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Separation of Weak Acids and Bases by Neutralization Dialysis

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Neutralization dialysis is a very effective deionization method and the transport of weak acids and bases is also facilitated by the neutralization reaction in the system. The transport rates of weak acids and bases increased with the increase of their dissociation constants.

Neutralization dialysis is a very effective deionization method[1,2] on the basis of Donnan dialysis[3] and it has found industrial applications such as in the desalination of aqueous solutions of carbohydrates and milk whey.[4] In the method, not only electrolytes but also weak acids and bases can be effectively transported and the preliminary result of the separation of weak acids and bases will be reported in this paper.

Permeation experiments were carried out for acetic acid and alcohols in a neutralization dialysis cell described elsewhere.[2] A two-compartment cell divided by an anion-exchange membrane was used for the separation of acetic acid and a three-compartment cell divided by an anion- and a cation-exchange membranes was used for the separation of alcohols. The anion- and cation-exchange membranes were Selemion AMV and CMV (Asahi Glass Co. Ltd.), respectively. The concentrations were determined by Shimadzu TOC-5000 total organic carbon analyzer.

Figure 1 shows three cases of the separations of acetic acid; case I: 10 mM CH_3COOH/Selemion AMV/10 mM NaCl; case II: 10 mM CH_3COOH/Selemion AMV/10 mM NaOH; case III: 10 mM CH_3COONa/Selemion AMV/10 mM NaOH. In case III, the solute of sodium acetate was dissociated almost completely but in the other cases, the solute of acetic acid was slightly dissociated. The transport rate of acetate ion was in the order of case II > case III > case I and the acetate ion was transported very rapidly against its concentration gradient when it was in the undissociated form in the source phase solution and exchanged with hydroxide ion in the membrane.

Acetic acid, HA, was used as the solute in cases I and II and its dissociation equilibrium is as follows.

$$HA = A^- + H^+, \qquad K_a = \frac{[H^+]\cdot[A^-]}{[HA]}, \qquad (1)$$

where K_a is the dissociation constant. Acetate ion is readily exchanged with the anion, L^-, in the membrane at the membrane surface as

$$A^- + \overline{L^-} = \overline{A^-} + L^-, \qquad K_{ex}(L^-) = \frac{[\overline{A^-}]\cdot[L^-]}{[A^-]\cdot[\overline{L^-}]}. \qquad (2)$$

In this equation, the line over the ion formula shows the ion in the membrane and $K_{ex}(L^-)$ is the selectivity coefficient of acetate ion exchange with other anion, L^-, in the membrane. After hydroxide ion is permeated to the source phase solution by the ion exchange reaction, neutralization reaction occurs between proton dissociated from acetic acid and the permeated hydroxide ion in case II according to the following equation.

$$OH^- + H^+ = H_2O,$$
$$K_w = [H^+]\cdot[OH^-], \qquad (3)$$

where K_w is the ion product of water. The total ion concentration in the membrane is equal to the ion exchange capacity, C_{ex}, as

$$C_{ex} = [\overline{A^-}] + [\overline{L^-}]. \qquad (4)$$

All of the reactions are combined in each case and the concentrations of acetate ion in the membrane are expressed as follows.

Case I: $HA + \overline{Cl^-} = \overline{A^-} + HCl$,

$$[\overline{A^-}] = \frac{C_{ex}}{\dfrac{C_{HCl}{}^2}{K_a\cdot K_{ex}(Cl^-)\cdot C_{HA}} + 1}. \qquad (5)$$

Case II: $HA + \overline{OH^-} = \overline{A^-} + H_2O$,

$$[\overline{A^-}] = \frac{C_{ex}}{\dfrac{K_w}{K_a\cdot K_{ex}(OH^-)\cdot C_{HA}} + 1}. \qquad (6)$$

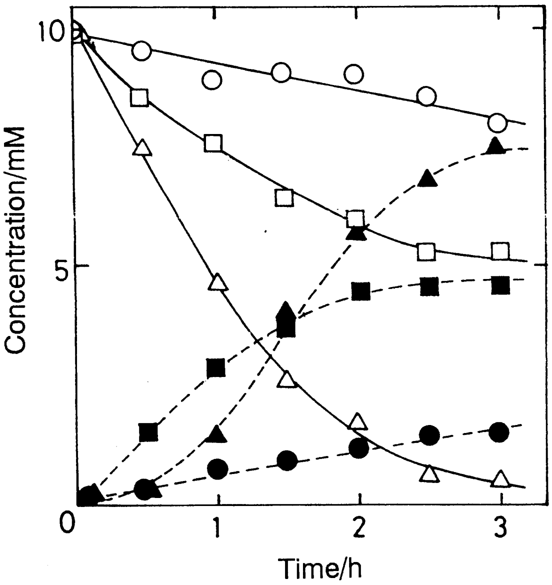

Fig. 1. Concentration change of acetate ion with time; ○ and ●, case I; △ and ▲, case II; □ and ■, case III; ○, △ and □, concentration change in compartment I; ●, ▲ and ■, concentration change in compartment II; compartment I, 10 mM acetic acid (cases I and II) or sodium acetate (case III); compartment II, 10 mM sodium chloride (case I) or sodium hydroxide (cases II and III); membrane area, 32 cm^2; solution volume, 0.1 dm^3.

Case III: $NaA + \overline{OH^-} = \overline{A^-} + NaOH$,

$$[\overline{A^-}] = \frac{C_{ex}}{\dfrac{C_{NaOH}}{K_{ex}(OH^-)\cdot C_{NaA}} + 1}. \qquad (7)$$

The acetate ion concentration at the membrane surface of the receiving phase side, alkali compartment, is very low at the initial stage and the flux is proportional to the concentration at the membrane surface of the source phase side. Then, the acetate ion concentration at the membrane surface of the source phase solution was calculated by those equations to compare the transport rates for three cases. Since the concentrations, C_{HCl} and C_{NaOH}, change with time, it is assumed that 10% of acetate ion was transported from 10 mM source phase solution, which is corresponded to the initial stage. If the selectivity coefficients, $K_{ex}(OH^-)$ and $K(Cl^-)$, are 0.53 and 5.9, respectively,[5] the ratio of the acetate ion concentration in the membrane for three cases is as follows.

$$[\overline{A^-}]_{case\ I} : [\overline{A^-}]_{case\ II} : [\overline{A^-}]_{case\ III} = 0.48 : 1 : 0.83. \qquad (8)$$

The difference of the transport rates of acetate ion for three cases is accounted for by the acetate ion concentration at the membrane surface, although the transport rate of acetate ion measured for case II is much larger than that for case III. The neutralization reaction may accelerate the uptake rate of acetate ion, which was also observed in the desalination of potassium chloride by neutralization dialysis.[1] Weak bases, such as ammonia or urea, can be also transported rapidly in this system.

The transport rate of other weak acids can be also facilitated on the same basis in neutralization dialysis. Alcohols are weak acid and the permeation properties

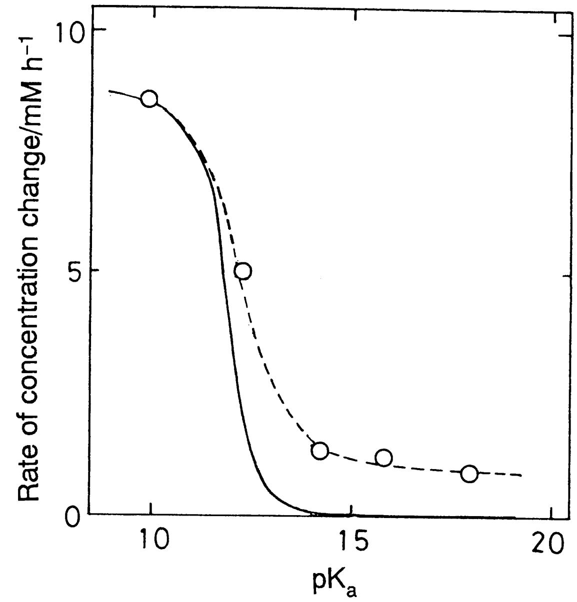

Fig. 2. Rate of concentration change vs. pK$_a$ of alcohols; ——, calculated value from Eq. 6 and the concentration change data of phenol; desalination compartment, 10 mM alcohol; alkali compartment, 10 mM NaOH; acid compartment, 10 mM HCl; membrane area, 60 cm^2; solution volume, 0.1 dm^3.

of some alcohols were investigated. Figure 2 shows the concentration change of alcohols in the source phase solution in the first one hour as a function of pK_a value. Alcohols used in this experiment were phenol (pK_a 10.0), 2,2,2-trifluoroethyl alcohol (pK_a 12.4), 2-chloroethyl alcohol (pK_a 14.3), ethyl alcohol (pK_a 15.9), and 2-propyl alcohol (pK_a 18.0). When pK_a < 10, the first term in the denominator of Eq. 6 is much smaller than 1 and the anion concentration at the membrane surface is C_{ex}. Then, the concentration change of alcohols was calculated from that of phenol and Eq. 6, which is shown as the solid line in Fig. 2. In the calculation, it is assumed that the steric effect on the permeation across the membrane and the selectivity coefficient are independent of the chemical species. The measured values of alcohols with large pK_a were much larger than the estimated values. It is known that the transports of aldehydes and sugars are facilitated by their dissociation in the hydroxide-type anion-exchange membrane[6,7] and thus the transport of those alcohols is also facilitated on the same basis.

There are much weak acids and bases such as metal hydroxide complex and fulvic acid dissolved in natural water and it has been very difficult to remove these species in water purification. Weak acids and bases as well as strong electrolytes can be effectively removed in neutralization dialysis and the neutralization dialysis is a very useful method in water purification.

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