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Neutralization Dialysis for Deionization

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In neutralization dialysis, cations are exchanged with protons across a cation-exchange membrane, while anions are exchanged with hydroxide ions across an anion-exchange membrane, and the effective deionization and the neutralization occur simultaneously on the base of Donnan equilibrium. The ion-exchange membranes are much more permeable to the electrolytes than the nonelectrolytes and their mutual separation is possible by this method.

Donnan dialysis is an ion-exchange membrane process based on Donnan equilibrium[1] and it has been used for salt enrichment.[2–5] Recently, we proposed a novel deionization method based on the principle of Donnan dialysis by the simultaneous use of a cation-exchange membrane and an anion-exchange membrane.[6] When a salt solution is separated from an acid solution with a cation-exchange membrane and from a base solution with an anion-exchange membrane, the cations in the salt solution are exchanged with protons, while the anions are exchanged with hydroxide ions, and deionization and neutralization occur simultaneously. This process can be called "neutralization dialysis," because salts are transported rapidly across the membrane by the great concentration gradients of protons and hydroxide ions caused by neutralization in the deionization compartment. Neutralization dialysis is a simple, continuous, and very effective process and its principle must also play an important role in biomembranes. Active transports coupled with proton antiport have been reported as the model of biomembranes,[7] but the ion transport will be enhanced much when it is coupled with neutralization reaction. This method will be quite profitable for desalination because of requiring a low energy and low cost and it may be able to substitute this deionization process for the ion-exchange process on ion-exchange resin. The ion-exchange membranes are much more permeable to electrolytes than nonelectrolytes and their complete mutual separation will be also reported in this report.

Experimental

The neutralization-dialysis cell, which is similar to the macromosaic cell,[8] and the schematic ion transport are shown in Fig. 1. Each compartment is 0.5 mm thick with a $2\times10\ \mathrm{cm}^2$ area. The solutions in deionization compartment D, in acid compartment A, and in base compartment B were cycled from respective reservoirs with tube pumps at a rate of $40\ \mathrm{cm\ min}^{-1}$. The ion-exchange membranes in the cell were Selemion AMV and CMV(Asahi Glass Co., Ltd.). In the dialysis experiment, $3\ \mathrm{cm}^3$ samples were collected from the solution of compartment D at a regular interval and the cation concentration, the specific resistance, and pH were measured with an atomic absorption spectrophotometer, a conductance cell, and a pH meter, respectively. The separation of electrolytes from nonelectrolytes was investigated with a mixed aqueous solution of potassium chloride and methyl alcohol. The concentration of methyl alcohol was measured with a total organic carbon analyzer.

Results and Discussion

A deionization experiment was carried out with the neutralization-dialysis cell and Fig. 2 shows the changes with time of the cation concentration, pH, and the specific resistance of the solution in compartment D. The ion concentration decreased and the specific resistance increased rapidly with time, and a deionized water with a specific resistance of 1 MΩ cm were obtained after 1.5 h.

In this process, Donnan equilibrium is set up across a membrane after an ample time and the ratios of the

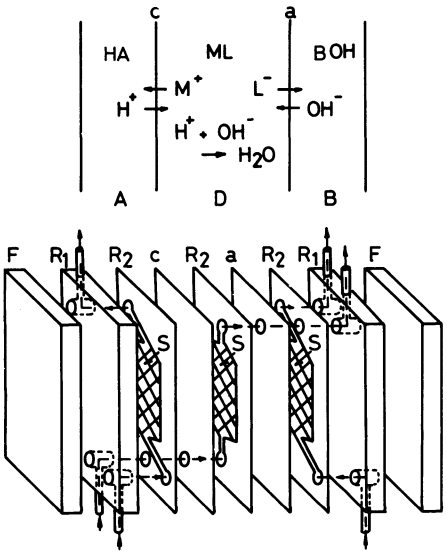

Fig. 1. Neutralization-dialysis cell and the schematic ion transport. a: Anion-exchange membrane, c: cation-exchange membrane. R_1 and R_2: silicone rubber sheet, S: spacer, F: acrylic resin frame.

ion concentrations in each compartment become

$$C_{A}^{M}/C_{A}^{H} = C_{D}^{M}/C_{D}^{H}, \tag{1}$$

$$C_{B}^{L}/C_{B}^{OH} = C_{D}^{L}/C_{D}^{OH}, \tag{2}$$

From the standpoint of thermodynamics, activities should be used for describing Donnan equilibrium but activity coefficients are assumed to be unity and concentrations are used in these equations for simplifying the discussion. In the equations, C is concentration, M, L, H, and OH are a monovalent cation, a monovalent anion, proton, and hydroxide ion, respectively, and A, B, and D are symbols of the compartments. When the volume of the acid solution is equal to that of the base solution and $C_{A}^{H}=C_{B}^{OH}$, $C_{A}^{M}=C_{B}^{L}$ and $C_{D}^{M}=C_{D}^{L}$. The material balance for the metal ion is

$$C_{A}^{M}V_{A} + C_{D}^{M}V_{D} = C_{0,D}^{M}V_{D} + C_{0,A}^{M}V_{A}, \tag{3}$$

where the amount of the ion in the cation-exchange membrane is ignored, and V and C_0 show the volume and the initial metal ion concentration of the solutions, respectively. From Eqs. 1 and 3, the final concentration of the metal ion in the deionization compartment is

$$C_{D}^{M} = (C_{0,D}^{M}V_{D}+C_{0,A}^{M}V_{A})/(C_{A}^{H}V_{A}/C_{D}^{H}+V_{D}). \tag{4}$$

Since protons and hydroxide ions combine to be water and their concentrations become 10^{-7} mol dm^{-3} ideally in compartment D, the equilibrated concentration in compartment D is calculated to be 3.8×10^{-10} mol dm^{-3} according to this equation in the case of Fig. 2. The pH decreased appreciably in the initial stage of the dialysis as shown in Fig. 2, because the transport rate of protons in the cation-exchange membrane differs from that of hydroxide ions in the anion-exchange membrane. Sulfuric acid and calcium hydroxide were used for acid and base in this experiment to decrease the leakage of co-ions across the membrane because polyvalent co-ions repel ion-exchange membranes strongly, but it can not be ignored in highly deionized solution.

In neutralization dialysis, the diffusion flux of metal ion across the membrane, J_M can be derived as the function of the ion concentration in the bulk solution. The ion flux is proportional to the concentration difference in the membrane as generally recognized[9] and it is

$$J_{M} = P(\bar{C}_{D}^{M}-\bar{C}_{A}^{M}), \tag{5}$$

where P, C_{D}^{M}, and C_{A}^{M} are the permeation constant, the concentration in the membrane adjacent to the deionization compartment, and that adjacent to the acid compartment, respectively.[4] The ion-exchange equilibriums apply at the interfaces of the membranes and the equilibrium constant, K is

$$K = (\bar{C}_{A}^{M}/C_{A}^{M})/(\bar{C}_{A}^{H}/C_{A}^{H}) = (\bar{C}_{D}^{M}/C_{D}^{M})/(\bar{C}_{D}^{H}/C_{D}^{H}), \tag{6}$$

where K is assumed to be constant on either side of the membrane. When the concentration of the exchangeable cation in the cation-exchange membrane is shown as C_{ex}, the relationship between each ion concentration in the membrane is

$$\bar{C}_{A}^{M} + \bar{C}_{A}^{H} = \bar{C}_{D}^{M} + \bar{C}_{D}^{H} = C_{ex}. \tag{7}$$

From Eqs. 5—7, J_M is expressed as the function of the ion concentration in the bulk solution by

$$J_{M} = C_{ex}P[1/(1+C_{D}^{H}/KC_{D}^{M}) - 1/(1+C_{A}^{H}/KC_{A}^{M})]. \tag{8}$$

According to this equation, it is predicted that J_M increases with increasing the ratio of C_{A}^{H} to C_{A}^{M} and becomes zero when Donnan equilibrium is attained across the membrane as shown in Eq. 1. J_M also increases with the decrease of C_{D}^{H} but the optimum value of C_{D}^{H} is 10^{-7} mol dm^{-3} because the anion flux can be also described in the same form as Eq. 8 and it should be equal to J_M for the most efficient

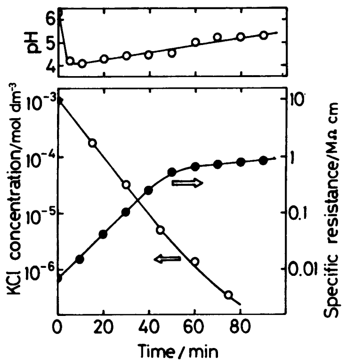

Fig. 2. Deionization by neutralization dialysis. Compartment A, 0.01 mol dm^{-3} H_2SO_4 (1 dm^3). Compartment B, 0.01 mol dm^{-3} $Ca(OH)_2$ (1 dm^3). Compartment D, 0.001 mol dm^{-3} KCl (75 cm^3).

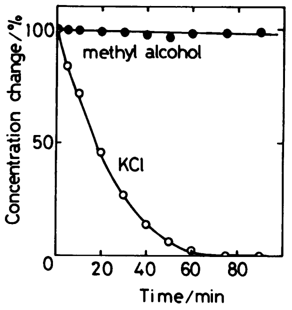

Fig. 3. Separation of potassium chloride from methyl alcohol. Compartment D, 0.1 mol dm^{-3} methyl alcohol+0.01 mol dm^{-3} KCl aqueous solution (100 cm^3). The other experimental conditions are the same as those of Fig. 2.

deionization.

The deionization capability was also confirmed when KCl was initially added to both acid and base solutions to be 0.1 mol dm^{-3} in the case of Fig. 2. The permeation rate decreased and the time taken to reach 10% of the initial concentration of the deionization compartment becomes about 5 times longer, but KCl was transported against its concentration difference as expected by above equations.

A dialytic separation of potassium chloride from methyl alcohol was also tried in this system and the result is shown in Fig. 3. The concentration change of methyl alcohol could be ignored (within 2%), while potassium chloride was effectively removed and its concentration became 0.2% of the initial concentration after 1.5 h. Since permeabilities of nonelectrolytes decreases rapidly with the increase of the molecular weight,[8] the loss of nonelectrolytes during the dialysis is much smaller in almost all the case than that showm in Fig. 3. A dialytic deionization of a mixed solution of electrolytes and nonelectrolytes is achieved effectively in this process.

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