Concentration and Separation of Metallic Ions from Aqueous Solutions by Using EC-PEG 4000 Alloy Membranes

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SYNOPSIS

The concentration and separation of some metallic ions have been achieved by complexing these species with suitable macromolecules or with water-soluble polymers in ultrafiltration. The effect of water-soluble poly(vinyl alcohol) (PVA) on the concentration and separation of Cu^{2+}, Ni^{2+}, and Fe^{3+} ions have been investigated by using EC-PEG4000 alloy membranes in ultrafiltration experiments. The water permeability of the membranes has been measured at various pressures. The permeability of these membranes for metal ions, however, has been recorded at constant pressure but at different pH values. The highest water-permeable membrane is also permeable for Cu^{2+} and Ni^{2+}, but it shows a considerable retention for Fe^{3+}, probably as a result of the hydrolysis of Fe^{3+}. The retentions of metallic ions and metallic ion–PVA couples have been determined at constant pressure but varying pH and polymer concentration values. It has been shown that Fe^{3+}/Ni^{2+} pairs can well be separated by using PVA. © 1993 John Wiley & Sons, Inc.

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.[1] In this method, the polymer must have high selectivity for the metal ion or ion 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 first proposed by Michaels.[2]

We attempted to concentrate Cu^{2+}, Ni^{2+}, and Fe^{3+} ions and to separate the metal ion couples from very dilute solutions by using PVA at varying pH and concentration values. Spectrophotometric data and ultrafiltration results were interpreted in terms of complexation reactions.

EXPERIMENTAL

Materials and Methods

PVA (MW $\simeq$ 14,000) was supplied by BDH; EC and PEG4000 used in preparation of EC-PEG4000 alloy membranes were obtained from Sigma and Merck, respectively. Cupric chloride, ferric chloride, and nickel chloride were obtained from Merck. All solutions were prepared with freshly distilled water.

The concentrations of Cu^{2+}, Ni^{2+}, and Fe^{3+} were determined by a Hitachi 100-60 double-beam UV spectrophotometer. EC-PEG4000 alloy membranes used in ultrafiltration experiments were characterized as having a molecular weight cut off value of 900.

Retentions for the metal ions were recorded in the presence and absence of PVA at various pH values. All experiments were performed at 25°C. The

quantitative analysis of metal ions that were retained were done spectrophotometrically.

The concentration of the retained metal ion was found by the following equation[3]:

$$R = 1 - \frac{C}{Co}$$

where C is the final metal ion concentration and Co is the initial feed concentration. The retention of a mixture of metal ions at the same conditions was also recorded.

RESULTS AND DISCUSSION

The water permeability of the EC-PEG4000 alloy membranes prepared has been measured at various pressures. The permeability of these membranes for metal ions, however, has been recorded at constant pressure but at different pH values. It has been noticed that the highest water-permeable membrane is also permeable toward Cu^{2+} and Ni^{2+}, but has also shown a considerable retention for Fe^{3+} as a result of the hydrolysis of Fe^{3+}.

The effect of PVA as complexing agent on the retention of metal ions (Cu^{2+}, Ni^{2+}, Fe^{3+}) was studied at different pH values. In the presence of complexing polymer at 25°C and 100 mmHg, retentions of Cu^{2+}, Ni^{2+}, and Fe^{3+} are shown in Table I.

In all cases, the retentions of metal ions increase with pH. The high retention of metal ions in the presence of PVA indicates a high degree of complexation. Ultrafiltration and spectrophotometric studies confirmed that PVA complexes with the metal ions. The stability constant of these complexes increases in the order $Fe^{3+} > Cu^{2+} > Ni^{2+}$. Maximum retention was obtained at 2×10^{-3} M metal ion and 2×10^{-3} unit g L^{-1} PVA concentrations. At these optimum concentrations, the optimum pH values were then determined. When the polymer : metal ion ratio was increased, the retention was

Table I Retentions for Cu^{2+}, Ni^{2+}, and Fe^{3+} Solutions at Different pH Values in the Presence of PVA (Temp = 25°C)

pH	%R(Cu²⁺)	pH	%R(Ni²⁺)	pH	%R(Fe³⁺)
1.0	20.0	3.1	27.0	1.0	48.0
3.1	22.0	5.1	35.0	2.0	50.5
5.1	30.5	6.9	46.3	3.1	54.5
6.0	52.8				

Table II Retentions for Fe^{3+}/Ni^{2+} and Fe^{3+}/Cu^{2+} Ion Couples in the Presence of PVA at pH 3.1

Complexing Polymer	Metal Ion Couples		%R
PVA	Fe³⁺/Ni²⁺	Fe³⁺ (54.5)	69.4
		Ni²⁺ (27.0)	26.0
	Fe³⁺/Cu²⁺	Fe³⁺ (54.5)	71.5
		Ni²⁺ (22.0)	20.0

The figures in parentheses are the retention values when the metal ions were used alone in complexation with PVA.

found to remain constant after the ratio of 1 : 1; due to concentration polarization. This critical ratio is also important in reflecting the selectivity of PVA toward complexing with Fe^{3+} and Ni^{2+}.

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 ion$_1$: metal ion$_2$: polymer ratio of 1 : 1 : 1. In all cases, the feed concentrations of each metal ion and polymer were fixed at 2×10^{-3} M and 2×10^{-3} unit g L^{-1}, respectively.

Fe^{3+}/Ni^{2+} and Fe^{3+}/Cu^{2+} ion couples were studied to separate Fe^{3+} ions in the presence of PVA at pH 3.1. The results are shown in Table II.

As can be seen from Table II, PVA selectively forms more stable complexes with Fe^{3+} than with Ni^{2+} or Cu^{2+}. The results show that an ion pair can be separated by polymer selective for the Fe^{3+} ion.
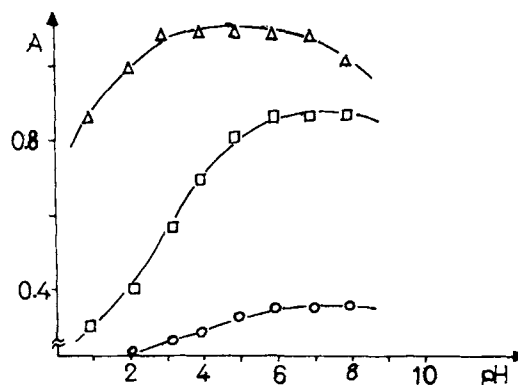

Figure 1 Effect of pH on complex formation between PVA and Cu^{2+}, Ni^{2+}, and Fe^{3+} metal ions. [PVA] = 2 $\times$ 10^{-3} units g L^{-1}, [Cu^{2+}] = [Ni^{2+}] = [Fe^{3+}] = 2 $\times$ 10^{-3} M. ($\triangle$) Fe^{3+}-PVA; ($\square$) Cu^{2+}-PVA; ($\bigcirc$) Ni^{2+}-PVA.

Table III   The Shifts in the Value of Wavelength Maxima (λ_{max}) of PVA and PVA Metal Ion Couples

Polymer	A	λ_{max} (nm)	Polymer + Metal Ion	A	λ_{max} (nm)
PVA	0.55	270	PVA + Fe^{3+}	1.17	290
			PVA + Cu^{2+}	0.87	274
			PVA + Ni^{2+}	0.64	274

To supply more evidence for the complexation of PVA with metal ions, UV-visible spectrophotometric studies were carried out. The absorbances of the aqueous solutions, prepared at the 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 III.

The maximum absorbance of PVA shifts to higher wavelengths upon complexing with Fe^{3+}, Cu^{2+}, and Ni^{2+} ions. The maximum shift ($\sim$ 20 nm) was observed with Fe^{3+}, indicating the formation of a stable PVA/Fe^{3+} complex and this observation supports the results of the ultrafiltration experiments. It has been demonstrated that OH groups on PVA coordinate the metal ion.[4]

The effect of pH on complexation is shown in Figure 1. The maximum absorbance values increase up to pH 6.1 for Cu^{2+} and Ni^{2+} and remains constant at higher pH values. However, for Fe^{3+}, maximum complexation is achieved at pH 3.0. At low pH values, the complexation of PVA 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 PVA/Fe^{3+} complex. Maximum absorbance corresponding the PVA/Fe^{3+} couple decreases at pH values higher than 3.0 because of the hydrolysis of Fe^{3+}.

In conclusion, the concentration and separation of the Fe^{3+} ion, from the Fe^{3+}/Ni^{2+} couple and the Fe^{3+}/Cu^{2+} couple by complexing with PVA in ultrafiltration involving the EC-PEG 4000 alloy membranes, can be proposed as a novel and suitable method.

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