

Diffusion Coefficients and Membrane Potential within Carrier Membrane by Reverse Transport System

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Abstract : The diffusion coefficients of ions in the reverse transport system using the carrier mediated membrane were estimated from the diffusional membrane permeabilities and the ion activity in membrane system. In the aqueous alkali metal ions-membrane system, diffusional flux of alkali metal ions driven by coupled proton was analyzed. The aqueous phase I contained NaOH solution, and the aqueous phase II also contained NaCl and HCl mixed solution. The concentration of Na ions of both phases were 10^0 , 10^{-1} , 10^{-2} , 5×10^{-1} and 5×10^{-2} mol·dm⁻³ and the concentration of HCl in aqueous phase II was always kept at 1×10^{-1} mol·dm⁻³. Moreover, the carrier concentration in liquid membrane was 10^{-2} mol·dm⁻³. The results indicated that the diffusion coefficients depend strongly on the concentration of both phases electrolyte solution equilibrated with the membrane. The points were interpreted in terms of the energy barrier theory. Furthermore, eliminating the potential terms from the membrane equation was derived.

Keywords : *diffusion coefficients, coupled proton, membrane permeability, liquid membrane, electrolyte solution, energy barrier theory*

1. Introduction

It was well-known that many studies have conducted on the facilitated transport across a liquid membrane with carriers by many researcher were reported [1,2]. In practice, it would be an attractive attempt to examine an effective material transport through the carrier membrane. At the same time, one should pay attention to elucidate the transport mechanism of such a liquid membrane. In our previous³ communications on the reverse transport process which have been done under such a

fundamental viewpoint, a reverse transport of sodium ion coupled to neutralization reaction was observed, and the results were analyzed by the irreversible description of system [4,5]. One of the important results was that the ion flux in the reverse transport process was not explained only as a conjugation with electrochemical activity, but also was derived by means of the membrane potential.

In order to take a step forward in previous study, the knowledge on the dynamics state of carrier mediated membrane will be required at present, and in fact, one may have an interest in the detailed roles of chemical reaction or facilitated transport ions in the liquid membrane [6-8].

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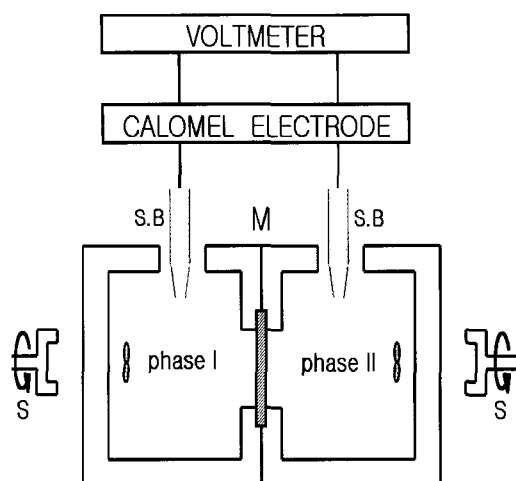
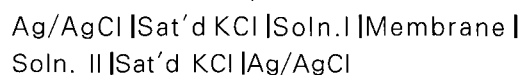


Fig. 1. Schematic membrane cell of membrane potential, Ion flux measured across separation membrane; M is membrane; S.B are salt bridge of KCl solution + agar; S is magnetic stirring meter for speed controller; phase I,II are electrolyte aqueous solution, respectively.

Thus, the additional experiments were carried out determining ion concentration within membrane and the development of new theoretical membrane equations in spite the previous treatments were presented in this work.

2. Experimental Section

2.1. Membrane System



The concentrations and the compositions of the electrolyte solutions were the same as the diagram above and shown Fig. 1. The equipment to measure partition coefficients was reported in the literature [3]. The respective electrolyte solutions were poured into the half compartments of cylindrical cell which was divided by glass wall [9]. The carrier concentration was 0.01 mol-dm^{-3} . The volume both sides of aqueous electrolyte solution is 15 mL, respectively. The prepared liquid membrane solution as a bulk liquid membrane was carefully floated on both phase I and phase II. All the phases including liquid membrane

phase were sufficiently stirred by the magnetic stirrer and all the measurements were carried out at 400 rpm, where the condition of the membrane-diffusion control was maintained. During the agitation, the special precaution was taken so as to avoid the disturbance of interface among phases.

2.2. Membrane Preparation

The supported liquid membranes were prepared on fluoropore filter (Model FP100, Sumitomo Electric Co. Ltd., Japan) with an average pore size of $0.10 \mu\text{m}$ by soaking it in 1-octanol solution with dissolved monensin carrier. The carrier concentration was $10^{-2} \text{ mol-dm}^{-3}$ and water was purified by double distillation, once from alkaline potassium permanganate solution.

2.3. Measurement of Ion Activity

After the system reached a steady state as 9 h or above, alkali cation ion activity across or within membrane was determined by an atomic absorption spectroscopy (Model 180-50, Hitachi Co. Ltd., Japan). Membrane potentials were measured by a pair of Ag/AgCl reference electrodes with a diameter of 2.5 mm connected to a potentiometer (Model 611, Orion, Co. Ltd., USA). The details of the determination of the concentration were already described elsewhere [10].

3. Results and Discussion

If the diffusional membrane permeability, P_a^0 and the concentration of ion α within the membrane, \bar{C}_a are known, the diffusion coefficient, \bar{D}_a can be calculated according to the relation,

$$P_a^0 = \bar{D}_a \bar{C}_a / \delta (a_a^I a_a^{II})^{1/2} = \bar{D}_a \beta / \delta \quad (1)$$

where δ denotes the membrane thickness $6 \times 10^{-2} \text{ cm}$, and a_a , the ionic activity of ions and β , the partition coefficients which is expressed as $\bar{C}_a / (a_a^I a_a^{II})^{1/2}$.

Table 1. The Partition Coefficients Value, β and Diffusional Membrane Permeabilities, P_{Na} , P_H of Cations in Membrane-electrolyte Solution System

C (mol · dm ⁻³)	β	P_{Na}^0 (cm · sec ⁻¹)	P_H^0 (cm · sec ⁻¹)
1×10^{-2}	2.17×10^{-2}	4.69×10^{-9}	1.37×10^{-7}
5×10^{-2}	4.26×10^{-3}	3.41×10^{-9}	1.14×10^{-7}
1×10^{-1}	3.80×10^{-3}	3.21×10^{-9}	0.90×10^{-7}
5×10^{-1}	1.35×10^{-3}	2.61×10^{-9}	0.76×10^{-7}
1×10^0	1.83×10^{-3}	2.18×10^{-9}	0.63×10^{-7}

Table 2. The Diffusional Coefficients of Sodium Ion and Proton Ion by Determined Membrane Equation(2) in Reverse Transport System

C (mol · dm ⁻³)	$\overline{D}_{Na} \times 10^6$ (cm ² · sec ⁻¹)	$\overline{D}_H \times 10^8$ (cm ² · sec ⁻¹)
1×10^{-2}	2.82	1.75
5×10^{-2}	6.03	2.37
1×10^{-1}	5.00	2.79
5×10^{-1}	7.81	3.89
1×10^0	4.28	5.08

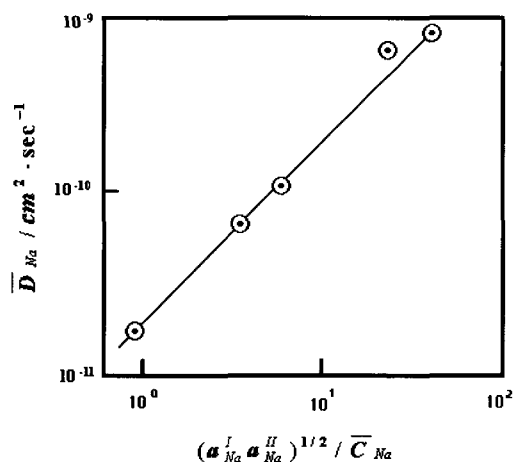
**Fig. 2.** A plot of diffusion coefficient of sodium ion within membrane vs. the partition coefficients.

Table 1 shows the partition coefficients of sodium ion together with the diffusional membrane permeabilities of sodium and proton ions obtained in the experiments. Thus the diffusion coefficient, \overline{D}_a was calculated from Equation (1) and listed in Table 2 and the result was described as a reciprocal function of

Table 3. The Ion Fluxes and Membrane Potentials of Sodium Ion in Various Concentrations of Membrane-electrolyte System by Coupled Proton Transfer

C (mol · dm ⁻³)	V_0 (mV)	J_{Na}^0 (mol · sec ⁻¹ · cm ⁻¹)
1×10^{-2}	-142.7	0.68×10^{-9}
5×10^{-2}	-112.1	1.12×10^{-9}
1×10^{-1}	-87.7	1.30×10^{-9}
5×10^{-1}	-49.5	1.98×10^{-9}
1×10^0	-38.8	2.36×10^{-9}

the partition coefficients, $(a_a^I a_a^{II})^{1/2} / \overline{C}_a$ in Fig. 2. As seen in Fig. 2, the obtained \overline{D}_a depended strongly on the sodium ion concentration and ranged between 10^{-9} to 10^{-11} cm²/sec which was less than that in the usual aqueous electrolytes solution. Moreover the linear relation between \overline{D}_a and $1/\beta$ in Fig. 2 was the same as that obtained in our earlier communication [11]. We have already presented the following equation to explain the concentration dependence of \overline{D}_a by taking into account the energy barrier, E for cations to across the membrane- aqueous solution interface as follow,

$$\begin{aligned} \overline{D}_a &= D_a^0 \exp[U - E]/RT \\ &= D_a^0 (a_a^I a_a^{II})^{1/2} \exp(-E/RT) \overline{C}_a \end{aligned} \quad (2)$$

where D_a^0 denotes the diffusion coefficient of cation in 1-octanol 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 $D_a^0 \exp(-E/RT)$, that is the product of the diffusion coefficient, D_a^0 and the exponential term of energy barrier E. It can be easily understood that the existence of the energy barrier E at the interface between membrane- aqueous solution makes the value of \overline{D}_a lower in comparison with the free diffusion coefficient. At present, we do not have any information about D_a^0 . If we assume that D_a^0 is constant and is in the order of 10^{-6} cm²sec⁻¹, the value of the energy barrier can be estimated as several

kcal/mole in the present system. This is a reasonable result, if compared with the result obtained in previous solid ion exchange membrane systems [2,3,12]. Thus it can be concluded that the energy barrier should be taken into account in the estimation of the diffusion coefficient of cation across the membrane.

In the previous study, we have 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 equations, we have

$$J_{Na}^0 = -J_H^0 \tag{3}$$

$$= -k(a_{Ha}^{II}a_{H}^I - a_{Na}^Ia_{H}^{II})$$

where,

$$k = \left\{ \frac{P_H^0 P_{Na}^0}{(P_{Na}^0 a_{Na}^I + P_H^0 a_H^I)(P_{Na}^0 a_{Na}^{II} + P_H^0 a_H^{II})^{1/2}} \right\} \tag{4}$$

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

Under the present experimental conditions, that is, when phase I contain only sodium hydroxide solution and a_H^I was negligible Equation (3) reduced to next equations.

$$J_{Na}^0 \cong ka_{Na}^I a_H^{II} \tag{5}$$

$$J_{Na}^0 \cong ka_{OH}^I a_H^{II} \tag{6}$$

Noted that Equation (5) is a simple and instructive form to understand the transport of sodium ion through this system. Equation (6) indicates that the reverse transport is generated with neutralization

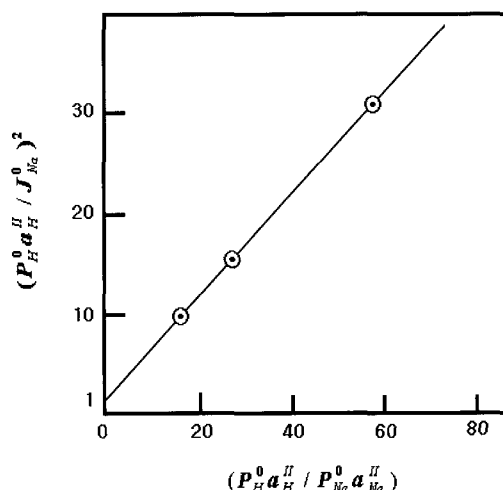


Fig. 3. The value of experimental verification for equation (7). Note that the straight line passes across unity at the intercept.

reaction. 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 Equation (6) still contains the potential terms through the diffusional membrane permeability.

The validity of Equations (5) or (6) was examined by using the results in which J_{Na}^0 , P_{Na}^0 and P_H^0 values were given in the previous work³. We can obtain Equation (7) by rearranging Equation (5).

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

Fig. 3 shows that the straight line passes through unity at the intercept and the relation among the sodium ion fluxes, the membrane permeabilities and the ion activities is satisfies the experimental results.

4. Conclusions

The analysis of membrane based on the irreversible description for the diffusion coefficient and ionic

activity can also be applied to the reverse transport system with the membrane-electrolyte aqueous solution system without the chemical reaction. The diffusion coefficients value of cation across membrane-electrolyte aqueous solution system was verified. The membrane equation indicates that the reverse transport is driven by the energy of neutralization reaction. A relation among the flux, the permeability and the partition coefficients of cations in electrolyte aqueous solution is presented and is verified by the experimental value.

Acknowledgements

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