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Selective Transport of Heavy Metal Ions across a Cation-Exchange Membrane with a Chelating Agent in the Receiving Phase

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Heavy metal ions can be selectively transported under the concentration gradient across a cation-exchange membrane with a chelating agent in the receiving phase. The selectivity depends on the complex formation constants of the ions with the agent. Metal ions are adsorbed into a cation-exchange membrane via the ion-exchange reaction and diffuse across the membrane. The desorption process is facilitated by the complexation in the receiving phase, which causes a large transport rate across the membrane. A transport equation was established and the theoretical values estimated by the equation and the permeation characteristics values obtained experimentally agreed well with the measured ion flux. The selectivity of the metal ions in the mixed solution is increased in the adequate concentration of the chelating agent in the receiving phase, when the chelate formation reaction may occur competitively between the ions with the agent in the receiving phase. The metal ions in the complex solution can be stripped as free ions across a cation-exchange membrane via the ion-exchange reaction with protons under a concentration gradient of acid.

Experimental

Each transport experiment was carried out with a flow type cell shown in Fig. 1 at room temperature. The cell was composed of two compartments, that is, source phase and receiving phase compartments, which were partitioned by a cation-exchange membrane (Asahi Glass Co. Ltd., Selemion CMV). Each solution was circulated from each reservoir to the compartment by a tubing pump at a rate of 30 mL min⁻¹. The membrane area was 10.5 cm² and the thickness of each compartment was ca. 1 mm. A spacer of nylon screen with the thickness of 1.16 mm was inserted in each compartment to control the thickness of membrane. The cell was mounted in a thermostated water bath.
compartment of the cell. In the transport experiment, aliquots of the solution of each phase were collected in a definite interval. The ion flux was calculated from the linear region of the concentration change of the receiving phase with time.

The transport and ion-exchange characteristics of the membrane were also obtained at room temperature to compare the experimental value of the flux with the calculated value using a theoretical flux equation. The ion-exchange capacity was obtained by immersing a Cu²⁺-type cation-exchange membrane (area, 4 cm × 4 cm) into 100 mL of 1 mol L⁻¹ HCl for over 1 hr and the desorbed copper(II) ion was determined. The immersion of the membrane into fresh HCl was repeated three times and the capacity was calculated from the summation of the determined values. The membrane thickness was measured to be 0.0107 cm with a micrometer; this value was used in the calculations. The rate constant of the ion-exchange reaction was obtained by immersing a cation-exchange membrane (area, 4 cm × 4 cm) into 100 mL of salt solution, aliquots of which were collected at definite intervals after the immersion to be analyzed. The constant was calculated from the initial concentration changes with time of the copper(II) ion and the sodium ion in the solution. The permeation coefficient was obtained in the transport experiment using two membranes, which were placed close together. After the permeation experiment from the source phase to the receiving phase across the two membranes, the membranes were taken out from the cell and the copper(II) ion concentration in each of two membranes was determined in a manner similar to the determination of the ion-exchange capacity. The coefficient was calculated from the concentration gradient obtained by the determined copper(II) ion concentration in the membrane and the measured copper(II) ion flux.

The metal ions other than alkaline metal ions were determined by an inductively coupled plasma atomic emission spectrophotometer (Seiko SPS1500VR), the alkaline metal ions were determined from the absorbance spectrum of the sample (Shimadzu AA-6700F), and the solution pH was measured by a pH meter (Toa HM-60S).

Results and Discussion

Figure 2 shows the transport behaviors of copper(II) ion in the cell. The membrane was sodium ion type at the beginning of the experiment. When the receiving phase was 2 mM sodium chloride aqueous solution, the fluxes were very small (0.022 × 10⁻⁸ mol cm⁻² min⁻¹). In the case of pure water as the receiving phase, the copper(II) ion in the receiving phase was not detected during 3 hours from the beginning in the experiment. When the receiving phase was 1 mM EDTA-2Na (C₆H₈O₇N₂O₂Na₂) aqueous solution, the flux was 2.6 × 10⁻⁸ mol cm⁻² min⁻¹ and the transport rate was facilitated extremely. The copper(II) ion is highly distributed from the aqueous solution to the cation-exchange membrane and the concentration change in the source phase was about the same for the EDTA solution as for the sodium salt solution in the receiving phase. The desorption process from the membrane to the receiving phase is facilitated in the case of EDTA solution because the copper(II) ion complexes with EDTA to become a chelate anion, the free copper(II) ion concentration in the receiving phase can be neglected due to the large complex formation constant, and there occurs a large concentration gradient between two phases across the cation-exchange membrane. When sodium chloride was added so as to be 10 mM in the EDTA-2Na solution of the receiving phase, the ion-exchange reaction between the sodium ion in the solution and the copper(II) ion in the membrane was enhanced and the flux increased to be 4.3 × 10⁻⁸ mol cm⁻² min⁻¹. Therefore, the ion-exchange process at the interface between the membrane and the receiving phase is also important in the transport of copper(II) ion to EDTA solution in the receiving phase.

Figure 3 shows the relationship between the copper(II) ion flux and the concentration of the solute in the receiving phase. The concentration point of sodium chloride in abscissa was different from that of the chelating agents to be compared with EDTA-2Na, which contains two moles of sodium per one mole of molecules. The flux strongly depends on the concentration of sodium chloride, while the flux depends little on the concentration of the chelating agents, whose stability constants of copper (II) complex are 10⁻¹⁸.8 for EDTA, 10⁻¹³.¹ for NTA (nitrilotriacetic acid), and 10⁻⁸.³⁵ for citric acid.
From Eqs. 2 and 3, Eqs. 6 and 7 can be derived.

\( J_s = k_1 \{ \text{Cu}^{2+} \}_s [\text{Na}^+]_s - k_{-1} [\text{Na}^+]_s [\text{Cu}^{2+}]_s \)  
\( J_r = k_{-1} [\text{Cu}^{2+}]_r [\text{Na}^+]_r - k_1 [\text{Na}^+]_r [\text{Cu}^{2+}]_r \)  

The meanings of these symbols are shown in Fig. 4. As shown in Fig. 4, copper(II) ion transport in this system can be explained by the ion-exchange process with sodium ion and the counter transport in the ion-exchange membrane. The transport is facilitated by the very low concentration of free copper(II) ion in the receiving phase for the complexation with the chelating agent in the receiving phase. The flux in the membrane phase, \( J \), can be described by using a permeation constant, \( P \).

\[ J = P \{ [\text{Cu}^{2+}]_s - [\text{Cu}^{2+}]_m \} \]  

In the stationary state, \( J_s = J_r = J \). Copper(II) ion complexes with EDTA in the receiving phase and the conditional complex formation constant, \( K' \), can be defined as follows, where \( C_Y \) is the concentration of EDTA.

\[ K'_C = [\text{Cu-Y}^2^-]_s/[\text{Cu}^{2+}]_s C_Y \]  

Since the complex formation constant is very large (\( K_C = 10^{18.8} \)), the free copper(II) ion in the receiving phase can be neglected and the second term in the right-hand side of Eq. 2 becomes zero. The ion-exchange capacity, \( C_{ex} \), is defined as follows.

\[ C_{ex} = 2[\text{Cu}^{2+}]_m + [\text{Na}^+]_m = 2[\text{Cu}^{2+}]_m + [\text{Na}^+]_m \]  

From Eqs. 2 and 3, Eqs. 6 and 7 can be derived.

\[ [\text{Cu}^{2+}]_m = (J + P[Cu^{2+}]_m)/P \]  
\[ [\text{Cu}^{2+}]_m = J/(k_{-1}[\text{Na}^+]_r) \]  

The following equation can be derived from Eqs. 6 and 7.

\[ [\text{Cu}^{2+}]_m = (J + P[J/(k_{-1}[\text{Na}^+]_r)^2])/P \]  

The initial concentration of copper (II) ion in the source phase is defined as \( C \) and the sodium concentration in the source phase is shown as follows.

\[ [\text{Na}^+]_s = 2C - 2[\text{Cu}^{2+}]_s \]  

From these equations, Eq. 11 can be derived.

\[ J = k_1 [\text{Cu}^{2+}]_s [\text{Na}^+]_s - 2J \{ [\text{Cu}^{2+}]_s + 1/[k_{-1}[\text{Na}^+]_r)^2 \}^2 \]

The flux in Eq. 11 is a function of \( [\text{Cu}^{2+}]_s \) and \( [\text{Na}^+]_r \) and the flux can be calculated for a source phase and receiving phase concentration when the membrane characteristic values of \( k_1 \), \( k_{-1} \), \( P \), and \( C_{ex} \) are obtained. Table 1 shows these values, which depend on the experimental conditions. The values \( k_1 \) and \( k_{-1} \) are dependent on the concentration because of the large concentration dependence of ion-exchange equilibrium constant and they were obtained in conditions similar to those for the transport experiment. The flux of copper(II) ion was calculated to be \( 2.9 \times 10^{-8} \) mol cm\(^{-2}\) min\(^{-1}\), while the measured flux was \( 2.6 \times 10^{-8} \) mol cm\(^{-2}\) min\(^{-1}\). These two values agreed well to each other, which shows the validity of Eq. 11. When the pseudo-equilibrium of the ion exchange reaction can be applied at the interface between the membrane and the receiving phase, Eq. 12 is valid in transport equations.

### Table 1. Characteristic Values of the Cation-Exchange Membrane (Selemion CMV)

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<tr>
<th>( C_{ex} ) (meq cm(^{-2}))</th>
<th>( k_1 ) /mol(^{-2}) cm(^3) min(^{-1})</th>
<th>( k_{-1} ) /mol(^{-2}) cm(^3) min(^{-1})</th>
<th>( P ) /cm(^{-1}) min(^{-1})</th>
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<td>2.65</td>
<td>4.78 ( \times 10^3 )</td>
<td>2.58 ( \times 10^9 )</td>
<td>2.1 ( \times 10^{-5} )</td>
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The value, \( C_{ex} \), is obtained for the ion exchange capacity of Cu\(^{2+}\) type cation-exchange membrane in the wet condition. The value, \( k_1 \), is the rate constant of adsorption of copper(II) ion to the membrane, which was obtained from the adsorption experiment using Na\(^+\)-type cation-exchange membrane and 1 mM copper(II) chloride solution. The value, \( k_{-1} \), is the rate constant of desorption of copper(II) ion from the membrane, which was obtained from the desorption experiment using Cu\(^{2+}\)-type cation-exchange membrane and 2 mM sodium chloride solution. The value, \( P \), is permeation constant of copper(II) ion to the membrane, which was obtained from the transport experiment using double Na\(^+\)-type cation-exchange membrane, 1 mM copper(II) chloride solution as the source phase, and 1 mM EDTA-2Na solution as the receiving phase.
Selective Transport of Heavy Metal Ions

\[ K_{ex} = \frac{[Cu^{2+}]_m[Na^+]^2}{[Na^+]_m^2[Cu^{2+}]} \]  

(12)

From Eqs. 2 and 12, Eq. 13 can be obtained.

\[ J = J_e = (k_e - k_d)\frac{[Cu^{2+}]_m[Na^+]^2}{[Na^+]_m^2[Cu^{2+}]} \]  

(13)

In this case, the flux is proportional to the second power of the sodium concentration in the receiving phase because \([Cu^{2+}]_m\) is determined by the copper(II) ion amount in the source phase and is constant approximately. This case is for the low concentration of sodium chloride in the receiving phase. Figure 3 shows the slope of 2 and the slope of the flux dependence on the sodium chloride concentration was about 2. The deviation from the value 2 was caused by the deviation of the activity coefficient from unity.

The fluxes of various divalent metal ions are compared in Fig. 5 for 1 mM EDTA-2Na in the receiving phase and 1 mM single chloride salt solution in the source phase. There is a tendency that the flux increases with the complex formation constant\(^{14}\) but there were some deviations in the relationship, which may be caused by the differences of the rate constants of the complex formation.\(^{15}\) The fluxes of various divalent metal ions were also obtained for 1 mM NTA-3Na (C\(_6\)H\(_6\)N\(_6\)O\(_6\)Na\(_3\)) or 1 mM trisodium citrate in the receiving phase, which showed similar tendencies.

The mutual separation of metal ions was tested for the mixed solution of manganese(II) and copper(II) ions. The flux of each metal ion and their ratio are shown in Fig. 6. In the case of single metal ion solution, the copper(II) ion flux is about twice the manganese(II) ion flux, as shown in Fig. 5. In the case of mixed ion solution, the selective permeability of copper(II) ion to manganese(II) ion shown as the flux ratio in Fig. 6 increased. There is a maximum value and the fluxes of both ions approaches to the same value when the concentration of the chelating agent in the receiving phase was too much for the metal ions. Therefore, one of the metal ions can be selectively enriched in the receiving phase when the amount of the chelating agent is approximately equal to that of the metal ion which one desires to enrich. In the condition, the competition of the chelate formation reaction may occur between the two ions in the receiving phase. The high selectivity was also observed in the cases for other chelating agents. The flux ratio of copper(II) ion to manganese(II) ion was 40 in the case when the receiving phase solution was 1 mM trisodium citrate and the source phase was the mixed salt solution of 1 mM copper(II) chloride and 1 mM manganese(II) chloride, while the flux ratio of copper(II) ion to manganese(II) ion was 5.5 in the case when the source phase was the single salt solution of 1 mM copper(II) chloride or 1 mM manganese(II) chloride.

It is better for heavy metal ions to be separated as free ions rather than in complexes. Therefore, stripping of a metal ion from the complex solution was tested with a three-compartment cell. Figure 7 shows the separation of copper(II) ion and magnesium ion. Magnesium ion was not permeated to the receiving phase. In this case, the flux is proportional to the second power of the sodium concentration in the receiving phase because \([Cu^{2+}]_m\) is determined by the copper(II) ion amount in the source phase and is constant approximately. This case is for the low concentration of sodium chloride in the receiving phase. Figure 3 shows the slope of 2 and the slope of the flux dependence on the sodium chloride concentration was about 2. The deviation from the value 2 was caused by the deviation of the activity coefficient from unity.

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ceiving phase solutions for trapping in the cation-exchange membrane between source phase and the receiving phase 1. In contrast, copper(II) ion was permeated to the receiving phases and free copper(II) ion was obtained in the receiving phase 2. The solution pH of the receiving phase 1 decreased gradually to be ca. 2.5 at last in this experiment. The pH change in the receiving phase 1 is a defect of this system, but it will be improved in our further study.

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References