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Separation of Cupric and Ferric Ions with a Cation-Exchange Membrane in the Presence of Complexing Agents

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Abstract

The separation of cupric and ferric ions in chloride solution has been studied with a cation-exchange membrane in a batch dialyzer. Citric acid, oxalic acid, malonic acid, succinic acid, ethylenedinitrilotetraacetic acid, and glycine have been employed as complexing agents used in the feed phase in order to increase the separation effect. The experimental results show that citric acid, compared to the others, is an effective complexing agent to increase the separation coefficient, T^{Cu}_{Fe}, from 0.5 to 50. The separation behavior depends on the pH of the complex solution, the stoichiometric ratios of complexing agents to metal ions, and the kinds of complexing agents, but is independent of counterion concentration in the stripping phase. The integral interdiffusion coefficients of cupric and ferric ions in Selemion CMV have also been evaluated and found to be $\overline{D}_{Fe\text{-}Na} > \overline{D}_{Cu\text{-}Na}$ at concentrations ranging from 0.0015 to 0.0085 M. In the absence of complexing agents, T^{Cu}_{Fe} falls in the neighborhood of the $\overline{D}_{Cu\text{-}Na}/\overline{D}_{Fe\text{-}Na}$ value when the pH is less than 2.0.

INTRODUCTION

Donnan dialysis using cation ion-exchange membranes is a potentially attractive process for the concentration of valuable metal ions or the removal of undesirable ions from aqueous solutions (*1–4*). Based upon Donnan membrane equilibrium (*5*), the metal ion can be continuously pumped into the stripping solution for the high concentration gradient of driving ion across the membrane. The interdiffusion of counterion in the ion-exchange membrane has been studied by many investigators (*6–10*). Numerous experimental results (*1–4*, *6*) support Donnan dialysis as a valuable

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process for the recovery of metal ions in water treatment and hydrometallurgical waste with low energy and operating cost.

The possibility of the application of Donnan dialysis of metal ions not only for preconcentration but also for separation has recently received much attention (*2*, *3*, *11–13*). Because of additional use of metal–complex agents, a cation-exchange membrane has the same function as a supported liquid membrane, which is characterized by its high selectivity to metal ions. Moreover, the higher exchange capacity and hydrophilic property of cation-exchange membranes make Donnan dialysis more effective in practice (*10–12*).

In this work, the application of cation-exchange membrane Donnan dialysis with complexing agents for the selective stripping of metal ions has been studied. Cupric and ferric ions were chosen for experimental investigation owing to the practical importance of separating these ions from hydrometallurgical waste effluents of copper mines (*3*). Organic complex agents such as citric acid, oxalic acid, malonic acid, succinic acid, glycine, and EDTA have been tested in a batch dialyzer in order to increase the separation effect of cupric ion and ferric ion. The effects of the concentrations and the kinds of complexing agents, the pH value of the feed solution, and the concentration of counterions on the flux of metal ions and separation coefficient have been investigated. The integral interdiffusion coefficients of cupric and ferric ions in chloride solution have been obtained from the experimental data.

THEORETICAL CONSIDERATIONS

In the interdiffusion of counterions A and B, concentration gradients exit across the membrane and the adhering Nernst diffusion films. Based on the assumption that the diffusion fluxes of co-ion and water are negligible, the integral interdiffusion coefficients of A and B ions in the membrane and Nernst film are (*10*)

$$D^{\mathrm{I}}_{\mathrm{AB}} = J^{\mathrm{I}}_{\mathrm{A}}\delta^{\mathrm{I}}/[C^{\mathrm{I}}_{\mathrm{A}} - C^{f}_{\mathrm{A}}] \tag{1}$$

$$\overline{D}_{\mathrm{AB}} = \overline{J}_{\mathrm{A}}l/[\overline{C}^{f}_{\mathrm{A}} - \overline{C}^{r}_{\mathrm{A}}] \tag{2}$$

$$D^{\mathrm{II}}_{\mathrm{AB}} = J^{\mathrm{II}}_{\mathrm{A}}\delta^{\mathrm{II}}/[C^{r}_{\mathrm{A}} - C^{\mathrm{II}}_{\mathrm{A}}] \tag{3}$$

where J_{A} and C_{A} are the flux and concentration of ion A, δ and l represent the thickness of the Nernst film and the membrane, respectively, and the superscripts I, II, —, f, and r refer to in Compartment I, in Compartment II, in the membrane phase, at the interface between Compartment I and the membrane, and at the interface between the membrane and Compartment II, respectively.

At steady state, the flux J_A is constant throughout the membrane and diffusion films, i.e.,

$$J_A^I = \bar{J}_A = J_A^{II} = J_A \tag{4}$$

Taking the overall mass balance across the membrane gives

$$J_A = (1/V^{II})S(dC^{II}/dt) = K_{A,0}(C_A^I - C_A^{II}) \tag{5}$$

where $K_{A,0}$ is the overall mass transfer coefficient.

The combination of Eqs. (1)–(5) yields

$$1/K_{A,0} = \delta^I/D_{AB}^I + l/\lambda_A\bar{D}_{AB} + \delta^{II}/D_{AB}^{II} \tag{6}$$

where λ_A is the distribution coefficient defined by $\lambda_A = \bar{C}_A/C_A$, and can be obtained directly from exchange equilibrium data.

The interdiffusion coefficient of metal ion in the liquid film D ($\sim 10^{-5}$ cm^2/s) is much greater than that in the membrane phase $\bar{D}$ ($10^{-7} \sim 10^{-8}$ cm^2/s) (*9*). The interdiffusion resistance within the membrane can be evaluated while neglecting the first and third terms on the right-hand side of Eq. (6) at vigorous stirring conditions. Thus, its value can be readily obtained experimentally from the following equation:

$$\bar{D}_{AB} = K_A l/\lambda_A \tag{7}$$

From the above kinetic description, the various kinds of metal ions with different integral interdiffusion coefficients should cause the difference in fluxes of metal ions owing to membrane selectivity. For the separation of metal ions with a cation-exchange membrane, the difference in fluxes of metal ions across the membrane must be enlarged since the flux of the metal ion is related to the integral interdiffusion coefficient and the concentration gradient across the membrane. There are two methods for the separation of metal ions, as follows.

(1) Separation of Ions Based on Difference in Charge

The Donnan equilibrium relationship holds between two solutions of opposite sides of the membrane (*1*). It is described as

$$(a_i^{II}/a_i^{I})^{1/Z} = \text{constant} \tag{8}$$

where a_i is the activity of *i*th cation of charge Z.

Inspection of Eq. (8) shows that cations of higher charge tend to concentrate preferentially over a lower charge owing to membrane selectivity (*1*, *2*, *12*). This will result in a difference of the integral interdiffusion coefficient so that metal ions with a different charge can be selectively stripped with a cation-exchange membrane.

(2) Separation of Ions with Different Complexing Agents

If the complexing agent is added in the feed, cations will compete with each other to react with complexing ligands to form complexes, which are hardly permeated through the membrane (*10–14*). The difference in the concentration gradients of free metal ions across the membrane can be obtained because of the difference in stability and quantity of the complex. Therefore, metal ions can be separated because of the discrepancy of fluxes resulting from the difference of their concentration gradients.

EXPERIMENTAL

Material

The homogeneous cation-exchange membrane used in this work was Selemion CMV, produced by Asahi Glass Co., Japan. The properties of the membrane were described in an earlier paper (*9*). Its thickness is 1.33×10^{-4} m. All electrolyte solutions were prepared from deionized water and extra pure chemicals without further purifications.

Apparatus

The stirred batch dialyzer used in this experiment consisted of two separable acrylic compartments. The membrane was sandwiched between compartments by two pieces of rubber gaskets to prevent leakage. The effective transfer area of the membrane was 4.3×10^{-3} m^2. The volume of one compartment was 5.5×10^{-4} m^3, another was half of that. Each compartment was equipped with a two-bladed stirrer. All runs were thermostatically controlled at 298 K.

Procedure

The membrane had to be changed to the same form before all experiments. This was done by a dialyzer cell filled with NaCl solution for at least 8 h until the original counterions in the membrane were completely replaced by sodium ions.

A pseudo-steady-state concentration distribution of counterions in the membrane was attained by feeding complex and stripping solutions for half an hour and renewing them with fresh solutions at the beginning of dialysis.

The complex solution contained ferric chloride, cupric chloride, complexing agent, and 0.1 *M* sodium chloride. The stripping solution usually contained 1.0 *M* sodium chloride except for other specifications. The volume of stripping solution was half that of complexing solution. During dialysis, a small amount of solution was taken from the stripping part at each preset time interval. The interdiffusion fluxes of metal ions were calculated from the linear slopes of concentration versus time curves with the least-square method.

The derivation of theory is based on the assumption that the volume of electrolyte solution is unchanged during all experiments. Therefore, the measured concentration of metal ions must be corrected by the following equation (*9*):

$$C_i = \{[V - v(i - 1)]C_i^* + \sum_{j=1}^{i-1} vC_j^*\}/V \tag{9}$$

where C_i is the corrected concentration of the *i*th sample, C_j^* and C_i^* are the measured concentrations of the *j*th and *i*th samples, respectively, and v is the volume of solution withdrawn at each time interval.

The distribution coefficients of counterions in the ion-exchange membrane were measured by the method suggested by Wallace and Ampaya (*8*, *15*). An atomic absorption spectrophotometer (Model 551, Instrumentation Laboratory Inc., USA) was used for the analysis of metal ions.

RESULT AND DISCUSSION

(1) Estimation of Integral Interdiffusion Coefficient in Membrane Phase

The integral interdiffusion coefficients for cupric ion and ferric ion in the ion-exchange membrane, Selemion CMV, were investigated in 0.0015, 0.0025, and 0.0085 *M* feed solutions, separately. The stripping solution was 1.0 *M* NaCl solution. The stirring rate in both compartments was kept at the same speed, and the effect of stirring rate was studied from 1200 to 1800 rpm at a constant temperature of 298 K. At each stirring rate the interdiffusion fluxes of cupric and ferric ions were determined from the slopes of linear relationships between concentration and time. By means of Eq. (5), the overall mass transfer coefficient $K_{A,0}$ can be calculated at each stirring rate. The experimental plots of the reciprocal of the overall mass transfer coefficients corresponding to cupric and ferric ions versus the reciprocal of the stirring rates are shown in Figs. 1 and 2, respectively. The linear relationship between them confirms that the behavior of mass

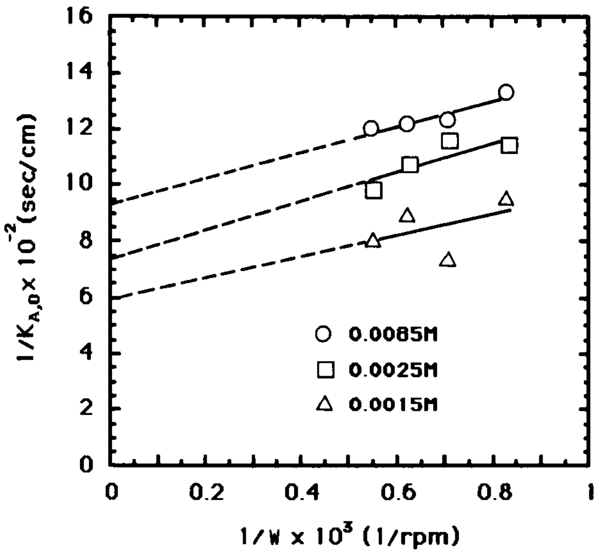

FIG. 1. The relation between the reciprocal of the stirring rate and the overall mass transfer coefficient under various concentrations of cupric ion at 298 K.

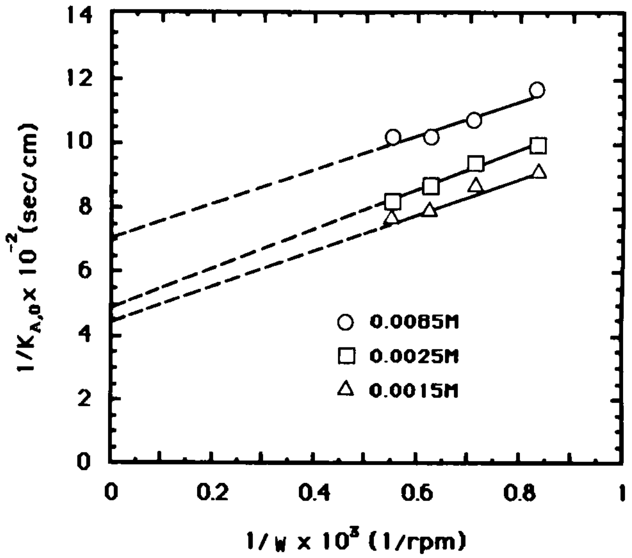

FIG. 2. The relation between the reciprocal of the stirring rate and the overall mass transfer coefficient under various concentrations of ferric ion at 298 K.

transfer is controlled by the membrane resistance as well as by the film resistance.

By extrapolating the data in Figs. 1 and 2 to infinite stirring condition, K_{Cu} and K_{Fe} were respectively obtained. Combining with distribution coefficients λ_A, which was obtained from the experiment of membrane equilibrium and thickness of membrane l, the integral interdiffusion coefficients of cupric ion $\bar{D}_{Cu\text{-}Na}$ and ferric ion $\bar{D}_{Fe\text{-}Na}$ in the membrane were estimated from Eq. (7) for each concentration. These results are given in Table 1.

As can be seen from Table 1, the integral interdiffusion coefficient of ferric ion is larger than that of cupric ion, and the $\bar{D}_{Cu\text{-}Na}/\bar{D}_{Fe\text{-}Na}$ value for each concentration is 0.8 (0.0085 *M*), 0.74 (0.0025 *M*), and 0.73 (0.0015 *M*). This can be explained by the Donnan membrane equilibrium relationship, Eq. (8), from the fact that the charge of ferric ion (3+) is larger than that of cupric ion (2+), the more highly charged cation is preferentially transferred across the membrane (*1–3*, *14*).

(2) Separation of Ions Based on Difference in Charge

The separation coefficient T_{Fe}^{Cu} is defined by

$$T_{Fe}^{Cu} = (J_{Cu}/C_{Cu,0})/(J_{Fe}/C_{Fe,0}) \tag{10}$$

where C_0 is the initial concentration of metal ion in the feed solution.

In order to study the separation of cupric and ferric ions based on their charge difference, mixed solutions of 0.0015 *M* $FeCl_3$ and 0.0015 *M* $CuCl_2$ were introduced into the feed comparment that contained 0.1 *M* NaCl solution. The 1.0 *M* NaCl solution was fed into the strippping part. Both solutions were stirred at 1600 rpm, and a further increase in stirring did not increase the flux. The permeation fluxes of cupric ion and ferric ion

TABLE 1
The integral Interdiffusion Coefficients of Metal Ions in Selemion CMV Membrane for Various Concentrations at pH 1.8 and 298 K

Ion species	Concentration (*M*)	$K_A \times 10^3$ (cm/s)	λ_A	$\bar{D} \times 10^7$ (cm^2/s)
Fe^{3+}	0.0085	1.57	84	2.57
	0.0025	2.30	158	2.06
	0.0015	2.61	196	1.89
Cu^{2+}	0.0085	1.10	63	2.06
	0.0025	1.37	129	1.51
	0.0015	1.68	172	1.38

TABLE 2
The Effect of pH in the Feed on Separation Coefficient and Permeation Flux at 298 K and $[CuCl_2] = [FeCl_3] = 0.0015\ M$

pH	$J_{Fe} \times 10^{10}$ (mol/cm²·s)	$J_{Cu} \times 10^{10}$ (mol/cm²·s)	T_{Fe}^{Cu}
1.8	12.0	4.7	0.5
2.2	11.0	5.5	0.6
2.4	6.5	7.8	1.6
2.6	5.5	14.3	3.2

were calculated, respectively, from the linear slopes of concentration versus time curves with the least-squares method, and the separation coefficients, T_{Fe}^{Cu}, were obtained from Eq. (10). These results are given in Table 2. It is indicated that the value of T_{Fe}^{Cu} is in the range of 0.5 to 1.0 and approaches the value of $\overline{D}_{Cu\text{-}Na}/\overline{D}_{Fe\text{-}Na}$ (0.7 ~ 0.8) at a pH below 2.4. This is in agreement with the foregoing discussion that membranes prefer the permeated transport of cations with higher charges.

It can be seen from Table 2 that the ferric ion flux decreases with an increase of cupric ion flux as the pH value of the feed solution increases. Consequently, the T_{Fe}^{Cu} value can be increased from 0.5 to 3.2 as the pH of the feed solution ranges from 1.8 to 2.6. This is due to the fact that the extent of hydration of ferric ion is over 90%, but that of the cupric ion is less than 10% at pH 3 (*17*). In Donnan dialysis, the permeation flux depends on the ion diffusivity as well as on the concentration gradient. Owing to the hydration of ferric ions, the concentration gradient of the ferric ion across the membrane is reduced with a decrease in the flux of the ferric ion. The precipitation of ferric hydration, resulting in membrane fouling, occurred at pH > 3.0 in the absence of a complexing agent (*16*, *17*).

(3) Separation of Ions with Different Complexing Agents

For the investigation of the complexing agent effect on the separation coefficient, T_{Fe}^{Cu}, the organic complexing agents including citric acid, oxalic acid, malonic acid, succinic acid, glycine, and EDTA were introduced, respectively, into the feed solution of 0.0015 *M* $FeCl_3$ and 0.0015 *M* $CuCl_2$ in each run. The fluxes of metal ions and the separation coefficient were measured under the same operating conditions as in the foregoing description and tabulated in Table 3. It is found that the permeation flux of ferric ion is always smaller than that of cupric ion, and the different values of T_{Fe}^{Cu} are obtained under the condition of various kinds of complexing agents.

TABLE 3
The Effect of Complexing Agent on Separation Coefficient and Permeation Flux at 298 K, pH 2.4, $\Phi = 0.6$, and $[CuCl_2] = [FeCl_3] = 0.0015$ *M*

	$J \times 10^{10}$ (mol/cm²·s)		
Complex agent	Fe	Cu	T_{Fe}^{Cu}
Citric acid	1.0	16.9	19.3
Oxalic acid	2.2	12.6	6.5
Malonic acid	1.9	10.3	6.0
Succinic acid	6.7	7.2	1.3
Glycine	3.3	11.7	4.0
EDTA	3.4	9.8	3.0
Without using	6.5	7.8	1.6

This is due to the fact that the stability constant of the ferric ion complex is larger than that of the cupric ion complex in all the complexing agents used (*16*, *17*). Thus, the ferric ion is easily captured by complex ligands to form complexes in competition with the cupric ion. The preferred permeation flux of the cupric ion is found to be due to the high concentration of free cupric ion in the feed, and the ferric flux is suppressed owing to its complexes which are hardly permeated through the membrane (*12–14*). The effect of various complexing agents on the separation of ferric and cupric ions is found to be in the order citric acid > oxalic acid, malonic acid > glycine, EDTA > succinic acid. Therefore, we focus attention on citric acid as the complexing agent in the following research.

Owing to complex formation, the pH value of the complexing solution and the stoichiometric ratio of the complexing agent, $\Phi = [\text{complexing agent}]/[FeCl_3] + [CuCl_2]$, are primary parameters on permeation flux and separating coefficient (*12*). In the experiment with mixed solution $FeCl_3$, $CuCl_2$, and citric acid in the feed compartment, the permeation flux, and separation coefficient were measured as the Φ ranged from 0 to 1.0 under various concentrations of metal ions at pH 2.4. These results are shown in Figs. 3–6 for metal ion concentrations of 0.0015, 0.0025, 0.005, and 0.0085 *M*, respectively. It is indicated that the value of T_{Fe}^{Cu} and the flux of cupric ion increase, but the flux of ferric ion decreases as Φ ranges from 0 to 0.6, and they approach a constant value when Φ increases from 0.6 to 1.0.

This can be explained from the fact that the stability constant of ferric ion with citric acid ($10^{13.5}$) is larger than that of cupric ion ($10^{7.2}$) (*16*), so that the ferric ions compete with the cupric ions for citric ligands in an

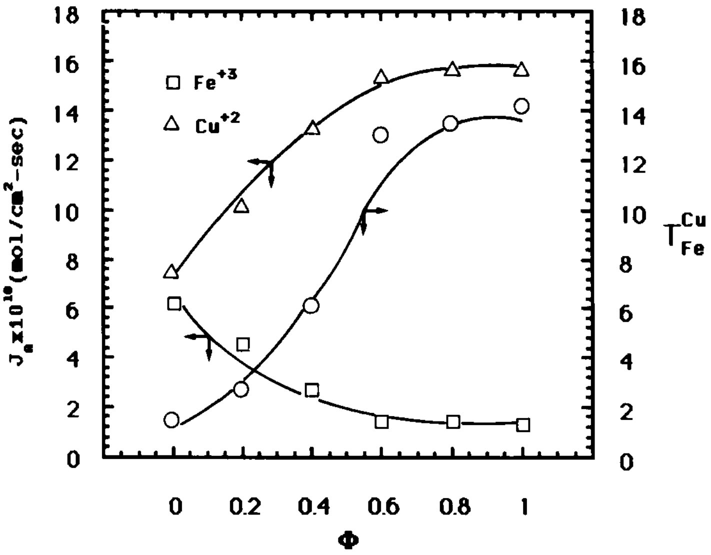

FIG. 3. The effect of the stoichiometric ratio of the complexing agent on the permeation flux of the metal ions and the separation coefficient for citric acid as the complexing agent in the feed solution at 298 K, pH 2.4, and $[CuCl_2] = [FeCl_3] = 0.0015\ M$.

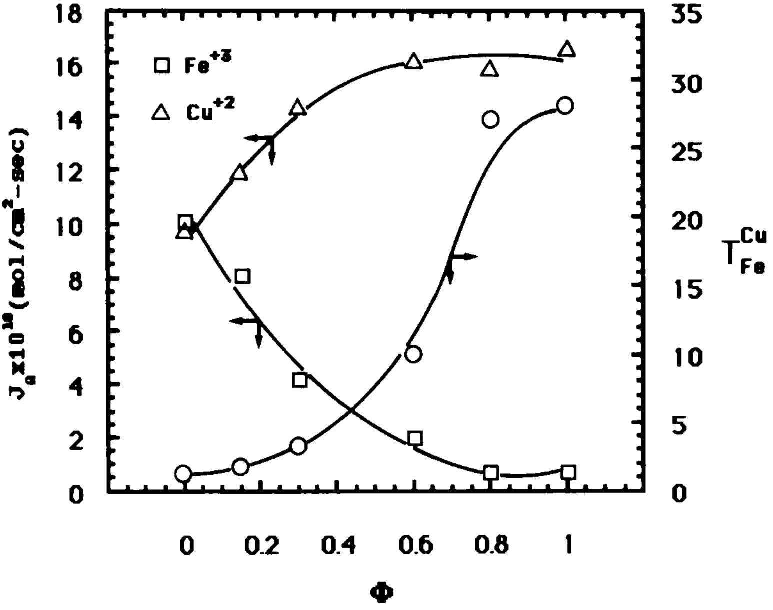

FIG. 4. The effect of the stoichiometric ratio of the complexing agent on the permeation flux of the metal ions and the separation coefficient for citric acid as the complexing agent in the feed solution at 298 K, pH 2.4, and $[CuCl_2] = [FeCl_3] = 0.0025\ M$.

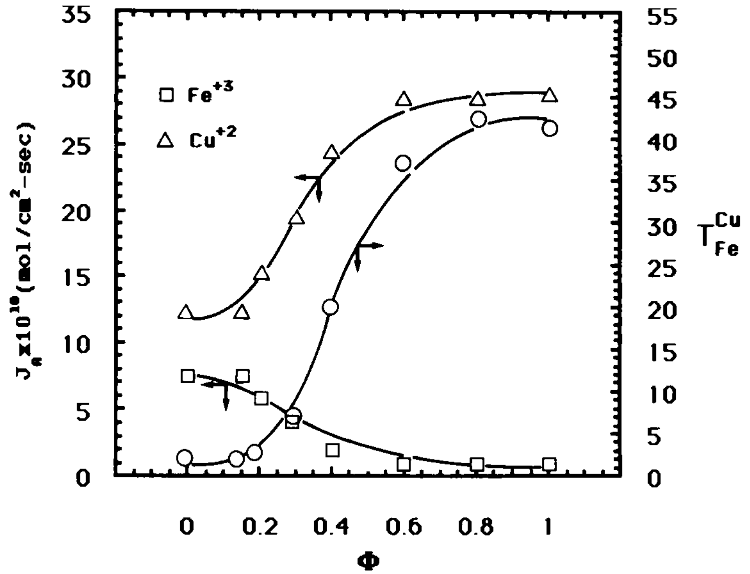

FIG. 5. The effect of the stoichiometric ratio of the complexing agent on the permeation flux of the metal ions and the separation coefficient for citric acid as the complexing agent in the feed solution at 298 K, pH 2.4, and [$CuCl_2$] = [$FeCl_3$] = 0.005 *M*.

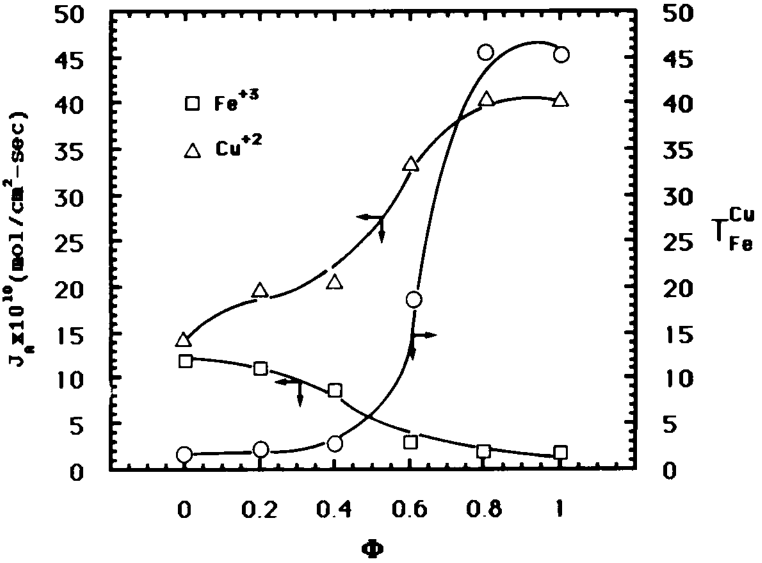

FIG. 6. The effect of the stoichiometric ratio of the complexing agent on the permeation flux of the metal ions and the separation coefficient for citric acid as the complexing agent in the feed solution at 298 K, pH 2.4, and [$CuCl_2$] = [$FeCl_3$] = 0.0085 *M*.

advantageous position to form complexes which hardly permeate through the membrane. Thus, the increase of Φ value leads to an increase in the formation of ferric ion complex as well as a decrease in ferric flux. Consequently, there is a steep increase of cupric ion flux and the separation coefficient, T_{Fe}^{Cu}. When $\Phi > 0.6$, i.e., the concentration of citric acid is larger than that of ferric ion, the ferric ions are almost captured by citric ligands to form complexes, so that ferric ion flux approaches a minimum value. However, cupric ions cannot overcome hydrogen ions for the residual amount of citric ligands to form complexes at low pH value because the stability constant of the cupric ion complex ($\sim 10^{7.2}$) is slightly greater than the dissociation constant of citric acid ($\sim 10^{6.4}$) (*16*). Thus, the difference of the concentration gradient between free cupric and ferric ions approaches the maximum, resulting in the optimal T_{Fe}^{Cu} value as Φ increases from 0.6 to 1.0. The optimal separation coefficient, T_{Fe}^{Cu}, is obtained as 14.0, 27.0, 42.0, and 45.0, respectively, for metal ion concentrations of 0.0015, 0.0025, 0.005, and 0.0085 *M*.

When EDTA is substituted for citric acid as the complexing agent, the effect of the stoichiometric ratio of permeation fluxes and separation coefficient is shown in Fig. 7 at a metal ion concentration of 0.0015 *M* and pH 2.4. As compared with Figs. 3 and 7, the result for EDTA used as a

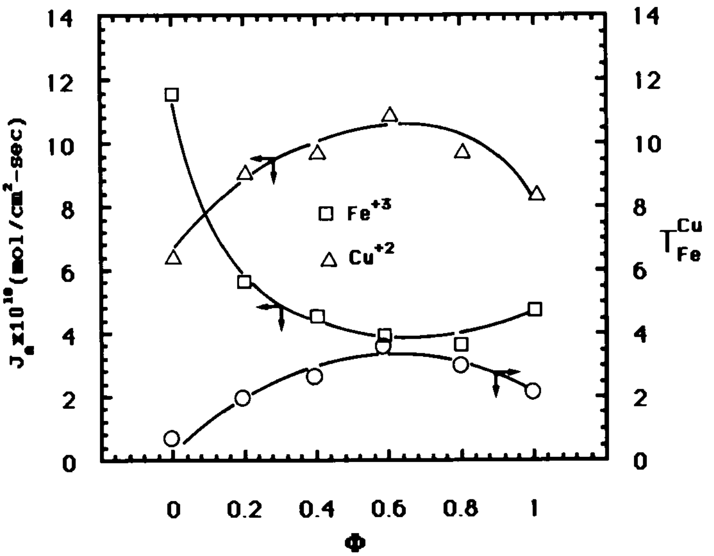

FIG. 7. The effect of the stoichiometric ratio of the complexing agent on the permeation flux of the metal ions and the separation coefficient for EDTA as the complexing agent in the feed solution at 298 K, pH 2.4, and $[CuCl_2] = [FeCl_3] = 0.0015$ *M*.

complexing agent is similar to citric acid at Φ ranging from 0 to 0.6. The separation coefficient, $T_{\mathrm{Fe}}^{\mathrm{Cu}}$, and the cupric ion flux increase, but the ferric ion flux decreases with Φ increasing because the stability constant of ferric ion with EDTA is still larger than that of cupric ion (*16*, *17*). But when $\Phi > 0.6$, the cupric ion flux and $T_{\mathrm{Fe}}^{\mathrm{Cu}}$ value may not maintain a constant as for the citric acid system, and decreases with the Φ value increasing because complexation of the cupric ion is occurring. This is due to the fact that the stability of the cupric ion complex ($\sim 10^{20.5}$) is smaller than that of the ferric ion complex ($\sim 10^{27.7}$), but it is much larger than the dissociation constant of EDTA ($\sim 10^{13.5}$) (*17*). Thus, cupric ions can overcome hydrogen ions to react with the residual quantity of complex ligands in the formation of a ferric ion complex at low pH values that may not occur in the case of citric acid.

Figure 8 shows that the separation coefficients, $T_{\mathrm{Fe}}^{\mathrm{Cu}}$, were obtained under various stoichiometric ratios of citric acid as the pH of the complexing solution ranged from 1.8 to 2.6 at metal ion concentrations of 0.0015 *M*. The result indicates that the effect of the stoichiometric ratio on the separation coefficient is in agreement with the foregoing discussion. It is noted that there is an increase in the separation coefficient as the pH of the complexing solution increases, and the optimal separation coefficient $T_{\mathrm{Fe}}^{\mathrm{Cu}}$

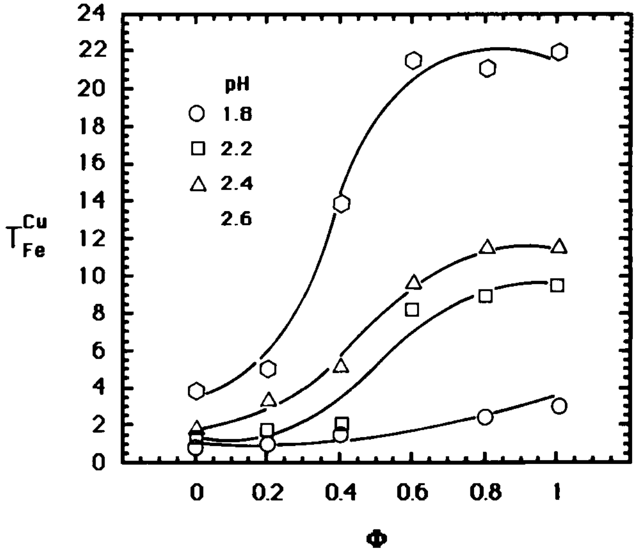

FIG. 8. The effect of the stoichiometric ratio of the complexing agent on the permeation flux of the metal ions and the separation coefficient under various pH values for citric acid as the complexing agent in the feed solution at 298 K, and $[\mathrm{CuCl_2}] = [\mathrm{FeCl_3}] = 0.0015$ *M*.

is obtained to be 1.8, 10.0, 12.0, and 22.0, respectively, for the pH of complexing solutions 1.8, 2.2, 2.4, and 2.6.

In order to study the pH effect on the separation coefficient, the mixed solutions of metal ions and citric acid were introduced into the feed solutions at constant Φ (1.0) under various pH values. The fluxes of metal ions and the separation coefficient were measured under the same operation conditions as in the foregoing description. These results are shown in Figs. 9, 10, and 11 for the metal ion concentrations of 0.0015, 0.0025, and 0.005 *M*, respectively. It is indicated that the relationship between the separation coefficient, T_{Fe}^{Cu}, and the pH of the complexing solution can be divided into three parts. First, T_{Fe}^{Cu} is increased sharply as the pH ranges from 1.8 to 2.5 because the permeation flux of the ferric ion decreases steeply while that of the cupric ion increases. Next, T_{Fe}^{Cu} is maintained at a constant pH value ranging from 2.5 to 4.5 due to the larger and constant difference of permeation flux between ferric and cupric ions. Last, the T_{Fe}^{Cu} is decreased steeply as the pH ranges from 4.5 to 6.5 owing to the steep decrease of cupric flux.

The reasonable explanation is that the dissociation extent of complexing ligands increases with increasing pH until the dissociation reaction of the complexing agent is completed. The pH value of complete dissociation of

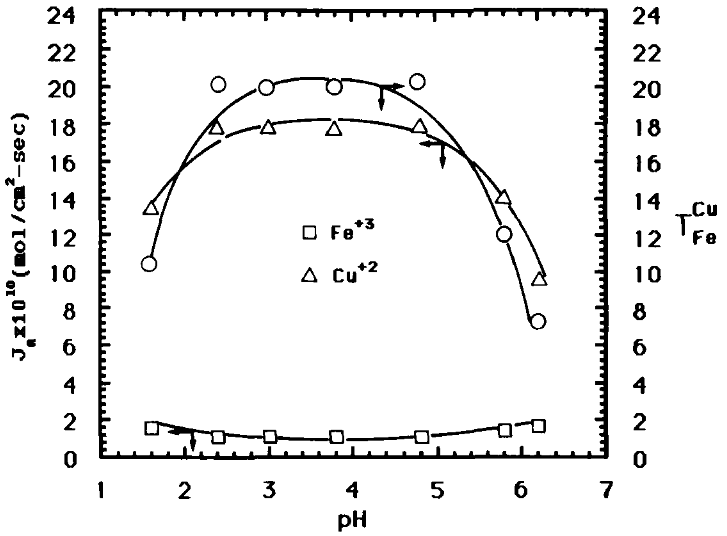

FIG. 9. The effect of pH on the permeation flux of the metal ions and the separation coefficient for citric acid as the complexing agent in the feed solution at 298 K, pH 2.4, Φ = 1.0, and $[CuCl_2]$ = $[FeCl_3]$ = 0.0015 *M*.

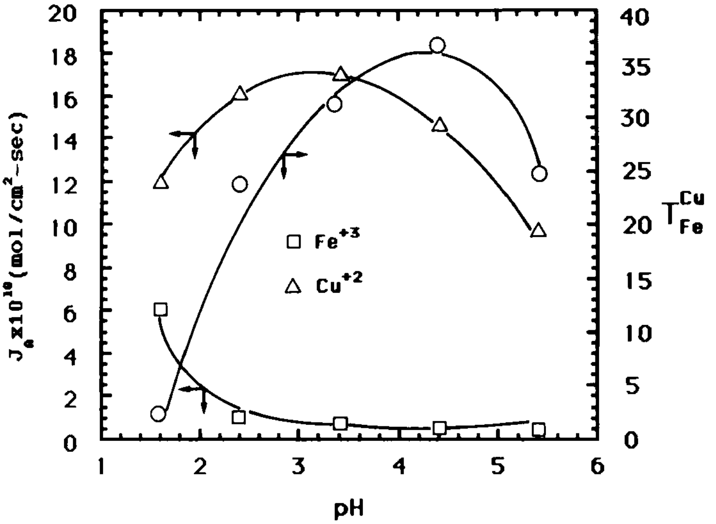

FIG. 10. The effect of pH on the permeation flux of the metal ions and the separation coefficient for citric acid as the complexing agent in the feed solution at 298 K, Φ = 1.0, and $[CuCl_2]$ = $[FeCl_3]$ = 0.0025 *M*.

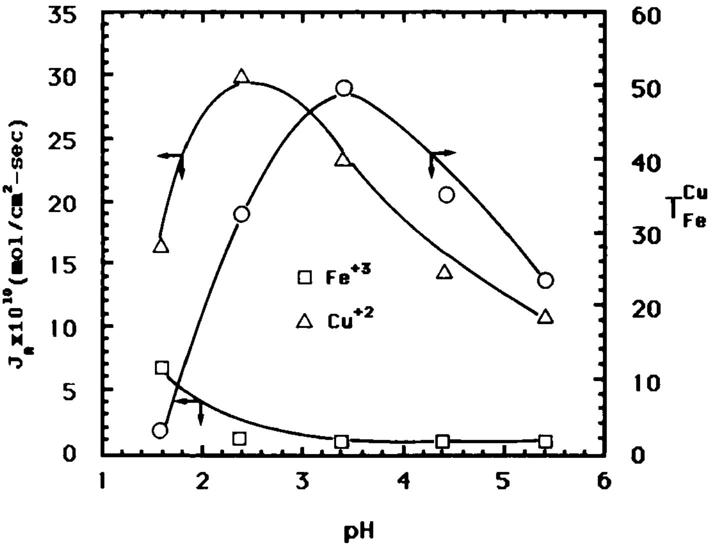

FIG. 11. The effect of pH on the permeation flux of metal ions and the separation coefficient for citric acid as the complexing agent in the feed solution at 298 K, Φ = 1.0, and $[CuCl_2]$ = $[FeCl_3]$ = 0.005 *M*.

citric acid is about 2.5 dependent on the concentration. Thus, if the pH is below 2.5 in the first stage, a higher pH is used and more ferric ion complex can be found, because the citric acid has been dissociated into more citric ligands. This leads to $T_{\mathrm{Fe}}^{\mathrm{Cu}}$ increasing rapidly with a steep decrease of ferric ion flux. In the second stage, where the pH ranges from 2.5 to 4.5, the ferric ion complex has been completed but the complexation of the cupric ion has not occurred owing to the high concentration of the hydrogen ion. Therefore, there is a large and constant difference between ferric ion flux and cupric ion flux, resulting in an optimal $T_{\mathrm{Fe}}^{\mathrm{Cu}}$ being obtained. In the third stage, where the pH is greater than 4.5, i.e., the concentration of hydrogen ion is less than $10^{-4.5}$ M, the cupric ions can compete with hydrogen ions for the citric ligands to form complexes in an advantageous position. The increase of the cupric complex leads to a decrease of the cupric ion flux, and the separation coefficient $T_{\mathrm{Fe}}^{\mathrm{Cu}}$ increases steeply as the pH increases from 4.5 to 5.5. The different optimal $T_{\mathrm{Fe}}^{\mathrm{Cu}}$ are 22.0, 38.0, and 50.0, respectively, for metal ion concentrations of 0.0015, 0.0025, and 0.005 M, and the optimum pH value ranges from 3.0 to 4.0 depending on the metal ion concentration.

As can be seen from Figs. 9 to 11, when a higher concentration of a metal ion is used, a higher separation coefficient $T_{\mathrm{Fe}}^{\mathrm{Cu}}$ can be obtained at a constant stoichiometric ratio under various pH values. Similar results can also be observed in Figs. 3 to 6 under various stoichiometric ratios at pH 2.4. This can be explained from the fact that the extent of ferric ion complexing is always greater than that of the cupric ion for citric acid as a complexing agent under various conditions. It tends to increase the amount of ferric complexing and, conversely, to increase the quantity of free cupric ion in the feed when the concentration of metal ion increases. This leads to enlarging the discrepancy of the concentration gradient across the membrane between ferric and cupric ions, so that a higher separation effect can be obtained due to the larger difference of permeation flux between them.

(4) The Influence of Sodium Ion in the Stripping Solution

Sodium ions were chosen as the driving ion in the permeation measurement. In the experiment with 0.0035 M $FeCl_3$ and 0.0035 M $CuCl_2$ in a feed solution of 0.1 M NaCl, the fluxes of ions and the separation coefficient were measured under various concentration of NaCl ranging from 0.1 to 1.5 M in the stripping solution. These results are shown in Fig. 12. It is found that there is a increase in the fluxes of both ferric and cupric ions with NaCl concentration of the stripping solution increasing, because a higher co-ion concentration of the stripping solution results in a larger driving force which enhances the increasing ionic flux. When the concentration of NaCl is larger than 1.0 M, the flux appears to approach a limiting

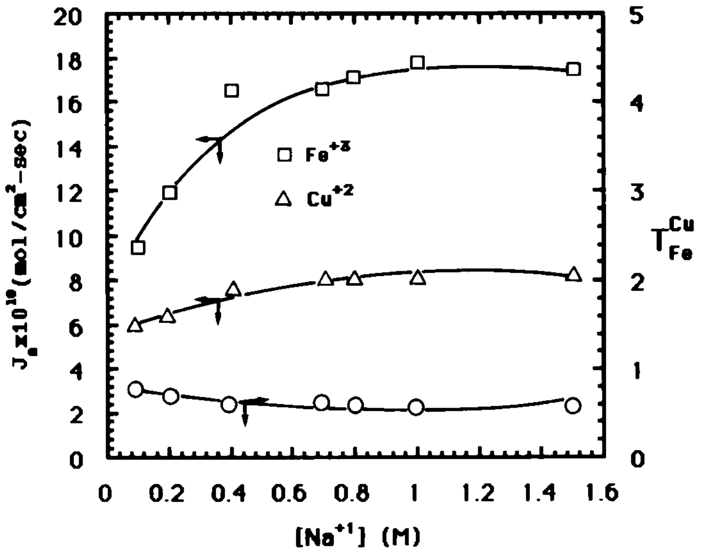

FIG. 12. The effect of concentration of the sodium ion in the stripping solution on the permeation flux of metal ions and separation coefficient at 298 K, pH 1.8, and [$CuCl_2$] = [$FeCl_3$] = 0.0035 *M*.

value because the resistant of mass transport is dominated by the characteristics of the membrane. It is noted that the separation coefficient, T^{Cu}_{Fe}, is almost not affected by the NaCl concentration because the sodium ion cannot permselective transport for metal ions. The result is in accordance with the derivation of Helfferich and Schlogl (*18*) that the flux ratio of ions across the membrane is independent of the condition in the stripping solution which does not contain any complexing agents.

CONCLUSION

The integral interdiffusion coefficients of ferric and cupric ions in Selemion CMV is found to be in the order $\overline{D}_{\text{Fe-Na}} > \overline{D}_{\text{Cu-Na}}$ and $\overline{D}_{\text{Fe-Na}}/\overline{D}_{\text{Cu-Na}}$ in the range of 0.7 to 0.8. By using suitable complexing agents in the feed, especially in the case of citric acid, it is found to be effective for the separation of ferric and cupric ions. The pH of a complexing solution and the stoichiometric ratio of the complexing agent to metal ions are the primary parameters of the separation effect. The higher concentration of a metal ion used, the better the separation effect that can be obtained. However, the separation coefficient is almost independent of the condition of the stripping solution when complexing ligands do not exit.

NOMENCLATURE

A, B	counterions A and B (—)
a	activity of ion in solution (—)
C_A	concentration of A in solution (mol/dm^3)
$\bar{C}_A$	concentration of A in membrane (mol/dm^3)
D_{AB}	integral interdiffusion coefficient in Nernst diffusion film (cm^2/s)
$\bar{D}_{AB}$	integral interdiffusion coefficient in membrane phase (cm^2/s)
J_A	ionic flux of counterion A (mol/cm^2·s)
$K_{A,0}$	overall mass transfer coefficient (cm/s)
K_A	apparent mass transfer coefficient at infinite stirring condition (cm/s)
l	thickness of membrane (cm)
S	effective transfer area (cm^2)
T^{Cu}_{Fe}	separation coefficient $J_{Cu}C_{Fe,0}/J_{Fe}C_{Cu,0}$ (—)
t	time (s)
V	volume of electrolyte solution in Compartment 2 (cm^3)
δ	thickness of Nernst diffusion film (cm)
λ_A	distribution coefficient, $\bar{C}_A/C_A$ (—)
Φ	stoichiometric ratio (—)
w	stirring rate (rpm)

Superscripts

I	in Compartment 1
II	in Compartment 2
f	at interface between Compartment 1 and membrane
r	at interface between Compartment 2 and membrane
—	in the membrane phase

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