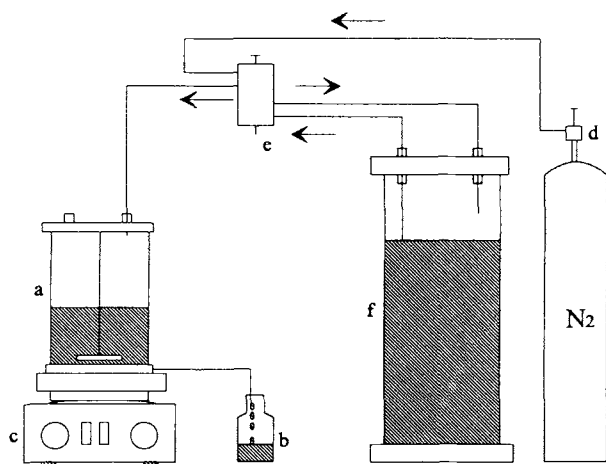


Figure 3 Experimental arrangement for the membrane filtration: (a) membrane filtration cell with polymer solution; (b) permeate; (c) magnetic stirrer; (d) pressure valve; (e) selector; (f) reservoir.

Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Sr(II), Zn(II)), which were simultaneously present in the solution.

Comparison of Poly(aziridine)s

Poly[1-(2-aminoethyl)aziridine] (BPEI) showed the strongest complexing properties with metal ions in conjunction with membrane filtration. Cu(II) was completely retained at pH 3, whereas at pH 1, it was not retained like all the other ions investigated. Fe(III), Cd(II), Ni(II), and Zn(II) can form stable complexes with BPEI under ultrafiltration conditions at pH 5. All the metal ions investigated were retained at pH 7, except for Sr(II).

Poly(1-acetylaziridine) (PAAZ) did not complex with metal ions under the conditions applied, except with Fe(III) and Cr(III), although it has the same backbone as that of poly[1-(2-aminoethyl)aziridine]. The retention of Fe(III) and Cr(III) was 10 and 16% at pH 3, respectively, and 72 and 18% at pH 5. However, all the metal ions but Sr(II) were quantitatively retained at pH 7. The higher retention values for the metal ions at pH 7 may be caused by the adsorption of the metal hydroxides onto polymer or on the surface of the colloidal particles, e.g., Fe(III)-colloidal particles.^{13,31}

Cu(II) forms the most stable complexes with PHEA in a pH range between 3 and 7. At pH 3, it was possible to separate Cu(II) ions from the other metal ions, whereas Sr(II) was only slightly retained. At pH 7, all metal ions, except for Sr(II), interacted with the polymer and were almost quantitatively retained.

The copolymer poly[1-(2-hydroxyethyl)aziridine-co-1-acetylaziridine] (HEA-AAZ) showed similar results to those of PHEA. All nine metal ions investigated were retained at pH 5, except for Co(II) and Zn(II). Sr(II) showed only a slight complexation over a pH range between 3 and 7 with this polymer; however, 94% of Co(II) and 88% of Zn(II) were retained at pH 7. At pH 3, only Cu(II) and Cr(III) ions formed complexes with the copolymer reflected in retention values of 76% for Cu(II) and 52% for Cr(III).

Poly[1-(2-aminoethyl)aziridine]oxine (POX) exhibited a much higher retention capability for several metal ions because of the salient complexing properties of the oxine.^{7,20} For example, even at pH 1, Fe(III), Cu(II), and Pb(II) were retained. At a higher pH, most metal ions were completely retained by POX. Only Sr(II) and Cr(III) ions were permeated at all pH values and also Zn(II) ions at pH 3.

Effect of Side Chains

The five polymers investigated can be considered as poly(aziridine) derivatives with different ligand groups as side chains, which have a pronounced effect in the coordination processes of the polymers with metal ions. Poly[2-(aminoethyl)aziridine] is a polymer, with saturated nitrogen donors (aminoethyl groups) on the polyaziridine backbone. The neutral saturated donor is widespread in ligands used in complex chemistry, because, on the one hand, it

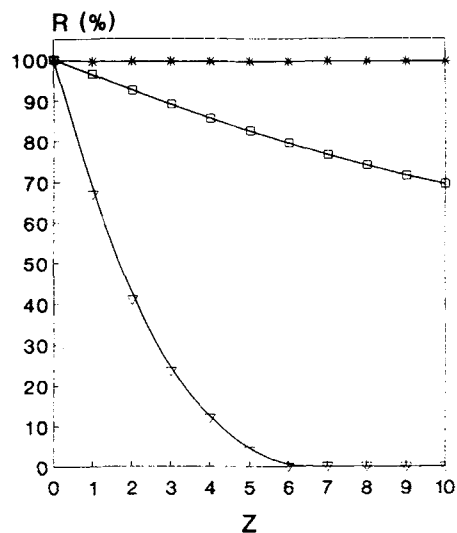


Figure 4 Retention profiles of the system Ni(II)/poly[(2-hydroxyethyl)-aziridine-co-1-acetylaziridine]. 2 wt % solution: (∇) = pH 3; (□) pH 5; (*) = pH 7.

Table I Comparison of the Retention of Poly[1-(2-aminoethyl)aziridine] (BPEI), Poly[(1-hydroxyethyl)-aziridine] (PHEA), Poly(1-acetylaziridine) (PAAZ), Poly[1-(2-hydroxyethyl)aziridine-co-1-acetylaziridine] (HEA-AAZ), and Poly[1-(2-aminoethyl)aziridine]-bound Oxine (POX) at Different pH Values (2 Wt % Polymer Solution, 20 mg L⁻¹ of Each Metal Ion, Filtration Factor Z = 10)

pH	Polymer	Retention (%)								
		Cr ³⁺	Fe ³⁺	Cd ²⁺	Co ²⁺	Cu ²⁺	Ni ²⁺	Pb ²⁺	Sr ²⁺	Zn ²⁺
1	BPEI	0	0	0	0	0	0	—	0	0
	PHEA ^a									
	PAAZ ^a									
	HEA-AAZ	7	6.5	0	0	0	0	0	0	0
	POX	0	75	0	0	80	20	99	0	0
3	BPEI	0	15	0	—	100	0	—	5	20
	PHEA	11	26	14	0	86	0	21	28	0
	PAAZ	16	10	0	0	0	0	0	0	0
	HEA-AAZ	52	13	14	4	76	0	11	4	0
	POX	—	98	88	95	100	40	99	0	0
5	BPEI	36	95	100	30	100	100	—	18	95
	PHEA	78	99	76	0	94	70	68	28	0
	PAAZ	18	72	0	0	0	0	26	0	0
	HEA-AAZ	89	96	80	0	88	72	69	21	0
	POX	48	98	90	95	100	100	99	0	95
7	BPEI	40	100	100	85	100	100	—	18	—
	PHEA	94	100	95	97	99	100	100	22	95
	PAAZ ^a									
	HEA-AAZ	93	100	90	94	93	95	100	17	88
	POX	—	98	95	95	100	100	99	10	95

^a The polymers are precipitated at these pH values.

provides a synthetically accessible site for the attachment of other chelating groups, e.g., EDTA, and, on the other hand, because the neutral nitrogen donor displays stronger complexing properties with many metal ions than does the neutral oxygen donor.

The metal ions investigated were not retained by BPEI in acidic solutions (pH 1 and pH 3). This can be interpreted by that the association reaction between amino groups with hydrogen ions is more pronounced than the metal complexation of the amino groups at both pH's. The only exception is that Cu(II) ions can be retained at pH 3, which may be caused by its high complex stability constant. For neutral solutions, the first point of interest is to characterize the affinity of each individual metal ion for the N donor group. The complexing properties of BPEI with metal ions can be assessed by using the first-step complex stability constant $\log K_1$ (NH₃) as an indicator for the affinity of N donors as reported by Hancock et al.³² The relationship between the retention values at pH 5 and 7 and $\log K_1$ (NH₃) is shown in Figure 5. The results indicate that the retention values of the BPEI are correlated

to the complex formation constants of NH₃ for the metal ions investigated, except for Co(II) at pH 5 and for Cr(III) at both pH.

Fe(III) and Cr(III) ions are known not to form complexes with amino groups.³² The retention of Fe(III) by BPEI is explainable by the formation of colloidal species at higher pH. Thus, the interaction between the polymer and the surface charges of the colloidal species causes the retention of Fe(III) during membrane filtration.^{13,31} However, Cr(III) was not retained because it can only form hydroxides under the experimental conditions investigated. The small retention of Cr(III) obtained may be caused by the adsorption of the hydroxides on the surface of the Fe(III)-colloids.¹³

PHEA, PAAZ, and HEA-AAZ can be viewed to contain neutral oxygen donor atoms introduced into the polyaziridine backbone. Like BPEI, all the metal ions were not retained by these polymers at pH 1 and 3. However, Cu(II) ions were retained at pH 3 because of its complexation with the OH groups in the side chains and the neutral nitrogen in the poly-

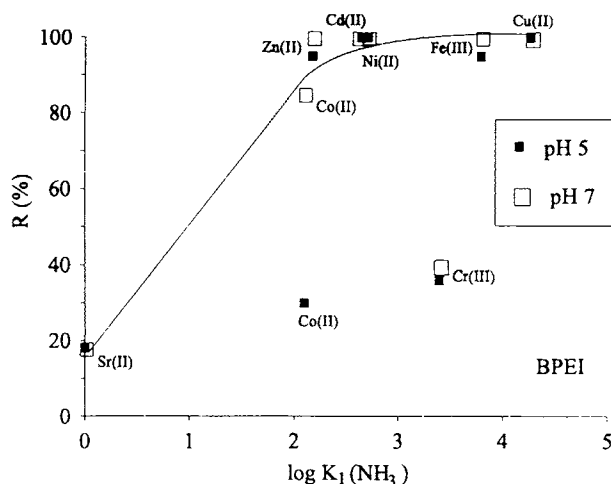


Figure 5 Relationship between the retention values of poly[(2-aminoethyl)aziridine] and $\log K_1(\text{NH}_3)$ for a series of metal ions.

mer backbone. The retention of Cr(III) (52%) by HEA-AAZ may be also caused by the interaction of Cr(III) with hydroxyl groups and carbonyl moieties. Similar to the BPEI, the affinity of the OH-containing polymers for metal ions can be characterized by using $\log K_1(\text{OH})$ values. The retention (R) profiles vs. $\log K_1(\text{OH})$ are shown in Figures 6 and 7.

The retention values for the metal ions by both polymers are almost consistent with the $\log K_1(\text{OH})$ values, except for Co(II) and Zn(II) at pH 5. These exceptions may be due to the steric effects by the introduction of the neutral oxygen donors.

The introduction of noncomplexing ligands such as acetyl groups into polyaziridine considerably reduces the complexing ability. Under the operating conditions, all the metal ions were not retained because of the poor complexing ability of the carbonyl moiety. The retention of Fe(III) at pH 5 can be traced back to the formation of Fe(III)-colloids similarly to the BPEI system. The adsorption of the Cr(III) and Pb(II) hydroxides onto the polymer or onto the Fe(III)-colloid particles might also explain their small retention values (Figs. 8 and 9).

The introduction of an analytical chelating reagent with a strong complexing power into the polymer chain can improve the general complexing ability of the polymer. As a further example, BPEI oxine (POX) was investigated in this study. As with the other polymers investigated, the retention of metal ions by POX is related to the metal complex stability constants of the monomeric oxine. Thus, Sr(II) ions cannot be retained by an aqueous solution of POX by reason of the small complex stability constant ($\log K_1 = 2.11$). In contrast, Fe(III) and Cu(II) have

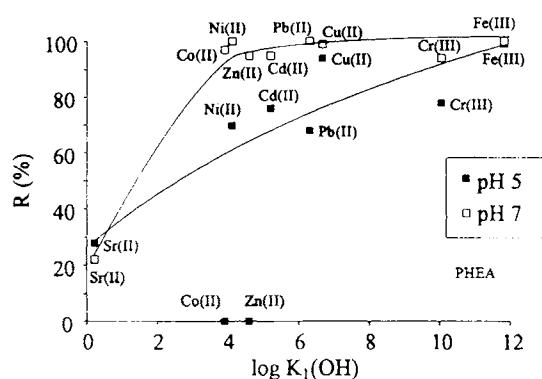


Figure 6 Retention of poly[(2-hydroxyethyl)aziridine] as a function of $\log K_1(\text{OH}^-)$ for a series of metal ions.

considerably higher complex stability constants (Fe-oxine, $\log K_1 = 11.4$; Cu-oxine, $\log K_1 = 12.1$),⁶ and, therefore, they were completely retained even at pH 1.

CONCLUSIONS

The metal-complexing properties of the five polyaziridines investigated are dependent on the complex-forming ability of the ligand groups in the side chains. The higher are the metal complex stability constants of the side-chain ligand groups of the polymer, the stronger is the interaction and complexation with the corresponding metal ions. The complexation was measured by the retention of the metal ions in an aqueous solution in combination with membrane filtration. The poly[(2-aminoethyl)aziridine]oxine showed the strongest complexing ability for the series of nine metal ions investigated due to the high complex stability constant of the oxine ligand. The introduction of non-

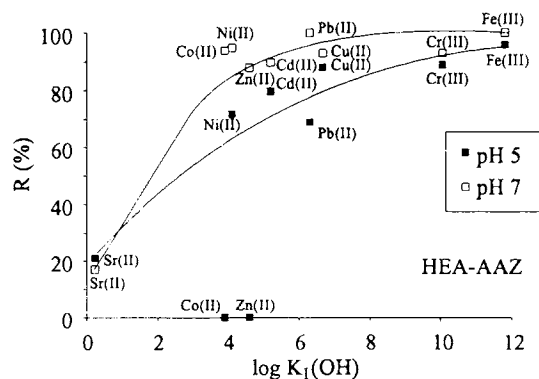


Figure 7 Dependence of the retention of poly[(2-hydroxyethyl)aziridine-co-1-acetylaziridine] and $\log K_1(\text{OH}^-)$ values for a series of metal ions.

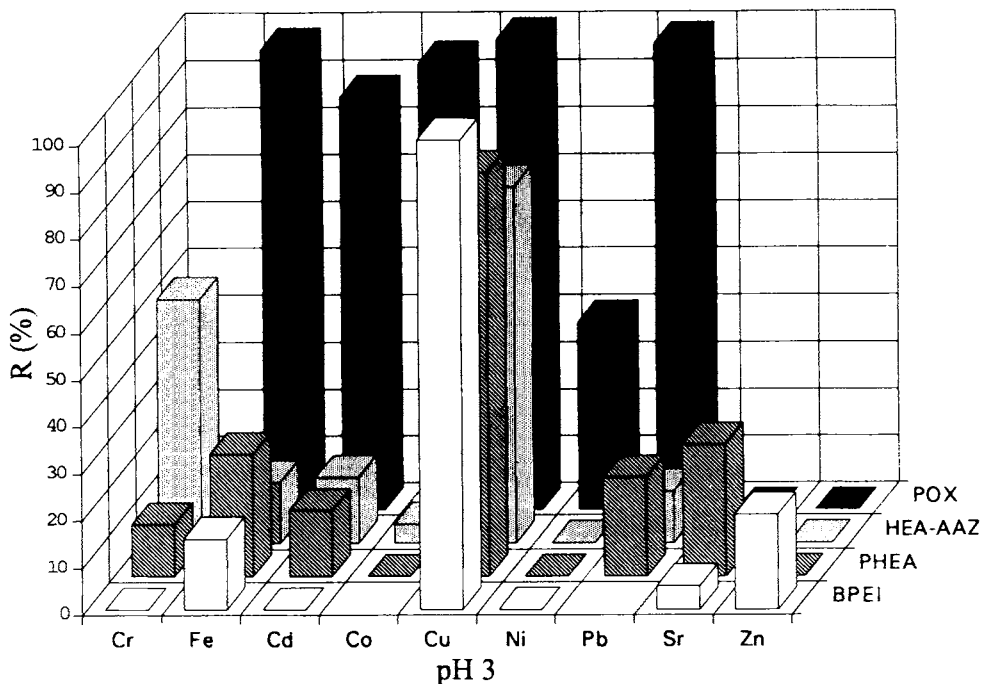


Figure 8 Comparison of the retention values of poly[(2-aminoethyl)aziridine], poly[(2-hydroxyethyl)aziridine], poly[(2-hydroxyethyl)aziridine-co-1-acetylaziridine], and poly[1-acetylaziridine] at pH 3.

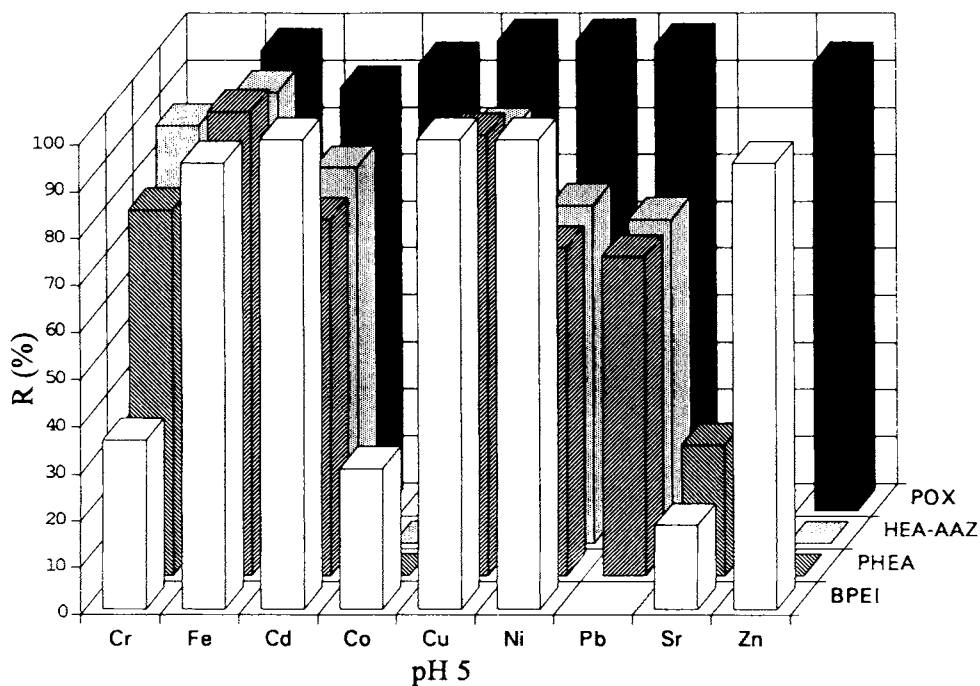


Figure 9 Comparison of the retention values of poly[(2-aminoethyl)aziridine], poly[(2-hydroxyethyl)aziridine], poly[(2-hydroxyethyl)aziridine-co-1-acetylaziridine], and poly[1-acetylaziridine] at pH 5.

complexing groups for metal ions led to a decrease of the complexing ability of the polymer showing significantly lower retention values. Evidently, the complexing ability of the corresponding monomeric analog cannot be applied solely for the evaluation of the complexing properties of the polymer as a whole because intramolecular interactions are also involved in the complexation process. As an approximation, however, the assessment of the complexing ability of the corresponding monomeric ligands allows one to design polymers with a high selectivity for various metal ions.

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