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Donnan Membrane Effect-Aided Separation of Metal Cyanide Complexes by Hyperfiltration through Cellulose Acetate Membranes

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Abstract

Permeation behavior of cyanide complexes of copper, zinc, and silver through cellulose acetate membranes was investigated in the presence of "activating salt" (succinate or polyvinyl sulfate). In hyperfiltration with high-performance membranes (CA-87), both activating salts effectively enhanced the permeability of negatively charged Group Ib metal (I) cyanide complexes (Donnan membrane effect); the phenomenon was caused by selective affinity of these metal cyanide complexes to the membrane phase. However, with low-performance membranes (CA-75) such selective permeations were reduced by a contribution of increased solute–solvent flow, and all the metal cyanide complexes showed relatively high permeabilities. The polymer-type activating salt, polyvinyl sulfate, did not permeate through the low-performance membrane but showed an effectiveness in enhancing the permeability of the cyanide complexes under low-pressurized conditions. Taking advantage of this, a new technique, a Donnan membrane effect-aided hyperfiltration-ultrafiltration, was developed for selective separation of metal cyanide complexes. A mutual separation of a mixture of silver and zinc cyanide complexes or a mixture of copper and zinc complexes was successfully achieved. The activating salt, polyvinyl sulfate, was recycled and reused in this separation system.

INTRODUCTION

A great number of basic and practical studies have been reported on a hyperfiltration process aimed for desalination (*1, 2*). These have naturally been concerned with the rejection characteristics of solutes and not with the permeation of some specific solutes through the hyperfiltration membrane. It would be meaningful if separation between solutes by simple filtration under hydraulic pressure could be attained. From this point of view, use of Donnan

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membrane effect (*3*) may be an effective means of enhancing the permeability of specific solutes in a solution subjected to hyperfiltration.

Hoffer and Kedem studied the negative rejection of hydrogen ion by hyperfiltrating ($CuSO_4 + H_2SO_4$) or ($CuCl_2 + HCl$) solution through a cationic charged membrane (*4*, *5*). Lonsdale et al. made a theoretical approach to such phenomena by studying the permbehavior of chloride ion in the presence of citrate ion through uncharged hyperfiltration membranes (*6*). Golomb hyperfiltrated a citrate-buffered gold plating rinse with a cellulose acetate membrane (*7*) and reported enhanced permeation or negative rejection of the dicyanoaurite(I) species. Later, Kamizawa et al. (*8*) restudied the same system and summarized the phenomena that a less permeable ion such as citrate improved the permeability of a more permeable ion of like charge such as $Au(CN)_2^-$.

In the previous paper (*9*) we investigated systems similar to gold plating rinse for the permeability of other metal cyanide complexes, and found that anionic cyanide complexes of only Group Ib family metal ions exhibited improved permeabilities as compared with other metal cyanide complexes. By taking advantage of this phenomenon, a selective enrichment of Group Ib metal cyanide complexes in the permeate and their separation from other coexisting metals could be achieved in the presence of "membrane-impermeable" citrate salt. However, in order for such a process to be of practical value, the impermeable salts or "activating salts" which affect the permeability of other ionic species must be recycled and reused effectively.

With respect to the above notion, a polymer electrolyte is considered to be a suitable choice for the activating salt, because a polymer is not permeable through a hyperfiltration membrane nor a thick ultrafiltration membrane. In the present report we deal with the effectiveness of polyvinyl sulfate as an activating salt. The permselectivity of cyanide complexes through cellulose acetate membranes of various salt or solute rejection performance is also investigated. A new technique, a Donnan membrane effect-aided hyperfiltration-ultrafiltration, is proposed for the selective separation of ionic solutes.

EXPERIMENTAL

Reagents

Cellulose acetate powder was purchased from Eastman Kodak Co. (acetyl content 39.8 ± 0.5%, ASTM viscosity 3 ± 1 s). Acetone and formamide, used for the preparation of membranes, were reagent-grade commercial products. Potassium polyvinyl sulfate was obtained from Wako Pure Chemical Co. (for colloidal titration, $n = 1500$ up, esterification degree 95.2%). Other reagents were also reagent-grade chemicals and used without further purification.

For our metal cyanide complex, a commercial reagent (sodium dicyanoargentite) or a combination of metal nitrates with potassium cyanide was used. Since silver(I), copper(I), and zinc(II) have relatively high complex stability constants with cyanide ion (Ag^+/CN^-: $\beta_2 = 21.1$, $\beta_3 = 22.0$; Cu^+/CN^-: $\beta_2 = 14.6$, $\beta_3 = 18.0$, $\beta_4 = 19.6$; Zn^{2+}/CN^-: $\beta_2 = 11.1$, $\beta_3 = 16.1$, $\beta_4 = 19.6$) (*10*), the complexes formed were stable under the present hyperfiltration conditions.

Membranes

Cellulose acetate membranes were prepared by a casting procedure similar to that described in the previous report (*9*). Cellulose acetate (17 g) was dissolved in a mixture of formamide (27 g) and acetone (56 g), and cast to a 200-μm thickness. The solvent was allowed to evaporate at 25°C for 30 s. The membrane was then treated with water at 0–4°C. Membranes with different solute-rejection characteristics were prepared by controlling the annealing temperature at 75, 80, and 87°C (CA-75, CA-80, and CA-87, respectively) in water.

Hyperfiltration

A batch-type hyperfiltration cell of 16.6 cm^2 effective membrane area and 300 mL feed capacity (Atsuryoku Kiki Engineering Co., Tokyo) was used. Permeation experiments were performed at 5–20 atm and 25°C. Before and after each permeation experiment, the membrane was successively tested for water flux with pressurized pure water, and the absence of any damage or deterioration during the experiment was confirmed.

The permeation experiments were carried out with 250 mL feed solutions. The first 5 mL of the permeated solution were discarded and the second 5 mL were collected. The metal concentration in the permeate was determined by atomic absorption spectrometry. The absorption measurement was often strongly affected by coexisting salts, which made it necessary to construct calibration lines appropriate to each solution system. The concentration of activating salts was determined indirectly by measuring the cation (potassium) concentrations by atomic absorption. The permeability (*P*) of solute was defined by

$$P = \frac{\text{concentration of solute in the permeate } (C'')}{\text{concentration of solute in the feed } (C')} \qquad (1)$$

RESULTS AND DISCUSSIONS

The structure and the concentration of activating salts are the important factors for the ion-selective separation through a membrane. Figure 1 shows the effect of two types of activating salts, succinate and polyvinyl sulfate, on the permeation behavior of dicyanoargentite, $Ag(CN)_2^-$, through cellulose acetate membranes. Under the experimental conditions (pH 6.7), both the activating salts exist as totally ionized species. With a high performance membrane (CA-87), the permeability of dicyanoargentite increased as the concentration of the activating salt increased, and succinate was more effective than polyvinyl sulfate in enhancing the permeability. Similar volumetric permeate fluxes were obtained for both the activating salts. With

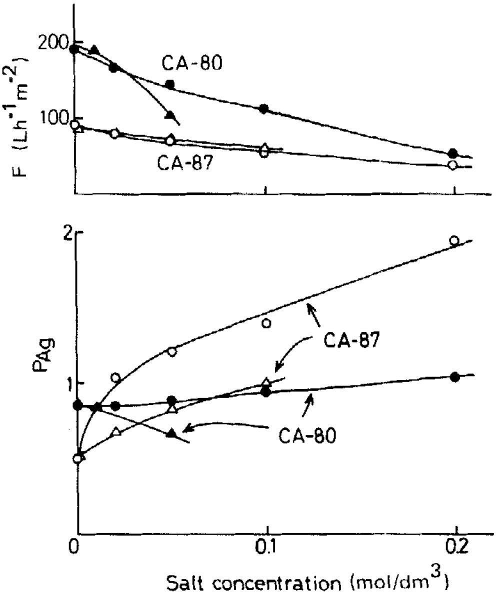


FIG. 1. Effect of activating salt concentration on the permeation behavior of dicyanoargentite (I). P_{Ag}, permeability of $Ag(CN)_2^-$; F, flux of permeate solution. Membrane: CA-80 (● succinate, ▲ polyvinyl sulfate), CA-87 (○ succinate, △ polyvinyl sulfate). Feed: 0.5 mM $NaAg(CN)_2$ with potassium succinate (pH 6.7) or potassium polyvinyl sulfate at 20 kg/cm^2 and 25°C. Concentration of polyvinyl sulfate is based on monomer unit.

a low performance membrane (CA-80), succinate induced only a minor increase in Ag permeability, and polyvinyl sulfate even caused a decrease. The fluxes decreased as the concentrations of the activating salts increased, as was observed with CA-87. However, with CA-80 the decrease in flux was much more pronounced for polyvinyl sulfate than for succinate.

Permeation behavior of a mixture of silver and zinc cyanide complexes was studied in the absence and in the presence of activating salt (Table 1). With a high-performance membrane (CA-87), enhanced permeability was observed only for the silver complex. The permeability of both the activating salts was very low. A similar behavior was reported for other transition metals in a previous paper (*9*). When a low performance membrane (CA-75) was used, the effect of the activating salts in enhancing permeation was not pronounced, since the permeability of the complexes was already high with this membrane. However, the enhancement was more distinct when the permeation was carried out at 5 atm rather than at 20 atm. Succinate was quite permeable through CA-75, but polyvinyl sulfate was permeable to only a limited extent.

To understand the permeation behavior of CA-75 in detail, the effect of activating salt concentration and operating pressure was studied further. Figure 2 shows the flux and the permeability in the filtration of a mixed solution of silver and zinc cyanide complexes. Under high operating pressure (20 atm), succinate was more effective in enhancing the permeability of complexes. A decreased permeability was observed with polyvinyl sulfate, as already noticed in Fig. 1. Under low operating pressure (5 atm), on the other hand, polyvinyl sulfate proved to be more effective than succinate. The permeability of both the silver and zinc complexes increased markedly as the concentration of polyvinyl sulfate increased.

A further investigation of CA-75 membrane showed that the permeability of zinc complex in the absence of activating salt changed markedly after

TABLE 1
Permeability of Metal Cyanide Complexes[a]

Activating salt	CA-87 (20 atm)[b]			CA-75 (20 atm)[b]			CA-75 (5 atm)[b]		
	P_{Ag}	P_{Zn}	P_{Act}	P_{Ag}	P_{Zn}	P_{Act}	P_{Ag}	P_{Zn}	P_{Act}
None	0.70	0.07	—	0.96	0.65	—	0.95	0.55	—
Succinate	1.40	0.09	0.03	1.04	0.94	0.81	1.01	1.01	0.86
Polyvinyl sulfate	1.00	0.03	0.01	0.99	0.57	0.06	1.49	0.99	0.10

[a] Feed: 0.5 m*M* $Zn(NO_3)_2$, 0.5 m*M* $AgNO_3$, and 4 m*M* KCN with 0.1 *M* activating salt; concentration of polyvinyl sulfate is based on monomer unit.

[b] Figures in parentheses indicate the pressure applied in the permeation study.

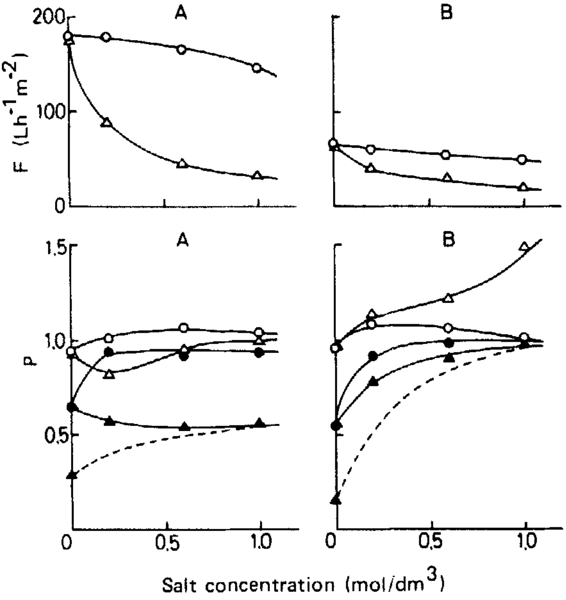


FIG. 2. Flux and permeability of a mixture of silver and zinc cyanide complexes as a function of activating salt concentration. P_{Ag} (○ succinate, △ polyvinyl sulfate), P_{Zn} (● succinate, ▲ polyvinyl sulfate): permeability of metal cyanide complex. F: flux of the permeate solution. Membrane: CA-75. Feed: 0.5 m*M* $AgNO_3$, 0.5 m*M* $Zn(NO_3)_2$, and 4 m*M* KCN with potassium succinate (pH 6.7) or potassium polyvinyl sulfate. Applied pressure: A, 20 kg/cm^2; B, 5 kg/cm^2. Dashed lines show the permeation behavior of "treated" membranes; the membranes were subjected to hyperfiltration treatment with 0.1 *M* polyvinyl sulfate before use.

hyperfiltration treatment with polyvinyl sulfate solution, which was not the case with succinate solution. This indicates that polyvinyl sulfate was adsorbed dynamically on the membrane, which caused the membrane to behave as if it was an anionic-charged membrane. The decreased permeability of zinc complex after hyperfiltration treatment with 0.1 *M* polyvinyl sulfate is also shown in Fig. 2 (dashed lines).

The permeation behavior under dialysis conditions was also investigated. A two-compartment glass cell (*10*) was separated by a cellulose acetate membrane. A "feed" solution containing metal cyanide complexes and activating salt was placed in one side of the cell (feed side), and an equal volume of pure water was placed in the other (permeate side). The permeation of silver and zinc complexes to the permeated side cell was monitored to give the time–concentration profiles shown in Fig. 3. When high performance membrane (CA-87) was used, the permeation of zinc did not take place, and succinate was found to be more effective than polyvinyl sulfate in enhancing the permeation of silver. This is in good agreement with the results of the hyperfiltration experiment in Table 1. On the other hand, when the low performance membrane (CA-75) was used, the enhanced permeation of zinc as well as of silver was observed, and polyvinyl sulfate was found to be more effectively enhancing than succinate for the permeation of both the metal cyanide complexes. These results again verify the usefulness of polyvinyl sulfate as an activating salt to attain the enhanced permeation of metal complexes through the low performance membrane.

In a hyperfiltration system, the permeation behavior of a solute can be described by the following phenomenological equations (*12*),

$$J_v = L_p(\Delta P - \sigma \Delta \pi) \tag{2}$$

$$J_s = B_s \Delta C_s + (1 - \sigma) J_v \bar{C}_s \tag{3}$$

where J_v is the volumetric flux and J_s is the flux of a solute. L_p and B_s represent permeability coefficients of solution and solute, respectively. σ is the reflection coefficient, and $\bar{C}_s$ is the average salt concentration in the membrane.

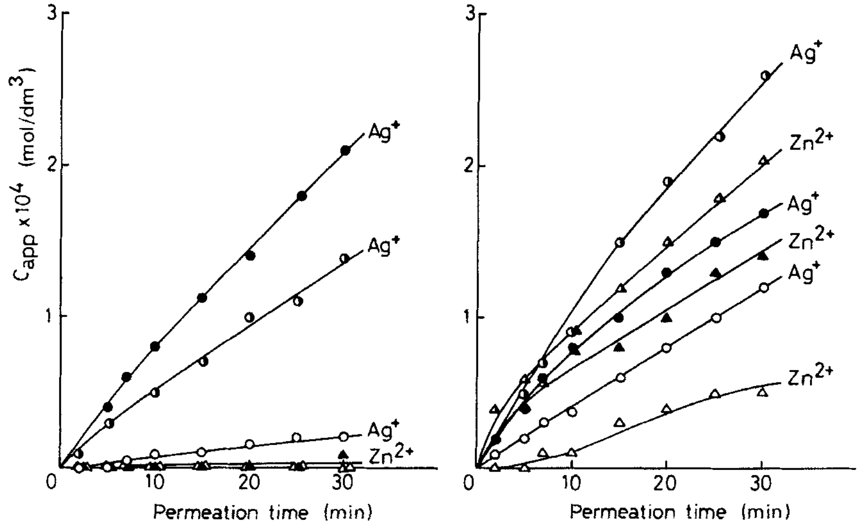


FIG. 3. Permeation of a mixture of silver and zinc cyanide complexes through a cellulose acetate membrane under unpressurized conditions. Membranes: CA-75, CA-87. Feed side: 0.5 m*M* $AgNO_3$, 0.5 m*M* $Zn(NO_3)_2$ and 4 m*M* KCN with 0.10 *M* activating salt (none: ○ Ag, △ Zn; succinate: ● Ag, ▲ Zn; polyvinyl sulfate: ◐ Ag, ◭ Zn). Permeate side: pure water.

For a high performance membrane, reflection coefficient σ is near unity, and Eq. (3) is rewritten as:

$$J_s = B_s \Delta C_s \tag{4}$$

Under the assumption that a partition equilibrium of solute exists between the membrane and the feed, the solute permeability coefficient (B_s) is proportional to the product of the partition coefficient (K_s) and the diffusion coefficient (D_s). Therefore it is found from Eq. (4) that the permeation behavior of the solute is dominated by partition and diffusion processes, and various reverse osmosis data for inorganic and organic salts have been explained by this model ("solution-diffusion model") (*13*).

However, when a membrane-impermeable ion coexists in the feed, the permeation behavior of permeable salts is significantly influenced by the so-called Donnan membrane effect. Consider that the concentration of membrane-permeable anion is C' and C'_m in the interface of the feed side and the membrane side, respectively, and the concentration of membrane-impermeable anion is X in the feed solution. Then the apparent partition coefficient β for the 1–1 electrolyte can be expressed as

$$\beta = C'_m / C' = K_s \sqrt{1 + (X/C')} \tag{5}$$

where K_s is a standard partition coefficient which is defined by the difference in the chemical potential of the solute between the membrane and the feed. Equation (5) suggests that the partition of the membrane-permeable anion to the membrane is significantly affected by the concentration of the membrane-impermeable anion (X). From Eqs. (1), (4), and (5), the permeability P can be represented as

$$P = \frac{C''}{C'} = \frac{\sqrt{1 + X/C'}}{1 + J_v/B_s} \tag{6}$$

Equation (6) indicates that permselectivity is basically dominated by the order of permeability coefficient of each solute (B_s) when the volumetric flux (J_v) is constant. However, the difference of solute permeability can be enhanced with the increase of membrane-impermeable anion concentration. Therefore, enhanced permeation by some specific salts may be achieved by using a high performance membrane. In fact, by using a high performance cellulose acetate membrane, Group Ib family metal cyanide complexes such as $\mathrm{Cu^I(CN)_2^-}$, $\mathrm{Ag^I(CN)_2^-}$, and $\mathrm{Au^I(CN)_2^-}$ can be concentrated in the permeate and separated from other transition metal cyanide complexes in the feed solution (*9*).

For a low performance membrane, however, the reflection coefficient is not near unity. In this case, the second term in Eq. (3) becomes significant and seems to lead to a diminished net Donnan Membrane effect; that is, the permeation of the solute is not dominated by the solution-diffusion mechanism. However, it is found from Eq. (2) that the volumetric flux (J_v) can be reduced by decreasing the operating pressure Δp, and hence the solute–solvent flow can be minimized. Then the contribution of solution-diffusion mechanism to the solute flux becomes dominant, and enhanced permeability can be expected in the presence of a membrane impermeable salt. In fact, enhanced permeation behavior can be realized under low pressure conditions (Fig. 2) and unpressurized conditions such as concentration dialysis (Fig. 3).

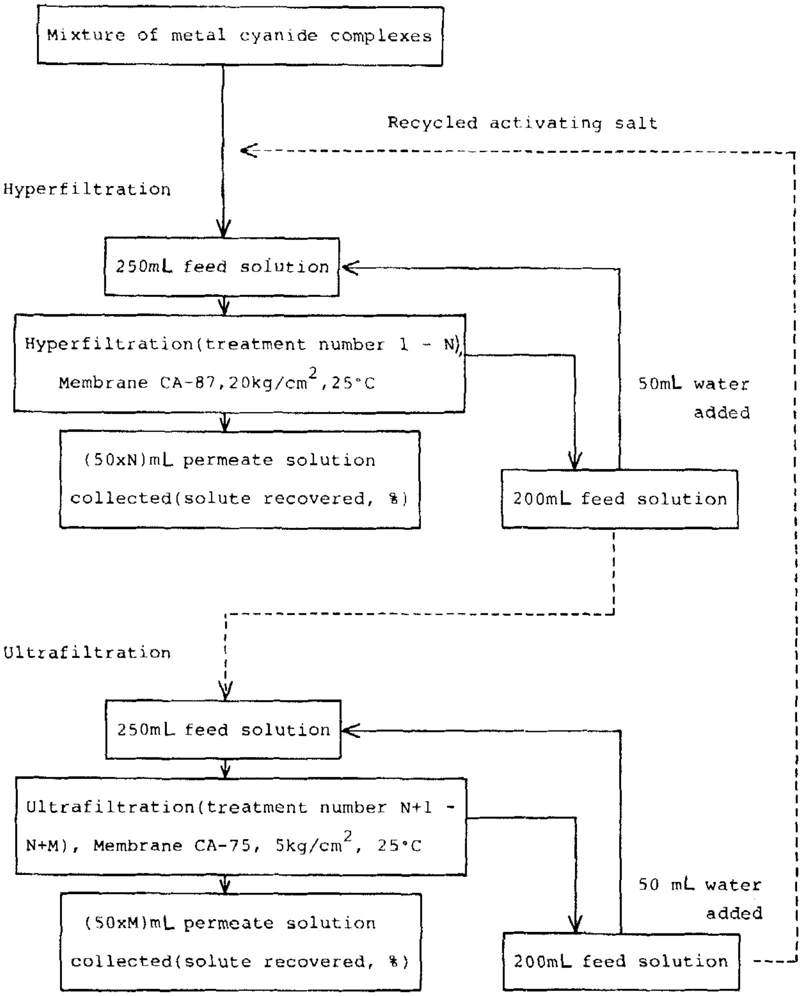
Based on the above considerations, a new hyperfiltration-ultrafiltration technique is proposed for the ion-selective separation of metals. Scheme I illustrates the principle for this sequential separation procedure.

Hyperfiltration: A 250-mL solution of a mixture of metal cyanide complexes is filtered in the presence of polyvinyl sulfate through a high performance membrane (CA-87). Fifty milliliters of the permeate is collected, and then 50 mL of pure water is added to the feed in order to keep the feed volume constant. The procedure is repeated until an appropriate recovery of metal complex in the permeate is achieved.

Ultrafiltration: After hyperfiltration treatment, the feed solution is subjected to filtration through a low performance membrane (CA-75) and a procedure similar to hyperfiltration is repeated until an appropriate metal recovery in the permeate is achieved. The feed solution which contains activating salt is saved for use in Hyperfiltration I for another mixture of metal complexes.

In a typical experimental study, a 0.5 m*M* solution of silver nitrate and zinc nitrate containing 4 m*M* potassium cyanide was treated according to the procedure in Scheme I. An 0.1-*M* polyvinyl sulfate solution was used as the activating salt. The result is shown in Fig. 4. After Treatment 7 (the last treatment with CA-87), 92% of silver was recovered in the permeate with a contamination of 15% zinc. Then, after ultrafiltration through a low performance membrane, 74% of zinc was recovered in the permeate with a contamination of 8% silver. The total permeation of polyvinyl sulfate in the hyperfiltration was negligible and was below 3% in ultrafiltration. These results verify the usefulness of this technique for separating a mixture of metal cyanide complexes in solution.

A similar separation was achieved with the cyanide complexes of copper and zinc. The permeation behavior of the copper species was markedly influenced by the cyanide concentration in the solution (Fig. 5). This is due to the fact that the copper(II) ion is quantitatively reduced to copper(I) ion in



SCHEME I. Hyperfiltration-ultrafiltration for ion selective separation of metals.

the presence of a stoichiometric amount of cyanide ions, producing the CA-87 membrane-permeable complex $Cu^{I}(CN)_2^-$. However, the addition of excess cyanide ion reduced the permeability because of the formation of such less permeable copper species as $Cu^{I}(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. Consequently, the addition of a fourfold molar excess of potassium cyanide ion to copper(II) nitrate yielded the maximum permeability of copper species in the presence of the activating salt potassium polyvinyl sulfate.

Figure 6 includes the permeation behavior of an equimolar mixture of copper and zinc salts in the presence of a fourfold molar excess of potassium cyanide to copper(II). In hyperfiltration through a CA-87 membrane, 95% of copper was recovered in the permeate with a contamination of 7% zinc. However, rather unexpectedly, the permeability of zinc was not enhanced by substituting the membrane from CA-87 for the low performance membrane CA-75. This behavior is reasonably explained because the anionic cyanide complex of zinc is not formed under the given conditions. Calculations based on the published stability constants of copper(I) and zinc(II) cyanide complexes support this belief. In fact, on further addition (at treatment number 10, Fig. 6) of a twofold molar excess of cyanide ion to copper salt, enhanced permeability of zinc was observed as expected from the results in Fig. 4. After this, 88% recovery of zinc was eventually obtained with a contamination of 5% copper.

Among various activating salts, a low molecular anion such as succinate was more effective as an activating salt than a polymer electrolyte (compared on a monomer unit basis) when a high performance membrane was used (hyperfiltration). This is simply because the polymer has a lower effective anion concentration or a lower anion activity. However, when a low performance membrane was used (ultrafiltration), the monomer electrolyte

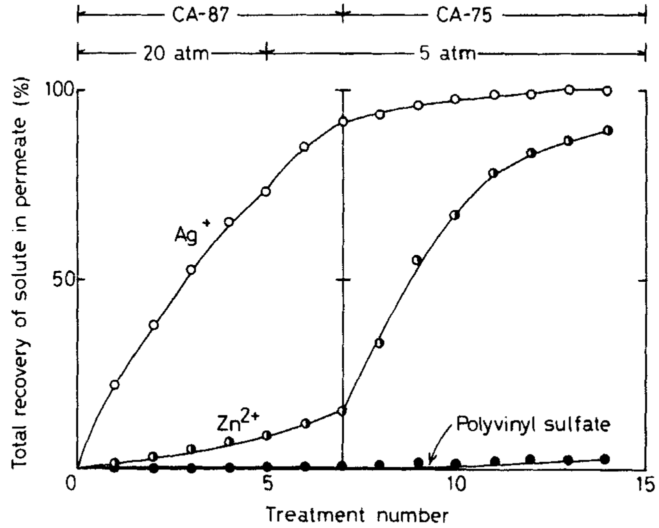


FIG. 4. Total recovery of silver and zinc cyanide complexes in the permeate according to hyperfiltration-ultrafiltration treatment (Scheme I). Feed: 0.5 m*M* $AgNO_3$, 0.5 m*M* $Zn(NO_3)_2$, and 4 m*M* KCN with 0.10 *M* potassium polyvinyl sulfate.

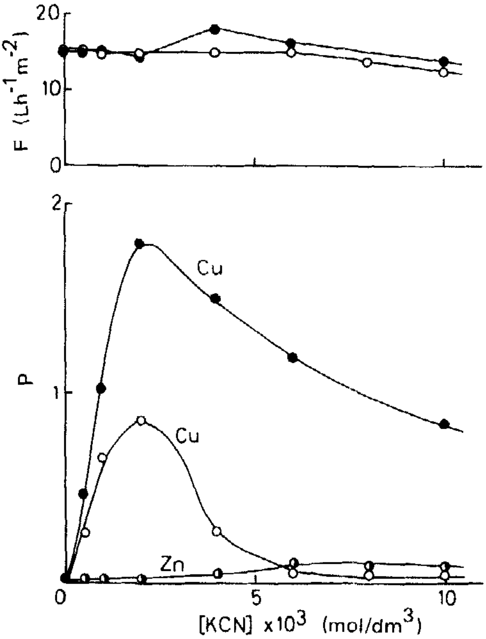


FIG. 5. Effect of potassium cyanide concentration on the permeability of metal. P: permeability of metal species (● succinate; ○, ◑ polyvinyl sulfate). F: flux of permeate solution. Membrane: CA-87. Feed: 0.5 mM $M(NO_3)_2$-KCN with 0.10 M activating salt. Applied pressure: 20 kg/cm^2.

no longer behaved as an activating salt because of its membrane permeability. Therefore, a polymer electrolyte such as polyvinyl sulfate is a more suitable activating salt for our purposes.

The Donnan membrane effect can be generated by the presence of membrane-impermeable salts in the feed solution. Under such hyperfiltration systems, the partition coefficient of a permeated salt is markedly influenced. However, it must be emphasized that the basic permselectivity is, in principle, not enhanced by the addition of a membrane-impermeable anion; the latter only increases the difference between the permeabilities of various ionic species. In this sense, the separation of metals in the present study is basically controlled by the difference in permselectivity of individual complexes or the affinities of the complexes to the cellulose acetate membrane. The ionic size, charge, and extent of hydration of the complexes as well as some intrinsic physico-chemical nature of the cellulose acetate membrane no doubt contributes to this peculiar permselectivity of metal cyanide complexes, the details of which are yet to be explored.

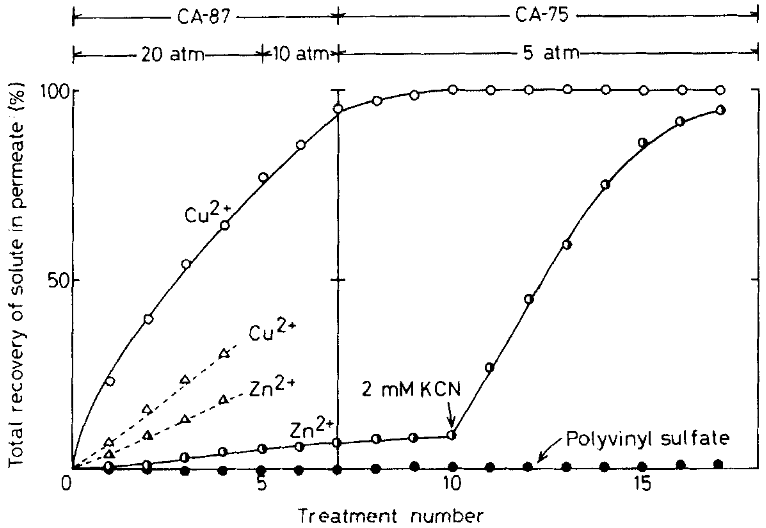


FIG. 6. Total recovery of copper and zinc cyanide complexes in the permeate according to the hyperfiltration-ultrafiltration treatment (Scheme I). Solid lines: Feed solution containing 0.5 m*M* $Cu(NO_3)_2$, 0.5 m*M* $Zn(NO_3)_2$, 2 m*M* KCN, and 0.10 *M* potassium polyvinyl sulfate was filtered; potassium cyanide (2 m*M*) was added at treatment number 10. Dashed lines: Feed solution containing 0.5 m*M* $Cu(NO_3)_2$, 0.5 m*M* $Zn(NO_3)_2$, 4 m*M* KCN, and 0.10 *M* potassium polyvinyl sulfate was filtered.

CONCLUSION

In hyperfiltration or ultrafiltration of ionic solutes, the presence of impermeable ions induces an increase in permeability of permeable ions of a like charge (Donnan membrane effect). The increase in permeability can even lead to a negative rejection or a concentration of permeable salts on the permeate side of the membrane. Potassium dicyanoargentite(I) is appreciably permeable through a cellulose acetate membrane annealed at 87°C (CA-87, hyperfiltration membrane), while zinc(II) cyanide complexes are not. Both the complexes are quite permeable through a cellulose acetate membrane annealed at 70°C (CA-70, ultrafiltration membrane). On the other hand, an anionic polymer electrolyte, potassium polyvinyl sulfate, is impermeable through either CA-87 or CA-70 membrane. By taking advantage of these permeability differences, a mixture of silver and zinc complexes can be separated by filtering through the two types of cellulose acetate membranes in the presence of polyvinyl sulfate. The complexes are concentrated in the permeate due to the Donnan membrane effect caused by the membrane-impermeable polymer electrolyte. The polymer was recovered in the feed side and reused. A mixture of copper and zinc complexes is separated in a similar manner. The principle of the present separation technique can be extended to cover any ionic solutes where intrinsic permeability differences between ions exist. Development of such ion-selective uncharged membranes is of vital importance to the success of this technique for general application.

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