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Selective Piezodialysis by Crown Ether Mosaic Membrane

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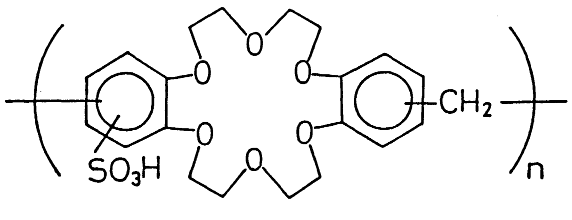
Piezodialysis behavior of mosaic membrane containing dibenzo-18-crown-6 structure was investigated. Depending on the ion exchange selectivity and the difference of hydration degree, selective piezodialysis behavior for alkali metal ions was obtained.

A charge mosaic membrane which has both cation exchange and anion exchange parts has known to have piezodialysis properties.[1-3] In the piezodialysis, hyperfiltrated salt is effectively concentrated in the permeate. Therefore, the piezodialysis is a useful method for salt enrichment and desalination.



PS-DB18C6

We have recently studied these systems with simplified components of membranes. One is a system of mosaic resin membrane in which fine ion exchange resins were dispersed into poly(vinyl chloride) (PVC) membrane.[4] The other is a macromosaic membrane system where cation and anion exchange membranes were functionally combined.[5] In the former system, resins of various types may be useful. If a specific ion exchange resin were used in this system, specific piezodialysis would be expected.

In the present study, we prepared a mosaic resin membrane containing dibenzo-18-crown-6 (DB18C6) structure as the cation exchange site, and investigated its selective piezodialysis behavior for alkali metal ions.

The cation exchange resin containing crown ether structure (PS-DB18C6) was synthesized by condensation polymerization of DB18C6 with formaldehyde[6] followed by sulfonation by chlorosulfonic acid. The ion exchange capacity was measured by the titration method[7)] to be 1.3 mequiv./g-dry resin. Amberlite CG-400 (3.7 mequiv./g-dry resin) was used for anion exchange resin. Both resins (finer than 200 mesh) were dispersed into PVC membrane in a similar manner as reported previously.[4)]

The ion exchange ability of PS-DB18C6 was investigated by adsorption experiment. Fifty milligrams of the resin of protonated form was suspended in an aqueous solution containing 1 mmol dm^{-3} alkali metal chloride and mechanically shaken until the equilibrium was attained (6 h). The change of metal ion concentration in the bulk solution was then measured by the flame analysis (Shimadzu AA-630-02). The diffusion flux was measured from the concentration change with time in the receiving solution by using a dialysis cell,[8)] in which a salt solution of 0.1 mol dm^{-3} and pure water were circulated separately into two chambers separated by a membrane. The membrane potential was determined with two glass cells separated by a membrane and equipped with calomel electrodes.[4)] A salt solution of different concentration (0.02 - 0.01 mol dm^{-3}) was circulated in each cell. The piezodialysis experiment was carried out using a batch type hyperfiltration cell and the permeation behavior was evaluated by enrichment factor, which is defined by the ratio of the concentration of permeated solution to that of feed solution.

In the adsorption experiment, specific adsorption behavior of alkali metal ions was observed for PS-DB18C6. Since the polymer of DB18C6 before sulfonation did not show any appreciable adsorbability under the present experimental condition, the observed adsorption of alkali metal ions must be due to ion exchange mechanisms . For the case of the ion exchange equilibrium, the relative affinity coefficient K_H^M was defined as follows,[9)]

$$K_H^M = \frac{[\overline{RM}]\,[H^+]f_{H^+}}{[\overline{RH}]\,[M^+]f_{M^+}} \qquad (1)$$

where $[\overline{RH}]$, $[\overline{RM}]$ and $[H^+]$, $[M^+]$ represent the concentrations of protons and metal ions in the resin and the bulk solution, respectively. f_{H^+} and f_{M^+} are the activity coefficients in the solution. The relative affinity coefficient of PS-DB18C6 is shown in Fig. 1 against

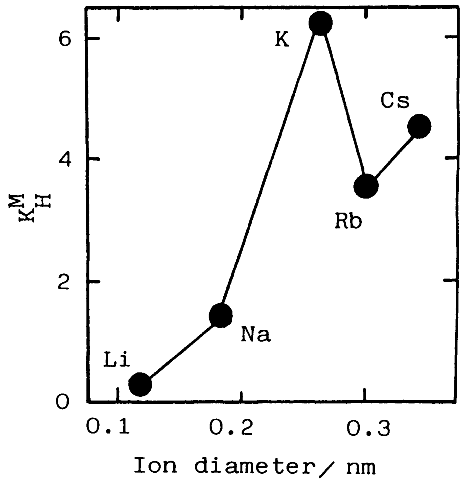


Fig. 1. Effect of ion diameter on the relative affinity coefficient.

PS-DB18C6 (50 mg) was shaken with 20 ml of 1 mmol dm^{-3} MCl solution.

the ion diameter of alkali metal ions. PS-DB18C6 has a selective ion exchange ability and the maximum affinity coefficient was obtained for potassium ($K_H^K = 6.3$). This behavior matches well with the property of DB18C6.[10]

Figure 2 shows the effect of the composition of anion exchange resin (CG-400) and cation exchange resin (PS-DB18C6) on the salt diffusion flux and the membrane potential. The packing form in the membrane is thought to become more closely with an increase of PS-DB18C6 fraction in the membrane, because PS-DB18C6 resin is less rigid compared with CG-400 resin. Therefore the salt diffusion flux decreases, on the whole, with an increase of the PS-DB18C6 composition. However, in the vicinity of membrane potential zero, the enhancement of salt diffusion was observed. This is a typical behavior of charge mosaic membranes, in which the circulating current ($I_{circulating}$) significantly affects the salt flux according to the following equation,[4])

$$J_s = I_{circulating}/F \qquad (2)$$

where F is the Faraday constant and J_s is the salt flux. Since the permeation resistance of potassium ion is high compared with that of sodium ion depending on interaction with PS-DB18C6, the circulating current effect is more pronounced in the case of sodium ion systems.

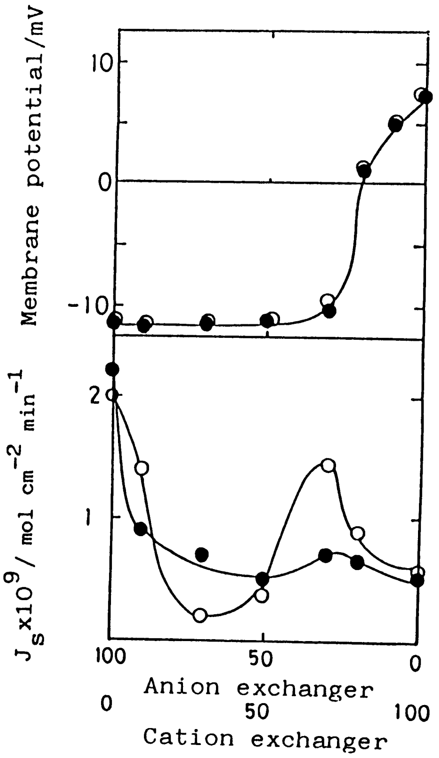


Fig. 2. Effect of membrane composition on membrane potential and diffusion flux.

Anion exchanger: CG-400
Cation exchanger: PS-DB18C6
● KCl, o NaCl

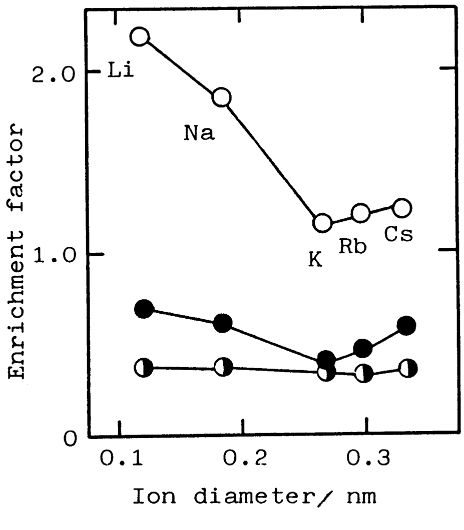


Fig. 3. Effect of ion diameter on enrichment factor.

Feed solution: 250 ml of 0.1 mmol dm^{-3} MCl solution
Applied pressure: 40 kg cm^{-2}
o PS-DB18C6-CG-400 (ion exchange capacity, 1:1) membrane
◑ CG-400 membrane
● PS-DB18C6 membrane

Piezoialysis behaviors for alkali metal salts were also investigated for the three types of membranes (Fig. 3). According to the properties of charged membrane,[11] the salt rejection behavior was observed for both PS-DB18C6 and CG-400 membranes. Only the mosaic membrane having equivalent amounts of cation and anion exchange capacities enriched the salt in the permeate in spite of the low volume flux (5 x 10^{-5} cm min^{-1}). In this system, depending on the ion exchange selectivity as shown in Fig. 1, a salt selective piezodialysis was obtained. The high enrichment factor of lithium ions must be due to a low frictional resistance of PS-DB18C6 and a large coupling effect with water flux[12] which was caused by the high degree of hydration of lithium ions. On the other hand, the enrichment factor of potassium ions showed a minimum value due to strong interaction of this ion with PS-DB18C6.

This selective piezodialysis is an interesting character of crown ether mosaic membrane. Further studies to obtain the membrane of this type possessing a high volume flux are still in progress.

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