Selective Permeation of Cadmium(II) Chloride Complex through Cellulose Triacetate Plasticizer Membrane Containing Trioctylmethylammonium Chloride Carrier

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A novel polymeric plasticizer membrane which is composed of cellulose triacetate as a membrane support, *o*-nitrophenyloctyl ether as a membrane plasticizer, and trioctylmethylammonium chloride as an anion-exchange carrier has been developed. Highly selective permeation of Cd(II) chloride complex through the plasticizer membrane was found to be obtained by the addition of EDTA in the receiving phase .

Certain heavy metal cations such as Pb(II) and Cd(II) are extracted into organic solvents as anionic metal halide complexes by liquid anion-exchangers.[1, 2] This system has been applied to continuous liquid membrane separations such as bulk liquid membrane separation and emulsion liquid membrane separation.[3] However, the unstability of these systems often poses a problem to practical industrial applications. To enhance the system stability and permeation efficiency, we have prepared a novel polymeric plasticizer membrane which is composed of cellulose triacetate (CTA) as a membrane support, *o*-nitrophenyloctyl ether (NPOE) as a membrane plasticizer, and trioctylmethylammonium chloride (TOMAC) as an anion-exchange carrier according to the procedure reported by Sugiura et al (Figure 1).[4,5] Although the permeation selectivity of Pb(II) and Cd(II) chloride complexes are influenced by the experimental conditions due to a difference in the Cd(II) retention in the membrane, we report herein that the addition of ethylenediamine tetraacetic acid (EDTA) in the receiving phase is very effective to achieve highly selective permeation and concentration of Cd(II) through the CTA plasticizer membrane.

In 10 cm^3 of chloroform, 0.20 g of CTA, 0.40 g of NPOE, and 0.40 g of TOMAC were dissolved. Of this solution, 3 cm^3 was poured into a glass culture dish (9.0 cm in diameter). After one day at room temperature, cold water was added and the membrane was peeled away from the dish. This procedure provided a stable, transparent film of 50 μm thickness. The obtained membrane was easily handled and stored under the dried condition.

In the present system, the liquid anion exchanger TOMAC functions as an anion-exchange carrier.[3] Heavy metal ions are selectively extracted at the membrane-source phase interface, transported through the plasticizer membrane to the membrane-receiving phase. Transport is driven by concentration gradients of both metal and chloride ions. As indicated in Figure 1, the membrane is permeable only to heavy metal and chloride ions. At equilibrium, the Donnan equilibrium equation is

$$[M^{2+}]_s[Cl^-]_s^2=[M^{2+}]_r[Cl^-]_r^2 \qquad (1)$$

where the subscripts s and r denote the source and receiving phases, respectively.[7] Thus, the metal ion species can be enriched in the receiving phase by a large concentration gradient of chloride ion across the membrane when the volume ratio of the receiving phase to the source phase is small.

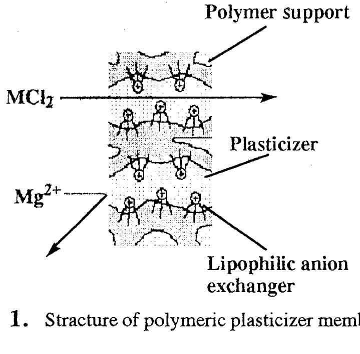

Figure 1. Stracture of polymeric plasticizer membrane.

The membrane transport experiments were first conducted in a cylindrical dialysis cell (membrane area, 0.8 cm^2) reported previously.[6] The source phase solution was a 250 cm^3 of 0.25 M (1 M = 1 mol dm^{-3}) $MgCl_2$ solution which contained 0.10 mM Pb(II) and Cd(II) (the pH was adjusted to 2.4 by HCl). The receiving phase was 5.0 cm^3 of pure water. The source and receiving phases were stirred with a magnetic stirrer (EYELA RC-2, Tokyo Rikakikai Co. Ltd.) and by circulating the solution with a peristaltic pump (EYELA MP-3, Tokyo Rikakikai Co. Ltd.), respectively. The cell was dipped into a thermostated water bath at 30°C. Metal ion concentrations in both the receiving and source phases were measured with a Hitachi 170-30 atomic absorption spectrophotometer. Plots of the enrichment factor (EF, the metal ion concentration in the receiving phase divided by the metal ion concentration in the source phase) versus time for competitive transport of Pb(II) and Cd(II) are presented in Figure 2. The EF for Cd(II) increased with time and reached value of 13.3 but EF for Pb(II) was 0.7 after 6 h. Thus Cd(II) chloride complex was found to be selectively concentrated in the receiving phase solution in the present condition.

To enhance the permeation efficiency, three compartment cell having a large membrane area (15.0 cm^2) was employed.[8] The source phase was a 250 cm^3 of 0.25 M $MgCl_2$ solution which contained 0.10 mM Pb(II) and Cd(II). The receiving phase (10 cm^3) was pure water. The source phase and receiving phase solutions were circulated from reservoirs through the outer two compartments and the central compartment, respectively, with the peristaltic pump at 30 °C. Figure 3 shows the results for the competitive transport of Pb(II) and Cd(II) with time. In this dialysis, a selective permeation was noted for Pb (II) over Cd (II), which is opposite selectivity recorded in Figure 2. Thus the EF values reached 12.0 for Pb(II) and 6.4 for Cd(II) after 5 h. Apparently the membrane area of the system affected the permeation selectivity for Cd(II) and Pb(II).

When the small membrane area (0.8 cm^2) was used for the dialysis, concentration of Cd(II) in the membrane became very high (4.7 x 10^{-6} mol/cm^2-membrane after 6 h). In this condition, the retention of Cd(II) in the membrane may be no

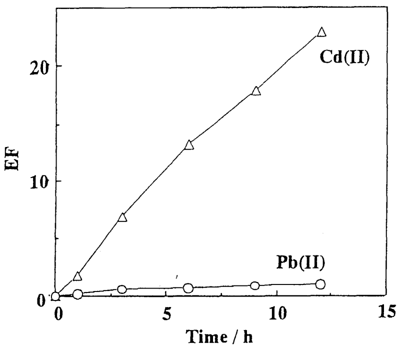

Figure 2. Enrichment factor (EF) of metal ions as a function of permeation time. Souce phase: 0.25 M $MgCl_2$ solution containing 0.1 mM Pb(II) and Cd(II) (250 cm^3, pH 2.4). Receiving phase: pure water (5 cm^3). Membrane area: 0.8 cm^2.

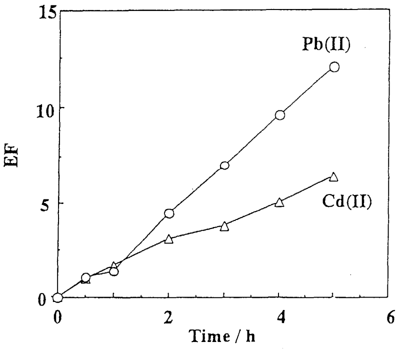

Figure 3. Enrichment factor (EF) of metal ions as a function of permeation time. Souce phase: 0.25 M $MgCl_2$ solution containing 0.1 mM Pb(II) and Cd(II) (250 cm^3, pH 2.4). Receiving phase: pure water (10 cm^3). Membrane area: 15 cm^2.

longer strong, which permitted an effective Cd(II) transport through the membrane. In contrast, the Cd(II) concentration in the membrane was low (0.5 x 10^{-6} mol/cm^2-membrane after 5 h) for dialysis with the large membrane area (15.0 cm^2). Under this condition, a strong retention of Cd(II) in the membrane prohibited the release of Cd(II) chloride complex at the membrane-receiving interface as reported previously.[3] Whereas the permeation of Pb(II) simply increased as an increase of the membrane area due to the low extractability of Pb(II) chloride complex into the membrane. Consequently, the permeation selectivity was changed from Cd(II) to Pb(II) by increasing the membrane area.

For practical separation of heavy metal ion, a large membrane area must be utilized. To improve the Cd(II) permeability in such a system, therefore, the Cd(II) retention in the membrane phase must be reduced. The EDTA is known as an effective complexing agent for heavy metal ions in aqueous solution. In fact, the 1:1 complex formation constants (log K) of EDTA with metal ion are 16.5 for Cd(II) and 18.0 for Pb(II), respectively.[9] Thus the addition of EDTA in the receiving phase may be effective to reduce the Cd(II) retention in the membrane phase. The EF values of Cd(II) and Pb(II) after 5 h as a function of EDTA (disodium salt) concentration in the receiving phase is shown in Figure 4 (experimental conditions are the same except for the addition of EDTA to those in Figure 3). As expected, the permeation of Cd(II) was effectively enhanced at above the EDTA concentration of 3 mM. It is interesting to note, however, that the permeation of Pb(II) was monotonously suppressed with increasing EDTA concentration. The enhanced Cd(II) permeation did not interfere the permeation of Pb(II), which was confirmed from single transport experiments. Thus the membrane extractable anionic EDTA-Pb(II) complex may be formed at membrane-receiving phase interface. Consequently, highly selective Cd(II) permeation was found to be obtained by the addition of EDTA in the receiving phase. This is a first example that the polymeric plasticizer membrane exhibited a superior separation efficiency and selectivity to the liquid membrane systems for concentration of Cd(II) from aqueous samples.

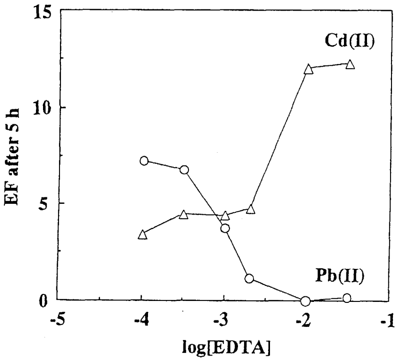

Figure 4. Enrichment factor (EF) of metal ions as a function of EDTA concentration in the receiving phase. Souce phase: 0.25 M $MgCl_2$ solution containing 0.1 mM Pb(II) and Cd(II) (250 cm^3, pH 2.4). Receiving phase: EDTA disodium solution (10 cm^3). Membrane area: 15 cm^2.

To elucidate these interesting phenomena for metal specific membrane separation, the detailed studies upon the partition behavior of metal chloride complexes to the polymeric plasticizer membrane and the flux analysis on the basis oh carrier mediate transport mechanism are actively underway in our laboratory.

References and Notes

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