막분리에서 액체막내의 이온투과현상

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Ion Transport Phenomena Within A Liquid Membrane on Membrane Separation

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요 약 : 분리용막을 이용한 역수송계에서 이온의 확산계수가 막내이온의 농도와 확산성 막투과 계수에 따른 변화를 검토하였다. 종래의 막－전해질수용액계에서 확산계수는 농도 프로파일에는 의존하지 않는다는 보고였다. 그러나 본 연구에서 확산계수는 외부의 전해질수용액에 강하게 의존하는 결과를 얻었다. 이 결과를 에너지장벽논리에 적용하여 이온의 flux식에서 Potential항을 무시한 새로운 막포텐셜식을 유도한 결과 식과 잘 맞는 것을 알았다. 이 식은 역수송계가 중화반응에서 생기는 에너지로 이온flux, 막투과계수 그리고 전해질용액의 활동도와의 관계에 대해서 고찰하였다.

Abstract : The diffusion coefficients of ion in the reverse transport system using the separation memranes were estimated from the diffusional membrane permeabilities and the ion concentration within membrane. The results indicated the diffusion coefficients depend strongly on concentrations of outer electrolyte equilibriated with the membrane. The result was interpreted in terms of the energy barrier theory. Furthermore, a new equation for the flux and membrane potential was drived by eliminating the potential terms. The equation indicated that the reverse transport system is driven by the energy of neutralization reaction. A relation among the flux, the permeability and the activity of electrolyte in solution is presented and verified by the experimental results.

INTRODUCTION

Many studies have accumulated concerning carrier-mediated transport across a liquid membrane with the simple carriers since the enlightened work on separation material by N. N. Li[1,2] was reported. In practice, it would be an attractive attempt to examine an effective material transport through the membrane. At the same time with the search of the material transport due to lower energy from the stand in chemical engineering, one should pay an attention to elucidate the transport mechanism in such a liquid membrane. In previous communication on the reverse transport process

which have been done under such a fundamental viewpoint,[3] a reverse transport of sodium ion coupled to neutralization reaction was observed, and the result was analyzed on the basis of a nonequilibrium thermodynamics.[4~6]

One of the important results was that the ion flux in the reverse transport process was not explained only as a conjugation with chemical reaction, but also was drived by means of the membrane potential.

In order to take a step forward in the previous study, the knowledge on the dynamic state of carrier-mediated ion will be required at present, and in fact, one may have an interest in the detailed roles of carrier ion or transport ion in the polymeric membrane(PM).[7]

Thus, the additional experiments were carried out determing ion concentration within the liquid polymeric membrane and the theoretical development of the previous treatments was presented in this work.

EXPERIMENTAL

Membrane

The PM used in this study was prepared by dissolving monensin into 1-octanol and the experimental conditions were the same as in the previous paper.[3] The carrier concentration was 0.01mol dm^{-3}.

System

The concentrations and the compositions of the electrolyte solutions used in this study were the same as those in the previous paper.[3] The respective electrolyte solutions were poured into the half compartments of cylindrical glass cell which was divided by glass wall. Each volume of aqueous electrolyte solutions (phase I and II) is 15 cm^3. The prepared liquid membrane solution (bulk membrane phase) was carefully floated over both phase I and II. The schematic diagram which is similar in most aspect to the one by J. H. Schulman et al.[8] Is shown in Fig. 1. Three phases including membrane phase were sufficiently stirred by the magnectic stirrers. In the agitation, the special

precaution was taken so as to avoid the disturbance of interface among phases.

Na ion Concentration Within the Liquid Membrane

After the system reached steady state, which is in need of 9 hrs more, Na ion concentration within membrane were determined by an atomic absorption spectroscopy(Hitachi Co. 180-50). The details for the determination of the concentration were already described elsewhere.[3,9,10]

RESULTS AND DISCUSSION

Provided the diffusional membrane permeability, $P\overset{0}{\alpha}$, and the concentration of ion α within the membrane, $\overline{C}\alpha$, are known, the diffusion coefficient, $\overline{D}\alpha$, can be calculated according to the relation.[11]

$$P\overset{0}{\alpha}=\overline{D}\alpha \ \overline{C}\alpha / \delta \, (a\overset{I}{\alpha} \, a\overset{II}{\alpha})^{1/2}=\overline{D}\alpha \ \beta / \delta \qquad (1)$$

where δ denotes the membrane thickness, 6×10^{-3} cm and a, the ionic activity, and β, the partition coefficient, which is expressed by $\overline{C}\alpha/(a\overset{I}{\alpha}a\overset{II}{\alpha})^{1/2}$. Table 1 shows the partition coefficients of Na ion together with the diffusional membrane permea-
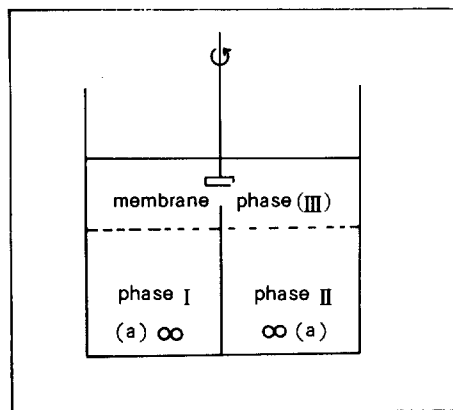

Fig. 1. Schematic diagram of the apparatus for the determination of concentration within the PM : I, II and III denote NaOH aqueous solution, NaCl+HCl aqueous solutions and monensin octanol solution, respectively.

Table 1. Partition Coefficients, β, Diffusion Coefficients, D_{Na}, and Diffusional Membrane Permeability, P_{Na}

$C/mol \cdot dm^{-3}$	β	$P_{Na}^{o}/cm \cdot s^{-1}$
1×10^{-2}	2.17×10^{-2}	4.69×10^{-9}
5×10^{-2}	4.26×10^{-3}	3.41×10^{-9}
1×10^{-1}	3.80×10^{-3}	3.21×10^{-9}
5×10^{-1}	1.35×10^{-3}	2.61×10^{-9}
1×10^{0}	1.83×10^{-3}	2.18×10^{-9}
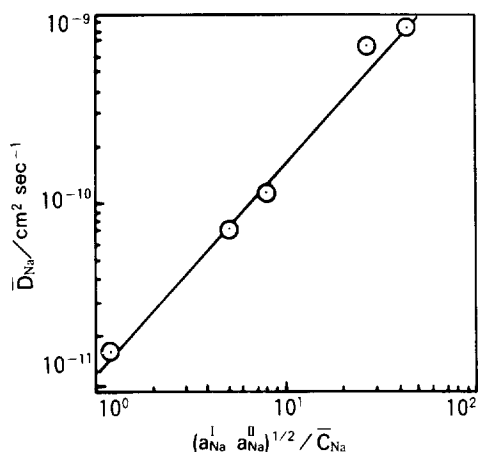
Fig. 2. A plot of $\bar{D}_{Na}$ vs. the inverse of partition coefficient.

bilities obtained in the previous study. Thus, the diffusion coefficient, $\bar{D}_{Na}$ were calculated by using equation(1), and the result was shown as a reciprocal function of the partition coefficients, $(a_{Na}^{I} a_{Na}^{II})^{1/2}$ $/\bar{C}_{Na}$ in Fig. 2. As seen in Fig. 2, the obtained $\bar{D}_{Na}$ depended strongly on the Na ion concentration and indicated the values of 1×10^{-9} to 1×10^{-11} $cm^2 sec^{-1}$ less than that in the usual aqueous electrolytes solution. Moreover, the linear relation between $\bar{D}_{Na}$ and $1/\beta$ in Fig. 2 was the same as that obtained in earlier communication.[12] One of the study has already presented the next equation to explain the concentration dependence of D_{Na} taking into account the energy barrier for ions to cross the membrane-solution interface, E,

$$\bar{D}_{Na} = D_{Na}^{o} \exp[(U-E)/RT] = D_{Na}^{o}(a_{Na}^{I} a_{Na}^{II})^{1/2}$$
$$\exp(-E/RT)/\bar{C}_{Na} \qquad (2)$$

where D_{Na} denotes the diffusion coefficient of Na ion in the membrane solvent and U, the energy of partition which can be replaced by the partition coefficient. According to equation (2), the slope of the linear relation in Fig. 2 represents D_{Na}^{o} exp $(-E/RT)$, i. e., the product of the diffusion coefficient, D_{Na}^{o} and exponential term of energy barrier, E.

It can be easily understood that the existance of the energy barrier, E at the interface between membrane and solution makes the values of $\bar{D}_{Na}$ lower in comparison with the free diffusion coefficient. At present, we do not have any information about D_{Na}^{o}. If we assume that D_{Na}^{o} is constant and is order of 10^{-6} $cm^2 sec^{-1}$, the value of the energy barrier can be estimated as several kcal/mole in the present system. This is a reasonable result, comparring to the result obtained in previous solid ion exchange membrane system.[12] Thus, it can be concluded that the energy barrier should be taken into account in the estimation of the diffusion coefficient of ion across the liquid membrane.

In the previous study,[3] it has presented the flux and potential equations to understand the reverse transport phenomena. In order to ensure the reverse transport from different viewpoint, the equations were reexamined in this study. Eliminating the potential terms from the flux and potential equation, we have,

$$J_{Na}^{o} = -J_{H}^{o} = -k (a_{Na}^{II} a_{H}^{I} - a_{Na}^{I} a_{H}^{II}) \qquad (3)$$

where

$$k = P_{H}^{o} P_{Na}^{o} / \{(P_{Na}^{o} a_{Na}^{I} + P_{H}^{o} a_{H}^{I})$$
$$(P_{Na}^{o} a_{Na}^{II} + P_{H}^{o} a_{H}^{II})\}^{1/2} \qquad (4)$$

Equation(3) implies that the fluxes of Na of H ions were apparently driven by the difference between the activities of Na and H ions in phase I and II. When $a_{H}^{I}/a_{H}^{II} = a_{Na}^{I}/a_{Na}^{II}$ holds, the system described by Eq. (3) reaches equilibrium.

Under the present experimental conditions, that is, when phase I contains only sodium hydroxide solution, and a_{H} is negligible, Eq. (3) is reduced to

$$J_{Na}^0 = k \ a_{Na}^I \ a_H^{II} \tag{5}$$

$$= k \ a_{OH}^I \ a_H^{II} \tag{6}$$

It is noted that Eq. (6) is a simple and instructive form to understand the transport of Na ion in this system. Eq. (6) indicates that the reverse transport is generated with coupled to the neutralization. However, one should not forget that the driving forces for the reverse transport are not only the energy of chemical reaction, but the membrane potential is also one of the driving forces in these systems. The reason is obvious from the facts that k in Eq. (6) still contains the potential terms through the diffusional membrane permeability.[13~15]

The validity of Eq. (5) or (6) was examined by using the results in which J_{Na}^0, P_{Na}^0 and P_H^0 were given in the previous paper.[3] We can obtain Eq. (7) by rearranging Eq. (5) as follow : [16]

$$(P_H^0 \ a_H^{II} / J_{Na}^0)^2 = 1 + P_H^0 \ a_H^{II} / P_{Na}^0 \ a_{Na}^{II} \tag{7}$$

Fig. 3 shows that the stright line passes through unity at the intercept and the relation among the Na ion fluxes, the membrane permeabilities and the ionic activities is satisfied well by the experimental results.

The following conclusion was drawn from this study : the analysis of membrane transport phenomena based on nonequilibrium thermodynamics
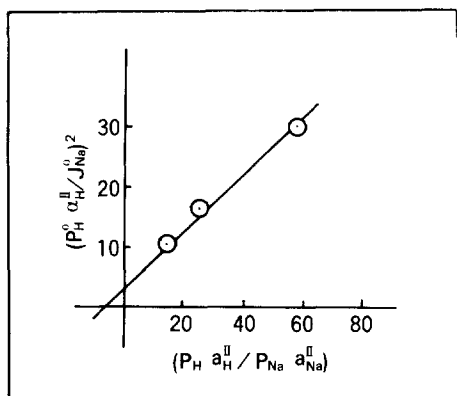

Fig. 3. Experimental verification of Eq.(7). Note that the straight line passes through unity at the intercept.

can also be applied to the reverse transport system as well as the membrane-electrolyte solution system without involving the chemical reaction.

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