Active and Selective Transports of Alkali Metal Ions through Hydrophobic Membrane

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Synopsis. The active and selective transport of alkali metal ions coupled with proton permeation, were observed through a dense hydrophobic membrane. The flux of alkali metal ions increased with the decrease in the degree of hydration. The behavior can be comprehended in terms of the asymmetrical permeabilities of ions through the hydrophobic membrane.

Active and selective transport phenomena have been intensively studied as models of biological membranes and with a view to the practical application in industry.[1,2] Active transport has been observed through a liquid membrane containing ionophore[3—5] and an artificial membrane with containing ion-exchange groups.[6—8] We wish to report herein the findings that a dense hydrophobic membrane are also revealed active and selective transport for alkali metal ions. Such specific transport, depending on the hydrophobic environment, is considered to play an important role in artificial and biological membranes.

Experimental

A thin and dense hydrophobic membrane was prepared by coating a fluorocarbon polymer (FEP-120 dispersion, purchased from the Dupont Co.) on a "fluoropore", porous support membrane (FP-010, obtained from the Sumitomo Electric Co., Ltd.; pore size, 0.1 μm), followed by melting at 300 °C.[9,10] The SEM studies indicated that the thickness of the polymer layer on the membrane surface was about 6 to 8 μm. A homogeneous and dense layer was formed on the support membrane.[9] The coating density of the membrane used in this experiment was 0.79 mg cm^{-2}.

The dialysis experiments were carried out with a cell in which 100 mL of an aqueous solution containing 1 mmol dm^{-3} of alkali metal salts (L-side) and 100 mL of an aqueous solution containing equimolar amounts of alkali metal salts in addition to 0.1 mol dm^{-3} additive salts for producing active transport (R-side) were circulated separately into two chambers divided by the hydrophobic membrane.[11] The change in the concentration of the metal ions with time in both chambers was measured by means of an atomic-absorption spectrophotometer (Shimadzu AA-630-02).

The transport number was determined with two glass cells separated by a membrane and equipped with calomel electrodes. A metal sulfate solution of a different concentration (0.01—0.001 mol dm^{-3}) was circulated in each cell.[12]

Results and Discussion

Figure 1 shows the change in the concentration of the alkali metal ions and the pH changes on the L-side and the R-side through the hydrophobic membrane. The concentration of potassium ions on the R-side increased with the decrease in the pH on the L-side. The permeation flux of sodium ions was low compared with that of potassium ions. These results indicate that the selective and active transport of the alkali metal ions occurred coupled with the proton permeation. The behavior can be explained as a consequence of the asymmetrical permeabilities of the cations and the anion through the membrane, because the hydrophobic membrane repels the penetration of highly hydrated ions. It should be noted that some permeation lags were observed in this system. That is, the increment of alkali metal ions in the R-side solution were somewhat low compared with the decreasing degree of the L-side solution. This suggests that the rate of ion-exchange migration in the membrane was slower than that of distribution into the membrane.

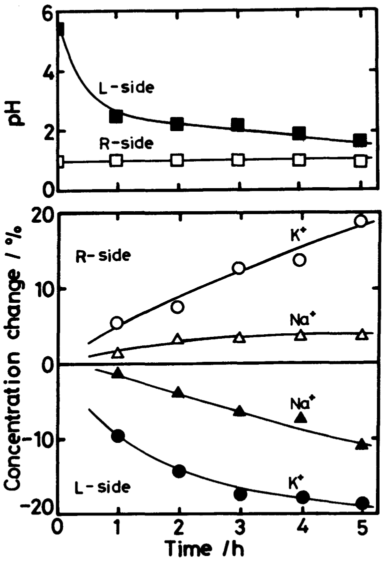

Fig. 1. Time-transport curves of Na$^+$, K$^+$ and pH through the hydrophobic membrane. L-side soln.: [Na_2SO_4]=[K_2SO_4]=1 mmol dm^{-3} (closed symbols). R-side soln.: [Na_2SO_4]=[K_2SO_4]=1 mmol dm^{-3}, [H_2SO_4]=0.1 mol dm^{-3} (open symbols).

These selectivities were only observed through a dense hydrophobic membrane. When the support membrane before coating was used as a barrier, an osmotic flow of water occurred and stable measurements could not be attained. To prevent such an osmotic flow, a coating density of at least 0.5 mg cm^{-2} was needed. The measurements are also considered to be difficult in the case of excess coating because of the low diffusibility of ions in the dense hydrophobic region of the membrane. Therefore, an appropriate amount of coating density (0.5—1.0 mg cm^{-2}) was required in these measurements.

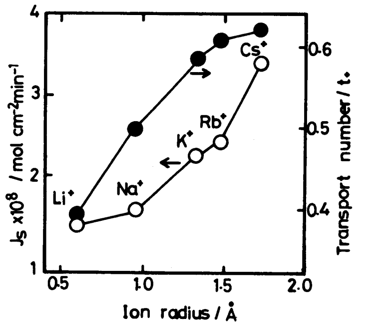

Fig. 2. Effect of ion radius on ion flux and transport number of permeate cations. ○: Ion flux (which were measured in the single component systems). L-side soln.: $[M_2SO_4]=1$ mmol dm^{-3}. R-side soln.: $[M_2SO_4]=1$ mmol dm^{-3}, $[H_2SO_4]=0.1$ mol dm^{-3}. ●: Transport number through the hydrophobic membrane.

Table 1. Effects of Additive Species on the Ion Flux[a)]

Additive	$J\times 10^8$/mol cm^{-2} min^{-1} K$^+$	Na$^+$	J_{K^+}/J_{Na^+}
H_2SO_4	2.38	0.69	3.4
HCl	1.39	0.79	1.8
NH_4Cl	0.20	0.27	0.7
LiCl	−0.55	−0.26	2.1

a) Measurements were carried out in the Na$^+$, K$^+$ binary system. L-side soln.: $[Na_mX]=[K_mX]=1$ mmol dm^{-3}. R-side soln.: $[Na_mX]=[K_mX]=1$ mmol dm^{-3}, [Additive]=0.1 mol dm^{-3} (X=Cl$^-$ or SO_4^{2-}, m=1 or 2).

The effect of the ion radius of alkali metal ions on the ion flux, as calculated from the initial change in the concentration on the R-side, is shown in Fig. 2. The measurements were carried out in a single-component system. The hydration degree of an ion is known to decrease with the increase in the ion radius.[13)] From the figure, the flux of metal ions is seen to increase with the decrease in the hydration degree. In a hydrophobic environment, a low-hydrated ion is considered to be more permeable. These differences in permeability depending on the hydration degree are also proved by the values of the transport numbers for the cations. As may be seen from the figure, the transport number of cations increased with the decrease of hydration degree, similarly with the propensity of the ion flux (Fig. 2).

The effect of additive species in producing the active transports is shown in Table 1. As the proton has a high permeability because of the different permeation mechanism (the transport number of protons through the membrane (t_{H^+}) was 0.69 for H_2SO_4), which is known as a proton-jump mechanism coupled with water molecules,[14)] the metal ions were effectively transported couples with proton permeation. However, when a cation with a low membrane permeability, such as the lithium ion, was used as the additive, the flux depending on the antiport mechanism decreased significantly, while, on the contrary, the symport permeation of alkali metal ions, coupled with the permeation of chloride anions, was found to occur. These results also indicate that asymmetrical permeabilities of ions through the hydrophobic membrane are the cause of these specific permeations.

In conclusion, the selective and active transport of alkali metal ions was found to be attained through a dense hydrophobic membrane prepared by coating a fluorocarbon polymer on a support membrane. We consider that the hydrophobic membrane is a useful model for studing an ion channel consisting of a hydrophobic environment. Further studies of these specific permeations for other ionic solutes are in progress.

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12) The transport number of the cation (t_+) was determined using the following equation:

$$E = \left(\left(\frac{1}{z_+} - \frac{1}{z_-}\right)t_+ + \frac{1}{z_-}\right)\frac{RT}{F}\ln\frac{a_R}{a_L}$$

Here, E is the membrane potential; z represents the ionic charge; R, T, and F are the gas constant, the absolute temperature, and the faraday constant respectively and a_R and a_L are the salt activities of the R-side and L-side solutions respectively.

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