Separation of Heavy Metal Ions with a Chelating Reagent Fixed in an Anion-exchange Membrane

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Abstract
The precipitation treatment of waste water of heavy metal ions as hydroxides is not efficient when their concentrations are very low. We propose a novel method to separate heavy metal ions with ethylenediaminetetraacetic acid (EDTA) fixed in an anion-exchange membrane. Cation-exchange membranes were placed at both sides of the membrane to avoid the desorption of the reagent by the ion-exchange with the co-ion in the solutions. Heavy metal ions in the source phase solution was selectively transported to the receiving phase of acid solution via the complexation with EDTA fixed in the anion-exchange membrane.

Key words: ion exchange, heavy metal ions, EDTA, complexation, waste water treatment, selective transport

1 Introduction
Mutual separation of solutes is an important subject in membrane technology and there have been many reports on the separation with membranes. The liquid membrane is an effective separation method [1,2] but the organic solvents and the carriers, which are expensive and toxic in most cases, are dissolved from the membrane into the aqueous solution. When one uses ion-exchange membranes, it is possible to separate solutes without organic solvents. We have reported the selective transport of heavy metal ions by using a cation-exchange membrane and ethylenediaminetetraacetic acid (EDTA) solution as the receiving phase.[3] However, further separation of heavy metal ions from EDTA is required in the system. Some chelating reagent fixed on the membrane has the potential to be an effective separation method of some solute via the specific complexation with the solute. It has been reported that the transport of olefins was facilitated via the complexation with silver ion fixed in the cation-exchange membrane [4] and that of aldehydes via the adduct formation with hydrogen sulfite fixed in the anion-exchange membrane.[5] Facilitated transport of carbohydrates were also reported across an anion-exchange membranes via the reaction of borate ion [6,7] or hydroxide ion [8] fixed on the membrane.

We have tried to permeate heavy metal ions selectively across an anion-exchange membrane via the specific reaction of the ions with EDTA fixed in the membrane. Heavy metal ions were selectively transported efficiently across the membrane in the system via the complexation with the metal ion. In this paper, we will report the permeation characteristics of the copper and potassium ions in the system and their transport mechanism.
2. Experimental

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, the source phase and the receiving phase compartments, which were partitioned by two cation-exchange membranes (Asahi Glass Co. Ltd., Selemion CMV) and an anion-exchange membrane (Asahi Glass Co. Ltd., Selemion AMV) allocated between the two cation-exchange membranes. Each solution was circulated from each reservoir to the compartment by a tubing pump at a rate of 30 cm³ min⁻¹. The source phase solution was 100 cm³ of mixed solution of 1 mmol dm⁻³ (mM) copper (II) chloride and 1 mM potassium chloride, and the receiving phase solution was 100 cm³ of 1 M hydrochloric acid, unless otherwise stated. The membrane area was 8.5 cm² and the thickness of the silicone rubber for each solution compartment was 3 mm. Three screen spacers with each thickness of 1 mm were inserted in each 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 membrane was pretreated as follows before the transport experiment to be changed to some ion type membrane. The cation-exchange membrane was immersed into 100 cm³ aqueous solution of 1 M hydrochloric acid or 1 M sodium chloride for 1 h to be changed to H⁺ or Na⁺ type. The anion-exchange membrane was immersed into 100 cm³ aqueous solution of 0.1 M EDTA (disodium ethylenediaminetetraacetate, Na₂H₂Y) for 1 h to be changed to H₂Y²⁻ type. The immersion was repeated three times in each fresh solution, and the membrane was rinsed with pure water. The order of the membranes was Na⁺ type, H₂Y²⁻ type, and H⁺ type from the source phase to the receiving phase. These three membranes were attached firmly to each other to have no interspace between each membrane by the spacers and the acrylic frame, and the screws were used for holding both acrylic frames.

The adsorption amount of metal ions to the membrane was measured by their desorption with 1 M hydrochloric acid solution after the 10 h permeation experiment.

Metal ions were determined by an atomic absorption spectrophotometer (Shimadzu AA-6700F), and the solution pH was measured by a pH meter (Toa HM-60S).

Fig. 2. Concentration change in source phase and receiving phase. The initial component of source phase was 1 mM copper (II) chloride and 1 mM potassium chloride, and that of receiving phase was 1 M hydrochloric acid; the volume of each solution was 100 cm³, and the membrane area was 8.5 cm².
3. Results and Discussion

Fig. 2 shows the result of permeation experiment. The initial concentration of copper ion and potassium ion was 1 mM in the source phase solution, and decreased significantly at first and then gradually. Sodium ion concentration increased with the decrease of copper and potassium ions, and hydrogen ion increased behind the increase of sodium ion. In the receiving phase, potassium ion increased gradually, but the copper ion increased significantly behind the increase of hydrogen ion in the source phase. There is a large selectivity between these ions for the complexation selectivity of EDTA. Figure 3 shows the effect of concentration on the fluxes of copper (II) ion and potassium ion and the selective permeability, which is defined as the ratio of the flux to the initial concentration of copper (II) ion divided by the ratio for potassium ion. The flux of copper (II) is approximately constant, but the flux of potassium increased and the selective permeability decreased with the source phase concentration for the same concentration of copper (II) ion and potassium ion in the source phase as shown in Fig. 3A. However, the selective permeability maintained a high value when copper (II) ion was 1 mM with the concentration change of potassium ion as shown in Fig. 3B for the high complexation selectivity of EDTA. Most of waste water contains much alkaline or alkaline earth metal ions with a little heavy metal ions and this selectivity as shown in Fig.3B is effective for the treatment of the actual waste water, although the selectivity to alkaline earth metal ions is lower than the result shown here for their higher complexation constants with EDTA than those of alkaline metal ions.

The concentrations of metal ions in the membrane after 10 h permeation experiment were measured and shown in Fig.4. The concentration of copper (II) ion was much higher than that of potassium ion in H$_2$Y$^{2-}$ type anion-exchange membrane, which shows that the selective permeation was caused by the selective complexation of EDTA in the anion-exchange membrane.

From these experimental results, the selective permeation mechanism can be explained as shown in Fig. 5. At first, (1) heavy metal ion in the source phase solution is exchanged with sodium ion in the cation-exchange membrane, and heavy metal ion is transferred to the membrane and the sodium ion is released to the solution; (2)
heavy metal ion diffuses in the cation-exchange membrane with the sodium ion diffusion in the opposite direction; (3) heavy metal ion in the cation-exchange membrane complexes with H$_2$Y$_2^-$ fixed in the anion-exchange membrane, and heavy metal ion is transferred to the anion-exchange membrane and the proton is released to the cation-exchange membrane.; (4) the complex ion diffuses in the anion-exchange membrane with the diffusion of H$_2$Y$_2^-$ in the opposite direction; (5) heavy metal ion in the complex is exchanged with hydrogen ion in the cation-exchange membrane, and heavy metal ion is transferred to the cation-exchange membrane and the hydrogen ion is bonded to Y$_4^-$ in the anion-exchange membrane.; (6) heavy metal ion diffuses in the cation-exchange membrane with the hydrogen ion diffusion in the opposite direction; (7) heavy metal ion in the anion-exchange membrane is exchanged with hydrogen ion in the receiving phase solution, and heavy metal ion is released to the solution and the hydrogen ion is transferred to the membrane; overall transport is the transport of heavy metal ion in the source phase solution to the receiving phase with the transport of hydrogen ion in the opposite direction. At the beginning of the permeation experiment, sodium ion is transferred to the source phase solution and then the transported ion is exchanged from sodium ion to hydrogen ion as shown in Fig. 2. Sodium ion fixed in the cation-exchange membrane prevents the significant pH decrease in the source phase solution.

The problem in this system is the formation of the precipitation, which may be some chelate, at the space between H$_2$Y$_2^-$ type anion-exchange membrane and hydrogen ion type cation-exchange membrane. The precipitation forming may be prevented by blocking the formation of dead space containing water between the membranes or by using an adequate chelating reagent other than EDTA. Further investigation for the improved membrane system will be reported later.

References