The Concentration and Separation of Cu$^{2+}$, Ni$^{2+}$, Fe$^{3+}$ Ions by Complexation with Poly(ethyleneimine) and Using A Suitable Membrane

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**Abstract**

The effects of water-soluble polymers on the concentration and separation of the aqueous solutions of the metal ions have been studied. EC-PEG 4000 alloy membrane was used as a filter for the concentration and separation of metallic ions. The permeability of this alloy membrane was studied, and it was found that it is permeable to Cu$^{2+}$ and Ni$^{2+}$ but not to Fe$^{3+}$ ions. The separation of metal ion pairs was performed by using this property of alloy membranes. In this study, the concentration of metal ions (Cu$^{2+}$, Ni$^{2+}$, Fe$^{3+}$) and the separation of metal ion couples have been recorded by using polyethyleneimine (PEI) at different pH values and polymer concentrations in accordance with the spectrophotometric results.

**INTRODUCTION**

Separation, purification, and concentration processes arise as important problems in industrial applications. Recently, conventional mass separation techniques such as distillation, crystallization, solvent extraction, etc., have been developed by utilizing semipermeable membranes. The concentration and separation of metal ions from their aqueous solutions by using semipermeable membranes can be realized by ultrafiltration. In this method, the polymer must have high selectivity for the metal ion or group, high binding capacity, narrow molecular weight distribution, and high water-solubility properties.

It is possible to form a complex between the polymer and the metal ion if the polymer shows a significant selectivity for the metal ion. Concentration and separation of metal ions can thus be achieved by complexing these species with a suitable water-soluble polymer. The principle of this process was proposed by Michaels [1].

**MATERIALS AND METHODS**

The poly(ethyleneimine) (PEI) used in this study was supplied from BDH. Cupric chloride, ferric chloride, and nickel chloride were obtained from Merck. Ethyl cellulose (EC) and polyethylene glycol

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(PEG 4000) used in the preparation of EC-PEG 4000 alloy membranes were obtained from Sigma and Merck, respectively.

**Preparation of alloy membranes**
EC-PEG 4000 alloy membranes are prepared by casting and recharacterized by the method given by Spychai et al [2]. Alloy membranes were obtained with PEG 4000 due to the fact that membranes without pores were only attained from ethyl cellulose. THF/CH$_2$Cl$_2$ and lactic acid were used as solvent and nonsolvent, respectively. After a relaxation period, the membrane casting solution was cast on a glass surface with a doctor blade. The films, which were immersed and precipitated in an n-hexane quench medium, were kept in an alcohol/water bath. Membranes obtained from EC only were not porous, but the addition of PEG resulted in the formation of pores. The membrane containing 20% PEG was suitable for ultrafiltration due to its water permeability and molecular weight cutoff (MWCO). The so-called molecular weight cutoff is the pure water flux. The EC-20% PEG membrane exhibited the highest water permeability and a MWCO of 900.

**Ultrafiltration experiments**
Ultrafiltration experiments were carried out in a stirred all (modified 401S Amicon cell) using the EC-20% PEG alloy membrane. The feed volume was 350 mL, the membrane surface was 18.5 cm$^2$. All experiments were performed at a pressure of 100 mmHg and 25°C. The pH of the feeds was adjusted to the desired values by addition of sodium hydroxide and hydrochloric acid.

The concentrations of Cu$^{2+}$, Ni$^{2+}$ and Fe$^{3+}$ were determined spectrophotometrically using a Hitachi 100-60 double-beam UV spectrophotometer. Cu$^{2+}$ concentration was measured at 430 nm as a diethyldithio-carbamate complex extracted with carbon tetrachloride, Ni$^{2+}$ as a dimethylglyoxime complex ($\lambda$=327 nm) extracted with chloroform, and Fe$^{3+}$ was determined in the form of a thiocyanate - Fe$^{3+}$ complex ($\lambda$=450 nm). The absorbances in the UV region of aqueous solutions of polymer and polymer ion complexes and the effect of pH on the complexation between polymer and metal ions were determined.

The equimolar mixture of the two metal ions in presence of the complexing agent was ultrafiltered. The concentrations of the metal ion and PEI were taken as 2x10$^{-3}$ M and 2x10$^{-3}$ gL$^{-1}$, respectively. The concentration of the retained metal ion was calculated by the following equation:

$$R = 1 - (C/C_o)$$ (1)

where C is the final metal ion concentration and $C_o$ is the initial feed concentration. The retention of metal ion pairs at the same conditions was also determined.

**RESULTS AND DISCUSSIONS**

Methods of separation using membranes are important economic developments of the last few years. Among them, ultrafiltration is the most economic [3-9]. The water permeabilities of the EC-PEG 4000 alloy membranes were measured at different pressures. The retention of metal ions at constant pressure but at different pH values was determined. It was found that the membrane is permeable to Cu$^{2+}$ and Ni$^{2+}$ but not to Fe$^{3+}$. Hydrolysis of Fe$^{3+}$ takes place at acid pH values.

The effect of PEI as complexing agents on the retentions of metal ions (Cu$^{2+}$, Ni$^{2+}$, Fe$^{3+}$) was studied at a pressure 100 mmHg and 25°C by using the EC-PEG 4000 alloy membranes. Retentions of Cu$^{2+}$, Ni$^{2+}$, Fe$^{3+}$ are shown in Figures 1,2,3 and
Figure 1. Effect of pH on retentions for Cu\textsuperscript{2+}-PEI, [Cu\textsuperscript{2+}]= 2\times10^{-3} M, [PEI]= 2\times10^{-3} units gL\textsuperscript{-1}. The open and solid symbols are pH values in the absence and presence of poly(ethyleneimine).

Figure 2. Effect of pH on retentions for Ni\textsuperscript{2+}-PEI, [Ni\textsuperscript{2+}]= 2\times10^{-3} M, [PEI]= 2\times10^{-3} units gL\textsuperscript{-1}. The open and solid symbols are pH values in the absence and presence of poly(ethyleneimine).

Figure 3. Effect of pH on retentions for Fe\textsuperscript{3+}-PEI, [Fe\textsuperscript{3+}]= 2\times10^{-3} M, [PEI]= 2\times10^{-3} units gL\textsuperscript{-1}. The open and solid symbols are pH values in the absence and presence of poly(ethyleneimine).

Table 1. Maximum retentions for Cu\textsuperscript{2+}, Ni\textsuperscript{2+} and Fe\textsuperscript{3+} solutions at different pH values in the presence of poly(ethyleneimine) (25°C).

<table>
<thead>
<tr>
<th>pH</th>
<th>%R (Cu\textsuperscript{2+})</th>
<th>pH</th>
<th>%R (Ni\textsuperscript{2+})</th>
<th>pH</th>
<th>%R (Fe\textsuperscript{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>37.0</td>
<td>3.1</td>
<td>52.0</td>
<td>2.0</td>
<td>30.0</td>
</tr>
<tr>
<td>3.1</td>
<td>52.0</td>
<td>5.1</td>
<td>44.0</td>
<td>3.1</td>
<td>52.0</td>
</tr>
<tr>
<td>5.1</td>
<td>76.0</td>
<td>6.9</td>
<td>65.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>86.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

summarized in Table 1.

In all cases, the binding capability between the complexing polymer and metal ion depends on pH and the retentions of metal ions increase with pH. The high retention of metal ions in the presence of PEI indicates a high degree of complexation increasing in the order of Cu\textsuperscript{2+} > Ni\textsuperscript{2+} > Fe\textsuperscript{3+}. PEI has a marked selectivity for Cu\textsuperscript{2+}. The retention of complex molecules with a branched or spherical structure is expected to be higher than that of linear elastic molecules with the same molecular weight. But this study, and the previous one [2], have shown that functional groups on the polymer (complexing agent) have a dominant effect in retention.

-CH\textsubscript{2}-CH\textsubscript{2}-N: + H\textsuperscript{+} ⇔ -CH\textsubscript{2}-CH\textsubscript{2}-NH\textsuperscript{+}

Protonation reaction

-CH\textsubscript{2}-CH\textsubscript{2}-N: + M\textsuperscript{m+} ⇔ -CH\textsubscript{2}-CH\textsubscript{2}-NM\textsuperscript{m+}

Complexation reaction

When the polymer:metal ion (weight/weight) ratio was increased, the retention was found to remain constant after the ratio of 1:1. Maximum retention was obtained at 2\times10^{-3} M metal ion and 2\times10^{-3} gL\textsuperscript{-1} PEI concentrations. The retentions are shown in Figures 4,5 and 6.

It is possible to separate any metal ion from an ion pair by using a polymer that exhibits a high selectivity for that metal ion. Equimolar mixtures of two metal salts were ultrafiltered in the presence of
complexing polymer. Polymer was added to the mixed salt feed to provide a metal ion1:metal ion2: polymer ratio of 1:1:1. In all cases, the feed concentrations of each metal ion and polymer were fixed at 2x10^{-3} M and 2x10^{-3} gL^{-1}, respectively. Cu^{2+}/Ni^{2+} and Cu^{2+}/Fe^{3+} ion couples were studied to separate Cu^{2+} ions in the presence of PEI at pH 5.1 and pH 3.1. The results are shown in Table 2. As can be seen from Table 2, PEI selectively forms more stable complexes with Cu^{2+} than with Ni^{2+} or Fe^{3+}. The results show that an ion pair can be separated by polymer selective for the Cu^{2+} ion.

**Table 2.** Retentions for [Cu^{2+}]/[Ni^{2+}] and [Cu^{2+}]/[Fe^{3+}] ion couples in the presence of poly(ethyleneimine) at pH 5.1 and 3.1.

<table>
<thead>
<tr>
<th>Complexing polymer</th>
<th>Metal Ion Couples</th>
<th>%R</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>[Cu^{2+}]/[Ni^{2+}]</td>
<td>Cu^{2+} (76.0) 78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni^{2+} (44.0) 22</td>
</tr>
<tr>
<td></td>
<td>[Cu^{2+}]/[Fe^{3+}]</td>
<td>Cu^{2+}(52.0) 51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe^{3+}(52.0) 47</td>
</tr>
</tbody>
</table>

To supply more evidence for the complexation PEI with metal ions, UV-visible spectrophotometric studies were carried out. The absorbances of the aqueous solutions, prepared at desired concentrations determined by ultrafiltration experiments, were recorded. The absorbance and wavelength maxima shift values for the metal ion-polymer couples are given in Table 3. The maximum absorbance of PEI shifts to higher wavelengths upon complexing with Fe^{3+}, Cu^{2+}, and Ni^{2+} ions. The maximum shift (~50 nm) was observed with Cu^{2+}, indicating the formation of a stable PEI/Cu^{2+} complex and this observation supports the results of the ultrafiltration experiments. It has been demonstrated that OH groups on PEI coordinate the metal ion [10].

The effects of applied pressure and pH of the aqueous solution on retentions for Cu^{2+}, Ni^{2+}, Fe^{3+} ions in the presence of PEI are given in Figure 7.
Table 3. The shifts in the value of wavelength maxima ($\lambda_{\text{max}}$) of PEI and PEI-metal ion couples.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Polymer + Metal Ion</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>2.63</td>
<td>PEI + Cu$^{2+}$</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>217</td>
<td></td>
<td>268</td>
</tr>
<tr>
<td></td>
<td>PEI + Ni$^{2+}$</td>
<td>3.16</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>PEI + Fe$^{3+}$</td>
<td>2.71</td>
<td>219</td>
</tr>
</tbody>
</table>

When the pressure and the pH of the solution increased the retentions of Cu$^{2+}$, Ni$^{2+}$, Fe$^{3+}$ ions increased.

The effect of pH on complexation is shown in Figure 8. The maximum absorbance values increase up to pH 5.1 for Cu$^{2+}$ and Ni$^{2+}$ and remains constant at higher pH values. However, for Fe$^{3+}$, maximum complexation is achieved at pH 3.1. At low pH values, the complexation of PEI with the metal ion is in competition with its protonation. At high pH values, complexation predominates due to decreasing H$^+$ concentration. However, at low pH values, the complexation of Fe$^{3+}$ is the primary reaction because of the stability of PEI/Fe$^{3+}$ complex. Maximum absorbance corresponding the PEI/Fe$^{3+}$ couple decreases at pH values higher than 3.0 because of the hydrolysis of Fe$^{3+}$.

The absorbance and wavelength maximum shift values for the PEI and PEI-metal ion pairs are given in Table 3. As clearly seen, shifts in the wavelengths and absorbances are indicators of the structural changes that occur on the molecules. Fe$^{3+}$, Ni$^{2+}$, and Cu$^{2+}$ form strong carbonyl complex. As a result of the interaction of Cu$^{2+}$, Ni$^{2+}$, and Fe$^{3+}$ with the nonbonding electrons in the carbonyl group of the alginic chain, a shift in the wavelength maxima takes place. This might be due to the n-π* transition. In conclusion, the concentration and separation of Cu$^{2+}$ ion from the Cu$^{2+}$/Ni$^{2+}$ couple and the Cu$^{2+}$/Fe$^{3+}$ couple by complexing with PEI and ultrafiltration of EC-PEG 4000 alloy membranes is proposed as a suitable method.

REFERENCES


