Polymer Bulletin 13, 307–311 (1985)

**Polymer Bulletin**



# *Membrane Filtration*

## Poly(Ethyleneimine) as Complexing Agent for Separation of Metal Ions Using Membrane Filtration

**E. Bayer, B. Ya. Spivakov*, and K. Geckeler**

Institut für Organische Chemie der Universität, D-7400 Tübingen, Federal Republic of Germany

Summary

The complexation properties of poly(ethyleneimine) were investigated for cobalt, nickel, zinc, cadmium, and copper using membrane filtration. The elution curves of each metal were determined at different pH values in homogeneous phase. Poly(ethyleneimine) was found to be an effective complexing agent and suitable for retention and separation of metals in aqueous diluted solutions.

## Introduction

Polymers with complexing properties have gained considerable importance in terms of their potential applications in chemistry and technology. Besides investigations on the complexation of metal ions with insoluble resins (1,2), recently a method for the application of polymeric complexing agents in homogeneous phase has been developed (3,4). To this end, a series of nitrogen and sulfur containing polymers with chelating properties was synthesized and applied for the enrichment and separation of metal ions in homogeneous phase using membrane filtration.

In this paper, we report on the complexation of metals by poly(ethyleneimine) (PEI) in aqueous solutions for potential enrichment and separation of metal ions. Retention of different divalent metal ions was investigated as a function of filtrate volume and pH.

## Experimental

The metal salt solutions, as well as hydrogen chloride and sodium hydroxide solutions, which were used to adjust pH, were prepared from analytical grade chemicals (Merck). Poly(ethyleneimine) ($\bar{M}$ = 30 000 - 40 000 g·mol$^{-1}$) was membrane filtrated and dried in vacuo prior to use.

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* On leave from the Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, Moscow, USSR

Metal concentration in the filtrate and retentate was determined by atomic absorption spectroscopy on a Beckman 1248 spectrometer, pH measurements were carried out with an E 512 pH-meter (Metrohm). Membrane filtration studies were performed with a unit consisting of a plexiglass cell, a membrane with exclusion rate 10 000 (Berghof, Tübingen), a plexiglass reservoir, a selector (CNC-10) and a regulator (MF 2-2, Amicon). The pressure of nitrogen (300 kPa) was kept constant during membrane filtration.

For the determination of metal ion retention aqueous solutions of PEI and metal nitrates or chlorides were placed into the filtration cell. The total volume in the cell was kept constant at 40 ml, polymer concentration was 1 % and metal concentration 10 ppm. The reservoir contained water at a pH adjusted to the same value as in the cell solution. The system was pressurized, the cell solution stirred for 5 min by a magnetic stirrer and then washed with the reservoir solution at a flow rate of about 5 ml/min. The filtrate fractions were collected and subjected to metal analysis. The metal content of the cell solution was controlled before and after each membrane filtration run.

## Results and Discussion

The complexing properties of soluble poly(ethyleneimine) were investigated by means of membrane filtration for several divalent metal ions as a function of pH. Using this technique, it is possible to study chelating effects of polymeric agents in homogeneous phase (3). The membrane filtration system consisted of filtration cell, reservoir, magnetic stirrer and pressure source (4). Poly(ethyleneimine) (PEI) with an average molecular mass of 30 000-40 000 g $mol^{-1}$ was used as polychelatogene in the cell as 1 % solution. This concentration was high enough as the polymer contained a great excess of complexing groups in comparison to the metal concentration. By addition of the divalent metal salts the polymer complexes were formed in the cell. The metal ions not bound to the polymer at the pH adjusted were washed out with an excess of the reservoir solution.

Retention effects are illustrated in Fig. 1 and 2, which were obtained from the quotient of metal concentration in filtrate and retentate. To this end, samples of membrane filtrate were taken and analyzed by atomic absorption spectroscopy in dependence of the volume of membrane filtrate.

In general, it can be stated that for the metals cobalt, nickel, zinc and cadmium practically no or only slight complexation takes place at low pH values ($\leq 3$), that corresponds to the theoretical curve (a) in Fig. 2. This exponential function can be described by the equation:

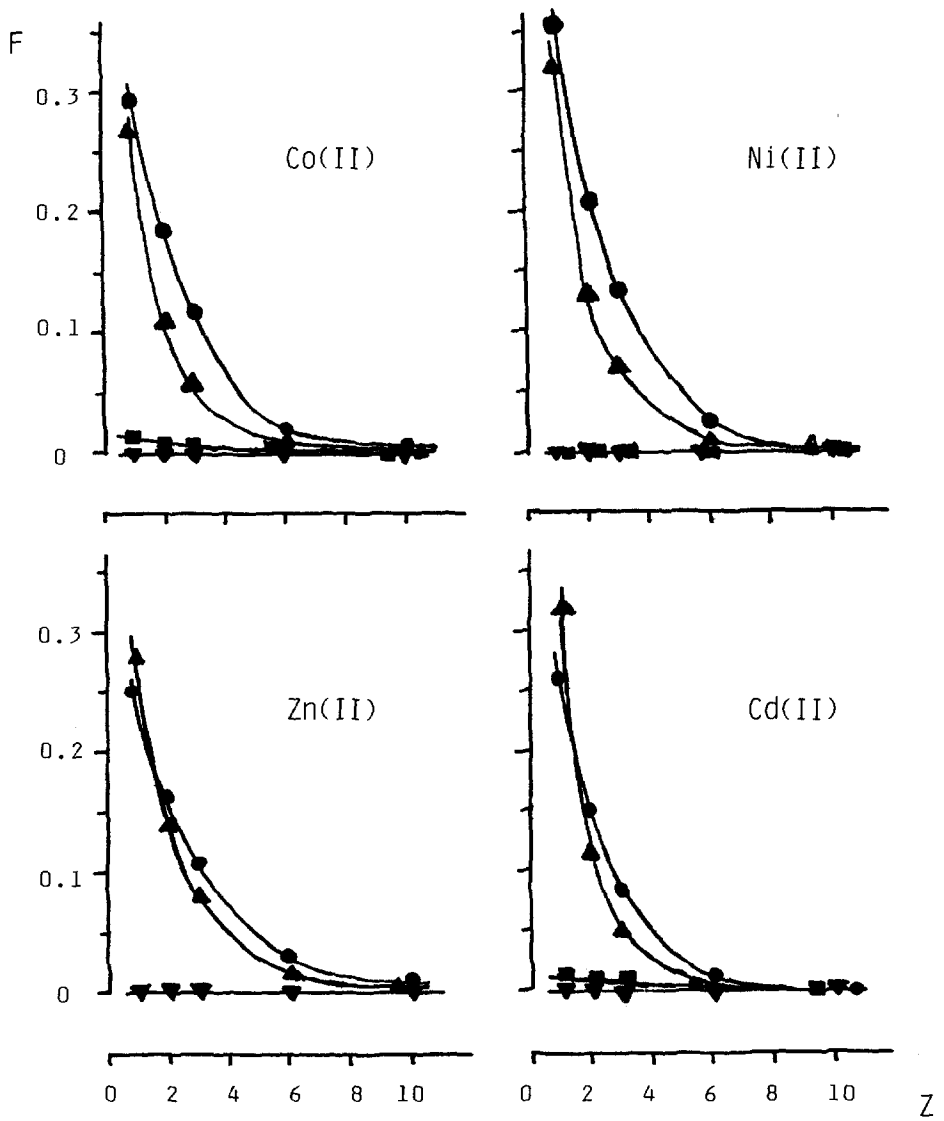


Fig. 1: Filtration quotient $F = C_f \cdot C_o^{-1}$ ($C_f$ = concentration in the filtrate, $C_o$ = initial concentration) for some divalent metal ions as a function of the ratio $Z = V_f \cdot V_o^{-1}$ ($V_f$ = volume of filtrate, $V_o$ = initial volume) at different pH values; PEI concentration 1 %), $C_o$ = 10 ppm; pH 2.1 (●), 3.2 (▲), 4.0 (■), 5.3 (▼).

$$C_f = C_o \cdot e^{-V_f/V_c}$$

where $C_f$ is concentration of metal in the filtrate, $C_o$ initial metal concentration, $V_f$ and $C_o$ are the volumes of filtrate and cell.

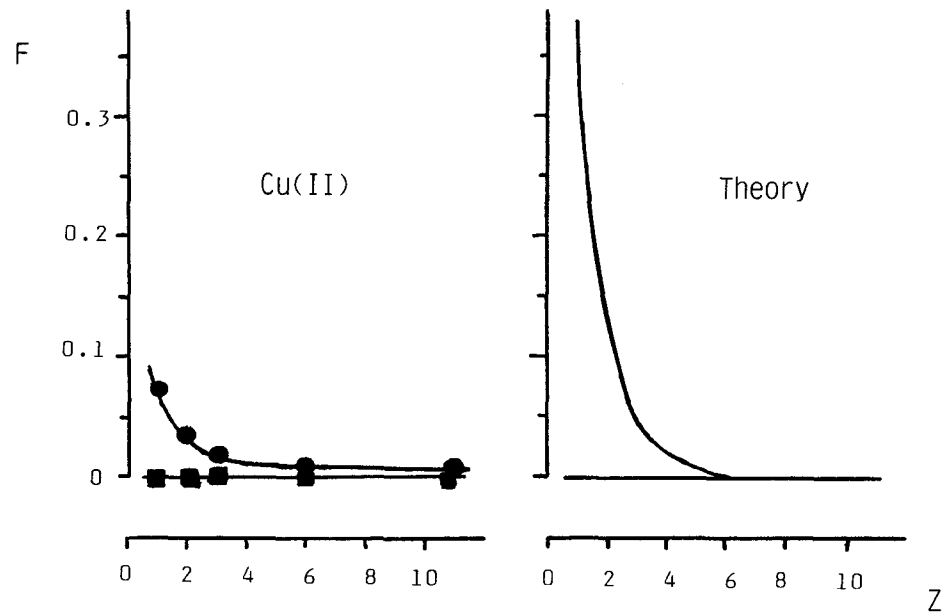


Fig. 2: Filtration quotient $F = C_f \cdot C_o^{-1}$ for copper and arbitrary metal ions as a function of the ratio $Z = V_f \cdot V_o^{-1}$; PEI concentration 1 %, $C_o$ = 10 ppm Cu(II); pH 2.1 (●), pH 3.2, 4.0, 5.3 (■); no retention (a), complete retention (b).

At higher pH values (pH 4 and 5) no metal ions could be determined in the membrane filtrate (Fig. 1). That means complete complexation by PEI and corresponds to the theoretical line (b) in the diagram (Fig. 2). Detailed studies showed that at pH 5 the retention was more than 99 % for all metals investigated. At pH 3 only copper was retained completely, whereas the other four metals were washed out in the filtrate. Thus, effective separation of one or of several metals simultaneously can be achieved at higher pH values.

In conclusion, PEI was found to be an interesting polymeric agent for the complexation of divalent metal ions in homogeneous phase and their retention during membrane filtration. Retention of metals showed a strong dependence on pH. At lower pH values copper, which forms more stable complexes with PEI, can be separated from all the other metals studied. Potentially, water-soluble polymeric reagents of such a type in combination with the procedure described could have applications in analytical separations as well as on a preparative scale.

Acknowledgement

The authors thank the Deutsche Forschungsgemeinschaft for financial support of this work.

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*Accepted February 11, 1985*