

## Salt Enrichment by a Novel Charged Mosaic Membrane

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A charged mosaic membrane with a parallel array of different negative and positive charges was prepared from microsphere gels. Several characteristics on the novel membrane were investigated through experiments concerning transport studies and membrane potentials. From analysis of the volume flux and salt flux based on irreversible thermodynamics, the reflection coefficients,  $\sigma$ 's values were less than unity and preferential salt transport across the charged mosaic membrane was suggested. Membrane potential did not indicate a constant value but the absolute value decreased rapidly in a short time. The time dependence of the membrane potential supported the interpretation of a salt flow in transport studies. From potential measurement, cationic and anionic transport numbers in the membrane were determined to be  $\bar{t}_K = 0.41$  and  $\bar{t}_{Cl} = 0.59$ , similar to the values in solution.

### 1. INTRODUCTION

Our goal is to materialize salt enrichment from sea water at low energy costs. In Japan consisting of islands, we have no natural resources except for salts in sea water. The effective production of salts from the ocean is one of the expected technological developments in Japan. The conventional techniques using membranes such as electrodialysis methods should be improved to become more effective because the present systems can not provide a highly concentrated salt solution. This is mainly caused by the membrane performance. As one of the potential techniques, a pressure dialysis using a charged mosaic membrane is proposed. The charged mosaic membrane is well known as the membrane containing two different charges within the matrix[1-4]. The two kinds of charges, anion and cation exchange groups, are arranged parallel to each other in the membrane and the array of charged groups links continuously from one membrane surface to the other surface. The charge distribution is supposed to induce concurrent migrations of cations and anions along the respective fixed charges(ion exchange sites) and to reject the nonelectrolyte. Then, preferential salt fluxes and the resultant separation between electrolyte and nonelectrolyte will be expected. Such a characteristic feature of the mosaic membrane is very attractive in

the membrane application to various field. In fact, since Sollner's foresighted study about the mosaic membrane[1-4], several investigations have been presented by many scientists but unfortunately the practical application has not been attained to up now[5-19].

Recently Nakamura et. al. developed the novel charged mosaic membrane using microsphere gels[20,21]. Before practical application, the fundamental properties of the membranes have to be characterized. In this study, the transport phenomena across the membrane and membrane potential were examined to understand the transport mechanism of salts from a fundamental point of view[22].

### 2. EXPERIMENTAL

#### 2.1. Membrane preparation

Firstly cationic microsphere gel(4VP/DVB) and anionic microsphere gel(SSNa/DVB) were dispersed in N-methyl-2-pyrrolidone and the matrix resin (polysulfone resin(80Wt%)/polyurethane (20Wt%)) was dispersed in the same organic solvent. Secondly, the mixed organic solutions were cast and thirdly the pyridine groups of 4VP were quaternarised to bear cationic charges[20,21]. In preparation of the membrane, theoretically identical quantities of positive and negative charges were introduced into

the membrane matrix but the absolute values were not verified yet experimentally at present. The membrane thickness was 50  $\mu\text{m}$  and the water content was 17~22%. The membranes were stored in 0.1  $\text{mol dm}^{-3}$  KCl solution before experimental use.

## 2.2. Transport studies

The experimental cell consisted of two half glass cells and the charged mosaic membrane was tightly clamped between the two cells. Temperature was kept at 25°C by constantly circulating water around the two glass cells during the experiment. Mainly two kinds of measurements, volume change and salt concentration change were measured as functions of time by using a graduated capillary and an electrode type conductive meter, respectively[23-26].

## 2.3. Membrane potential

The cell for membrane potential measurement is essentially the same one as the one for transport studies except for the insertion of a capillary or conductive meter. Instead of this, a pair of KCl agar bridges were put into the glass cells. The membrane potentials in a tenfold concentration difference of KCl across the charged mosaic membrane were measured by digital potentiometer connected to calomel electrodes through agar bridges[27,28].

## 3. RESULTS and DISCUSSION

According to irreversible thermodynamics concerning transport phenomena, the characteristic parameters of a membrane such as its filtration coefficient,  $L_p$ , reflection coefficient,  $\sigma$ , solute permeability,  $\omega$  can be defined as follows[22],

$$L_p = (J_v / \Delta \Pi_s)_{\Delta P=0, \sigma=1} \quad (1)$$

$$\sigma = (1/L_p)(J_v / \Delta \Pi_s)_{\Delta P=0} \quad (2)$$

$$\omega = (J_s / \Delta \Pi_s)_{\Delta P=0} \quad (3)$$

where  $J_v$  and  $J_s$  are volume flux and salt flux which can be obtained from volume changes in time and salt concentration changes in time respectively, and moreover,  $\Delta \Pi_s$  is the osmotic pressure calculated from the concentration differences of salt or saccharose across membrane. It should be noticed that  $J_v$  has a negative sign for the transport direction from pure water to solution. Under the condition

given at each subscript, one can obtain the membrane parameters experimentally and discuss the membrane performances through these parameters[23-26]. That is,  $L_p$  represents the water transport index across membrane,  $\sigma$ , the separation index between water(solvent) and solute by the membrane and  $\omega$ , the solute transport index across the membrane.

Before transport study, first of all, the separation potential of the charged mosaic membrane for electrolyte / nonelectrolyte was examined. The result in Fig.1 indicated that the separation in a mixed solution of glucose / KCl was satisfying and the glucose molecules are almost rejected by the membrane.

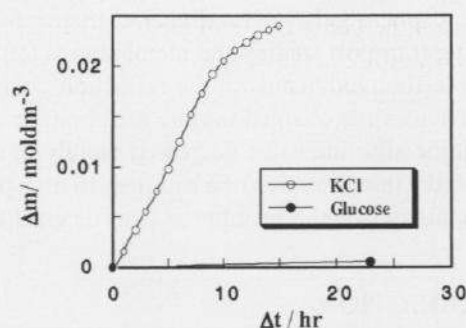


Fig.1. Separation potential of a mixed solution of KCl and glucose.  $\Delta m$  vs.  $\Delta t$  in water / mixed solution of KCl and glucose system. Meaning of each symbol is assigned in figure.

Based on the above fact, a saccharose can be easily rejected by the membrane because the molecule is larger than glucose and it is capable to produce sufficient osmotic pressure in the water /

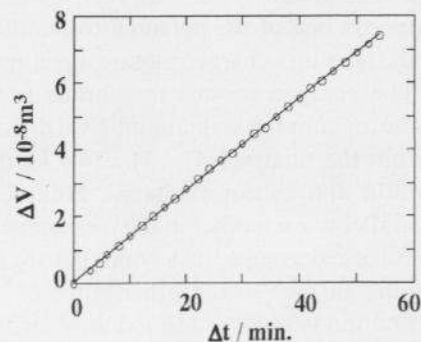


Fig.2. Typical example of volume changes across charged mosaic membrane.  $\Delta V$  vs.  $\Delta t$  in water / 0.5  $\text{mol dm}^{-3}$  saccharose system.

saccharose system. When  $0.5 \text{ mol/dm}^3$  saccharose is inserted into one side of cell system as typical example, the volume change driven by the osmotic pressure can be plotted as a function of time in Fig.2 where the decreased volume changes were taken as the positive values. The relation turned out to be linear within the range of time examined and was suggested to reflect the steady state. Accordingly the volume flux,  $J_v$  was deduced from the slope of the linear relation by taking into account the effective membrane area,  $3.14 \times 10^{-4} \text{ m}^2$  [18,19]. In addition, experiments in a similar system which contained an identical amount of KCl in both solutions across the membrane, were carried out in order to know the influence on the volume flux in presence of electrolytes. Inserting the volume flux into Eq.(1), one can obtain the filtration coefficient,  $L_p$  which means solvent(water) permeability through the membrane.  $L_p$ 's values in the presence of KCl were depicted in Fig.3. As seen in Fig.3, the values were almost

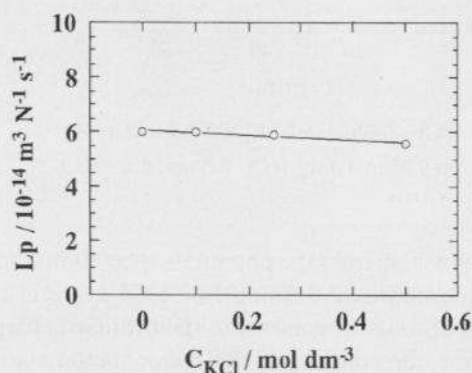


Fig.3. Dependence of  $L_p$  on KCl concentration.  $L_p$  is filtration coefficient and calculated from Eq.(1).

independent of the KCl concentrations in ranges from zero to  $0.5 \text{ mol/dm}^3$ . In this case, the presence of KCl gave no effect for water permeability through the membrane and  $5.9 \times 10^{-14} \text{ m}^3 \text{N}^{-1} \text{s}^{-1}$  for  $L_p$  was determined as an average value. In the system where only KCl instead of saccharose was inserted into the half cell, the KCl flow due to the concentration gradient takes place across the membrane. Occurrence of KCl flow means the reduction of KCl concentration difference across the membrane and the osmotic pressure due to KCl concentration difference decreases. As a result, volume flux of solvent was reduced. From the viewpoint of separation between solute and solvent,

Table 1. Dependence of  $\sigma L_p$  and  $\sigma$  on KCl concentration.

KCl $\text{mol dm}^{-3}$	$\sigma L_p$ $10^{-14} \text{ m}^3 \text{N}^{-1} \text{s}^{-1}$	$\sigma$
0.10	-1.0	-0.17
0.15	0.68	0.12
0.25	1.00	0.17
0.50	1.51	0.26
0.63	1.69	0.29

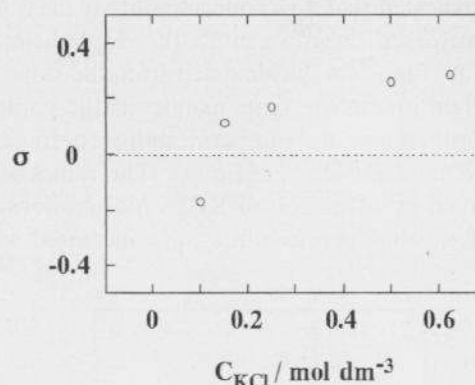


Fig.4. Dependence of  $\sigma$  on KCl concentration.  $\sigma$  is reflection coefficient and calculated from Eq.(2).

the increase of KCl flux means that the separation index,  $\sigma$  becomes less than unity. Using Eq.(2),  $\sigma L_p$  can be obtained from the volume fluxes in water / KCl system and the values are given in Table 1. It should be noticed that  $\sigma L_p$  turns out to become negative with decreasing KCl concentration in the system. Provided that the water permeability would be constant, independent of the presence of KCl, and equal to  $5.9 \times 10^{-14} \text{ m}^3 \text{N}^{-1} \text{s}^{-1}$ ,  $\sigma$  can be estimated to be as given in Fig.4. The values were also summarized for several KCl concentrations together with  $\sigma L_p$  in Table 1. As expected from the values of KCl fluxes, a negative value of  $\sigma$  appears as the KCl concentrations decrease.

In a comparative study with the ordinary charged membrane, the filtration coefficient,  $L_p$ , in the present charged mosaic membrane was almost of the same order as those of ion exchange membranes [7,19,23-26]. Interestingly the reflection coefficient,  $\sigma$  has a relatively low value, although generally  $\sigma$  is close to unity in the ordinary ion ex-



change membrane. Furthermore, the dependence of  $\sigma$  on the electrolyte concentration was obviously recognized and in case of the dilute electrolyte concentration, it became negative. It was suggested according to irreversible thermodynamics that the salts can be preferentially transferred across the membrane[22].

As mentioned above, the fact that  $\sigma$  in water / KCl system becomes less than unity is attributed to the generation of a salt flux across the membrane. The solute fluxes in systems with several KCl concentrations were observed experimentally and the results indicated that KCl concentrations in the water phase increased linearly against the elapsed times. The solute flux,  $J_s$  was calculated from the slope of the straight line in the same manner as the volume flux. Furthermore, the salt permeability coefficient,  $\omega$ , was obtained in terms of Eq.(3). The values of  $\omega$  were given as a function of KCl concentrations in Fig.5. The solute permeabilities,  $\omega$ 's increased with

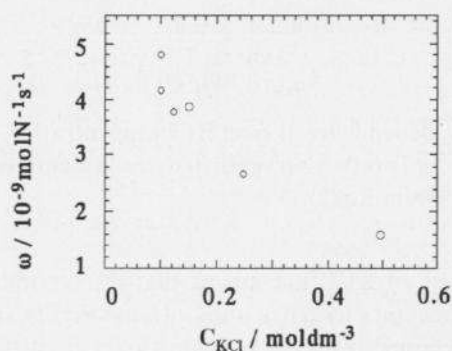


Fig.5.  $\omega$  vs. KCl concentration.  $\omega$  is salt permeability coefficient and calculated from Eq.(3).

the decrease of KCl concentrations and the result contrasted with the decrease of  $\sigma$ . Both  $\omega$  and  $\sigma$  obviously confirm the existence of KCl transport through the charged mosaic membrane. The  $\omega$ 's values reflecting KCl transport were a  $10^2$  fold more than that of the transport through the ordinary charged membrane[7] and the result supported the above interpretation of  $\sigma$ . These thermodynamic parameters such as  $\sigma$  and  $\omega$  in this study, indicate that the application of the charged mosaic membrane will be promising in enrichment of the salt or getting the pure water from the ocean.

It is interesting to view the charged structure in membrane from a different aspect. In general, the

membrane potential reflects the relative ionic transport through the charged membrane having monotonic ion exchange groups. In other words, measurement of the membrane potential gives us the transport number of the counterion within the charged membrane. In case of the charged mosaic membrane having two different ion exchange groups, the membrane potential would be certainly influenced by the transport of cation and anion in the membrane. If the exchange capacities of cation and anion in the membrane are equal and the symmetrical salt like KCl is also used as electrolyte solution, it is predicted that the membrane potential would be zero because both ionic transport numbers are almost 0.5. Figure 6

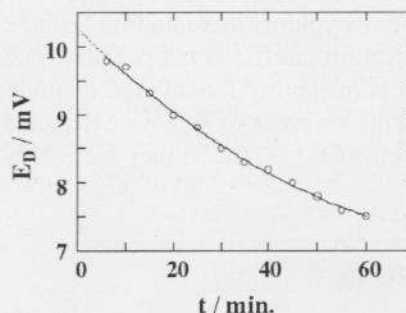


Fig.6. Diffusion potential,  $E_D$  vs. elapsed time,  $t$  in  $0.05 \text{ mol dm}^{-3}$  KCl /  $0.5 \text{ mol dm}^{-3}$  KCl system.

shows typical membrane potentials in a  $0.05 \text{ mol/dm}^3$  KCl / membrane /  $0.5 \text{ mol/dm}^3$  KCl system as a function of time. In contrast to the ordinary charged membrane, the potential of the system largely varied with the elapsed time as seen in Fig.6. The rapid reduction of potential means that the KCl flow takes place across the charged mosaic membrane and it can be said that the fact is consistent with the low  $\sigma$  or increase of  $\omega$  indicated before. Accordingly the potential - time dependence may be considered as a diffusion potential rather than the steady membrane potential. Thus, in this case it would be suitable to use Henderson's equation for diffusion potential as follows,

$$E_D = \frac{RT}{F} \left( \frac{t_+/z_+ + t_-/z_-}{t_+/z_+ - t_-/z_-} \right) \ln C^I/C^{II} \quad (4)$$

Before inserting the potential values into the equation, the potential values were extrapolated to  $t = 0$  to obtain the initial diffusion potential. Cationic and anionic transport numbers in the charged mosaic

Table 2. Transport Numbers,  $\bar{t}_K$  and  $\bar{t}_{Cl}$  in Membrane

$\bar{t}_K$ ( $t_K$ )	$\bar{t}_{Cl}$ ( $t_{Cl}$ )
0.41 (0.49)	0.59 (0.51)

Values in parentheses represent transport numbers in solution[29]

membrane were then calculated from the potential values in terms of Eq.(4) and given together with the values in solution in Table 2[29]. A slight difference between the values in membrane and solution was recognized but as a whole the cationic and anionic transports through the charged mosaic membrane were of the same degree as those in solution and therefore the transport as a salt was inferred. The slight difference between  $\bar{t}_K$ (0.41) and  $\bar{t}_{Cl}$ (0.59) can not be explained at present, but K ions may be more or less immobilized within the membrane and the mobility of K ions may be depressed.

#### 4.CONCLUSION

In this work, a stable charged mosaic membrane made of microsphere gels was prepared. The filtration coefficient,  $L_p$  concerning water transport across the membrane was of the same order as that of ordinary charged membrane,  $5.9 \times 10^{-14} \text{ m}^3 \text{N}^{-1} \text{s}^{-1}$ . At certain KCl concentrations, the membrane indicated a negative reflection coefficient,  $\sigma$  which suggests preferential salt transport compared to solvent transport. The interpretation was also supported by salt flow and membrane potential measurements. As a result, the charged mosaic membrane turned out to be promising for enrichment of salt, desalination or separation between electrolyte and nonelectrolyte.

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