PII: S0032-3861(97)10107-0

Polymer Vol. 39 No. 18, pp. 4199–4204, 1998

0032-3861/98/$19.00+0.00

Effect of polymer composition in intermediate layer on water splitting in bipolar membranes

Tadashi Hosono and Akihiko Tanioka*
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama Meguro-ku, Tokyo 152, Japan
(Received 21 May 1997; revised 21 August 1997; accepted 8 September 1997)

The relationship between the water splitting effects and the chemical composition of the intermediate layer has been studied. Firstly, the membrane resistance decreases if a quaternary ammonium group or a carboxyl group is inserted in the intermediate layer instead of a secondary or tertiary amino group, which implies that the water dissociation occurs not only due to the catalytic effect of the secondary or tertiary amino group but also to the electrical field. Secondly, it is proved that the current efficiency is determined by the ion exchange capacity in the anion and cation exchange layers, but not by the chemical structure of intermediate layer. Thirdly, it is also evidenced that the membrane which has a thick intermediate layer showed a high conductivity before the critical point of thickness of the intermediate layer, which means an increase in the reactive region of the water. In this study, we could not find evidence that the chemical reaction model is superior. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: bipolar membrane; water splitting; intermediate layer; chemical reaction model; second Wien effect)

INTRODUCTION

A bipolar membrane is composed of one cation-selective layer joined to one anion-selective layer in series. It is well known that rectification is observed in current and voltage properties and water splitting occurs at the boundary between the anion and cation layers[1–7]. The water splitting mechanism has been discussed for a long time. Mafé and coworkers at first explained the water splitting using the Donnan effect and the Nernst–Planck equation; water molecules dissociate into cations (H^+) and anions (OH^-) in accordance with the second Wien effect[8–11]. The efficiency of the water splitting is explained as a function of the dielectric constant in the boundary surface. On the other hand, Simons and coworkers suggested that the water splitting was caused by the chemical reaction of secondary or tertiary amino groups with water molecules[12–14].

In a previous paper, it was proved that the water splitting occurred between the sulfonic acid group layer and the quaternary ammonium group layer without the existence of secondary or ternary amino groups[15,16]. This result seems to show that the second Wien effect model is more reasonable than the chemical reaction model. However, we still cannot abandon the idea of the latter case because there is a possibility that the quaternary ammonium group on the membrane intermediate surface is temporarily decomposed into a tertiary amino group during the application of voltage[17]. Recently, Mafé and co-workers also suggested that the chemical reaction model is preferable over the second Wien effect model, because there was no evidence to support the second Wien effect model from their experiments[18,19].

In this study, three types of bipolar membranes which had different amino groups in the anion exchange layer, different polyelectrolytes in the intermediate layer, and different intermediate thickness of poly(styrene) were prepared in order to confirm the reasonable water-splitting mechanism in the membrane. Based on the current efficiency, current–voltage characteristics and membrane resistance of those bipolar membranes cited above, the water-splitting mechanism was examined.

EXPERIMENTAL

Samples

Three types of membranes which had different amino groups in the anion exchange layer, different polyelectrolytes in the intermediate layer, and different intermediate thickness of poly(styrene) were prepared.

Case I: different amino group type. Five kinds of bipolar membranes which had different chemical compositions of amino groups were prepared. For the preparation of the anion exchange layer, a dimethylformamide (DMF) solution of poly(styrene) and poly(chloromethylstyrene) (Asahi Chemicals), to which *N,N*-dimethyl-1,3-diaminopropane and *N,N,N′,N′*-tetramethyl-1,3-diaminopropane were added in order to introduce positively charged groups of secondary and quaternary amines, was stirred for 1 min and cast on a glass plate surrounded by a rectangular frame (13 × 10 cm) of about 1 mm thickness to dry at 105°C for 4 min in air after standing for 4 min at room temperature. The mixing ratio of *N,N*-dimethyl-1,3-diaminopropane to *N,N,N′,N′*-tetramethyl-1,3-diaminopropane was varied from 100 to 0, as shown in *Table 1*, with the ratio of the quaternary ammonium group in the membrane (called M-50, M-63, M-75, M-88, M-100). The number in the sample names shows the existing ratio (by %) of quaternary amine in the membranes. Subsequently, a DMF solution of sulfonated poly(butadiene-co-styrene) rubber (Asahi Chemicals) was cast quickly on the top surface of an anion exchange layer surrounded by the rectangular frame to dry at 105°C for

---

* To whom correspondence should be addressed: E-mail: atanioka@o.cc.titech.ac.jp

Table 1 Ratio of each diamine in the DMF solutions of diamines, and ratio of quaternary ammonium group in anion-selective layer of bipolar membrane

Sample	N,N-Dimethyl-1,3-propanediamine	N,N,N′,N′-Tetramethyl-1,3-propanediamine	Ratio of quaternary ammonium group in membrane
M-50	100	0	50.0
M-63	75	25	62.5
M-75	50	50	75.0
M-88	25	75	87.5
M-100	0	100	100.0

Table 2 Polymer of intermediate layer, concentration of solution in intermediate layer (*C*), degree of hydration and thickness of samples

Sample	Polymer of intermediate layer	*C* (M)	Degree of hydration (%)	Thickness (μm)
01AA	Poly(acrylic acid)	0.1	35.8	120
01PAS	PAS	0.1	36.2	122
1AA	Poly(acrylic acid)	1.0	32.5	124
1PAS	PAS	1.0	36.3	119

C represents concentration of polymer repeating unit in solution for intermediate layer

10 min in air for the preparation of the cation exchange layer. The glass plate was cooled to room temperature and soaked in 0.1 mol dm^{-3} aqueous solution of potassium chloride to peel off the membrane. Thus the bipolar membrane was obtained. The swelling by water is prevented by polymer crosslinking. The charged groups are assumed to be distributed homogeneously, and the intermediate region between the anion and cation exchange layers is very clear without a thin water layer. The membrane charge densities of the cation exchange layer and the anion exchange layer (in the case of M-100) were *ca.* 0.65 mol dm^{-3} and *ca.* 0.92 mol dm^{-3}, respectively, which were determined from membrane potential measurements.

Case II: different polyelectrolyte type. First, for the preparation of the anion exchange layer, a dimethylformamide (DMF) solution of poly(styrene) and poly (chloromethylstyrene) (Asahi Chemicals), to which *N,N,N′,N′*-tetramethyl-1,3-diaminopropane was added in order to introduce positively charged groups of quaternary amine, was stirred for 1 min and cast on a glass plate surrounded by a rectangular frame (13 × 10 cm) of about 1 mm thickness to dry at 105°C for 4 min in air after standing for 4 min at room temperature. Secondly, an aqueous solution of poly (diallyl dimethyl ammonium chloride) (PAS-H) composed of quaternary ammonium groups or an aqueous solution of poly(acrylic acid) (PAA) composed of carboxyl groups, whose concentrations defined by the polymer repeating unit were 0.1 and 1.0 mol dm^{-3}, was cast on the anion exchange layer to dry at 105°C for 2 min in air. Finally, DMF solution of sulfonated poly(butadiene-co-styrene) rubber (Asahi Chemicals) was cast quickly on the intermediate layer to dry at 105°C for 10 min in air for the preparation of the cation exchange layer. The glass plate was cooled to room temperature and soaked in a 0.1 mol dm^{-3} aqueous solution of potassium chloride to peel off the membrane. Thus the bipolar membrane was obtained. The characteristics of these samples are listed in *Table 2* (01AA, 01PAS, 1AA and 1PAS, where 01 means 0.1 mol dm^{-3} and 1 means 1.0 mol dm^{-3}, and PAS indicates PAS-H, AA the acrylic acid).

Case III: different intermediate thickness type. First, for the preparation of the anion exchange layer, a dimethylformamide (DMF) solution of poly(styrene) and poly(chloromethylstyrene) (Asahi Chemicals), in which *N,N,N′,N′*-tetramethyl-1,3-diaminopropane was added in order to introduce positively charged groups of quaternary amine, was stirred for 1 min and cast on a glass plate surrounded by a rectangular frame (13 × 10 cm) of about 1 mm thickness to dry at 105°C for 4 min in air after standing for 4 min at room temperature. Secondly, a DMF solution of poly(styrene) (PS), whose concentrations defined by the polymer repeating unit were 0.2, 0.4, 0.6, 0.8 and 1.0 mol dm^{-3}, was cast on the anion exchange layer to dry at 105°C for 2 min in air. Finally, a DMF solution of sulfonated poly(butadiene-co-styrene) rubber (Asahi Chemicals) was cast quickly on the intermediate layer to dry at 105°C for 10 min in air for the preparation of the cation exchange layer. The glass plate was cooled to room temperature and soaked in 0.1 mol dm^{-3} aqueous solution of potassium chloride to peel off the membrane. Thus the bipolar membrane was obtained. The characteristics of these samples are listed in *Table 3* (called 02PS, 04PS, 06PS, 08PS, 10PS).

Current–voltage and current efficiency measurements

Measurements of the voltage via a salt bridge under a constant applied current were carried out using a laboratory-scale electro-dialytic cell composed of two compartments, as shown in *Figure 1*[15,16,20]. The two compartments were separated by a bipolar membrane having an effective area $A_m = 8$ cm^2, and a Pt electrode (anode) and a Ni electrode (cathode) were installed at the anion exchange layer and at the cation exchange layer, respectively. The distance between the anode and cathode was 8 cm and the volume of each compartment was 300 ml. In the anode side cell 1 mol dm^{-3} of NaOH, and in the cathode side cell 1 mol dm^{-3} of HCl were added in order to eliminate the ion concentration change due to the electrochemical reaction at the electrodes and the water dissociation. A constant current was applied for 60 min. by a direct current source (Kikusui PAB 18-1A), and the voltage was measured by a glass electrode (TOA HS-205C) via a KCl salt bridge.

Table 3 Concentration of poly(styrene) (PS) in DMF solution (*C*), width of intermediate layer, degree of hydration and thickness

Sample	Concentration of PS solution (M)	Thickness of intermediate layer (μm)	Degree of hydration (%)	Thickness of bipolar membrane (μm)
02PS	0.2	1.52	37.5	116
04PS	0.4	1.03	31.2	123
06PS	0.6	1.34	35.3	126
08PS	0.8	1.50	35.9	117
10PS	1.0	1.49	38.0	123

C represents concentration of polymer repeating unit in solution for intermediate layer

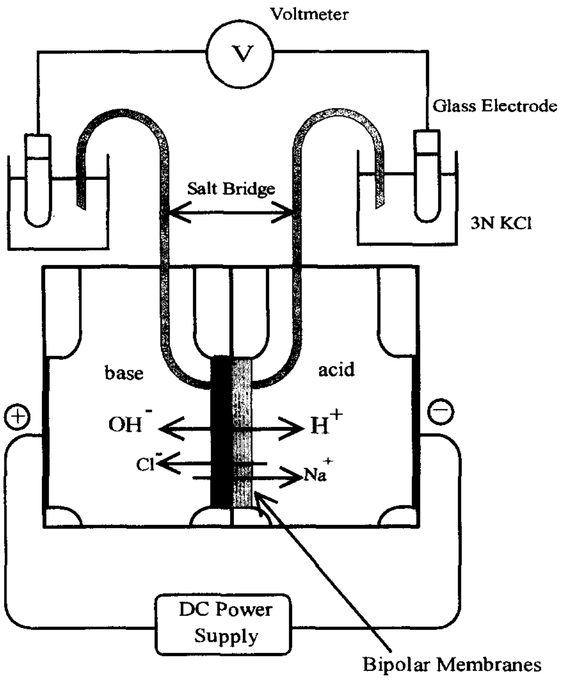


Figure 1 Electrodialysis cell used for voltage–current measurements and current efficiency measurements: anion and cation exchange layers face the anode and cathode, respectively

The current efficiency (CE) was determined by the following equation [21].

$$CE = 1 - \frac{\text{transported electrical charge by Na}^{+} + \text{transported electrical charge by Cl}^{-}}{\text{transported total electrical charge}} \quad (1)$$

where the total electrical charge is mediated by Na^+, Cl^-, H^+ and OH^-. In order to determine CE, the concentrations of Na^+ in the cathode side cell and Cl^- in the anode side cell were measured using a Na ion electrode (TOA Na-125B) and a Cl ion electrode (TOA Cl-125B), respectively. Prior to the measurements, the calibration curves between the potential difference and the concentration were already determined.

RESULTS AND DISCUSSION

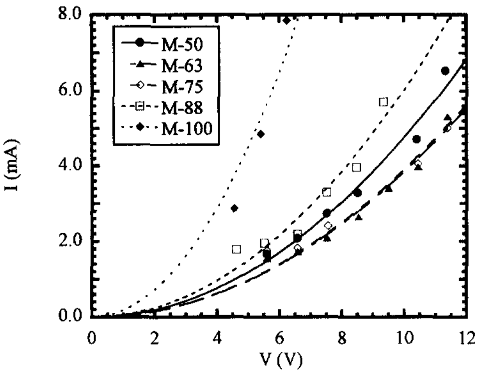


Figure 2 Current–voltage characteristics of Case I type membranes. M-50, M-63, M-75, M-88, M-100 indicate 50, 63, 75, 88 and 100% for the existing ratio of the quaternary amine in the membranes

In *Figure 2*, the current–voltage curves of Case I type membranes are shown. If rectification occurs, the current cannot be found under the applied voltage. However, the current increases with an increase in voltage, which proves the water splitting in the membrane. The magnitude of the current is the order of M-100 > M-8 > M-50 > M-75~M-63 at the same voltage. The M-100 membrane is composed of quaternary ammonium groups and has no secondary or tertiary amino groups. The anion-exchange layer of the other bipolar membranes, except M-100, include the secondary amino groups. The ion exchange capacity of the polyelectrolyte composed of quatenary amino groups is larger than that with secondary or tertiary amino groups. On the other hand, secondary and tertiary amino groups improve the water dissociation ability of the membrane. It is thought that a large amount of water is dissociated into H^+ and OH^- in the anion exchange layer composed of secondary amino groups but the secondary amino groups prefer to release H^+ in the discharged state under the applied voltage, which reduces the effective charge density in the membrane to decrease the water splitting ability. This is the reason why the current magnitudes of M50, M63, M75 and M88 are much smaller than that of M100. In *Figure 3*, the membrane resistances are shown as a function of the percentage of quaternary ammonium groups at a constant current of 5 mA. They decrease with the increase in the quaternary ammonium group percentage, which also implies that a high water splitting effect is observed for the membrane with a large amount of quaternary ammonium groups.

Considering the results cited above, it is proved that the anion exchange layer should be composed of quaternary

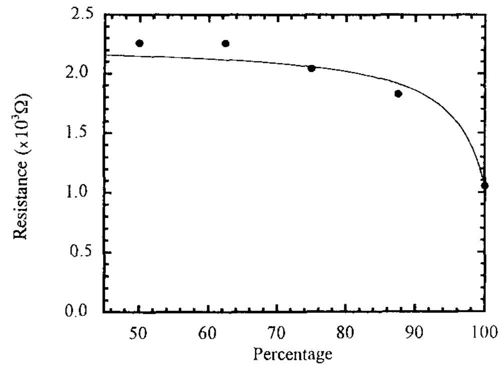


Figure 3 Resistance of the bipolar membrane at a constant current of 5 mA as a function of the percentage of quaternary ammonium groups

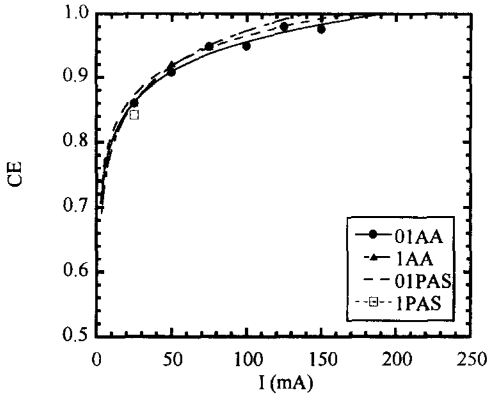


Figure 5 Current efficiency curves of the Case II type membranes as a function of the applied current

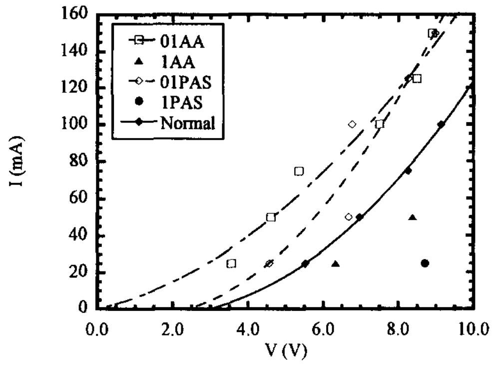
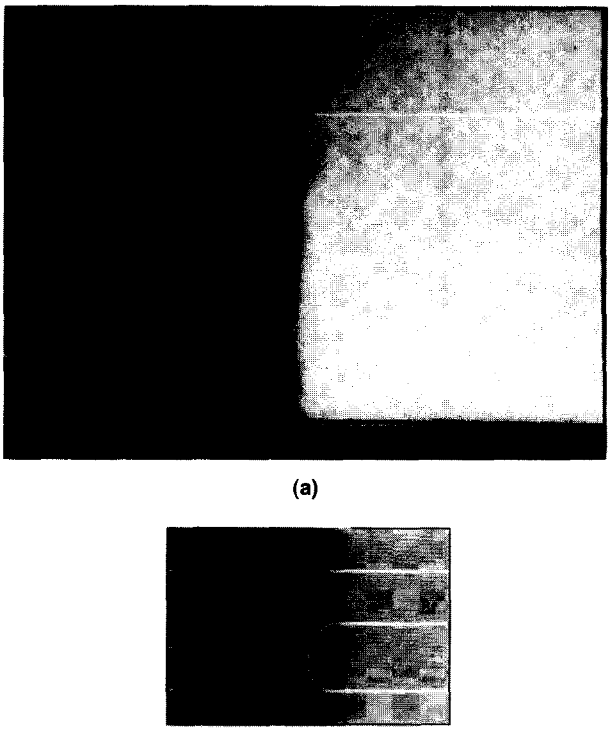


Figure 4 Current–voltage characteristics of Case II type membranes where the compounds of the intermediate layers are different. 01AA represents the 0.1 mol dm^{-3} of poly(acrylic acid), 1AA 1 mol dm^{-3} of poly(acrylic acid), 01PAS 0.1 mol dm^{-3} of PAS-H, 1PAS 1 mol dm^{-3} of PAS-H and normal, no compound (which corresponds to M-100 in Case I) in the intermediate layer



(a)

(b)

Figure 6 (*a*) EDAX photograph of a cross-section of a bipolar membrane composed of quaternary ammonium and sulfonic acid groups. The right side is the positive charge layer and the other is the negative one. (*b*) Schematic diagram of (*a*). The Br$^-$ line profile ascends from left to right, on the other hand, the K$^+$ line profile descends

ammonium groups. It has been pointed out that the intermediate layer plays an important role in the water dissociation. If the intermediate layer is composed of secondary or tertiary amino groups, but the anion exchange layer is composed of quaternary ammonium group, the water-splitting effect is accelerated. Therefore, it is very important to discuss the role of the intermediate region. In *Figure 4* the current voltage characteristics of Case II bipolar membranes are shown. In this figure, normal means the M-100 membrane in *Table 1*. The currents of 1AA and 1PAS are smaller than that of the normal sample at the constant voltage, which shows the increase in membrane resistance. These samples could not form the very thin intermediate layer between the cation and anion exchange layers because of the high concentration of the polymers which increase the membrane resistance. On the other hand, the currents of 01AA and 01PAS are larger than that of the normal sample at the constant voltage, which shows a decrease in membrane resistance. PAS is composed of quaternary ammonium groups and AA carboxyl groups. It is very hard to consider that these charged groups play a catalytic role in water dissociation in the membrane intermediate layer. Therefore, the very thin intermediate layer of PAS or AA plays an important role in producing a high electrical field for water dissociation. In *Figure 5*, the current efficiency (CE) is shown as a function of applied current for the samples of 01AA, 1AA, 01PAS and 1PAS. We could not find a significant difference among the samples. The cation and anion exchange layers of these membranes have the same structures, chemical compositions and thicknesses. The ionic selective permeabilities of the cation exchange layers and the anion exchange layers are the same for those membranes. It is suggested that the most important effect determining the current efficiency in water splitting by the bipolar membrane is the selective ionic permeability in the anion and cation exchange layers.

It is impossible to remove the intermediate layer from the bipolar membrane in order to investigate the water-splitting effect. The intermediate layer has not been studied experimentally. Mafé *et al.*[11] defined that the intermediate layer is produced only if voltage is applied. Therefore, they considered that the fixed charge density is altered as a step function from negative to positive at the intermediate layer.

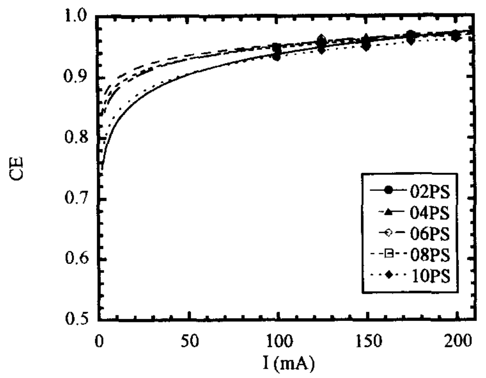


Figure 7 Current efficiency curves of the Case III type membranes as a function of the applied current. 02PS, 04PS, 06PS, 08PS and 10PS indicate the concentrations of poly(styrene) corresponding to 0.23, 0.4, 0.6, 0.8 and 1.0 mol dm^{-3} of the segment units, respectively

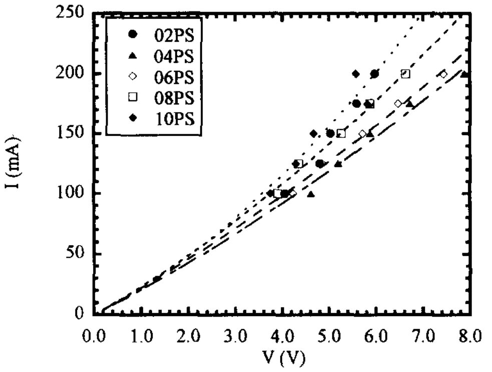


Figure 8 Current–voltage characteristics of Case III type membranes where the thickness of the intermediate layer is changed by controlling the concentration of poly(styrene)

In *Figure 6a*, the photograph of the energy-dispersion X-ray spectrometry (EDAX) of a cross-section of the normal bipolar membrane is shown after the counter ions of each layer are exchanged with 2 M KBr for 24 h. The vibrating white lines show the concentration profiles of K^+ and Br^-. The right white phase is the positively charged layer and the upper white line indicates the concentration profile of Br^-; the left black phase is the negatively charged layer and the upper white line indicates that of K^+. *Figure 6b* shows a schematic diagram of *Figure 6a*. The Br^- line profile ascends from left to right, but on the other hand, the K^+ line profile descends. The curved region is considered as an intermediate layer and the thickness can be determined to be about 1.5 μm. *Figure 6* shows that the fixed charge changes from negative to positive or positive to negative gradually and the thickness is the order of μm. In this experiment, the thickness of the intermediate layer was changed by inserting various very thin poly(styrene) layers in the intermediate layer in the Case III membranes (called as 02PS, 04PS, 06PS, 08PS and 10PS). In *Table 3*, the width of each sample, which was determined by EDAX, is also listed. We could change the thickness from 1.03 to 1.52 μm. In *Figure 7*, the current efficiency of the CASE III membranes is shown as a function of the current. We could not find a difference among them above 120 mA, which implied that we used the same anion and cation exchange layers for each sample. In *Figure 8*, the current–voltage characteristics of those bipolar membranes are shown. The current magnitude at a constant voltage above 5.0 V is nearly the order of 02PS > 10PS > 08PS > 06PS > 04PS, which corresponds with the order of intermediate thickness as shown in *Table 3*. The more the thickness is increased, the larger the current is at constant voltage. In *Figure 9* membrane resistances are plotted as a function of the width of the intermediate layer at constant currents of 100, 150 and 200 mA. This figure also shows that an increase in the intermediate thickness decreases the resistance. Usually, a thin intermediate layer is considered to show a low resistance[21,22]. However, these results are the opposite of the previous results. The increase in the intermediate layer is considered to enlarge the reactive layer for the water dissociation. Therefore, in this region, many dissociated ions exist to reduce the resistance.

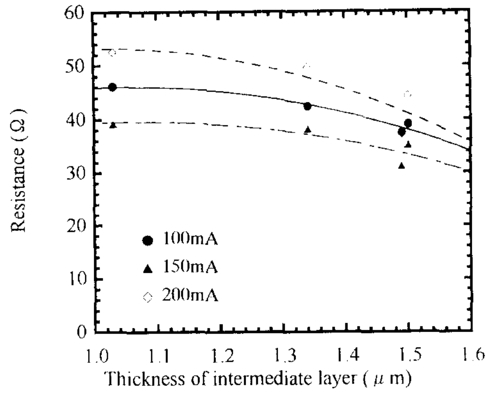


Figure 9 Resistance of Case III type membranes as a function of the thickness of the intermediate layer

ACKNOWLEDGEMENTS

We are most grateful to Mr. Hamada and Mr. Yamamura of Asahi Chemicals Co., Ltd., for providing us with the samples and for helpful suggestions.

REFERENCES

1. Bassignana, I. C. and Reiss, H., *J. Membrane Sci.*, 1983, **15**, 27.
2. Mauro, A., *Biophys. J.*, 1962, **2**, 179.
3. Coster, H. G. L., *Biophys. J.*, 1965, **5**, 669.
4. Aritomi, T., van den Boomgaard, Th. and Strathmann, H., *Desalination*, 1999, **104**, 13.
5. Nagasubramanian, K., Chlanda, F. P. and Liu, K.-J., *J. Membrane Sci.*, 1977, **2**, 109.
6. Thompson, R., Paleologou, M. and Berry, R. M., *Tappi J.*, 1995, **78**, 127.
7. Chlicott, T. C., Coster, H. G. L. and George, E. P., *J. Membrane Sci.*, 1995, **100**, 77.
8. Wien, M. and Schile, J., *Phys. Z.*, 1931, **32**, 545.
9. Onsager, L., *J. Chem. Phys.*, 1934, **2**, 599.
10. Ramirez, P., Manzanares, J. A. and Mafé, S., *Ber. Bunsenges. Phys. Chem.*, 1991, **95**, 499.
11. Mafé, S., Manzanares, J. A. and Ramirez, P., *Phys. Rev. A*, 1990, **42**, 6245.
12. Simons, R., *Desalination*, 1979, **28**, 41.
13. Simons, R., *Nature (London)*, 1979, **280**, 824.
14. Simons, R. and Khanarian, G., *J. Membrane Biol.*, 1978, **38**, 11.
15. Tanioka, A., Shimizu, K., Miyasaka, K., Zimmer, H. J. and Minoura, N., *Polymer*, 1996, **37**, 1883.
16. Shimizu, K., Tanioka, A., *Polymer*, 1997, **38**, 5441.
17. Tanioka, T., Mafé, S. and Ramirez, P., *Bulletin Soc. Sea Water Sci., Jpn.*, 1997, **51**, 66.
18. Ramirez, P., Rapp, H. J., Reichle, S., Strathmann, H. and Mafé, S., *J. Appl. Phys.*, 1992, **72**, 259.
19. Ramirez, P., Rapp, H.-J., Mafé, S. and Bauer, B., *J. Electroanalytical Chem.*, 1994, **375**, 101.

20. Yokoyama, M., Tanioka, A. and Miyasaka, K., *J. Membrane Sci.*, 1989, **43**, 165.
21. Moussaoui, R. El., Pourcelly, G., Maeck, M., Hurwitz, H. D. and Gavach, C., *J. Membrane Sci.*, 1994, **90**, 283.
22. Strathmann, H., Rapp, H. -J., Bauer, B. and Bell, C. M., *Desalination*, 1993, **90**, 303.