

PREPARATION AND APPLICATION OF WATER-SOLUBLE POLYMER-METAL COMPLEXES

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Abstract - A series of water-soluble polymers and derivatives with chelating groups has been prepared and investigated for the complex formation with various metals. The complexation of basis polymers, such as poly(ethyleneimine), poly(vinylamine), and poly(acrylic acid), as well as copolymers was carried out in homogeneous phase. Membrane filtration allowed continuous or discontinuous separation of the polymer chelates from metallic ions not bound to the polymer. The polymer complexes remained water-soluble independent of the chelated metal and the polymeric ligand. Studies on the dependency of the capacities of the polymers upon various parameters and methods for regenerating the polymeric ligands are described. The introduction of chelating groups, e.g. pyridine-2-alimine, thiourea, iminodiacetic acid, 8-hydroxy quinoline, and hydroxyaniline, to the macromolecules by polymer-analogous reaction or by copolymerization improved significantly the selectivity for the metals cobalt, nickel, copper, cadmium, palladium, mercury, silver, gold, and platinum. By the use of membrane filtration in the preparation and application of water-soluble polymer-metal complexes it is possible to recover metal ions from solutions in a short time and in homogeneous phase.

INTRODUCTION

Water-soluble polymer complexes are not only of theoretical importance but also of increasing practical interest, since they involve the potentiality of versatile applications in chemistry. Insoluble chelating resins, on the contrary, have considerable disadvantages, such as reaction in heterogeneous phase and long contact times.

Up to present, many investigations have been carried out in this field, particularly on synthesis and properties of soluble polymer ligands and coordinating groups (Ref. 1-10).

In general, there are three requirements with which polymers as chelating agents should comply: sufficient solubilizing power of the constitutional repeating unit which provides water-solubility of the polymer complexes, a great number of functional groups of the complexing agent for a high capacity, and a high molecular weight which allows an easy separation by usual methods from the metal not bound to the polymer. Preferable for these studies are molecular masses between 10 000 and 100 000. Molecular masses of polymers smaller than 10 000 are not suitable because of separation problems in membrane filtration. Therefore, all prepared macromolecular ligands consisted of molecular mass fractions greater than 10 000, which was verified by membrane filtration.

Possibilities for the synthesis of polymer chelating agents are the following:

- 1) Preparation of polymers with chelating units, e.g. poly(vinylamine), poly(ethyleneimine).
- 2) Polymerization of monomers already bearing the complex forming group, e.g. acrylic acid, vinylmethyl ketone, vinylsulfonic acid.
- 3) Polymerization of monomers containing protected functional groups with following polymer-analogous deblocking reaction, e.g. poly(vinylalcohol) from poly(vinylacetate).
- 4) Conversion of side chains or functional units in order to form or to change complexing groups, e.g. hydrolysis of poly(1-vinyl-2-pyrrolidinone)

to poly(vinylimino butyric acid).

5) Polymer-analogous derivatization of functional heteroatom units, e.g. poly(ethyleneimine).

Water-solubility is provided by a high content of hydrophilic groups, e.g. amino, hydroxyl, carboxyl, amide and sulfonic acid groups, or hydrophilic units of the polymer backbone, e.g. ether or imino groups.

In principal, both possibilities for the preparation of functionalized polymers, copolymerization and polymer-analogous derivatization have been examined and successfully applied to polymeric chelates.

We illustrate here new developments in preparation of water-soluble polymer complexing agents and their complexes with various metals by means of membrane filtration as well as investigations on cleavage of the metal from the chelating polymer with recovering the polymer ligands.

RESULTS AND DISCUSSION

Membrane Filtration

Membrane filtration (Ref. 11,12) was carried out in a system as depicted in Fig. 1. The membrane filtration unit consists of the membrane filtration cell with a magnetic stirrer, the coupled reservoir, the dialysate reservoir, the selector and the pressure source (Ref. 13). Using a selector allows the addition of the washing fluid simultaneously corresponding to the elution volume and therewith continuous membrane filtration. In the cells symmetric membranes which are prepared from polyamides, polysulfones, or cellulose derivatives are used. They are stable in aqueous medium and available in a great variety of retention properties (Ref. 13).

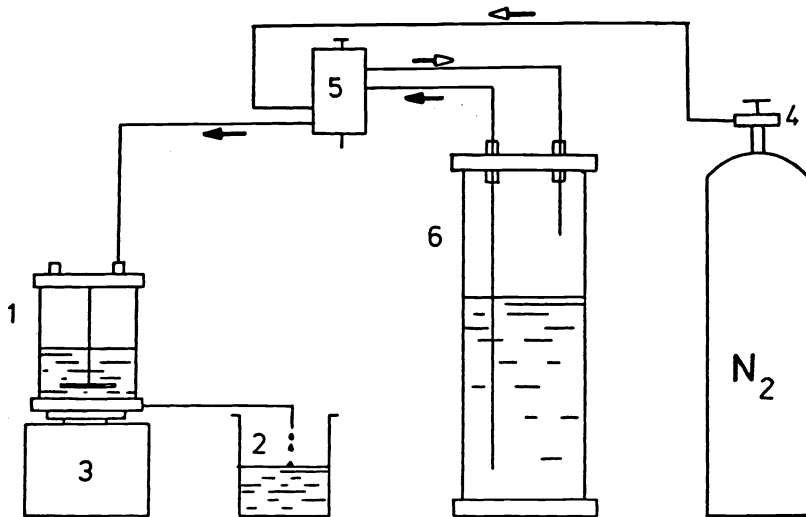


Fig. 1. Membrane filtration unit (system "Amicon").

- 1 Filtration cell with solution of polymeric complex
- 2 Membrane filtrate
- 3 Magnetic stirrer
- 4 Pressure trap
- 5 Selector
- 6 Reservoir with solution of metal salt

For analytical investigations on the metal uptake, solution volumes of about 250 ml were used. The complexing polymer solution was placed into the membrane filtration cell and the metal salt solution added from the reservoir. The polymer concentration in the cell was constant. After isolation of the complex formed, the proportion of non-bound ions could be determined by atomic

absorption spectroscopy of the filtrate which was collected in fractions. The flow rate depends on the type of membrane and, above all, on the membrane surface. For simple membrane filtration systems 300 to 500 ml per hour are average values.

Beside stirred cells there are thin-channel systems in which the solution is flowing continuously over the membrane in very shallow channels, and hollow-fiber-systems (Ref. 13,14) in which microtubular membranes with extremely large surfaces are used. These systems are advantageous for greater quantities because of the better relationship between membrane surface and solution volume.

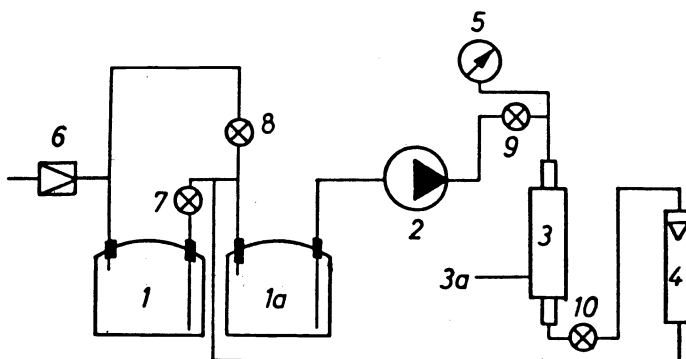


Fig. 2. Membrane filtration unit (system "Berghof")

- 1 Reservoir for solution of metal salt
- 1a Reservoir for chelating polymer
- 2 Pump
- 3 Modul (membrane fibers)
- 3a Membrane filtrate
- 4 Flow metre
- 5 Manometer
- 6 Pressure trap
- 7-10 Valves

These systems have a substantially higher flow rate and are recommendable above all for highly diluted metal salt solutions. For example, for a filter surface of 0.5 m² the flow rate is about 10 h for a 3 % solution of poly-(ethyleneimine). Ultrafilter and hollow fiber membranes allow the separation at high flow rate and at moderate pressure (20-40 psi).

The relationship between concentration and volume for membrane filtration is expressed by the following equation (Ref. 13):

$$\ln \frac{C_0}{C_1} = \frac{V_1}{V_0}$$

- C₀ = original macrosolute content
- C₁ = final macrosolute content
- V₀ = original volume
- V₁ = final volume

The proportionality allows the determination of final macrosolute content or filtrate volume if the other parameters are known. The flow-rate is inversely proportional to the logarithm of the concentration of retained solute. The flow-rate diminishes as the concentration of retained solute increases. In practical use, a 5fold volume of the washing solution referred to the cell solution yielded 99 % separation of the low-molecular excesses.

The "wash-out" process is documented graphically in Fig. 3.

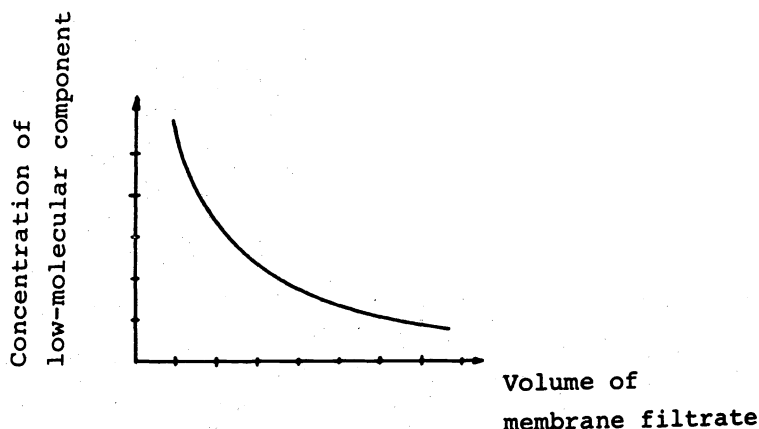


Fig. 3. "Wash-out" process during membrane filtration. Concentration of low-molecular components is plotted versus the volume of membrane filtrate.

Capacity and Enrichment

The capacity of soluble polymer complexing agents is influenced by various factors, chiefly steric and statistical ones. According to the calculations of Flory (Ref. 15), the maximal conversion for a reaction of two neighbouring groups is about 85 % of all available functional groups. Usually there is not only intramolecular, but also intermolecular complexation because of the coordination number of metal ions greater than two. Hence follows an additional depression of conversion. Other functional groups of the polymer which do not take part in metal complexation influence also capacity and selectivity by linking and screening effects (Ref. 16,17,18). The dependence of capacity on concentration of the polymer solution differs from polymer to polymer. Generally, sterical hindrance diminishes the capacity if a certain concentration of solution is exceeded.

The capacity C is defined as

$$C = \frac{M \cdot V}{P_m}$$

M = initial concentration of metal salt (mg/l)

V = metal-free volume of the membrane filtrate (l)

P_m = quantity of polymer (g)

A very strong dependency exists between capacity and pH, influenced by both type of functional group and type of metal ion. Generally, we obtained a curve as depicted in Fig. 4 for this relationship.

The optimum pH value can be determined experimentally for every polymer complex. In all cases of the complexes investigated, at pH = 2 the metal was split off from the polymeric ligand, signalized by the disappearance of the complex colour.

In some cases, if the solubility of the polymer complex causes problems, it is recommendable to carry out reactions at a lowered pH. Thereby, the macromolecular complex remains water-soluble.

The main factors for the enrichment of metals from dilute aqueous solutions by this method are the following:

- solubility of the polymeric complexing agent,
- capacity of the chelating polymer, and
- concentration of metal salt solution.

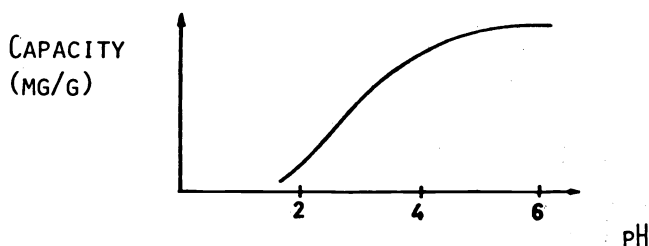
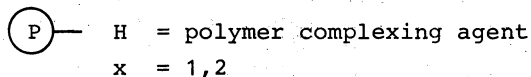
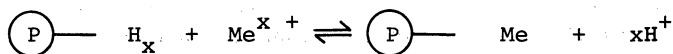


Fig. 4. Capacity (mg metal/g polymer) as a function of pH.

Other methods for the enrichment of metal ions from aqueous solutions involve considerable disadvantages because of reaction in heterogeneous phase, e.g. ion exchange resins (Ref. 19,20,21). Similar to such resins, soluble polymer complexing agents can be regenerated after separation of the excess metal salt solution. For this separation process membrane filtration was found to be especially suitable, particularly because of the possibility of continuous procedure.

Therefore, the main task in this field is to optimize the three factors. As lower limits one should consider polymer solutions of 1 % and capacities of 0.1 g metal/g polymer. Furthermore, the metal uptake should be reversible in order to recover the polymer chelating agents. The reverse reaction can be carried out by means of acids, stronger ligands or electrolysis. The easiest way is the cleavage of complexes by acids. Hence, chelating polymers are chosen which satisfy the following equation:



For a known capacity of a polymer and on the premises of quantitative complexation we can define the enrichment rate E , which depends at a certain pH essentially on polymer capacity, concentration of polymer and metal solution (Ref. 22).

$$E = 10 \frac{P_c C}{M}$$

P_c = concentration of polymer (%)

C = capacity ($\frac{\text{mg}}{\text{g}}$)

M = initial concentration of metal salt (mg/l)

Quantitative studies on complex formation of water-soluble polymer chelating agents necessitate the addition of a defined volume of a solution containing a defined metal concentration to the polymer solution and determination of the non-bound metal in the membrane filtrate. For the graphical presentation, the concentration of the metal salt in the filtrate is plotted versus the volume of the filtrate. Therefrom, characteristic enrichment curves are obtained. Two extreme types of curves are given in Fig. 5.

The break of curve in Fig. 5b represents the limit of capacity of the polymer ligand. Curves without break (Fig. 5a) indicate that no complexation has taken place but only simple adsorption of the metal to the polymer. In this case, metal concentration increases quickly up to the initial maximum concentration. On the contrary, in Fig. 5b the membrane filtrate contains metal ions only after some time. The metal-free fractions of the diafiltrate volume are represented by the part of curve parallel to the abscissa.

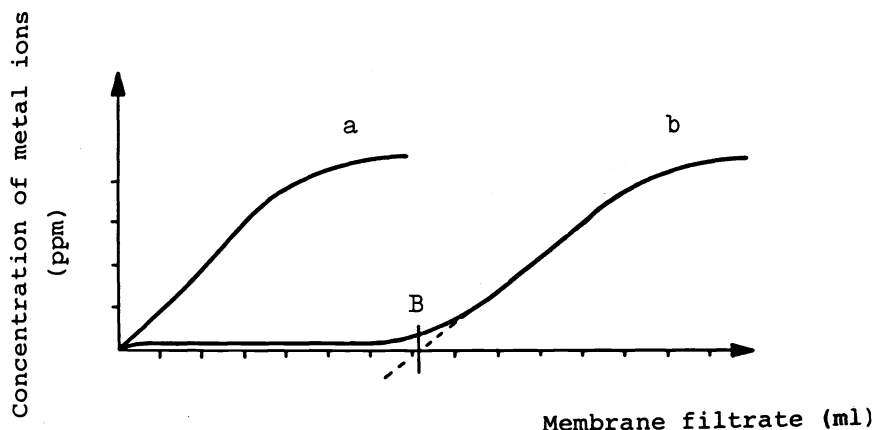
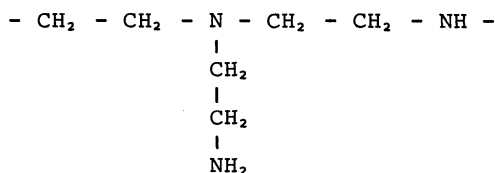


Fig. 5. Enrichment curves for polymer ligands in membrane filtration. a) No complexation: Immediate increase of concentration of metal salt in the filtrate. b) Quantitative complexation: Retarded appearance of metal ions in the filtrate (straight line parallel to the abscissa) with following continuous increase up to the initial concentration. B indicates the limit of capacity.

Polymer Ligands and Derivatives

Poly(ethyleneimine) possesses quite a number of advantages as polymer chelating agent, such as good water-solubility, high content of functional groups, good physical and chemical stability, and suitable molecular weights. Depending on the polymerization process, there are different ratios of amino groups. We used commercially available poly(ethyleneimine) (Polymin P, BASF) with equivalent ratios of primary, secondary and tertiary nitrogen atoms (1:1:1).



The average molecular mass of Polymin P was 30 000 - 40 000. The high content of primary amino groups allows suitable modification of the polymer and branching provides good properties for membrane retention. Contrary to poly(ethyleneimine) itself, the complexes prepared could be easily isolated as dry powders which were not hygroscopic. This can be explained by screening of the ionic groups by the metal ions. In consequence, there is depression of the hydrophilic properties and hindered hydration.

The data for some complexes are presented in Table 4. As best results, 0.37 g copper was bound by 1 g poly(ethyleneimine). In agreement with the Irving-Williams series (Ref. 23), ions of higher valence are less strongly bound.

For preliminary studies we investigated the selectivity of complexation of poly(vinylamine) and derivatives. Complex formation of bivalent metallic ions proceeded almost quantitatively. Some examples are shown in Table 1 and Table 2 (Ref. 9, 24).

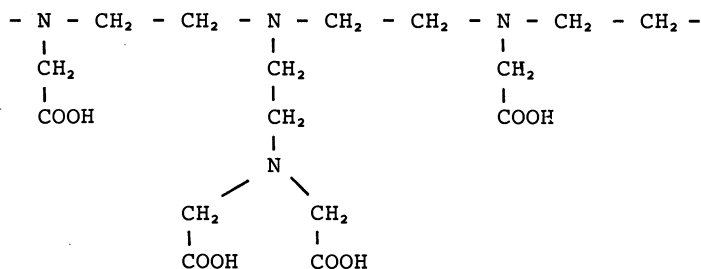
The knowledge of application of imino acetic acids as complex forming agents dates back to the early fifties and was investigated (Ref. 25). These complexes exhibit great stability, good water-solubility, and a wide spectrum of chelated metals (Ref. 26). We prepared polymeric imino acids by reaction of poly(ethyleneimine) with chloroacetic acid.

TABLE 1. Capacities of poly(vinylamine) for copper and nickel

Metal ion	pH	Capacity (mg/g)	Molar capacity (mmole/g)
Cu ²⁺	6	153	2.4
Ni ²⁺	6	72	1.2
Ni ²⁺	4	35	0.6

TABLE 2. Comparison of capacities of poly(vinylamine) derivatives

Structure unit of polymer ligand	pH	Capacity: mg/g (mmole/g)			
		Cu ²⁺	Ni ²⁺	Fe ²⁺	Hg ²⁺
$ \begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{N} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \quad \\ \text{COOH} \quad \text{COOH} \end{array} $	5.5	148 (2.3)	45 (0.8)	25 (0.5)	--
$ \begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{NH} \\ / \quad \backslash \\ \text{S}=\text{C} \quad \text{N}-\text{CH}_3 \end{array} $	2.5	35 (0.6)	16 (0.3)	14 (0.2)	365 (1.8)



The fully reacted acid polymer is insoluble in water but becomes water-soluble as sodium salt. Practically quantitative binding of copper (II) to the sodium salt proceeds at pH 6-7 but metal uptake greater than 0.12 g Cu/g renders the polymer insoluble. Therefore, we used partially reacted polymers with sufficient solubility.

Two examples are presented in Fig. 6 and Fig. 7 with molar ratios of polymer nitrogen to acetic acid of 3:1 and 2.5:1. In the first case the capacity limit was at a pH of 2.5 with a capacity of 7.5 mg Cu (II) per gram polymer or 2.3 mmole Cu(II)/g polymer. An increasing content of chelating groups yielded a better acid stability and the maximal capacity obtained was 0.1 g Cu/g polymer.

Selectivity studies for copper, nickel and zinc are summarized in Fig. 8, which demonstrates the extremely high stability of the copper chelates.

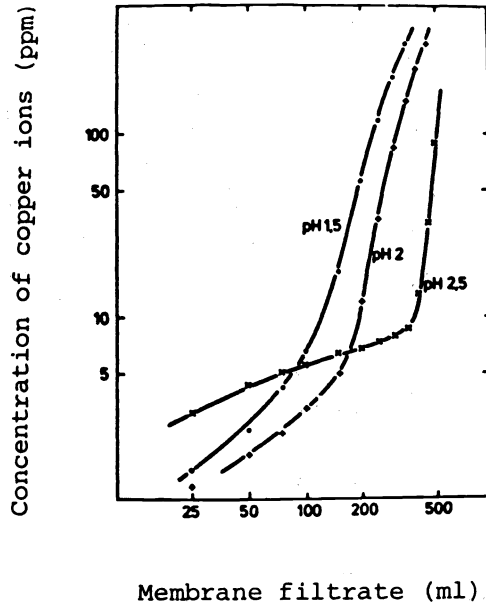


Fig. 6. Metal uptake (solution of 1000 ppm Cu) of poly(ethyleneimine acetic acid) (5 % solution) with a molar ratio of 3 : 1 (polymer N : acetic acid) at different pH values.

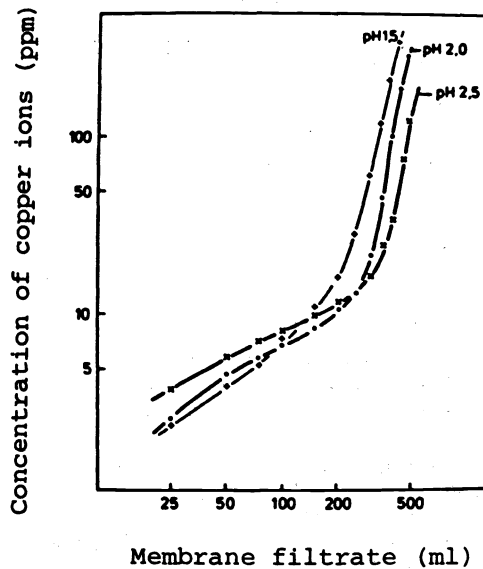


Fig. 7. Metal uptake (solution of 1000 ppm Cu) of poly(ethyleneimine acetic acid) (5 % solution) with a molar ratio of 2.5 : 1 (polymer N : acetic acid) at different pH values.

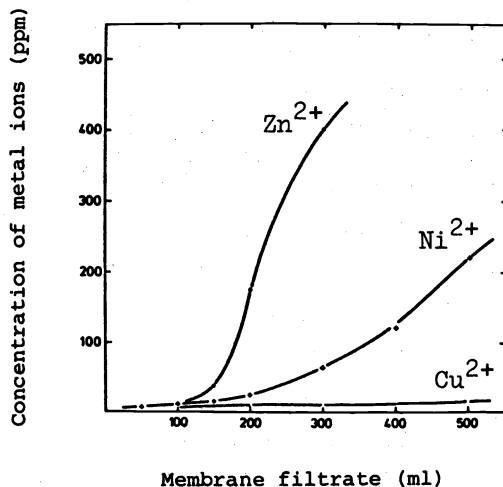
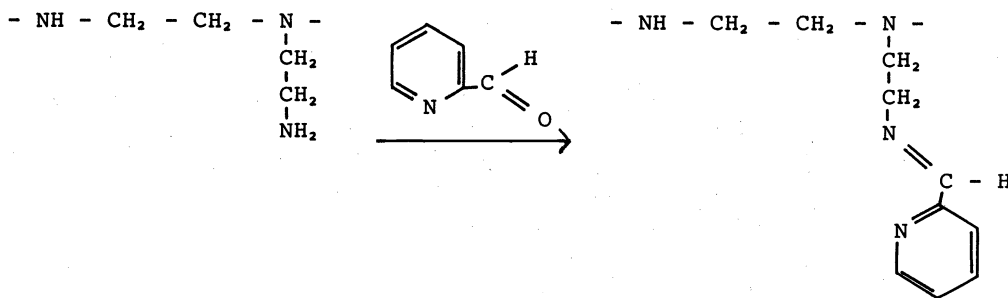


Fig. 8. Comparison of copper, nickel, and zinc in complexation with poly(ethyleneimine acetic acid) at pH 3.5. Metal salt solution of 500 ppm Me^{2+} , 5 % solution of polymer ligand.

Selective Chelating Groups

As iron-selective complexing polymers, derivatives of poly(ethyleneimine) with 1,2-dimine groups were synthesized. The 1,2-dimine group is known as chelating group with selectivity for iron as well as a group forming stable and water-soluble iron complexes (Ref. 27). By reaction of the primary amino group of the polymer with pyridine-2-aldehyde, the pyridine-2-aldimine structure (Ref. 28,29) in the polymer derivative was obtained.



The pH-dependence of the iron complex with this polymer is shown in Fig. 9. At pH = 5.0 complex formation proceeded almost quantitatively, whereas at pH = 3.5 a considerable amount of Fe (II) was not bound to the polymer by complex formation.

The polymeric complex corresponds to a 2:1-chelate, calculated from elemental analysis. It is water-soluble and stable against a solution of 1 N perchloric acid in acetic acid but cleaved by dilute mineral acids.

Infrared spectroscopy of the Fe (II) complex showed the bathochromic displacement of the C=N-frequency (100 cm^{-1}), as was expected (Ref. 30).

Attempts to prepare the corresponding monomeric chelating molecule were successful. The formation of the iron complex, however, failed because of polymerization reaction of the aziridine derivative.

Poly(ethyleneimine), which was quaternized with alkylating agents, was found to have selective properties for noble metals similar to the thiuronium group, which has been reported in literature (Ref. 31,32). We reached maximal capacities of 1.55 g Au^{3+} , 0.82 g Hg^{2+} and 0.63 g Pt^{4+} per gram polymer at a pH range of 2.5 - 3.5. Methyl iodide, ethyl bromide and dimethyl sulfate served as alkylating agents. The complexation curve for poly(ethyleneimine)

which was reacted with dimethyl sulfate is given in Fig. 10.

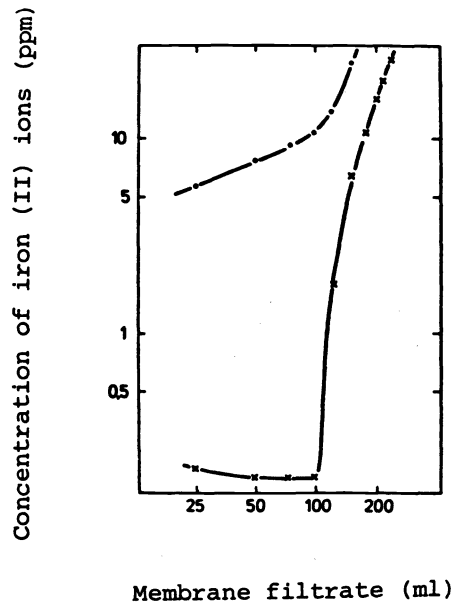


Fig. 9. Metal uptake (solution of 100 ppm Fe^{2+}) of poly(ethyleneimine pyridine-2-alimine) (1 % solution) at pH 3.5 (---) and pH 5 (-x-x-).

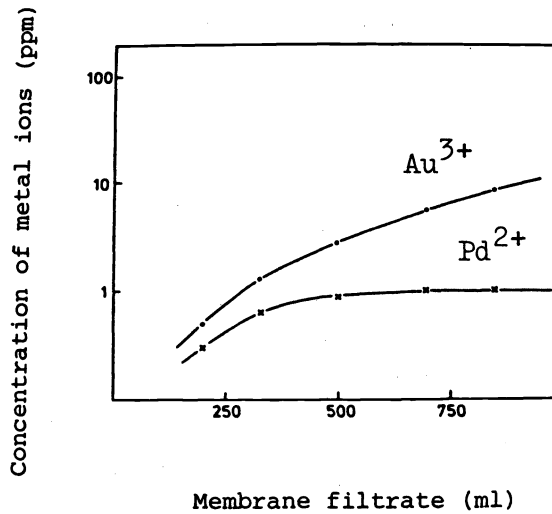
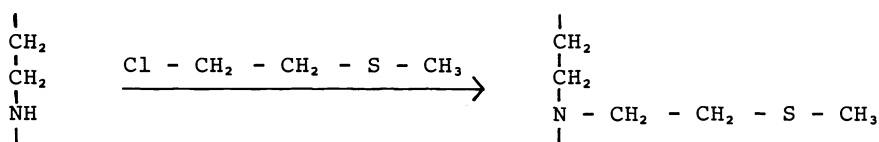


Fig. 10. Comparison of metal uptake from a solution containing Au^{3+} (40 ppm) and Pd^{2+} (40 ppm) in a solution of Cu^{2+} (1000 ppm) at pH 1,7 for poly(ethyleneimine) quaternized with dimethyl sulfate.

It is shown that palladium is bound from acid solutions in high yields, whereas gold exhibits an inferior tendency for complexation. The methyl sulfide derivative, which can be obtained by reaction with 2-chloroethyl methylsulfide, had similar selective properties.



This polymer complexes almost quantitatively both palladium and gold (Fig.11)

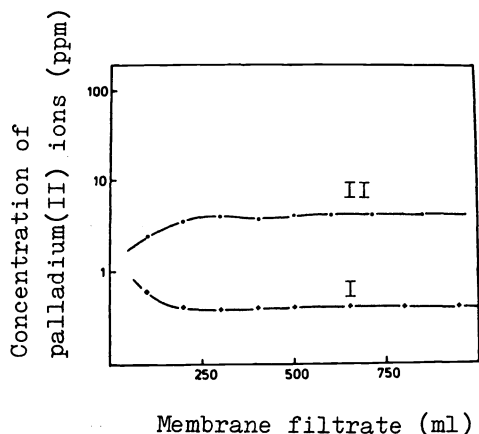
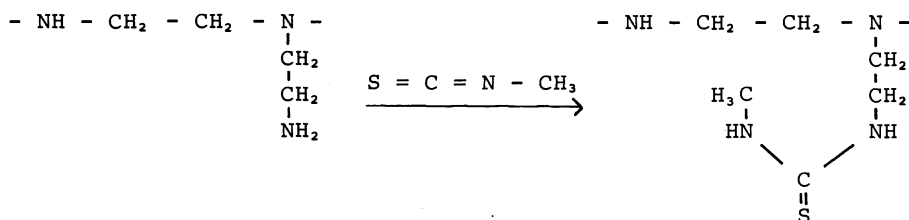


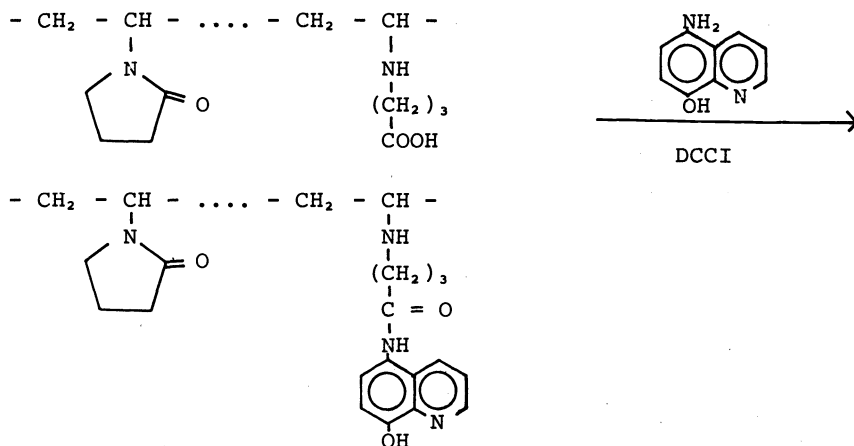
Fig. 11. Complexation behaviour of poly(ethyleneimine N-ethyl methyl sulfide) (I) and poly(ethyleneimine N-methyl thiourea) (II) at pH 1.5 for Pd^{2+} (40 ppm) in a solution of Cu^{2+} (1000 ppm).

Linear polythiourea can be obtained by reaction of poly(ethyleneimine) with N-methylisothiocyanate.

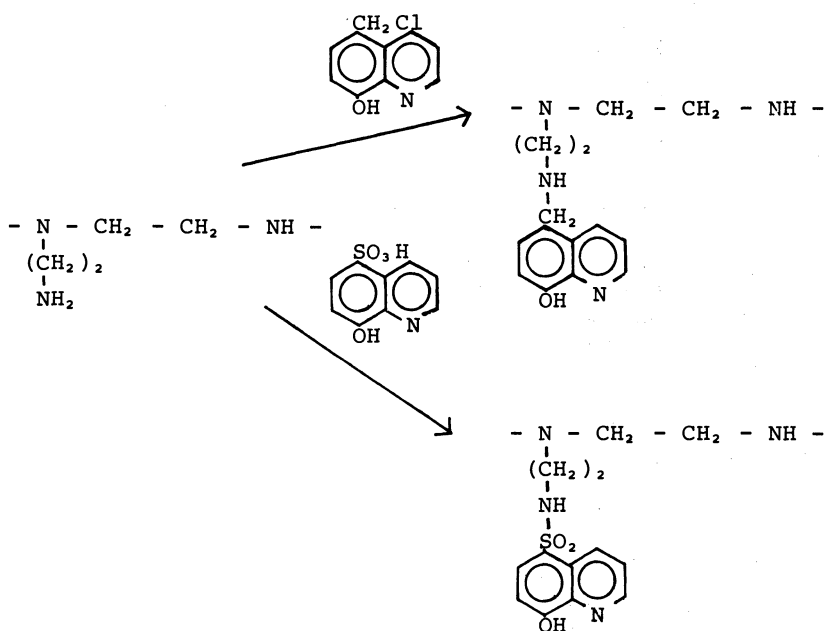


Direct polymerization of the corresponding aziridine derivative yielded molecular weights which were too small for the membrane filtration system. Therefore it is advantageous to prepare the complexing polymer by polymer-analogous reaction. The enrichment factors of these polymer were in the range of 10^3 . That means, for example, that a solution with originally 500 ppm Hg^{2+} contained less than 0.5 ppm after the complexation and separation process.

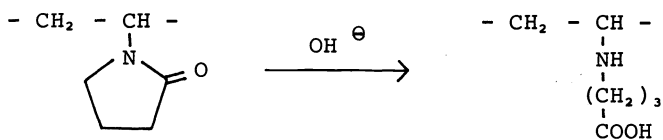
Excellent complexation properties have been reported for 8-hydroxy quinoline and derivatives (Ref. 33,34). These coordinating groups have been bound to polymers by polymer-analogous coupling using dicyclohexyl carbodiimide (DCCI) as coupling reagent (Ref. 35,36). For instance:



Polymer-analogous fixation reactions were also used for poly(ethyleneimine):



A water-soluble polymer with carboxyl groups was obtained by partial hydrolysis of poly(1-vinyl-2-pyrrolidinone) (Ref. 37). The copolymer yielded contained about 15 % comonomer units.



Other polymers employed, such as poly(acrylic acid), poly(1-vinyl-2-pyrrolidone-co-acrylic acid), poly(1-vinyl-2-pyrrolidone-co-allyl thiourea) and poly(vinylsulfonic acid), were commercially available or prepared by usual methods. Some results are summarized for comparison of different metals and polymer ligands in Table 3.

TABLE 3. Comparison of capacities of poly(ethyleneimine) and derivatives

Structure unit of polymer ligand	Name of polymer	Metal ion	pH	Capacity (mg/g)	Molar capacity (mmole/g)	Theoretical capacity* (mmole/g)
- CH ₂ - CH ₂ - NH -	Poly(ethyleneimine)	Co ²⁺	4	105	1.8	
		Ni ²⁺	4	135	2.3	
		Cu ²⁺	4	180	2.8	3.88
		Cd ²⁺	4	185	1.6	
- CH ₂ - CH ₂ - N - (CH ₂) ₂ N / \ CH ₂ CH ₂ COOH COOH	Poly(ethyleneimine acetic acid)	Cu ²⁺	4	130	2.0	
		Pd ²⁺	2.5	80	0.8	3.88
		Ag ⁺	2.5	40	0.4	
- CH ₂ - CH ₂ - N - (CH ₂) ₂ NH / \ S = C NH - CH ₃	Poly(ethyleneimine N-methyl-N-thio-urea)	Au ³⁺	2.5	180	0.9	
		Pt ⁴⁺	2.5	135	0.7	4.65
		Hg ²⁺	4	100	0.5	
-CH ₂ -CH-.....-CH ₂ -CH- N CH ₂ O NH / \ S=C NH ₂	Poly(1-vinyl-2-pyrrolidone-co-allylthio-urea)	Au ³⁺	2.5	172	0.9	
		Hg ²⁺	4	92	0.5	1.48

* The theoretical capacity is calculated on the basis of content of functional groups and on the premises of a coordination number of 4^{18,38}.

UV and IR Spectroscopy

Several characterization methods are appropriate for the investigation of macromolecular chelates. Especially important are ultraviolet and infrared spectroscopy, elemental analysis, and atomic absorption spectroscopy. Determination of equilibrium constants and studies on the behaviour during electrolysis provide additional characteristic values.

UV-spectroscopic studies on the composition of polymer complexes were carried out according to the method of continuous variation (Ref. 39). Typical results are shown in Fig. 12 and 13. The break of curve in these diagrams, in which extinction values are plotted versus mole fraction, indicates the composition of the polymeric complex.

For the copper complex of poly(ethyleneimine) the value x is 0.65 (Fig. 12). Consequently, the composition of the complex $\text{Cu}(\text{PL})_n$, where PL represents the polymer ligand, could be calculated by the equation

$n = \frac{x}{1-x}$. Therefrom resulted $n \approx 2$, which means that two constitutional repeating units of poly(ethyleneimine) are the ligands of one Cu^{2+} -ion.

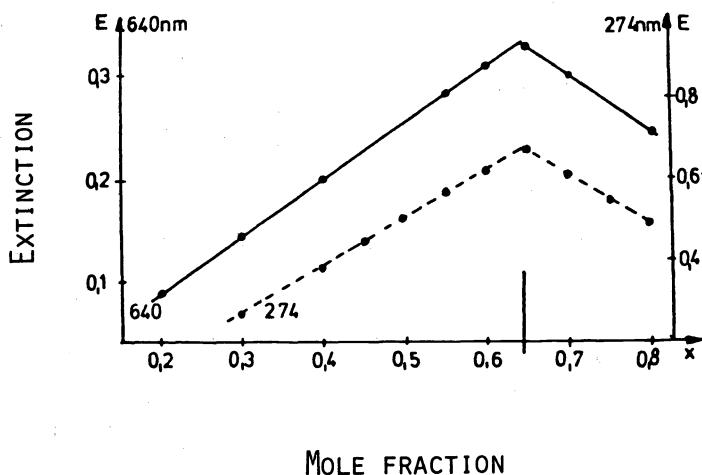


Fig. 12. Extinction curves of the poly(ethyleneimine)-copper complex at different wavelengths for the determination by continuous variation. Extinction is plotted versus mole fraction.

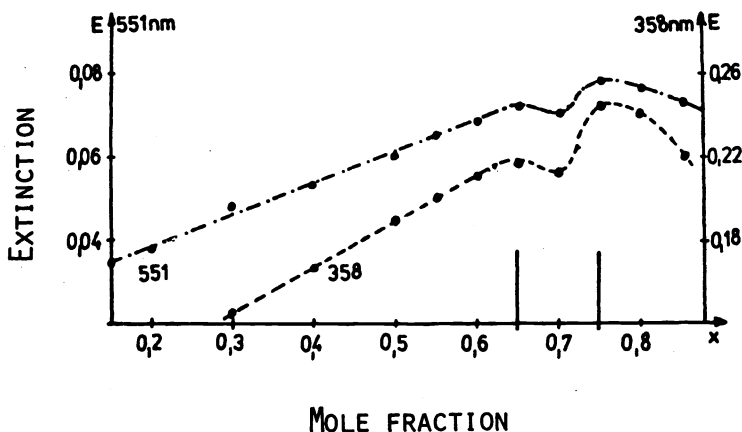


Fig. 13. Extinction curves of the poly(ethyleneimine)-nickel complex at different wavelengths for the determination by continuous variation.

For the nickel complex of poly(ethyleneimine), two maxima were found in the extinction curves. The two maxima at $x = 0.65$ and $x = 0.75$ correspond to the complexes $Ni(PL)_2$ and $Ni(PL)_3$. Attempts to distinguish between complexes with coordination numbers four and six by magnetic measurements were not successful. The pH-dependence of the coloured complexes was also studied by UV-spectroscopy. Fig. 14 shows the extinction curves for two examples, the copper and nickel complexes of poly(ethyleneimine).

These extinction curves are not suitable for quantitative determination of the content of metallic ions because of a strong dependency on the polymer content, even at a constant pH-value. This determination requires calibration curves for different concentrations of metallic ions and for different concentrations of polymer ligand. The exactness and the convenience of the determination by means of atomic absorption spectroscopy is not reached by far.

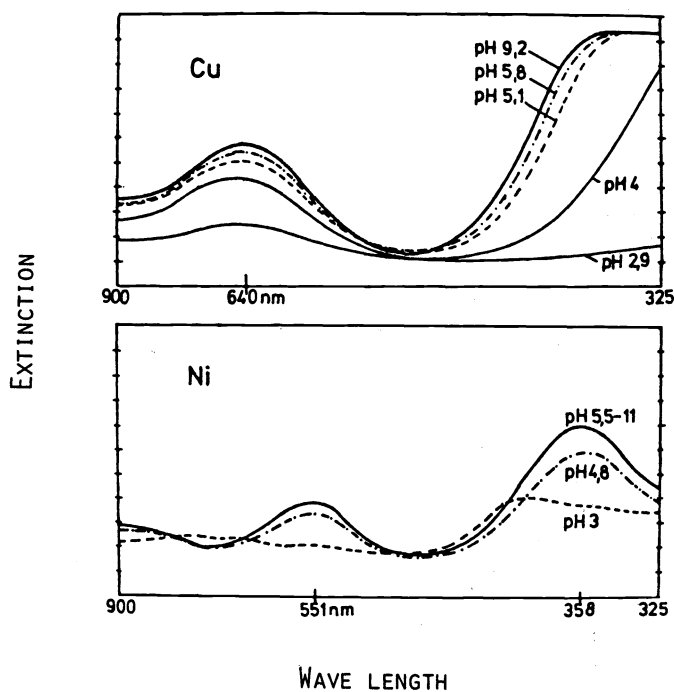


Fig. 14. Absorption spectra of complexes of poly(ethyleneimine) with copper and nickel at different pH values.

Infrared spectra of the investigated complexes of poly(ethyleneimine) are shown in Fig. 15.

Identification of the characteristic bands is limited to two functional groups and therefore not difficult. Complexation of this polymer with metal ions yielded mainly a displacement of the C-N-valence vibration to lower wave numbers. The detailed values are summarized in Tab. 4.

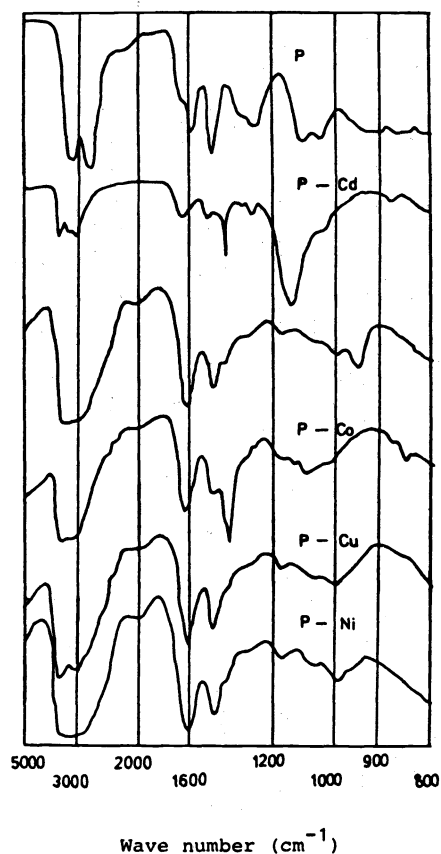


Fig. 15. Infrared spectra of poly(ethyleneimine) (P) and some metal complexes.

TABLE 4. Infrared spectroscopy data of complexes of poly(ethyleneimine) (P)

Complex	Wave number (cm ⁻¹)				
	N - H	C - H	N - H	C - H	C - N
P - UO ₂	3400 s	2950 s 2850 s	1630 s	1470 s 1390 m 1300 w	1150 - 900 (940)
P - Cu	3400 s	2950 s 2850 s	1640 s	1460 s 1390 m 1300 w	1150 - 900 (1000)
P - Ni	3500 s	2500 s	1650 s	1400 s 1390 m 1300 w	1150 - 900 (1000)
P - Co	3400 s	3000 s	1630 s	1470 m 1390 s 1300 w	1150 - 900 (1100)
P - Cd	3400 m	2950 m 2850 m	1630 m	1460 m 1390 s 1300 w	1120 s
P	3500 s 3300 s	2930 s 2840 m	1590 m	1455 s 1350 m 1290 m	1150 - 900 (1150)

The extent of displacement of the C-N-vibration served also for evaluation of the relative stability of the formed complexes. These series of stability were confirmed by determination of the equilibrium constant of complexes as well as by "mixed loading" studies.

The different complexes of poly(ethyleneimine methylthiourea) can be divided in two types by infrared spectroscopic studies, for which examples are given in Fig. 16.

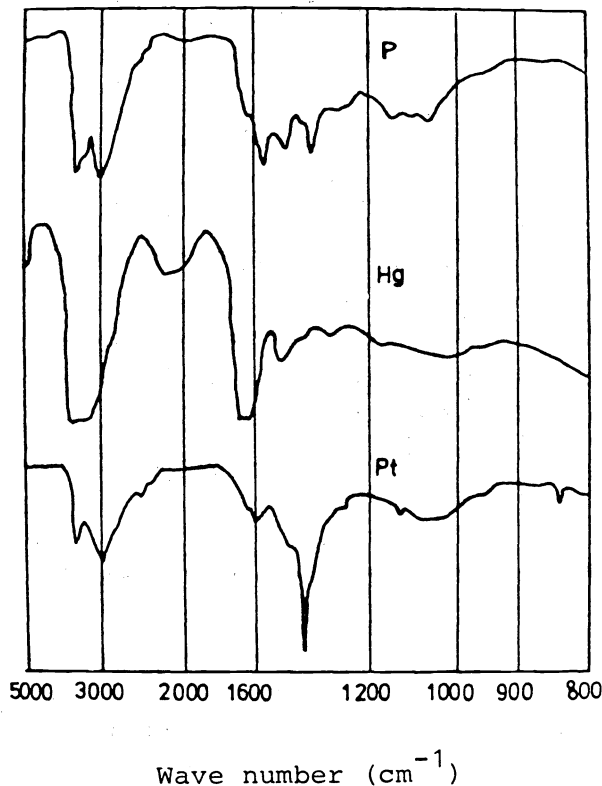
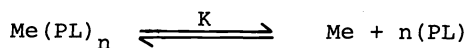


Fig. 16. Infrared spectra of poly(ethyleneimine methyl thiourea) (P) and the mercury and platinum complex.

In the case of the platinum complex, a strengthening and a displacement from 1360 to 1380 cm^{-1} of the C=S band could be observed. Mainly N-coordination of platinum was concluded from the displacement of $\nu_{\text{C-N}}$ to inferior and of $\nu_{\text{N-H}}$ to elevated wave numbers. On the other hand, the C=N C=S-band is completely missing in the spectrum of the mercury complex but the other displacements are existing. That means that there is sulfur as well as nitrogen coordination of the mercury ion.

Equilibrium Constants

For the complex forming reaction:



where is

Me = metal

PL = chelating unit of polymer ligand, and

n = coordination number of metallic ion,

the equilibrium constant K can be expressed by the following equation (Ref. 40):

$$K = \frac{\alpha(\alpha \cdot n \cdot C)^n}{1 - \alpha} \quad \begin{array}{l} C = \text{concentration of complex} \\ \alpha = \text{dissociation constant} \end{array}$$

The molar ratio method (Ref. 41,42) renders it possible to determine the dissociation constant spectro-photometrically. To this end, the extinction values were plotted versus the molar ratio of reagent to metal. The extinction values for a certain wave length were obtained by measuring a series of solutions at a constant pH containing a constant quantity of metal salt but different quantities of complex forming reagent.

The quantitative relations for the calculation of the dissociation constant from the extinction values are defined as follows:

$$\alpha = \frac{E_m - E_c}{E_m} \quad \begin{array}{l} E_m = \text{maximum extinction} \\ E_c = \text{extinction for a defined} \\ \quad \text{coordination number} \end{array}$$

Fig.17 shows the extinction curve of the poly(ethyleneimine)-copper complex, wherefrom an equilibrium constant of $K = 9.1 \cdot 10^{-16}$ could be calculated.

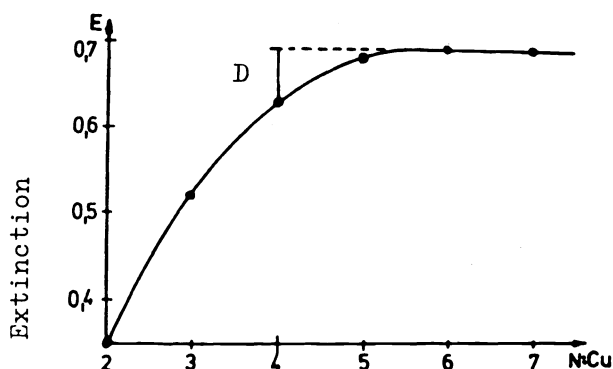


Fig. 17. Extinction curve of the poly(ethyleneimine)-copper complex for the determination of the dissociation constant according to the "molar ratio" method. Extinction is plotted versus the ratio of ligand N to copper. D represents the difference between maximal extinction and the extinction for the coordination number 4.

Determination of the dissociation constant according to the molar ratio method failed in the case of the nickel complex. The reason was that no curve could be obtained with a constant maximal extinction but with two maxima as depicted in Fig. 18. That indicates only the formation of complexes with coordination numbers of four and six.

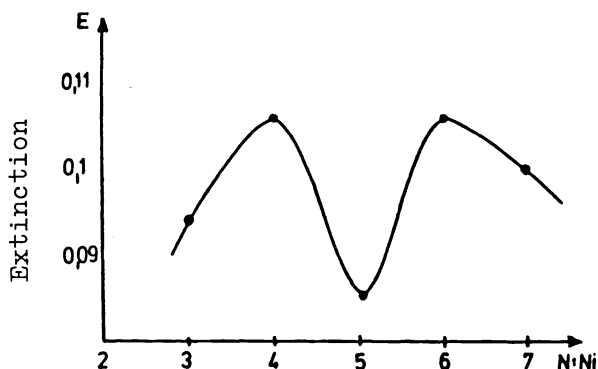


Fig. 18. Extinction curve of the poly(ethyleneimine)-nickel complex according to the "molar ratio" method.

"Mixed loading" and Selectivity

The selectivity of polymeric chelating agents for certain metals and the relative stability of the complexes formed can be investigated by simultaneous addition of different metal ions to the solution of the polymer ligand. This procedure for determination of stability series we call "mixed loading". The detailed results of these experiments are listed in Table 5, summarized in Table 6, and illustrated in Fig. 19.

TABLE 5. "Mixed loading" studies for different metals

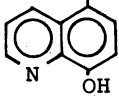


Structure unit of polymer ligand	Colour of complex	Cu ²⁺	Co ²⁺	Ni ²⁺	Au ³⁺	Pt ⁴⁺	Total
1 - CH ₂ - CH ₂ - NH -	Violet	60	28	20	90	36	234
2 $\begin{array}{c} - \text{CH}_2 - \text{CH}_2 - \text{N} - \\ \\ (\text{CH}_2)_2 \\ \\ \text{N} \\ / \quad \backslash \\ \text{S} = \text{C} \quad \text{NH} - \text{CH}_3 \end{array}$	Blue	49	32	32	54	52	219
3 $\begin{array}{c} - \text{CH}_2 - \text{CH}_2 - \text{N} - \\ \\ (\text{CH}_2)_2 \\ \\ \text{N} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \quad \\ \text{COOH} \quad \text{COOH} \end{array}$	Blue	68	9	18	21	80	186
4 - CH ₂ - CH - COOH	Violet	6	1	1	70	94	172
5 - CH ₂ - CH - NH - (CH ₂) ₃ - COOH	Colourless	2	1	1	100	15	119
6 $\begin{array}{c} - \text{CH}_2 - \text{CH} - \\ \\ \text{NH} - (\text{CH}_2)_3 - \text{CO} \\ \\ \text{NH} \\ \text{N} \quad \text{OH} \end{array}$ 	Brown	100	6	6	40	18	170
7 $\begin{array}{c} - \text{CH}_2 - \text{CH}_2 - \text{N} - \\ \\ (\text{CH}_2)_2 \\ \\ \text{NH} \\ \\ \text{CH}_2 \\ \\ \text{N} \quad \text{OH} \end{array}$ 	Green-brown	20	4	4	60	100	188
8 $\begin{array}{c} - \text{CH}_2 - \text{CH}_2 - \text{N} - \\ \\ (\text{CH}_2)_2 \\ \\ \text{NH} \\ \\ \text{O}_2\text{S} \\ \\ \text{N} \quad \text{OH} \end{array}$ 	Brown	45	36	35	16	40	182

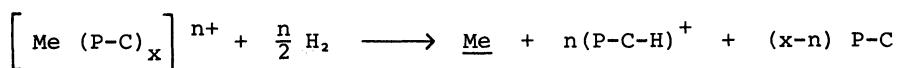
TABLE 6. Selectivity series of some polymer ligands

Number of polymer ligand	Complex stability and selectivity for metal ions
<u>1</u>	Au ³⁺ > Cu ²⁺ > Pt ⁴⁺ > Ni ²⁺ ~ Co ²⁺
<u>2</u>	Au ³⁺ ~ Pt ⁴⁺ ~ Cu ²⁺ > Ni ²⁺ ~ Co ²⁺
<u>3</u>	Pt ⁴⁺ > Cu ²⁺ » Au ³⁺ ~ Ni ²⁺ > Co ²⁺
<u>4</u>	Pt ⁴⁺ > Au ³⁺ » Cu ²⁺ ~ Ni ²⁺ ~ Co ²⁺
<u>5</u>	Au ³⁺ » Pt ⁴⁺ > Cu ²⁺ ~ Ni ²⁺ ~ Co ²⁺
<u>6</u>	Cu ²⁺ » Au ³⁺ > Pt ⁴⁺ > Co ²⁺ ~ Ni ²⁺
<u>7</u>	Pt ⁴⁺ » Au ³⁺ » Cu ²⁺ > Co ²⁺ ~ Ni ²⁺
<u>8</u>	Cu ²⁺ ~ Pt ⁴⁺ > Ni ²⁺ ~ Co ²⁺ > Au ³⁺

Studies by other methods on these properties, such as IR-spectroscopy, displacement experiments, and determination of equilibrium constant, confirmed the results. Generally, it can be stated that in these series the polymer ligand containing carboxyl groups exhibited the best selectivity. Polymer ligands with low selectivity are poly(ethyleneimine) and the thiourea derivative whereas the acetic acid derivative, poly(acrylic acid) and particularly the hydrolyzed poly(1-vinyl-2-pyrrolidinone), which is highly selective for gold, represents chelating agents with excellent selectivity.

Cleavage by Electrolysis

Beside the other methods for cleaving the metal from the polymer as mentioned above, we investigated the application of electrolysis to this purpose. The deposition of metallic ions in the form of the element during electrolysis necessitates a certain potential, called potential of deposition. The primary reaction, the formation of molecular hydrogen from hydrogen ions, is followed by the electrodeposition of the metal at the cathode. We may write the equation for the electrodeposition as follows:



Me = metal

P-C = polymer-bound chelating group

n = ionic charge number

x = coordination number

The part of ionized polymer ligand is converted by successive reactions to the uncharged polymer ligands, so that there is a complete recovery of the used polymer. For a full recovery it is necessary to avoid destruction of the polymer ligand by oxidation at the anode. To this end, we placed an ion exchange membrane between the space of anode and cathode in order to separate them. Fig. 20 shows the electrolysis cell.

The experimental results are summarized in Table 7.

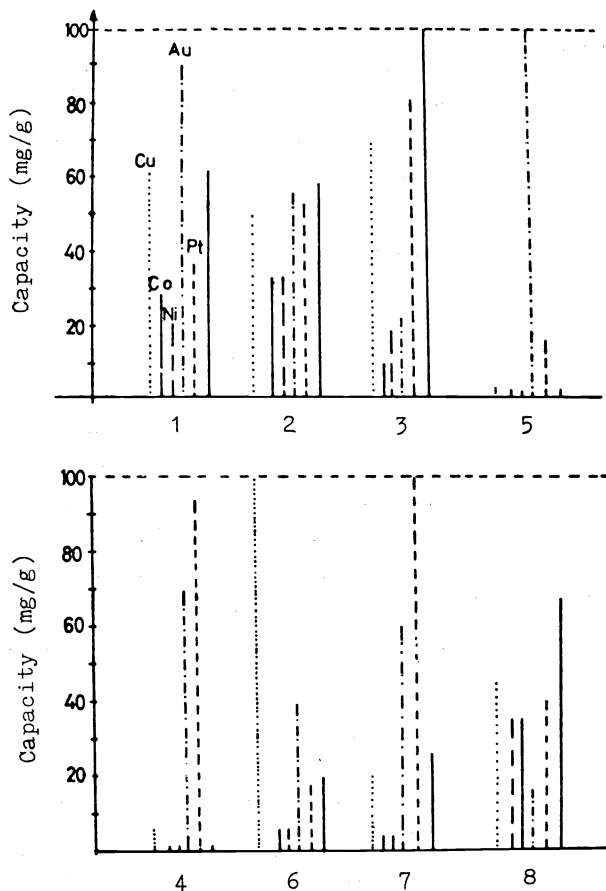


Fig. 19. Comparison of capacities in "mixed loading" studies of transition metals for some chelating polymers. For the numbers refer to Table 5.

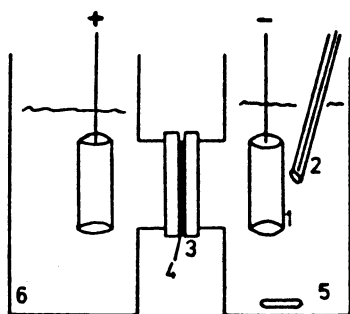


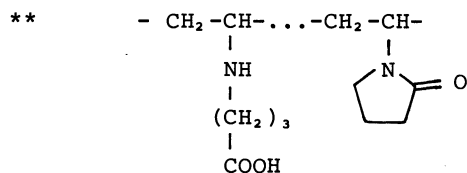
Fig. 20. Electrolysis cell with ionic exchange membrane.

- | | | | |
|---|-------------------------|---|---|
| 1 | Platinum net electrode | 5 | Solution of conductivity salt and polymer complex |
| 2 | Calomel electrode | 6 | Solution of conductivity salt |
| 3 | Teflon joint | | |
| 4 | Ionic exchange membrane | | |

TABLE 7. Experimental data of electrolysis studies

No.	Metal	A*	B*	C*	D*	E*	F*	G*	H*	H*
			(V)	(mg)	(mg)	(mg)	(mg)	(mg/g)	(mg/g)	(%)
<u>1</u>	Cu ²⁺	0.1 N KCl	-1.0	31.6	30.9	0.7	29.1	158	145.5	92
	Cu ²⁺	1 N NH ₃ / NH ₄ Cl	-1.1	31.6	30.3	1.3	28.8	158	144	91
	Ni ²⁺	0.1 N KCl	-1.2	60	No deposition of metal, generation of gas					
	Ni ²⁺	1 N NH ₃ / NH ₄ Cl	-1.2	60	No deposition of metal, generation of gas					
	Cd ²⁺	1 N KCl	-0.85	185	120	64	182	185	182	98
<u>2</u>	Cu ²⁺	0.1 N KCl	-1.0	34	33.5	0.5	34	170	170	100
	Au ³⁺	0.1 N KCl (Pt/Pt)	-1.3	39.6	No deposition of metal, potential of de- position was not reached					
	Au ³⁺	0.1 N KCl (Pt/Cu)	-1.3	39.6	No deposition of metal, generation of gas					
	Hg ²⁺	1 N KCl	-0.1	210	134.5	74.2	198	210	198	94
<u>3</u>	Cu ²⁺	1 N NH ₃ / NH ₄ Cl	-1.0	28.8	27.5	1.2	28.7	144	143.5	99
	Ag ⁺	1 N NH ₃ / NH ₄ Cl	50 mA const.	40	---	4	28	40	28	70
<u>4</u>	Cu ²⁺	0.1 N KCl	-1.0	27.5	25.5	2.0	27.1	137.5	135.5	98
<u>8</u>	Cu ²⁺	0.1 N KCl	-1.1	38	36.2	1.7	38	190	190	100
<u>9</u> **	Cu ²⁺	0.1 N KCl	-1.05	7	6.5	0.5	6.9	35	34.5	99

- * A Conductivity salt
 B Deposition potential
 C Initial total quantity of metallic ions
 D Deposited quantity of metal
 E Residual content of metal
 F Reloading of metal
 G Capacity before electrolysis
 H Capacity after electrolysis



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