

Material Transport Properties of Polymer–Gel Composite-Charged Mosaic Membrane with and without Reinforcement [II]

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ABSTRACT: The charged mosaic membranes (CMM) without reinforcement and the composite charged mosaic membrane (CCMM) with reinforcement were investigated in terms of solute and solvent transport. The composite charged mosaic membrane (CCMM) with reinforcement showed a unique transport behavior such as preferential material transport L_p and ω . Filtration coefficient, L_p and salt permeability coefficient ω were estimated by taking account of active layer thickness of composite polymer gel. The L_p and ω values of CCMM with reinforcement were larger than those of charged mosaic membrane (CMM) without reinforcement. On the other hand, the reflection coefficient of

CCMM σ showed negative value, which suggested the preferential material transport to solvent transport. This indicates that σ was independent of active layer thickness. Furthermore, the results of transport properties of CCMM with reinforcement were supported by the membrane potential measurements. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3507–3513, 2006

Key words: composite charged mosaic membrane; negative reflection coefficient; transport number; active layer; reinforcement

INTRODUCTION

Cation and anion exchange membranes have been mainly used for salt enrichment from seawater by electrodialysis on the industrial scale. At present, a further development of the charged membrane system with new functional groups is required to increase the efficiency in the desalination of seawater or to recover waste solutions containing heavy metals. Desalting of seawater is important, in particular; the technology will become inevitable in big cities because the rapid increase of population and the industrial development demand huge quantities of water. The techniques using membrane, such as electrodialysis, or reverse osmosis method should be improved to be more effective. As one of the potential techniques, a pressure dialysis using charged mosaic membrane, CMM, is proposed.

In previous studies^{1–6} the transport behavior of solvent and solute across the CMM was reported and the unique characteristics of the mosaic membrane, such as the preferential solute transport was observed as well. Also, the comparison of transport properties of monovalent anions through anion exchange membranes of CMM, and CMM prepared from microspheres were studied as well.^{7–8} In this study, we are motivated to investigate the transport material properties of composite charged mosaic membrane (CCMM), which contains cationic and anionic polymer–gel microsphere with and without reinforcement. Furthermore, from electrochemical aspect, the membrane potentials of CCMM/electrolyte solution system were measured, and the transport numbers were estimated. The study of membrane potential provides the information regarding the transport behaviors of both cation and anion through the membrane. In this study, the results of CCMM with reinforcement are compared to the results of the CMM without reinforcement to understand the transport mechanism from basic viewpoint.

EXPERIMENTAL

Materials and membrane preparation

Firstly, cationic microsphere polymer–gels polyvinylpyridine/divinylbenzene copolymer, and anionic

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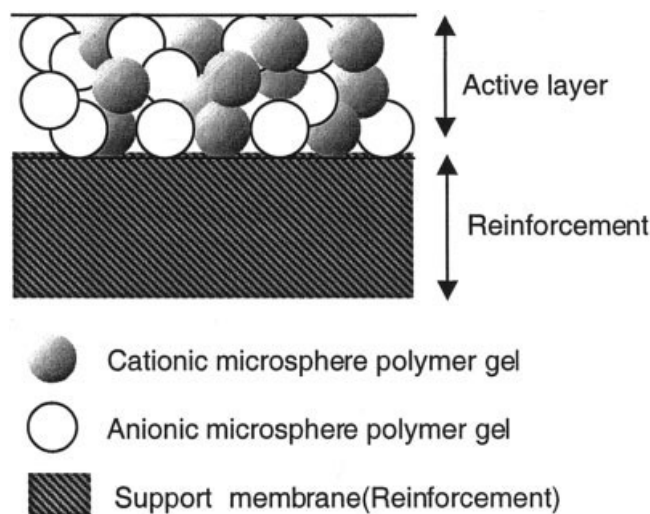


Figure 1

microsphere polymer gel, polystyrene sulfonic acid sodium salt/divinylbenzene copolymer were prepared. The detailed procedures for the preparation of the mosaic membrane were described elsewhere.^{6,9-10} Schematic model of the charged composite mosaic membrane (CCMM) with support (reinforcement) was shown in Figure 1. Here, in this study, the membrane without support film, CMM, consists of only active layer. The "active layer" stands for a part of polymer gel-charged mosaic membrane (CMM) structure. The total membrane thickness is reported by Dainichiseika Color and Chemicals Mfg. Co. (Japan) to be about 50 μm . Lithium chloride (LiCl), sodium chloride (NaCl), cesium chloride (CsCl), potassium chloride (KCl), tetramethylammonium chloride (Met_4NCl), and tetraethylammonium chloride (Et_4NCl) were purchased from ABIOS Co., Ltd. (Japan).

Transport studies

The cell for experiment consisted of two half cells. The charged mosaic membranes were tightly clamped between two half-glass cells by using silicon rubbers to avoid leak of solution from the contact position between membrane and the orifice of cells. Each cell volume is 25 mL and the effective membrane area is 3.14 cm^2 . Temperature of glass cells was kept at constant 25°C by circulating thermostated water around the two cells during experiment. The volume change and salt concentration change were measured as functions of time by using graduated glass capillary and pencil-type conductance electrode, in cell 1 or cell 2, respectively. Volume flux and solute flux were estimated from volume change versus time and concentration change versus time by taking account of membrane area, respectively.¹¹⁻¹⁴ In this study, the volume

flux and solute flux were examined in two different situations, system I and system II, separately.

System I

A 0.5 mol dm^{-3} aqueous sucrose solution and distilled water were separately placed in both cell 1 and cell 2, across the composite polymer-gel CMM. Furthermore, to examine the effects of added salt, the KCl concentrations in both cells were changed from 0.01 to 0.5 mol dm^{-3} . The increase of volume, ΔV , against time, Δt , was determined as positive. The dependence of ΔV on different salt concentration was not clearly observed (see Fig. 2).

System II

In this system, aqueous KCl solution and distilled water were inserted into cell 1 and cell 2, respectively, and KCl concentrations were changed from 0.01 to 1 mol dm^{-3} . The decrease of volume, ΔV against time, Δt was determined as negative. The dependence of ΔV on the different salt concentration was observed (See Fig. 3). Also, the dependence of the slope, $\Delta V/\Delta t$ that represents J_v , on different salt concentration was not linear as shown in Figure 3(a).

Membrane potential

The cell used for membrane potential measurement was the same one used for the transport studies case. Instead of capillary or conductive meter, a pair of silver/silver chloride electrodes was inserted into both glass cells. The electrolyte concentrations in cell 1

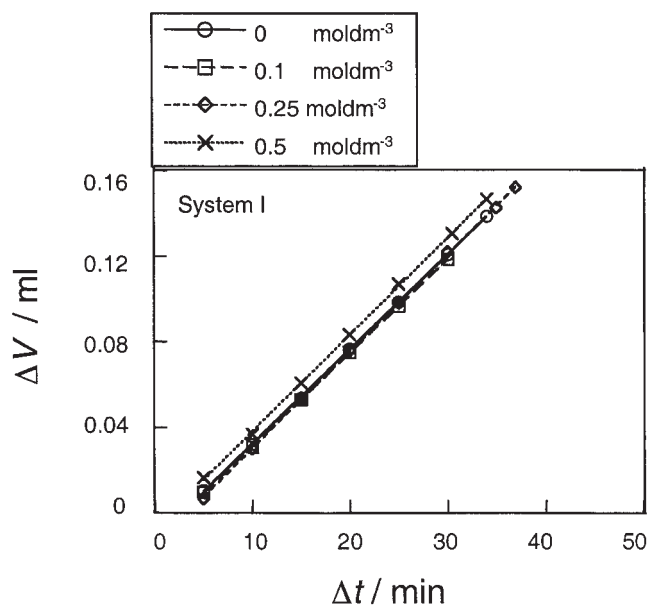


Figure 2

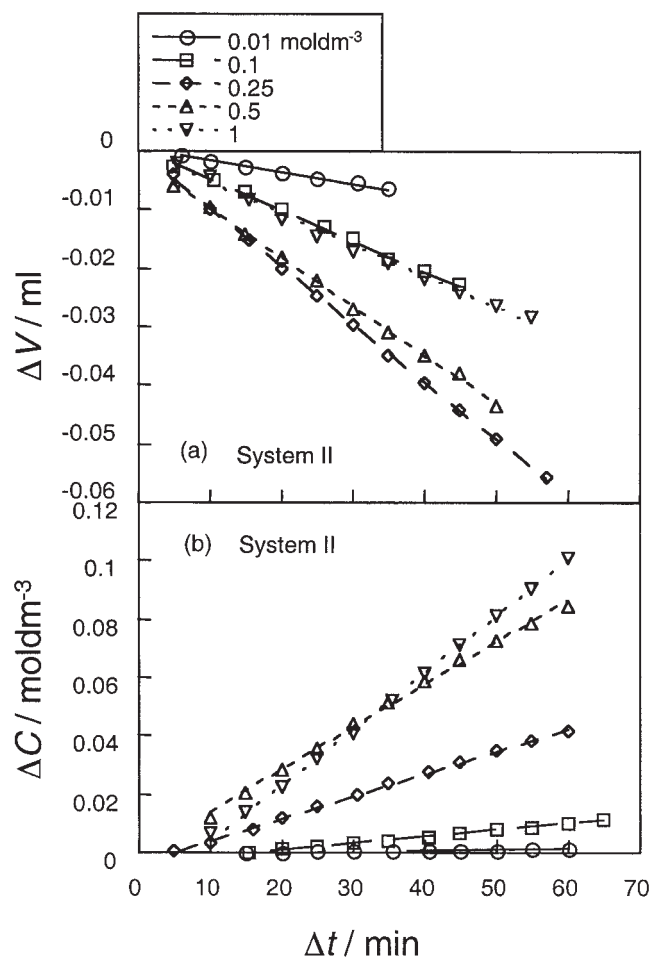


Figure 3

were changed to 0.5, 0.025, 0.01, and 0.005 mol dm⁻³ and that in cell 2 was kept constant at 0.05 mol dm⁻³. The potentials in each system were measured as a function of time by using a digital potentiometer (ORION RESEARCH, Microprocessor ionalyzer/901). Because the membrane used in this study can easily permeate both anion and cation, so the concentration difference in both phases becomes zero, and then the value of membrane potential disappear within finite time. Hence at each respective concentration, the value of potential at $t = 0$, by extrapolating the linear relation between the potential and time to zero, was defined as the initial diffusion potential. Six kinds of electrolytes including organic salts for membrane potential measurements were examined.

RESULTS AND DISCUSSION

Figure 2 shows the volume changes versus time in system I by using sucrose as impermeable solute. The volume changes of CCMM with time indicated linear relationship, irrespective to the different added KCl concentrations. This means that the system I is in

steady state within examined time. Similarly, Figures 3(a-b) show both the volume change and KCl concentration change with time in system II. Figure 3(a) showed linear relationship with steady state in the range of the examination time, however the direction of volume change of CCMM in system II was opposite to that in system I, as shown in Figure 2. This means that KCl diffusion, and water transport due to osmotic pressure induced by KCl concentration difference across polymer gel mosaic membrane, take place concurrently. As the transport rate of the sucrose molecule across the membrane is very slow,¹ the positive values of water transport, which induced by sucrose concentration are larger than that dragged by KCl diffusion. Hence it would be reasonable that the volume flux in system I appeared as positive flow. This indicates that the sucrose molecules are inhibited by the entangled polymer chains of the mosaic membrane to permeate through the mosaic membrane. The difference between systems I and II is that whether the system contains sucrose or not.

Filtration coefficient L_p

Based on the presence of sucrose, polymer chains in the membrane inhibit the sucrose molecules, the sucrose molecule can't easily permeate through the membrane because the molecule is larger than glucose.¹ This leads to produce osmotic pressure difference in the water/sucrose in system I. The volume change caused by the osmotic pressure, when 0.5 mol.dm⁻³ sucrose is inserted into one side of the cell, is given as a function of time. The relation turned out to be linear within the range of examined time. Accordingly, the volume flux, J_v , and solute flux, J_s , were deduced from the slope of the linear

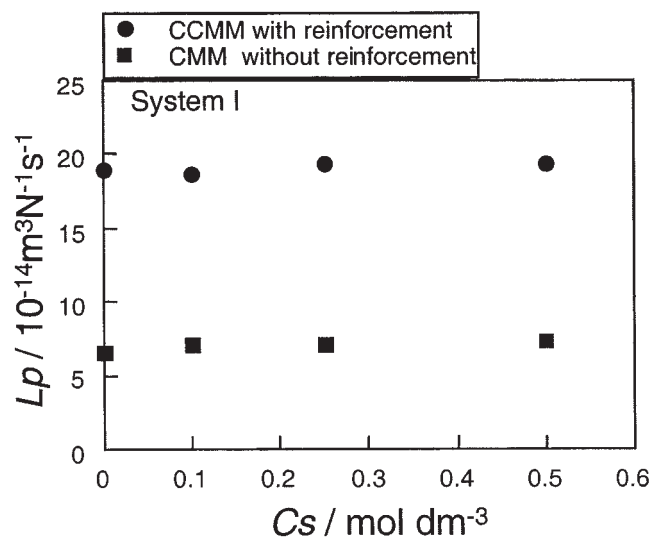


Figure 4

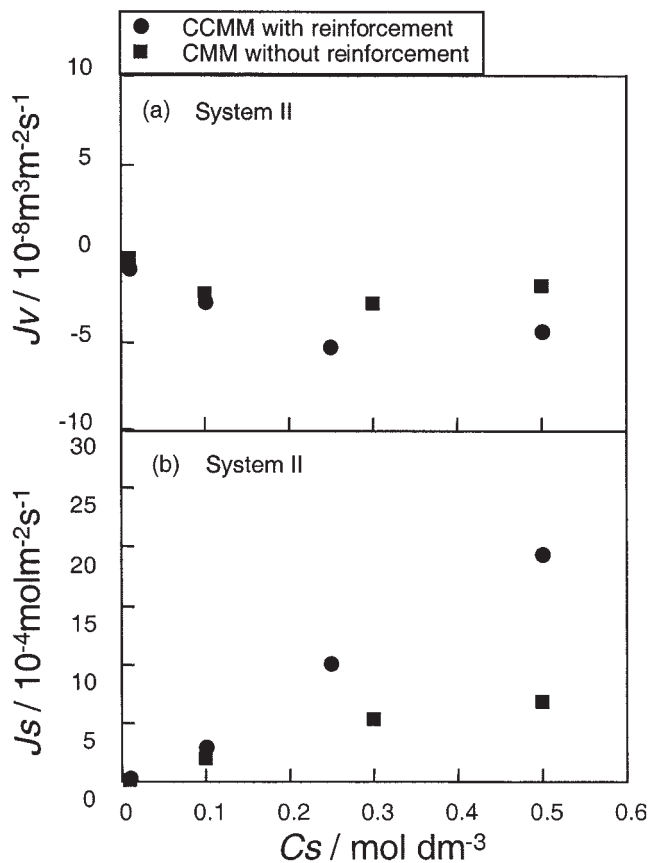


Figure 5

relation by taking into account the effective membrane area. Inserting the volume flux into eq. (1), one can obtain the filtration coefficient, L_p . L_p represents water transport index (water permeability) across membrane. The changes of the values of L_p of CCMM with reinforcement together with the values of CMM without reinforcement, in the presence of different KCl concentrations, were shown in Figure 4. Figure 4 indicated that the L_p of membrane was not affected by the existence of electrolytes in the outer solutions. In general, the values were almost independent on KCl concentrations in the range 0–0.5 mol dm⁻³. This means that the presence of KCl had no effect on water permeability through the membrane. In comparative study with CMM without reinforcement, L_p values of CCMM with reinforcement became larger than that of CMM without reinforcement. It is known that the transport properties are inversely proportional to the membrane thickness. Even though the thickness of the membrane used in our study was constant (50 μm), different transport properties of charged mosaic membrane, with and without reinforcement, were observed. Explanation of this result will be discussed together with the solute permeability part (see Fig. 6)

Reflection coefficient σ and salt permeability coefficient ω

In Figures 5 (a–b), solvent fluxes J_v and solute flux J_s of CMM with and without reinforcement were plotted as function of KCl concentration in system II. The values of J_v and J_s are obtained from volume changes in time and salt concentration in time, respectively. One can note that the values of J_v show negative sign for the transport direction from pure water to solution, while J_s values show positive sign for the transport direction from solution to water. It can be mentioned that the J_v and J_s values of CMM with and without reinforcement showed an observable difference, especially near 0.3 mol dm⁻³, of KCl. One can estimate from Figure 5, the reflection coefficient, σ , and salt permeability, ω , from the solvent and solute fluxes in system II, respectively. The resulting σ and ω were replotted as shown in Figures 6(a–b), respectively. Figure 6 (a) showed that the σ values of CCMM with reinforcement and CMM without reinforcement were almost the same. Also Figure 6(a) indicated that the values of σ in the examined concentration ranges were negative. Negative σ values means that the preferential salt transport was enhanced over the solvent transport, which is very important for practical pressure dialysis process. The

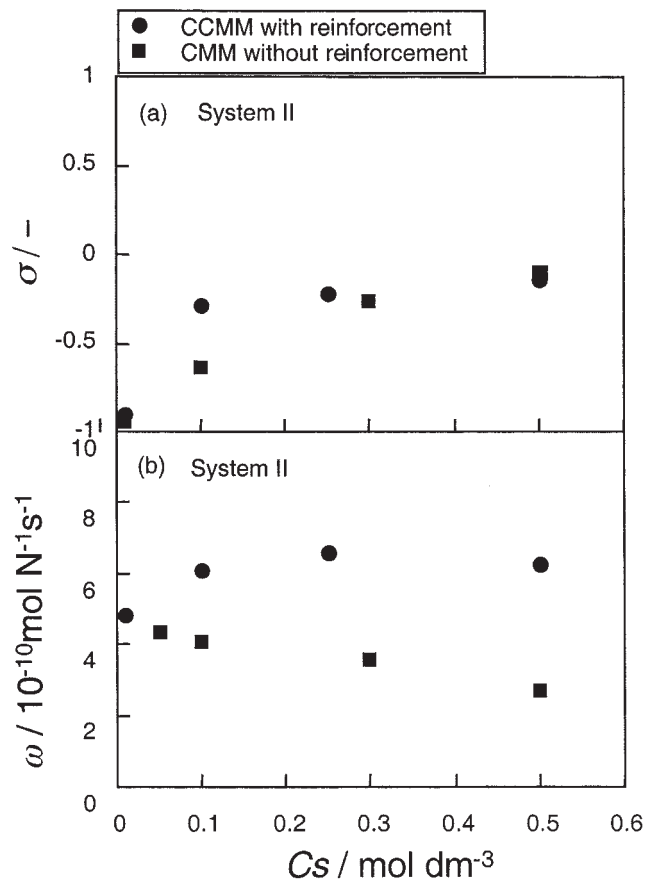


Figure 6

negative σ values were attributed to the enhancement of the salt flux across the mosaic membrane. The salt flux across the polymer mosaic membrane was explained in terms of the presence of cationic and anionic polymer exchange-active sites inside the mosaic membrane. From viewpoint of separation between solute and solvent, the increase of KCl flux means that the separation index σ becomes less than unity. On the other hand, ω values were given as a function of KCl concentrations in Figure 6(b). Figure 6(b) showed remarkable difference of ω values between two CMMs with and without reinforcement. This means that the CCMM with reinforcement was more permeable than CMM without reinforcement, for water transport and KCl transport as seen in Figures 5 and 6 (b). The L_p values in Figure 5 and ω values in Figure 6 (b) suggest that they may be possibly related to the active layer of composite polymer-gel in the membrane. In the other words, solvent and solute transports depend strongly on the active layer thickness of polymer composite membrane, while the relative ratio of solute velocity to solvent velocity, σ , did not depend on the membrane thickness. This gives us the necessity to consider the active layer thickness of the polymer mosaic membrane in this study. From the fact mentioned above, the equations used for evaluation of L_p , σ , and ω did not include a term of active layer thickness δ .

According to Kedem and Katchalsky¹⁵⁻¹⁶, membrane parameters, L_p , σ and ω under appropriate experimental conditions were given as follows,

$$L_p = - \left(\frac{J_v}{\Delta\Pi} \right)_{\Delta P=0, \sigma=1} \quad (1)$$

$$\sigma = - \frac{1}{L_p} \left(\frac{J_v}{\Delta\Pi} \right)_{\Delta P=0} \quad (2)$$

$$\omega = \left(\frac{J_s}{\Delta\Pi} \right)_{J_v=0, \Delta P=0} \quad (3)$$

The membrane parameters in Figure 4 and Figure 6 were estimated using eqs. (1)–(3). As described above, the equation having a term of active layer thickness is necessary to explain the discrepancy between CMM and CCMM¹⁷. The equations, which predict the membrane thickness, are given as eqs. (6) and (7) as follows

$$J_v = \frac{L_p'}{\delta} (\Delta P - \sigma \Delta \Pi) \quad (4)$$

$$J_s = C_s^a (1 - \sigma) J_v + \frac{\omega'}{\delta} \Delta \Pi \quad (5)$$

Comparing eqs. (1)–(3) with eqs. (4)–(5), one can obtain the relation between present and previous L_p or ω , as follows,

TABLE I
The L_p and Active Layer Thickness

	L_p ($10^{-14} \text{ m}^3 \text{ N}^{-1} \text{ s}^{-1}$)	Thickness ($\delta/\mu\text{m}$)
CMM without reinforcement	7.07	50
CCMM with reinforcement	19.1	18.5

$$L_p' = L_p \cdot \delta \quad (6)$$

$$\omega' = \omega \cdot \delta \quad (7)$$

Equations (6) and (7) indicate that the transported quantities of L_p and ω , across the membrane are inversely proportional to the membrane thickness. By considering the membrane thickness (50 μm) as reference, and by using eq. (6), the thickness of the active layer of CCMM was estimated as 18.5 μm , (see Table I). The higher values of L_p and ω of CCMM with reinforcement compared with the CMM without reinforcement are possibly explained based on the fact that the thickness of the active layer of membrane is 18.5 μm . As the membrane gets thinner, the functional groups of anionic and cationic polymers are segregated to the upward direction at the surface¹⁸. This may increase the efficiency of the functional groups at the surface to form active sites that lead to increase in transport properties, L_p and ω of CCMM. On the other hand, at a larger membrane thickness (50 μm), the functional groups of used polymers are migrated into the bulk of membrane because of the entanglement effect¹⁹, which led to a decrease in the number of active sites at the surface. Accordingly, the transport properties, L_p and ω , of CMM are decreased. In contrast, σ did not show remarkable dependence on active layer thickness in this study.

Reproduction of J_v and J_s

To verify the effect of the active layer thickness of CCMM on the transport properties, J_v and J_s of the composite membrane were reproduced from the previous results, using an active layer thickness of 18.5 μm . (Figs.7(a–b)). As seen in Figures 7(a–b), the predicted solid lines were satisfactorily fitted with the experimental results of CCMM. Regarding the minimum observed around 0.3 $\text{mol} \cdot \text{dm}^{-3}$ in Figure 7(a), it is presumed that salt diffusion and osmotic flow may be competitive in that condition. In other words, at relative dilute salt concentration range, the diffusion force dominates over osmotic force. However at higher salt concentration range, the osmotic flow dominates the total flow. As a result, the CCMM exhibited an excellent transport performance.

Membrane potential

To investigate the effect of the active layer concept on the membrane potentials, the membrane potentials for different electrolytes were measured. Figure 8 shows the results of membrane potentials of CCMM with reinforcement and CMM without reinforcement. A little difference between the potentials of membranes with and without reinforcement was observed. Moreover the transport numbers of cation, t_+ were estimated by Nernst equations and the values are summarized in Table II. t_+ gives the index of ionic mobility of cation inside the membrane or in the solution. The t_+ values did not show remarkable difference between CCMM with reinforcement and CMM without reinforcement. This means that the membrane potential did not depend on the membrane thickness and composition of porous support film. It can be mentioned that the t_+ in the mosaic membrane behaves like that in KCl electrolyte solution. It gives the evidence that the salt transport through the membrane was almost the same as the behavior in the solution. So, both ions (K^+ and Cl^-) move easily within membrane material because of presence of active sites of cationic and anionic polymer in the membrane. One can conclude

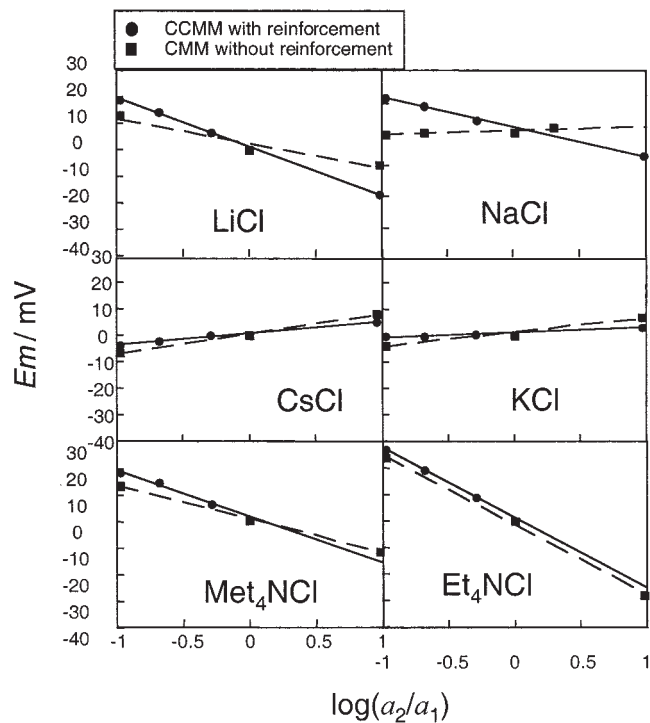


Figure 8

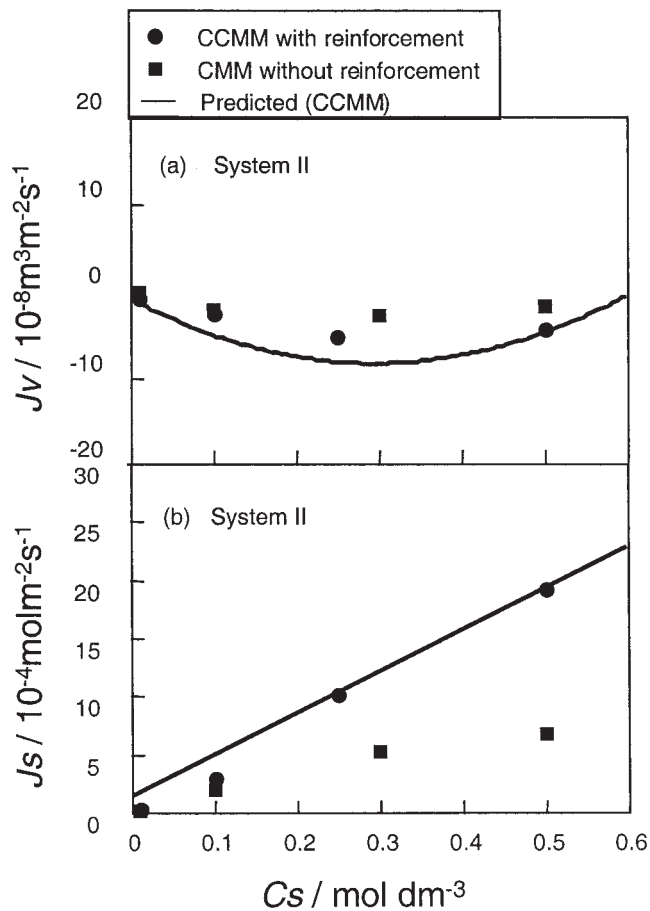


Figure 7

that the mobility of ions in the membranes CCMM and CMM behaves approximately in the same trend.

CONCLUSIONS

The active layer thickness of the polymer gel in the CCMM was estimated from the thickness of the membrane without support. The L_p values in CCMM membranes with reinforcement were larger than that L_p values in CMM membrane without reinforcement. The L_p and ω values suggest that the physical quantities be possibly related to the active layer of composite polymer-gel in the membrane. In other words, L_p and ω depend strongly on the active layer thickness of polymer composite membrane, while the relative ratio of solute velocity to solvent velocity, σ , did not depend on the membrane thickness. This makes us to consider the active layer thickness of the polymer mosaic membrane as shown in the modified eqs. (6) and (7). The negative σ values were attributed to the enhancement of the salt flux across the membrane. This salt flux across the polymer-gel mosaic membrane was explained in terms of the presence of cationic and anionic polymer exchange sites inside the mosaic membrane. From viewpoint of separation between solute and solvent, the increase of KCl flux means that value of separation index σ becomes less than unity. In contrast, there was no remarkable difference between the reflection coefficient σ and the membrane potential E_m values of CCMM and CMM.

TABLE II
Cationic Transport Number t_+

	t_+ ^a						
	LiCl	NaCl	KCl	CsCl	Met ₄ NCl	Et ₄ NCl	
CMM	0.49	0.45	0.55	0.56	0.39	0.28	
CCMM	0.35	0.42	0.52	0.54	0.36	0.28	
In solution ^b	0.32	0.39	0.49	–	–	–	

^a t_+ was calculated from membrane potential results.

^b The values were calculated for molar conductivities at 25°C.²⁰

Assumption that the difference between the performance of the membrane with and without reinforcement depends only on the thickness of active layer turned to be reasonable. Also, the CCMM is reinforced without losses of the original properties of CMM. A CCMM might be potentially used for pressure dialysis.

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