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Extractive Permeation of Zinc(II) and Cadmium(II) Chloride Complexes through Anion-Exchange Membrane

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Extractive permeation is demonstrated in the permeation of Zn(II) and Cd(II) chloride complexes through an anion-exchange membrane. A selective permeation between Cd(II) and Zn(II) was observed. This selectivity well corresponded to the sorption selectivity with an anion-exchange resin. Under the large concentration gradient of chloride ions across a membrane, Cd(II) chloride complex was selectively enriched in the receiving solution. The concentration ratios between the source and the receiving solution after 40 h reached 5.8 for Cd(II) and 1.2 for Zn(II) when chloride ions of 0.5 mol dm^{-3} were added to the source solution.

Solvent extraction is known to be a useful method to confirm and separate metal ions from solutions.[1] In this method, the separation selectivity is enhanced by a specific reaction between the metal ions and the complexing agents. A hydrophobic complex formed in an aqueous solution is selectively extracted into organic solution and a hydrophilic complex is retained in the aqueous solution (masking). To make a continuous process of such a system, liquid membrane systems have been developed.[2] However, the unstability of these systems pose a large problem to the practical industrial applications. In this respect, separation systems using polymer membranes are prominent.

Regarding the hyperfiltration process, Nguyen et al. reported that metal ions could selectively be ultrafiltrated using a reaction of metal ions with water-soluble macromolecules.[3] Similar attempts were also made by Lee and co-workers.[4] Selective hyperfiltration of a heavy-metal acetylacetonate complex through a hydrophobic polystyrene membrane was reported by Igawa et al.[5] A chelate-forming heavy metal was selectively transported through the polystyrene membrane by some coupling process with a solvent flow under hydraulic pressure. In the dialysis process, Wallece introduced a "Donnan dialysis" system for membrane separation, in which the Donnan equilibrium principle[6] was applied to a dialysis system utilizing separation by an ion-exchange membrane.[7] By applying a high-concentration gradient of receiving electrolytes across a cation-exchange membrane, the metal ions can be effectively enriched against the concentration gradient into the receiving solution. Wallece[7] and Davis et al.[8] reported an enrichment of metal ions, such as uranil ion, according to this method. A selective enrichment of metal ion by using a reaction with chelating agents was also shown by Wallece[7] and Cox et al.[9–11]

During the course of our study we studied the production of a polymer membrane which exibits selective separation ability similar to that of the liquid membrane systems.[12–17] For a selective permeation of metal ions through the membrane, certain metal species must first be preferentially sorbed into the membrane over other metal species in the solution. However, the interaction of the hydrated metal ions and conventional polymeric membranes and the difference in ionic radii among metal ions are generally slight for metal separation. This fact suggests the difficulty in achieving the selective separation of metal ions by the polymer membranes.

On the other hand, some metal ions are known to complex with halide ions to form metal halide complexes as follows:

$$\mathrm{M}^{2+} + \mathrm{X}^- \overset{K_1}{\rightleftarrows} \mathrm{MX}^+ \tag{1-1}$$

$$\mathrm{MX}^+ + \mathrm{X}^- \overset{K_2}{\rightleftarrows} \mathrm{MX}_2 \tag{1-2}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\mathrm{MX}_{m-1}^{-(m-1)} + \mathrm{X}^- \overset{K_m}{\rightleftarrows} \mathrm{MX}_m^{-(m-2)} \tag{1-m}$$

Here, K_m stands for the m-th successive complex formation constants between metal (M^{2+}) and halide (X^-) ions. These complexes are selectively extracted into an organic solution containing an anion exchanger, such as lipophilic quaternary ammonium salts.[1] According to the differences in the formation constants of metal ions with halide ions and the interaction between metal halide complexes and extractant cations, the selective extraction behavior of metal ions has been observed. A similar selective sorption has been reported for anion-exchange resins.[18] Therefore, a membrane having an anion-exchange group (anion-exchange membrane) is expected to show an excellent separation ability for metal halide complexes. In this separation method, the metal ion is selectively sorbed (or "extracted") into the membrane as an anionic halide-complex form and transfers across the membrane to the opposite-side solution. Furthermore, the large concentration difference of halide ions across the membrane is expected to cause an "uphill" transport of metal halide complexes due to Donnan equilibrium.

The aim of this present study was to examine and verify the above-mentioned hypothesis. We investigated the sorption and permeation behavior of Zn(II) and Cd(II) chloride complexes with the anion-exchange resin and membrane.

Experimental

Stock solutions of Zn(II) and Cd(II) chlorides (in 0.1 mol dm^{-3} HCl or HNO_3) and $MgCl_2$ solution were stored in polyethylene bottles. Metal chloride solutions were prepared by mixing and diluting these stock solutions. The concentrations of the metal ions were measured with a Shimadzu AA-630-02 atomic absorption spectrophotometer. The reagents used in the study were reagent-grade commercial products and were used without further purification.

Anion-exchange resin (Amberlite CG-400, Rohm & Hass Co., Ltd.) was purified by treating with 1 mol dm^{-3} NaOH. 1 mol dm^{-3} HCl and finally by washing with pure water. The ion-exchange capacity was 3.7 mequiv/g-dry resin. The anion-exchange membrane (Selemion AMV, ion-exchange capacity: 2.0—2.3 mequiv/g-dry membrane) was provided by Asahi Glass Co., Ltd. The membrane was soaked twice in 1 mol dm^{-3} HCl and pure water prior to an experiment.

The sorption experiments were performed according to a previously described procedure.[12] One-tenth of a gram of resin (finer than 100 mesh) was suspended in 10 cm^3 of a $MgCl_2$ solution containing 1 mmol dm^{-3} Zn(II) and Cd(II) (the solution pH was adjusted to 1.7 by HCl); the mixture was shaken on a mechanical shaker until equilibrium was attained (12 h). After filtering the solution the residual concentration of metal ion was then measured by atomic absorption spectrophotometry. The sorption behavior of metal ions was estimated by means of the degree of sorption (S) and distribution ratio (D):

$$S(\%)=\frac{[\mathrm{M}]_\mathrm{i}-[\mathrm{M}]_\mathrm{f}}{[\mathrm{M}]_\mathrm{i}}\times 100 \tag{2}$$

and

$$D(\mathrm{mL\,g^{-1}})=\frac{[\mathrm{M}]_\mathrm{i}-[\mathrm{M}]_\mathrm{f}}{[\mathrm{M}]_\mathrm{i}}\times\frac{V_\mathrm{w}}{W_\mathrm{m}}, \tag{3}$$

where $[\mathrm{M}]_\mathrm{i}$ and $[\mathrm{M}]_\mathrm{f}$ are the initial and final metal concentrations, respectively. V_w is the volume of the solution (cm^3), and W_m the weight of the resin (g).

The dialysis experiments were carried out by using a cylindrical glass cell, as shown in Fig. 1. The membrane was attached to the bottom of a cell with silicone packing (effective membrane area is 1.1 cm^2). A clamp and screws made from polycarbonate were used to prevent contamination by metal ions. The cell, which contained 5 cm^3 of pure water as a receiving solution, was dipped into 97 cm^3 of the source solution containing various concentrations of $MgCl_2$ and 0.1 mmol dm^{-3} metal ions (the pH was adjusted to 2.7 by HNO_3). The solutions were magnetically stirred, and the concentration change of metal ions after 40 h in the source and the receiving solution were measured. The experiments were carried out in a water bath at 30 °C.

Results and Discussion

Sorption of Zn(II) and Cd(II) Chloride Complexes. Some metal ions are known to form anionic metal complexes with halide or pseudohalide ions such as Cl^-, Br^-, I^-, and SCN^- in solution.[19] These complexes are expected to interact selectively with the anion-exchange site in the membrane. In the present study we investigated the sorption and permeation behavior of Zn(II) and Cd(II) chloride complexes. Figure 2 shows the sorption behavior of Zn(II) and Cd(II) on the anion-exchange resin under various concentrations of chloride ion. Cd(II) sorption increased significantly with an increase in the chloride concentration. This indicates that Cd(II) is sorbed in the form of an anionic chloride complex, such as $CdCl_n^{2-n}$. The selective sorption was observed for Cd(II) over Zn(II). The successive stability constants (K_m) for Zn(II) and Cd(II) are reported as follows:[19] $\log K_m$ of Zn(II): -0.49 (m=1), 0.51 (m=2), -0.09 (m=3); $\log K_m$ of Cd(II): 1.58 (m=1), 0.65 (m=2), 0.12 (m=3). As can be seen from the values, the difference in the sorption of these ions on the anion-exchange resin can mainly be attributed to a difference in the complexation ability with chloride ions. In general, the ion-exchange

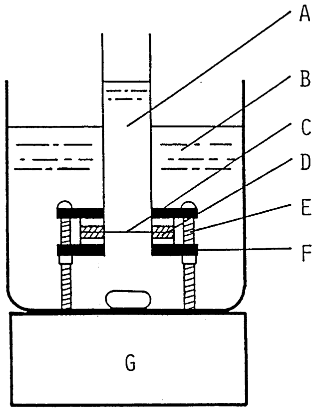

Fig. 1. Dialysis cell: (A) receiving solution, (B) source solution, (C) membrane, (D) silicone packing, (E) screw, (F) clamp, (G) magnetic stirrer.

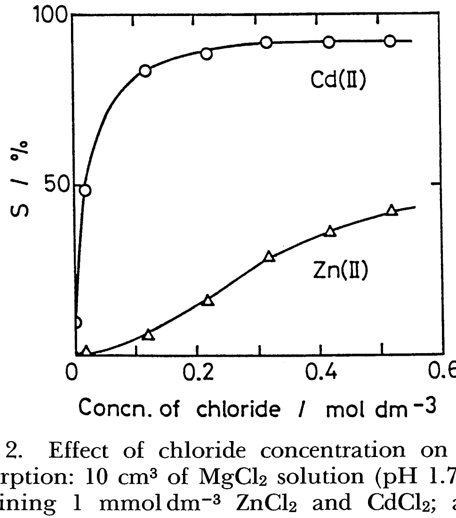

Fig. 2. Effect of chloride concentration on metal sorption: 10 cm^3 of $MgCl_2$ solution (pH 1.7) containing 1 mmol dm^{-3} $ZnCl_2$ and $CdCl_2$; anion-exchange resin, 0.1 g; (○) Cd(II); (△) Zn(II).

resins show a high sorption ability for less-hydrated ions.20) Therefore, the difference in hydrophobic nature of metal chloride complexes is considered to also affect the sorption selectivity.

Mechanism of Sorption. When the ion pair is formed between the anion-exchange site and the metal chloride complexes, the following equations can be used:

$$n(\mathrm{RCl})_\mathrm{r} + (\mathrm{M}^{2+})_\mathrm{a} + 2(\mathrm{Cl}^-)_\mathrm{a} \overset{K_\mathrm{ex}}{\rightleftarrows} (\mathrm{R}_n\mathrm{MCl}_{n+2})_\mathrm{r} \tag{4}$$

and

$$K_{ex} = [\mathrm{R}_n\mathrm{MCl}_{n+2}]_\mathrm{r}/[\mathrm{RCl}]_\mathrm{r}^n[\mathrm{M}^{2+}]_\mathrm{a}[\mathrm{Cl}^-]_\mathrm{a}^2, \tag{5}$$

where R represents the anion-exchange site in the resin, and subscripts "r" and "a" denote the resin and the aqueous phase, respectively. Equation 5 can be expressed logarithmically as

$$\log \beta D = 2\log[\mathrm{Cl}^-]_\mathrm{a} + n\log[\mathrm{RCl}]_\mathrm{r} + \log K_\mathrm{ex}, \tag{6}$$

where D and β represent the distribution ratio of the metal ions and the coefficient related to the chloride ion concentration, respectively. When the overall stability constant is β_i, the values of D and β can be defined by

$$D = [\mathrm{R}_n\mathrm{MCl}_{n+2}]_\mathrm{r}/\sum_{i=0}^{m}[\mathrm{MCl}_i^{2-i}]_\mathrm{a} \tag{7}$$

and

$$\beta = \sum_{i=0}^{m}\beta_i[\mathrm{Cl}^-]_\mathrm{a}^i. \tag{8}$$

In the case that the concentration of $(\mathrm{R}_n\mathrm{MCl}_{n+2})_\mathrm{r}$ is negligible compared with that of $(\mathrm{RCl})_\mathrm{r}$, the value of $[\mathrm{RCl}]_\mathrm{r}$ in Eq. 6 can be regarded as being constant. Therefore, the relationship between $\log \beta D$ and $\log[\mathrm{Cl}^-]_\mathrm{a}$ is readily estimated from Eq. 6. This relationship for the sorption of Zn(II) and Cd(II) chloride complexes on the resin is shown in Fig. 3. The activities of the chloride ions (a_{Cl^-}) were calculated using the Debye-Hückel equation.21) Both plots gave a straight line with a slope of 2, suggesting that the reaction depicted in Eq. 4 indeed took place.

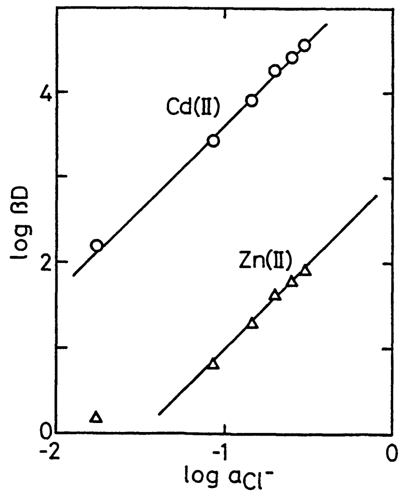

Fig. 3. Sorption of metal chloride complexes as a function of chloride activities in solution: plots according to Eq. 6. Conditions and symbols are similar to those in Fig. 2.

We have recently reported that the Cd(II) chloride complex is sorbed on the crown ether resin in the ion-association form of $\mathrm{K}^+\cdot\mathrm{CdCl}_3^-$ (anion-exchange sorption). In this system, when magnesium chloride was used as a complexing salt, which has little interaction with crown ether in the resin, Cd(II) sorption was negligible.17) The sorption of metal chloride complexes was also negligible for a porous polystyrene resin, which consists of a matrix of the anion-exchange resin. Hence, the sorption of metal chloride complexes with the anion-exchange site is the main reaction for this sorption.

Unfortunately, the n-value was not determined in the present study because of difficulties in evaluating the $[\mathrm{RCl}]_\mathrm{r}$ value in Eq. 6. However, we consider that n-values of 1 or 2 may be favorable in comparison with the ion-association extraction systems reported.22)

Permeation of Zn(II) and Cd(II) Chloride Complexes. On the basis of the selective interaction of metal chloride complexes with the anion-exchange site mentioned above, a selective permeation of metal ions through an anion-exchange membrane can be expected. The permeation mechanism of this system is shown in Fig. 4 (a 1:1 ion-pair was assumed between metal halide complex and ion-exchange site in the membrane for simplicity; n=3 in Eq. 4). In this permeation, the metal ions are selectively sorbed (or "extracted") in the form of metal chloride complexes, and transported to the receiving solution due to a migration of a metal chloride complex between the fixed-carriers (anion-exchange site) in the membrane. As can be seen from the figure, the membrane is permeable only to the metal and the chloride ions in the system. Therefore, the free energy change (ΔG) of the system is simply expressed6) as

$$\Delta G = RT\ln\frac{[\mathrm{M}^{2+}]_\mathrm{R}[\mathrm{Cl}^-]_\mathrm{R}^2}{[\mathrm{M}^{2+}]_\mathrm{S}[\mathrm{Cl}^-]_\mathrm{S}^2}, \tag{9}$$

where R is the gas constant and T is the absolute

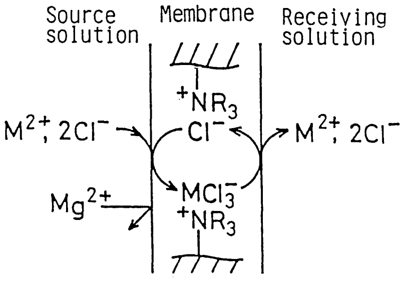

Fig. 4. Permeation mechanism of metal chloride complexes through anion-exchange membrane.

temperature. Subscripts "S" and "R" denote the source and the receiving solution, respectively. At the equilibrium condition, ΔG becomes zero, and Eq. 9 becomes:

$$\frac{[M^{2+}]_R}{[M^{2+}]_S} = \frac{[Cl^-]_S^2}{[Cl^-]_R^2}, \tag{10}$$

This equation should be more complicated, because the concentration of free metal ion varies with the reaction of complex formation between metal and chloride ions. However, it qualitatively indicates that matal ion can be enriched in the receiving solution due to the large concentration gradient of chloride ion across the membrane. Under the present conditions, $MgCl_2$ was added to the source solution in large excess. Therefore, a selective uphill transport of the metal ions also can be expected in this system.

Figure 5 shows the effect of the chloride ion concentration on the permeation of Zn(II) and Cd(II) through the anion-exchange membrane. The permeation of Cd(II) increased significantly with an increase in the chloride ion concentration, and Cd(II) was selectively enriched in the receiving solution, as expected. The concentration ratios of the source and receiving solution after 40 h reached 5.8 for Cd(II) and 1.2 for Zn(II) when chloride ions of 0.5 mol dm^{-3} were added to the source solution. Apparently, the Zn(II) chloride complex was less permeable through the membrane. This was due to the low sorptivity of Zn(II) in the membrane. Consequently, the selective permeation of Cd(II) to Zn(II) could be attained in this system. The decrememt of both metal ions in the source solution showed higher values compared to the increasing degree of the receiving solution. This suggests that the anion-exchange membrane retained metal chloride complexes to some extent. However, the retention amounts of metal ions calculated from the mass balances were very small: the values after 40 h were 0.09 mmol/g-dry membrane for Cd(II) and 0.07 mmol/g-dry membrane for Zn(II), respectively, when the chloride concentration in the source solution was 0.5 mol dm^{-3}. Therefore, the migration of metal chloride complexes between a fixed carrier in an anion-exchange membrane can readily occur in this dialysis.

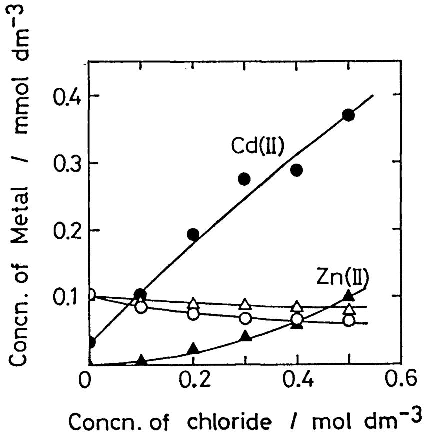

Fig. 5. Permeation behavior of metal chloride complexes through anion-exchange membrane: source solution, 97 cm^3 of $MgCl_2$ solution (pH 2.7) containing 0.1 mmol dm^{-3} $ZnCl_2$ and $CdCl_2$; receiving solution, 5 cm^3 of pure water; metal concentration in the source solution (○, Cd(II); △, Zn(II)), in the receiving solution (●, Cd(II); ▲, Zn(II)).

Equation 10 indicates that the degree of metal enrichment increases with an increase in the chloride ion concentration. However, the leakage of additive salts ($MgCl_2$) also increases with an increase in the $MgCl_2$ concentration because of a decreasing Donnan repulsion effect in the membrane. This phenomenon causes a negative effect for the permeation of metal ions, since the retention of metal chloride complexes in the membrane increses with increasing chloride concentration in the receiving solution. Therefore, optimum conditions are considered to exist in this system. Details of these effects are now under investigation.

In conclusion, it was found that the selective transport of Cd(II) chloride complexes can be observed through an anion-exchange membrane. The permeation selectivity of the metal ions was essentially induced by a selective uptake of metal chloride complexes into the anion-exchange membrane. Hence, an extractive permeation similar to liquid membrane systems could be attained in the present system.

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