

# Transport Coefficients Across A Charged Mosaic Membrane III

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**Abstract:** Various characteristics of ion transport properties of a charged mosaic membrane with a parallel array of positive and negative functional charges were investigated. From the analysis of the volume flux, it was found that the salt flux based on nonequilibrium thermodynamics, preferential salt transport across the charged mosaic membrane. Transport properties of the magnesium sulfate(MgSO<sub>4</sub>) and sucrose across the charged mosaic membrane were estimated. As a result, metal salts transport depended largely on the charged states and molecular weight otherwise nonelectrolyte solution was rejected under all experimental conditions. On the other hand, the reflection coefficient  $s$  indicated the negative value that suggested preferential material transport and was independent of charged mosaic thickness.

**Keywords:** transport property, charged mosaic membrane, electrolyte solution, nonequilibrium thermodynamics

## 1. Introduction

The aim was to elucidate the transport coefficient across a charged mosaic membrane. By an ion exchange membrane, most cation or anion cannot permeate without applied current; while so-called a charged mosaic membrane having two different fixed charges in the membrane matrix can simultaneously permeate both cation and anion of concentration difference. In previous studies[1-4], we reported the transport behavior of solvent and solute across the charged mosaic membrane and indicated the unique characteristics of salt solution across the charged mosaic membrane, such as the preferential solute transport. This means that one of the membrane parameters,  $\sigma$  estimated from flux measurements indicates the negative value and the separation between solute and solvent or between electrolyte and nonelectrolyte will be realized. Charged mosaic membranes are well known as membranes containing two different

fixed charges within the matrix. The two kinds of charges, cation and anion exchange groups are arranged parallel with each other inside the membrane and the array of charge groups' links continuously from one membrane surface to the other. Thus, preferential salt fluxes and a resultant separation between electrolyte and nonelectrolyte can be expected.

## 2. Experimental

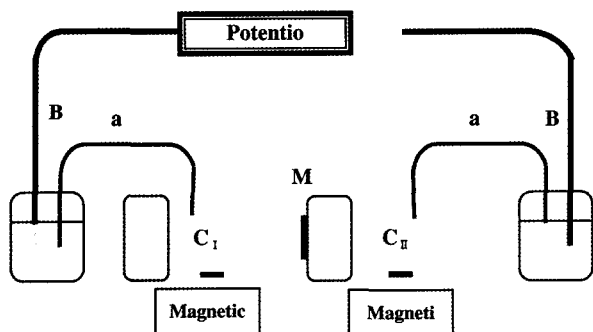
### 2.1. Materials

All the composite charged mosaic membranes in this study were kindly supplied from Dainichi Seika Industry Co.Ltd(Japan). The detailed procedure to make the membrane was described in literatures. Other reagents were purchased from Sigma(St.Louis,U.S.A). All reagents were used without further purification.

### 2.2. Flux Coefficients

The flux measurements were carried out by using two glass cells shown in Figure1. The membranes were tightly inserted between two cells by using silicon

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**Fig.1** Schematic apparatus of membrane potential measured: C<sub>I</sub>,C<sub>II</sub>, volume of solution(25 mL), respectively, B, reference electrode, a is KCl saturated salts bridge, M is charged mosaic membrane.

rubbers in order to avoid leak of solution from the contact surfaces. Each cell volume was 25 mL and the membrane area was 3.14 cm<sup>2</sup>. Temperatures of glass cells were kept at 25°C by circulating constant water surrounding the cells during the experiment. Time changes of volume and concentration in cell 1 or cell 2 were measured respectively using a graduated glass capillary or a pencil-type conductance cell. Volume flux and solute flux were evaluated from volume change versus time or concentration change versus time by taking account membrane area, 3.14 cm<sup>2</sup>. In this study, the volume flux and solute flux were examined in different two situations, systems I and II.

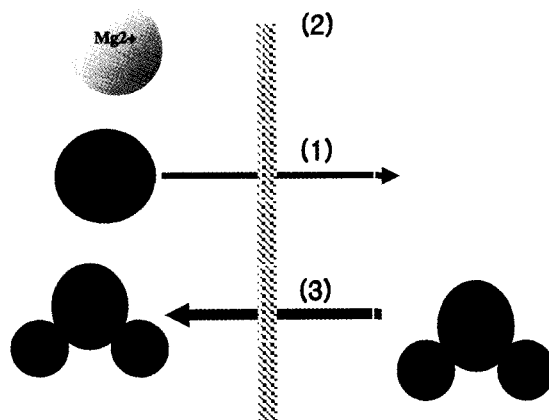
**System I:** in this system, aqueous MgSO<sub>4</sub> solution and distilled water were inserted into cell 1 and cell 2, respectively, and MgSO<sub>4</sub> concentrations were changed from 0.001 to 0.1 mol dm<sup>-3</sup> in Figure 2.

**System II:** in cells 1 and 2 across the charged mosaic membrane, 0.5 mol dm<sup>-3</sup> aqueous saccharose solution and distilled water were placed, respectively. Furthermore, in order to examine the added salt effects, equal amounts of MgSO<sub>4</sub> were inserted into both cells and the MgSO<sub>4</sub> concentrations were changed from 0.1 to 0.001 mol dm<sup>-3</sup>.

In the system I is produced by the difference between the water flux induced by MgSO<sub>4</sub> diffusion and osmotic flow as shown in Figure 3.

### 2.3. Membrane Potential

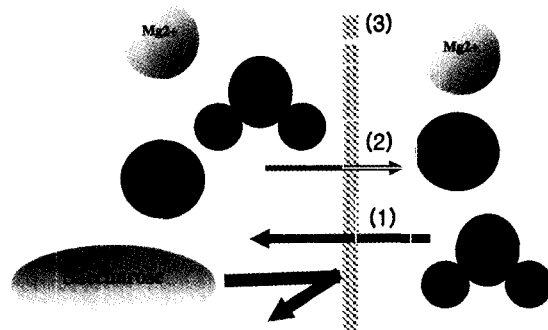
The cell for membrane potential measurements was



#### System I

MgSO<sub>4</sub> | charged mosaic membrane | water

**Fig. 2.** Simple schematic of ion transport phenomena across a membrane.



#### System II

MgSO<sub>4</sub> + Saccharose | Charged mosaic membrane | MgSO<sub>4</sub>

**Fig. 3.** Simple schematic of ion flux phenomena across a charged mosaic membrane.

essentially the same one as the transport studies. The electrolyte concentrations in cell 1 were changed from 0.1 to 0.005 mol dm<sup>-3</sup> and that in cell 2 was kept at constant 0.05 mol dm<sup>-3</sup>. The potentials in the systems were measured as a function of time by using a digital potentiometer (Orion research 902). The values of  $t = 0$  in those figures were adopted membrane potential.

## 3. Results and Discussion

The volume change versus time in system I using sucrose as impermeable solute indicated linearity. All

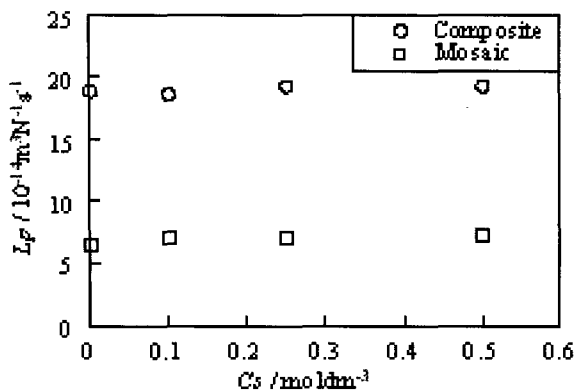


Fig. 4. Dependence of water permeability on the salt concentration in system I.

the other relations with various added  $\text{MgSO}_4$  concentrations in system I also indicated linearity. This means the systems are in steady state within the examined time. Similarly, the volume change and  $\text{MgSO}_4$  concentration change versus time in system II were obtained as linear relations being steady state. However, the direction of the volume change in system II was opposite to that in system I.

### 3.1. Filtration coefficient, $L_p$

As described in experimental section, taking account of membrane area for the slopes of straight lines, one can obtain volume flux and solute flux. In addition, according to equations in previous studies, three important membrane parameters,  $L_p$ ,  $\sigma$  and  $\omega$  can be estimated.  $L_p$  is filtration coefficient that means water permeability or water affinity with membrane and is given in Figure 4 along with those about the charged mosaic membrane without reinforcement. In Figures 4 and 5 the obtained  $L_p$ 's values were given as added  $\text{MgSO}_4$  concentrations and the result indicated the water affinity in membrane was not affected by existence of electrolytes in outer solutions. On the other hand, in comparison with charged mosaic membrane without reinforcement,  $L_p$ 's values in composite membrane became larger than that in the charged membrane without reinforcement. This result seems to be inconsistency because material transports depend on membrane thickness and the values are almost the same in both

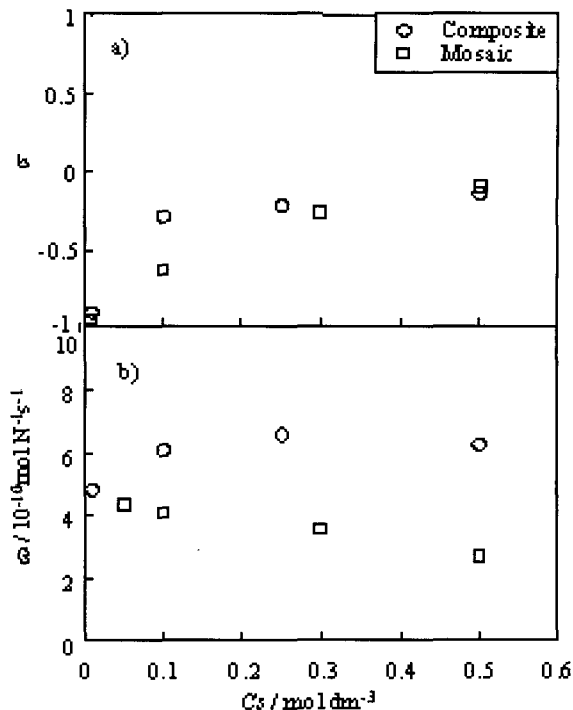


Fig. 5. a) and b) Reflection coefficients and salt permeabilities obtained using charged mosaic membrane.

membranes. The result will be discussed later along with that in solute permeability.

### 3.2. Reflection Coefficient $\sigma$ and Salt Permeability Coefficient $\omega$

In Figures 6a and 6b, the reflection coefficients and salt permeability coefficients estimated from the results in system II were given along with the previous results. Regarding  $\sigma$ , the values were almost the same as those in previous studies and indicated the negative values in the examined concentration ranges as seen in Figure 3a. Negative  $\sigma$  implies the preferential salt transport over solvent transport and is very important for practical pressure dialysis. On the other hand,  $\omega$  values indicated the different values between charged mosaic membranes and present membranes were more permeable than the previous membrane for water transport and  $\text{MgSO}_4$  transport as seen in Figure 5b. Those two values,  $L_p$  and  $\omega$  suggesting the physical quantities are closely related to charged functional groups in the total membrane thickness.

### 3.3. Practical Phenomenological Equation

In the case of two flows about solute and solvent, practical phenomenological equations can be given as follows:

$$J_v = L_p(\Delta p - \sigma_s \Delta \Pi_s) \quad (1)$$

$$J_s = C_s(1 - \sigma_s)J_v + \omega_s \Delta \Pi_s \quad (2)$$

where  $J_v$  and  $J_s$  are volume flux and solute flux which can be obtained from volume changes with time and concentration changes with time, respectively.  $L_p$  is defined as the filtration coefficient (water permeability). The  $\sigma_s$  is defined as reflection coefficient. The  $\omega_s$  is defined as permeability coefficient. According to Kedem and Katchalsky, membrane parameters across charged mosaic membrane,  $L_p$ ,  $\sigma$  and  $\omega$  in appropriate experimental conditions were given as following equations,

$$L_p = - \left( \frac{J_v}{\Delta \Pi} \right)_{\Delta P=0} \quad (3)$$

$$\sigma = - \frac{1}{L_p} \left( \frac{J_v}{\Delta \Pi} \right) \quad (4)$$

$$\omega = \left( \frac{J_s}{\Delta \Pi} \right)_{J_v=0, \Delta P=0} \quad (5)$$

The membrane parameters in Figure 5 and Figure 6 were estimated using Eqs.(3)-(5). As described above, the improved equation containing information about active layer thickness would be convenient to explain the discrepancy between present and previous results.

Here, the dissipation function can be written,

$$\phi = J_s \cdot \frac{d\mu_s}{dx} + J_w \cdot \frac{d\mu_w}{dx} \quad (6)$$

Where s stands for solute and w solvent.

As the chemical potential of solvent is  $\mu_w = \mu_w^0 + \bar{V}_w P + \mu_w^c$ , where a symbol of superscript c is the concentration dependent part,

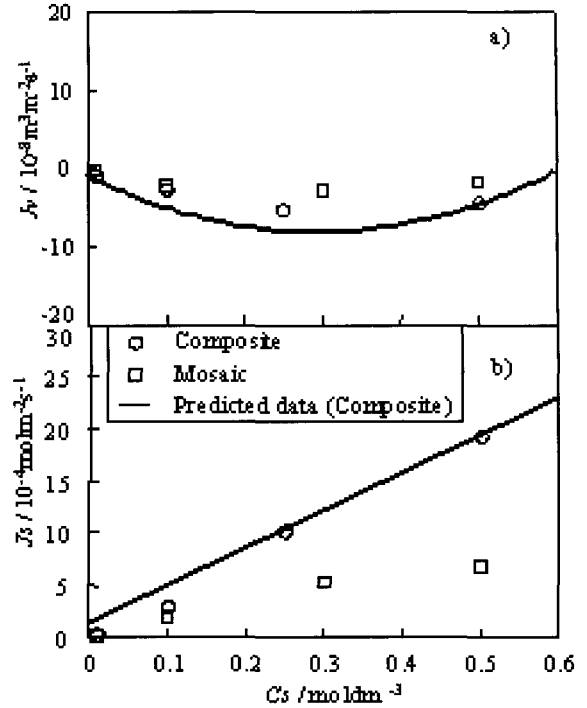


Fig. 6. a) and b) Comparison of experimental data with predicted data of a composite membrane in volume and salt fluxes.

$$d\mu_w = \bar{V}_w dP + d\mu_w^c \quad (7)$$

In the same way, the chemical potential of solute is written

$$d\mu_s = \bar{V}_s dP + d\mu_s^c \quad (8)$$

If a membrane is ideal, the concentration dependent part of solvent,  $d\mu_w$  can be replaced by osmotic pressure,  $-V_w d\Pi$ . Integrating over membrane thickness, one can obtain the following equations,  $d\mu_w^c$  can be replaced by osmotic pressure  $-V_w d\Pi$ . Then, Eq. (8) can be reduced to

$$d\mu_w = \bar{V}_w (dP - d\Pi) \quad (9)$$

On the other hand, Gibbs-Duhem equation in this case can be written as follows

$$\sum_{j=1}^{k-1} n_j d\mu_j^c = -n_w d\mu_w^c$$

$$n_s d\mu_s^c = n_w \overline{V_w} d\Pi$$

$$d\Pi = \frac{n_s}{n_w \overline{V_w}} d\mu_s^c = C_s^a d\mu_s^c \quad (10)$$

Substituting Eq.(10) into Eq.(8) gives

$$d\mu_s = \overline{V_s} dP + d\Pi / C_s^a$$

Thus the dissipation function, Eq.(6) can be rewritten to

$$\phi = (J_w \cdot \overline{V_w} + J_s \cdot \overline{V_s}) \frac{dP}{dx} + \left( \frac{J_s}{C_s^a} - J_w \cdot \overline{V_w} \right) \frac{d\Pi}{dx}$$

The phenomenological equations are described as follows,

$$J_v = L_{11} \frac{dP}{dx} + L_{12} \frac{d\Pi}{dx}$$

$$J_D = L_{21} \frac{dP}{dx} + L_{22} \frac{d\Pi}{dx} \quad (11)$$

where  $J_v = J_w \cdot \overline{V_w} + J_s \cdot \overline{V_s}$  and  $J_D = \frac{J_s}{C_s^a} - J_w \cdot \overline{V_w}$

Adding  $J_v$  and  $J_D$  gives

$$J_v + J_D = J_w \overline{V_w} + J_s \overline{V_s} + \frac{J_s}{C_s^a} - J_w \overline{V_w}$$

$$= \frac{J_s}{C_s^a} (1 + \overline{V_s} C_s^a) \approx \frac{J_s}{C_s^a} \quad (12)$$

First equation of Eqs.(11) can be rewritten to  $\frac{dP}{dx} = \frac{J_v}{L_{11}} - \frac{L_{12}}{L_{11}} \frac{d\Pi}{dx}$ . So  $J_s$  may be given as follow.

$$J_s = C_s^a \cdot J_v + C_s^a J_D$$

$$= C_s^a \cdot J_v \left( 1 + \frac{L_{21}}{L_{11}} \right) + C_s^a \left( L_{22} - \frac{L_{12} L_{21}}{L_{11}} \right) \frac{d\Pi}{dx} \quad (13)$$

$$= C_s^a \cdot J_v (1 - \sigma) + \omega \frac{d\Pi}{dx}$$

Where  $L_{11} = Lp'$ ,  $\sigma = -\frac{L_{12}}{L_{11}}$   $\omega = C_s^a (L_{22} - \frac{L_{12}^2}{L_{11}})$ .

And  $J_v$  may be given as follows.

$$J_v = Lp' \frac{dP}{dx} + L_{11} \frac{L_{12}}{L_{11}} \frac{d\Pi}{dx}$$

$$= Lp' \left( \frac{dP}{dx} - \sigma \frac{d\Pi}{dx} \right) \quad (14)$$

As summarizing the practical phenomenological equation allowing for the membrane thickness will be given as follows,

$$J_v = Lp' \left( \frac{dP}{dx} - \sigma \frac{d\Pi}{dx} \right)$$

$$J_s = C_s^a \cdot J_v (1 - \sigma) + \omega \frac{d\Pi}{dx}$$

Integrating Eqs(14) and (13) over membrane thickness, one can obtain the following equations

$$J_v = \frac{Lp'}{\delta} (\Delta P - \sigma \Delta \Pi) \quad (15)$$

$$J_s = C_s^a (1 - \sigma) J_v + \frac{\omega'}{\delta} \Delta \Pi \quad (16)$$

where  $Lp'$  or  $\omega'$  are parameters taking account of membrane thickness and  $\delta$  is membrane thickness. Compared Eqs.(3)-(5) with Eqs.(8)-(9), one can obtain the relation between present and previous  $Lp$  or  $\omega$  as follows,

$$Lp' = Lp \cdot \delta \quad (17)$$

$$\omega' = \omega \cdot \delta \quad (18)$$

Eqs. (17) and (18) reasonably satisfy the condition that transported quantity across membrane is inversely proportional to the membrane thickness. This means that if active layer consists of same materials, the flux should depend on only the thickness of the active layer irrespective of membrane with or without reinforcement. From previous study[1,6], the thickness of active layer

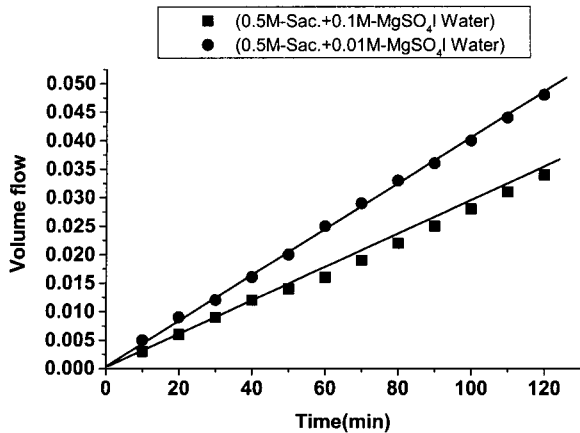


Fig. 7. Volume flux vs. functional time variable across a charged mosaic membrane.

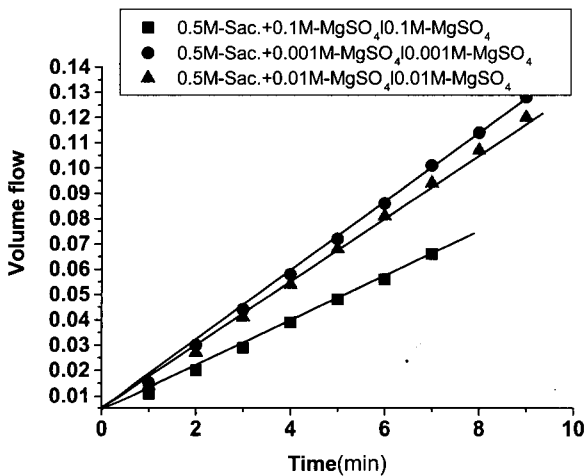


Fig. 8. Volume flux vs. functional time variable across a charged mosaic membrane.

in membrane without support film is already known as  $50 \mu\text{m}$ . Then, taking  $50 \mu\text{m}$  as reference, the thickness of the present active layer was estimated, determined as  $18.5 \mu\text{m}$ ,  $L_p$  or  $\omega$  indicating large values would be reasonable. That is the thinner the membrane thickness, the larger the volume of salt flux is, while  $\sigma$  is independent of active thickness

### 3.3. Reproduction of $J_v$ and $J_s$

In order to verify the active layer thickness of composite membrane,  $J_v$  and  $J_s$  about the composite

membrane was reproduced from the previous result using  $18.5 \mu\text{m}$  thickness and given in Figures 6a and 6b. As seen in Figure 6, the predicted solid lines were satisfactorily accord to the experimental results in the composite charged mosaic membrane. As a result, the composite charged mosaic membrane was proved to exhibit the excellent transport performance. The potential application to pressure dialysis was expected.

## 4. Conclusions

In this work,  $\text{MgSO}_4$  and water transports under the mixed  $\text{MgSO}_4$  and saccharose solution system were investigated. Two kinds of measurements, volume flux and solute flux, were performed. Volume fluxes across charged mosaic membrane could be classified into osmotic flow of water due to  $\text{MgSO}_4$  concentration difference, water flow dragged by  $\text{MgSO}_4$  diffusion, and osmotic flow of water due to saccharose and they were found to be additive. In addition, it was elucidated that the presence of nonelectrolyte solution can easily change the direction and the magnitude of volume fluxes. From the results, it was suggested that a efficient salt enrichment can be performed by controlling the direction of the solvent osmosis and one can expect negative salt rejection.

## Acknowledgement

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