

Concentration and Separation of Aqueous Solutions of Cu^{2+} , Ni^{2+} , Fe^{3+} by Dextran

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SYNOPSIS

The effects of water-soluble polymers on the concentration and separation of the aqueous solutions of the metal ions have been studied. The separation of metal ions can be possible by ultrafiltration-complexation process. The effect of Dextran, which is a water-soluble polymer, on the concentration and separation of metal ions (Cu^{2+} , Ni^{2+} , Fe^{3+}) have been investigated by using EC-PEG 4000 alloy membranes. The permeability of these membranes for metal ions has been recorded at constant pressure but different pH values. It has been noticed that the highest water-permeable membrane is also permeable towards Cu^{2+} and Ni^{2+} , but has shown a considerable retention for Fe^{3+} as a result of the hydrolysis of Fe^{3+} . The retentions of metallic ions and metallic-ion-Dextran couples have been determined at constant pressure but different pH and polymer concentration values. It has been shown that $\text{Fe}^{3+}/\text{Ni}^{2+}$ and $\text{Fe}^{3+}/\text{Cu}^{2+}$ couples can be separated by using Dextran. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The ultrafiltration is the most economic technique for the separation of metal ions by means of membrane process (electrodialysis, reverse osmosis, microfiltration, gas separation, etc.);¹ in addition, the osmotic pressure is very low in the ultrafiltration process.²

It is known that ultrafiltration is an effective method of purifying proteins from low molecular weight solutes but that it is not very specific in extracting a protein from other contaminant proteins because the difference between the dimensions of these compounds is not great enough to afford efficient separation.³ This principle has been successfully applied to the separation of metal ions by ultrafiltration after complexation with complexing macromolecules.

The retention capability of the membranes is affected by the shape, largeness, charge, and deformation of solute.⁴ The molecular weight of the solute is indirect. As a general rule, the linear elastic mol-

ecules are less retained than the branching and the spherical macromolecules having the same molecular weight. In our previous work,⁵ we had utilized the ultrafiltration technique for the separation of metal ions in the presence of PVA [poly(vinyl alcohol)] as the complexing agent.

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 Dextran at different pH values and polymer concentrations and determined in accordance with the spectrophotometric results.

EXPERIMENTAL

Materials and Methods

EC-PEG 4000 alloy membranes were prepared from EC (ethyl cellulose, Sigma) and PEG (polyethylene glycol, Merck, $M_w \sim 4000$) by the phase inversion process. THF/ CH_2Cl_2 (tetrahydrofuran/dichloromethane) system was used as solvent and lactic acid as nonsolvent. The membranes obtained from EC only were not porous, while addition of PEG resulted in the formation of pores. The membrane containing 20% PEG was suitable for ultrafiltration

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due to its water permeability and molecular weight cutoff (MWCO). The water permeability is a measure of the ability to transport fluid volume under the action of a pressure difference across the membrane. 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. Cupric chloride, ferric chloride, and nickel chloride were obtained from Merck. All solutions were prepared with freshly distilled water.

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 cm². 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.

In ultrafiltration, the effects of pH, concentration of the solutions of Cu²⁺, Ni²⁺, Fe³⁺, pressure, temperature, and rotational speed on the retention of the metal ions were studied. Because the EC-PEG 4000 alloy membranes are not stable to high temperatures, all experiments were performed at 25°C. Retentions were obtained for metal ions in the presence and absence of Dextran T-40 (Pharmacia, *M_w* ~ 40000) at different pH values and constant rotational speed.

The retention of a mixture of metal ions at the same conditions was also recorded.

Each metal ion was characterized by its retention,⁶ *R*:

$$R = 1 - \frac{C}{C_0}$$

where *C* is the final metal ion concentration and *C*₀ is the initial feed concentration. *R* is time dependent because at constant pressure the flow of solvent and solution diminish due to concentration polarization. The water permeability of the membranes remained

Table I Retentions for Cu²⁺, Ni²⁺, Fe³⁺ Solutions at Different pH Values in the Presence of Dextran (Temp = 25°C)

pH	%R(Cu ²⁺)	pH	%R(Ni ²⁺)	pH	%R(Fe ³⁺)
1.0	32.0	3.1	40.2	1.0	52.0
3.1	37.0	5.1	57.0	2.0	65.0
5.1	52.5	6.9	67.0	3.1	77.2
6.0	62.5				

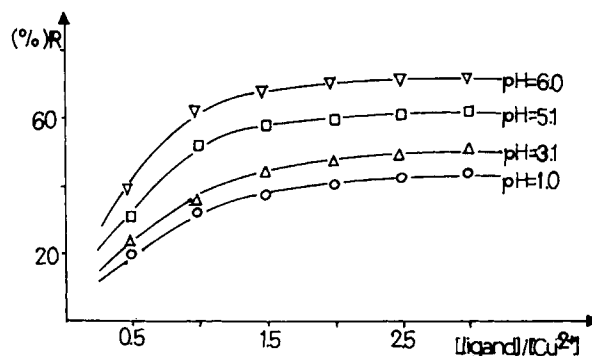


Figure 1 Change in retentions of cupric ions in the presence of Dextran with [Dextran]/[Cu²⁺] ratio at four pH values. [Cu²⁺]: 2 × 10⁻³ M.

constant after 2 h and, consequently, the UF process was applied for 2 h before spectrophotometric measurements.

The concentrations of Cu²⁺, Ni²⁺, Fe³⁺ were determined by spectrophotometry with "Hitachi 100-60" double beam spectrophotometer. Cu²⁺ was measured at 430 nm as a diethyldithiocarbamate complex extracted with carbontetrachloride, Ni²⁺ as a dimethylglyoxime complex (λ = 327 nm) extracted with chloroform, and Fe³⁺ was determined in the form of a thiocyanate-Fe³⁺ complex (λ = 450 nm).

RESULTS AND DISCUSSION

The water permeability of the membranes produced 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 towards Cu²⁺ and Ni²⁺ but has shown a considerable rejection for Fe³⁺ as a result of the hydrolysis of Fe³⁺.

The effect of Dextran as complexing agents on the retentions of metal ions (Cu²⁺, Ni²⁺, Fe³⁺) was studied at a pressure 100 mmHg and at 25°C by using the EC-PEG 4000 alloy membranes. Retentions of Cu²⁺, Ni²⁺, Fe³⁺ are shown in Table I.

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 Dextran indicates a high degree of complexation increasing in the order of Cu²⁺ < Ni²⁺ < Fe³⁺. Dextran has a marked selectivity for Fe³⁺.

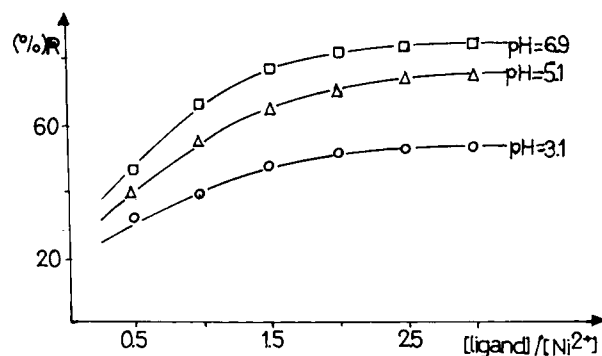


Figure 2 Change in retentions of nickel ions in the presence of Dextran with $[\text{Dextran}]/[\text{Ni}^{2+}]$ ratio at four pH values $[\text{Ni}^{2+}] : 2 \times 10^{-3} \text{ M}$.

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 $2 \times 10^{-3} \text{ M}$ metal ion and $2 \times 10^{-3} \text{ unit g} \cdot \text{L}^{-1}$ Dextran concentrations. The retentions are shown in Figures 1, 2, and 3.

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 $2 \times 10^{-3} \text{ M}$ and $2 \times 10^{-3} \text{ unit g} \cdot \text{L}^{-1}$, respectively.

$\text{Fe}^{3+}/\text{Ni}^{2+}$ and $\text{Fe}^{3+}/\text{Cu}^{2+}$ ion couples were studied to separate Fe^{3+} ions in the presence of Dextran pH 3.0. The results are shown in Table II.

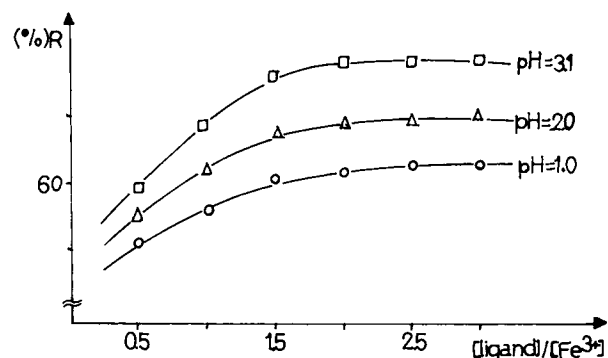


Figure 3 Change in retentions of ferric ions in the presence of Dextran with $[\text{Dextran}]/[\text{Fe}^{3+}]$ ratio at four pH values $[\text{Fe}^{3+}] : 2 \times 10^{-3} \text{ M}$.

Table II Retentions for $\text{Fe}^{3+}/\text{Ni}^{2+}$ and $\text{Fe}^{3+}/\text{Cu}^{2+}$ Ion Couples in the Presence of Dextran at pH 3.0

Complexing Polymer	Metal Ion Couples		%R
Dextran	$\text{Fe}^{3+}/\text{Ni}^{2+}$	Fe^{3+} (77.2)	80.0
		Ni^{2+} (40.2)	82.4
	$\text{Fe}^{3+}/\text{Cu}^{2+}$	Fe^{3+} (77.2)	82.4
		Cu^{2+} (37.0)	12.2

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

As can be seen from Table II, when Dextran was added into the $\text{Fe}^{3+}/\text{Ni}^{2+}$ and $\text{Fe}^{3+}/\text{Cu}^{2+}$ mixtures, Cu^{2+} and Ni^{2+} have showed a low degree of retention, while for Fe^{3+} it has been over 80%. Dextran 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 a polymer selective for Fe^{3+} ion.

In order to supply more evidence for the complexation of Dextran 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 complexation of Dextran with the metal ions has been proved by its wavelength maxima shift from 266 nm to 287 nm with Fe^{3+} , to 270 nm with Ni^{2+} , and to 270 nm with Cu^{2+} . The maximum shift ($\sim 20 \text{ nm}$) was observed with Fe^{3+} , indicating the formation of stable Dextran/ Fe^{3+} complex, and this observation sup-

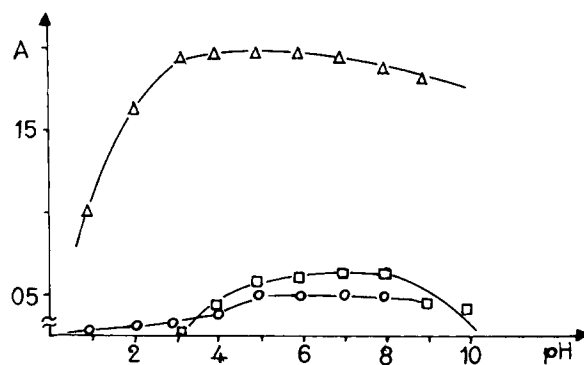


Figure 4 Effect of pH on complex formation between Dextran and Cu^{2+} , Ni^{2+} , Fe^{3+} metal ions. $[\text{Dextran}] = 2 \times 10^{-3} \text{ units g} \cdot \text{L}^{-1}$, $[\text{Cu}^{2+}] = [\text{Ni}^{2+}] = [\text{Fe}^{3+}] = 2 \times 10^{-3} \text{ M}$. (Δ) Fe^{3+} -Dextran, (\blacksquare) Cu^{2+} -Dextran, (\circ) Ni^{2+} -Dextran.

ports the results of the ultrafiltration experiments. It has been demonstrated that OH groups and oxygen atoms on Dextran coordinate the metal ion.⁷

The effect of pH on complexation is shown in Figure 4. The maximum absorbance values increase up to pH = 6.0 for Cu²⁺ and Ni²⁺ and remain constant at higher pH values. However, for Fe³⁺, maximum complexation is achieved at pH = 3.1. At low pH values, the complexation of Fe³⁺ is the primary reaction because of the stability of Dextran/Fe³⁺ complex. On the other hand, at high pH values, hydrolysis of Fe³⁺ predominates.

In conclusion, the concentration and separation of Fe³⁺ ion from Fe³⁺/Ni²⁺ couple by complexing with Dextran in ultrafiltration involving the EC-PEG 4000 alloy membranes can be proposed as a novel and suitable method.

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