

# Selective permeability of grafted nylon-6 membranes: 2. Potassium chloride permeation in acrylic acid grafted membranes

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The permeation of potassium chloride through  $\gamma$ -irradiated nylon-6 membranes grafted with acrylic acid (AA) was investigated. The permeability of potassium chloride increases with increasing levels of grafting in the membrane. It was found that the theory of permeation of electrolyte through ionic membranes (derived from the phenomenological equation) was applicable to the permeation of potassium chloride through AA-grafted membranes with high levels of grafting. The effective concentration of fixed charge determined by the Donnan membrane equilibrium exhibited almost the same value in the grafted membrane regardless of the levels of grafting. It was found that a tortuosity factor was dominant through affecting the permeation of KCl through the membrane. This may be considered as an interference factor in a homogeneous membrane.

(Keywords: ionic membrane; permeability coefficient; tortuosity factor; effective concentration of fixed charge; Donnan membrane equilibrium)

## INTRODUCTION

In part 1 of this series of papers<sup>1</sup>, the diffusive permeability of urea and potassium chloride through nylon-6 membranes grafted with acrylamide (AM) and acrylic acid (AA) was investigated. It was found that the free volume concept of diffusion<sup>2-5</sup> (in homogeneously water-swollen membranes) could explain the permeation of solutes through both of these types of membranes (AM and AA) when the grafting was >100%. However, the diffusion coefficient of potassium chloride through AA-grafted membranes showed remarkable dependence on concentration of solute.

In this paper, the dependence of the permeability coefficient of potassium chloride on concentration of salt solution is studied in detail. The results are discussed using the theoretical equation derived from the phenomenological equation<sup>7</sup>, and the dominant factors affecting the permeation of potassium chloride through AA-grafted nylon-6 membrane are considered. Furthermore, a comparison with results of the Donnan membrane equilibrium method is also made, so as to clarify features of the permeation of potassium chloride.

## EXPERIMENTAL

### Materials

Nylon-6 film ( $1.5 \times 10^{-3}$  cm in thickness) produced by Unitika Co. Ltd. was used. The degree of crystallinity of the biaxially stretched film determined by X-ray diffraction<sup>8</sup> was 45.7%. The sample was washed with 0.1% nonionic surfactant aqueous solution, and the acrylic acid

(AA) was distilled under reduced pressure before use. The potassium chloride and other chemicals were of analytical grade, and used without further purification.

### Graft copolymerization

The nylon-6 film (ca. 0.5 g) was dried under reduced pressure at 50°C for 20 h, and irradiated under a nitrogen atmosphere by <sup>60</sup>Co  $\gamma$ -rays with an exposure rate of  $1.0 \times 10^6$  R h<sup>-1</sup> for 1 h at room temperature. Graft copolymerization onto the irradiated nylon-6 films was carried out in a reaction system containing AA-water (20:80 wt%) under nitrogen atmosphere at 30°C. The liquor-to-material ratio was maintained 400:1. After graft copolymerization, the sample was washed with distilled water and extracted with hot water. The grafting percentage was expressed as the weight percent increase (based on the original weight of the sample). The AA-grafted membranes were kept in 0.1% potassium chloride aqueous solutions in the dark.

### Diffusive permeability

The diffusive permeability of potassium chloride was measured by the use of a dialysis cell consisting of two compartments at  $25 \pm 0.1^\circ\text{C}$ . The ratio,  $r$ , of the higher concentration  $C'$  to lower concentration  $C''$  was kept at 5, 10, 15, and 20, and  $C''$  was changed from  $5 \times 10^{-4}$  to  $1 \times 10^{-1}$  mol l<sup>-1</sup>. The permeability coefficient,  $P$  (in cm<sup>2</sup> s<sup>-1</sup>) was calculated according to the equation

$$\ln(C' - C'') / (C' - C'' - 2C_i) = 2PA\tau / \delta V \quad (1)$$

where  $C'$  and  $C''$  are the initial concentrations of the

solution (in the lower and the upper compartments respectively),  $C_1$  is that part of the solution transported from the lower compartment to the upper one at a time  $t$  (seconds),  $\delta$  is the membrane thickness (cm), and  $V$  is the volume of each compartment ( $\text{cm}^3$ ).

#### Membrane thickness

The sample was immersed in a solution with the same concentration as the solution in the upper compartment of the dialysis cell. After equilibrium, the membrane thickness was measured by a microscope.

#### Chlorine ion in water-swollen membrane

The weighed membrane grafted with AA was immersed in  $0.2 \text{ mol l}^{-1}$  potassium chloride (KCl) aqueous solution for one day at room temperature. The sample was removed from the KCl solution and any excess removed from the membrane surface. The sample was then placed in a known amount of distilled water, and the potassium chloride extracted by ultrasonic irradiation for 2 h. The composition of chlorine in the membrane was analysed colorimetrically ( $460 \text{ nm}$ )<sup>9</sup>, and the concentration of chlorine ions in the swollen membrane,  $\bar{C}_-$ , expressed as moles per litre of water in the swollen membrane.

#### Concentration of the fixed charge in the membrane

To convert the polyelectrolyte completely into the acidic form, the AA-grafted nylon-6 membrane was immersed in 0.1% hydrochloric acid for one day at room temperature. To remove the hydrochloric acid adsorbed the membrane was then washed with distilled water (until the water was chlorine free) and dried under vacuum prior to weighing. The grafted membrane in acidic form was immersed in a known amount of 0.01 N sodium hydroxide solution for one day at room temperature, and the amount of carboxyl group on the grafted membrane was determined by back titration with 0.01 N hydrochloric acid solution. The concentration of the fixed charge in the grafted membrane,  $X$ , was expressed as moles per litre of water in the swollen membrane.

## RESULTS AND DISCUSSION

The permeability coefficient,  $P_{2,13}$ , of potassium chloride through AA-grafted membranes was determined at a lower concentration  $C'' = 1.0 \times 10^{-2} \text{ mol l}^{-1}$  and a ratio of concentration of electrolyte  $r = 20$ . The relationship between the  $P_{2,13}$  of potassium chloride and the levels of grafting is shown in Figure 1. Although potassium chloride could not permeate through the AA-grafted membrane of less than 60% grafting, the  $P_{2,13}$  of potassium chloride raised with the levels of grafting. In the range of about 60–100% grafting the  $P_{2,13}$  of potassium chloride showed a very small value, but increased with increases in the levels of grafting. Similar results were obtained for the permeation of urea through AA-grafted membranes<sup>1</sup>; membranes of <100% grafting showed a different behaviour from membranes of >100% grafting. The changes in behaviour of the permeability with the levels of grafting may be due to the non-uniformity of the fine structure of the grafted membrane<sup>1</sup>. AA-grafted membranes of 252% and 415% grafting which have a high degree of hydration were chosen. These are regarded as homogeneous membranes. The influence of the concentration of potassium chloride on the permeability

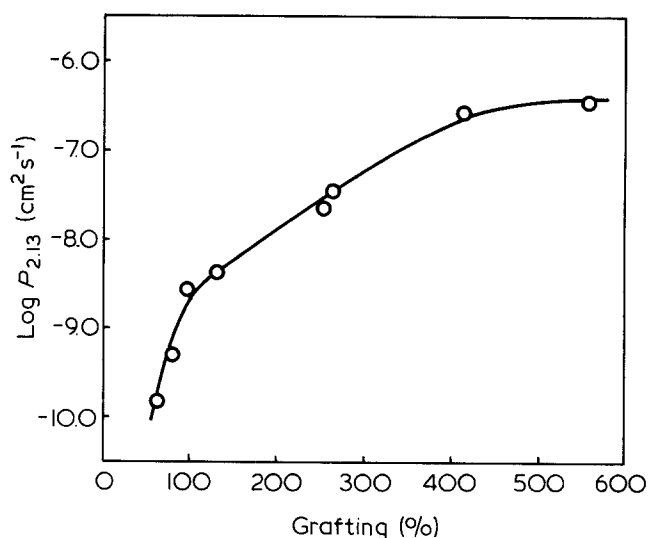


Figure 1 Dependence of  $\log P_{2,13}$  on grafting percentage for AA-grafted nylon-6 membrane

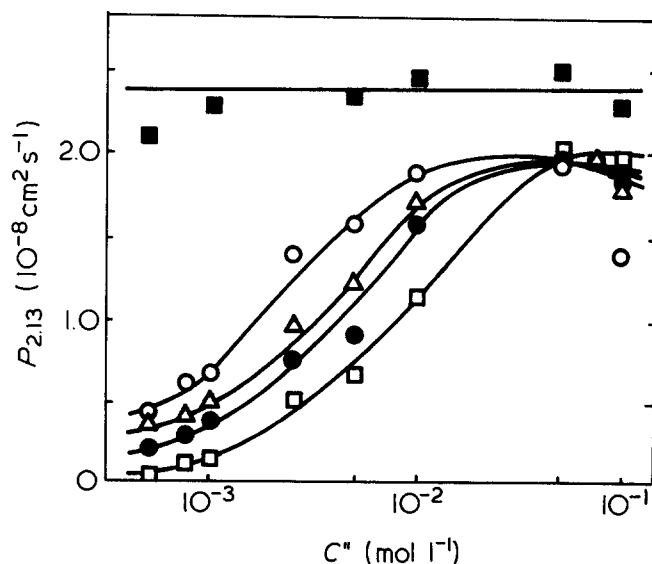


Figure 2 Relationship between the permeability coefficient and the concentration of potassium chloride (for AA-grafted nylon-6 membrane of 252% grafting and AM-grafted nylon-6 membrane of 310% grafting) (○) AA,  $r=20$ ; (△) AA,  $r=15$ ; (●) AA,  $r=10$ ; (□) AA,  $r=5$ ; (■) AM,  $r=20$

coefficient was investigated. Figure 2 shows the relationship between  $P_{2,13}$  and the concentration  $C''$ , for AA-grafted membranes of 252% grafting (at various values of the ratio,  $r$ ), and also for grafted membranes of 310% grafting (at  $r=20$ ). The  $P_{2,13}$  of AM-grafted membranes (which are regarded as non-ionic) showed almost the same value at various concentrations of potassium chloride. However, the  $P_{2,13}$  of AA-grafted membranes increased with increases in the concentration,  $C''$ , and the ratio,  $r$ . In all the curves the values converged in the higher concentration region ( $C'' > 5 \times 10^{-2} \text{ mol l}^{-1}$ ). Similar results were observed in AA-grafted membranes with 415% grafting, but the values of  $P_{2,13}$  were larger than those of the membrane with 252% grafting. The features in Figure 2 are almost the same as those reported by previous authors<sup>7</sup>.

Tasaka *et al.*<sup>7</sup> derived theoretical equations based on the phenomenological equations from the permeation of potassium chloride through an interpolymer membrane

of collodion and sulphonated polystyrene. In dilute solution where  $\bar{C}_- \ll \phi X$  can be assumed, the permeability coefficient,  $P_{2,13}$ , of 1-1 electrolyte through an ionic membrane is given by equation (2):

$$P_{2,13} = [RTl_-(r+1)/\phi X]C'' \quad (2)$$

where  $\bar{C}_-$  is concentration of electrolyte in the membrane,  $X$  is the concentration of fixed charge,  $l_-$  is the mobility of the co-ion in the membrane,  $r$  is the ratio of  $C'$  to  $C''$ , and  $\phi$  is a parameter expressing the non-ideality of the solution. This is denoted as  $\bar{y}_p/\bar{y}_\pm$ ;  $\bar{y}_p$  is the activity coefficient of the counterion in the charged membrane. However, if the mobility of the anion  $l_-$  is almost the same as that of cation  $l_+$  (such as potassium chloride) in the swollen membrane,  $P_{2,13}$  at higher concentration is given by equation (3).

$$P_{2,13} = RTl_- \quad (3)$$

It is shown in Figure 2, that  $P_{2,13}$  for AA-grafted membranes converged to a constant value at higher concentrations regardless of the concentration of potassium chloride,  $C''$ , and the ratio of concentrations,  $r$ . Therefore, it is considered that the permeability of potassium chloride through AA-grafted membranes with high levels of grafting apparently follows equation (3) in the high concentration region. In order to examine the permeation behaviour in the low concentration region,  $P_{2,13}$  was plotted against the ratio,  $r$ , for each concentration,  $C''$  (selected in the range of concentration from  $5.0 \times 10^{-4}$  to  $5.0 \times 10^{-3} \text{ mol l}^{-1}$ ). The results for membranes with 252% grafting are shown in Figure 3. The  $P_{2,13}$  increased linearly with  $r$  for each concentration. Similar results were obtained for membranes with 415% grafting. Subsequently, the values of  $P_{2,13}$  (at  $r=1$ ) were replotted against concentration,  $C''$ , for both membranes, and the result is shown in Figure 4. The plot of  $P_{2,13}$  vs.  $C''$  for both membranes gives a straight line passing through the origin. Thus, it is assumed that equation (2) can be applied to the permeation of potassium chloride in the low concentration region. However, the slopes of the straight lines are not equal to each other (the slope of the membrane with 415% grafting is larger than that of the membrane with 252% grafting). The values of the slopes,

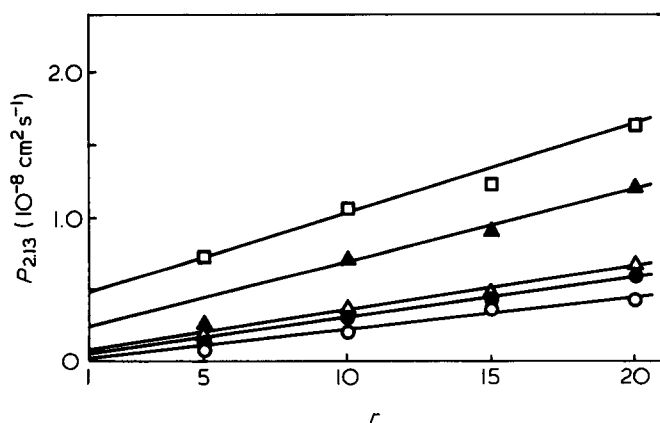


Figure 3 Relationship between the permeability coefficient and the concentration ratio,  $r$ , for AA-grafted nylon-6 membrane of 252% grafting. ( $\square$ )  $C'' = 5.0 \times 10^{-3} \text{ mol l}^{-1}$ ; ( $\blacktriangle$ )  $C'' = 2.5 \times 10^{-3} \text{ mol l}^{-1}$ ; ( $\triangle$ )  $C'' = 1.0 \times 10^{-3} \text{ mol l}^{-1}$ ; ( $\bullet$ )  $C'' = 7.5 \times 10^{-4} \text{ mol l}^{-1}$ ; ( $\circ$ )  $C'' = 5.0 \times 10^{-4} \text{ mol l}^{-1}$

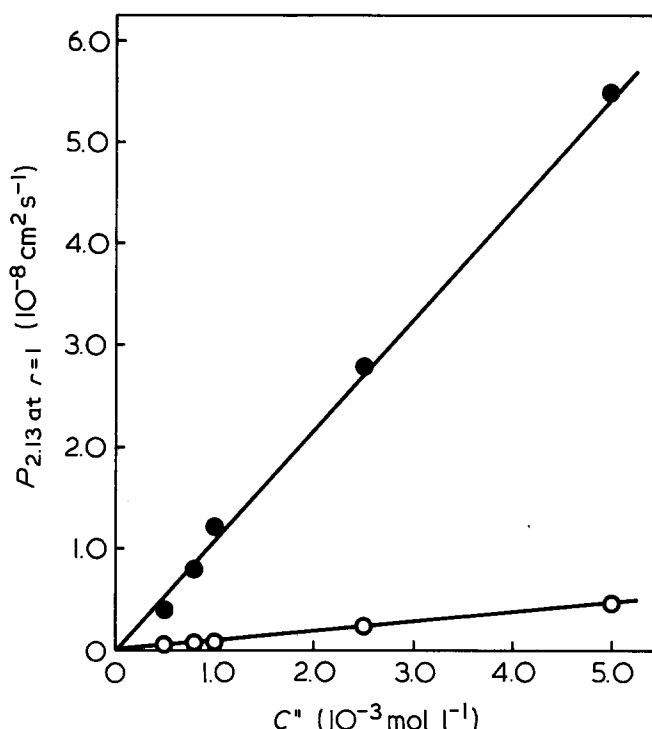


Figure 4 Dependence of  $P_{2,13}$  at  $r=1$  on the concentration of potassium chloride for AA-grafted membrane. ( $\circ$ ) 252% grafting; ( $\bullet$ ) 415% grafting

Table 1 Tortuosity factor,  $f$ , mobility of co-ions in aqueous solution,  $l_-^0$ , and effective concentration of fixed charge,  $\phi X$ , for AA-grafted nylon-6 membranes

Graft-on (%)	$RTl_-/\phi X$ ( $\text{cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$ )	$f \times 10^2$	$l_-^0 \times 10^{16}$ ( $\text{cm}^2 \text{ mol}^{-1} \text{ erg}^{-1} \text{ s}$ )	$\phi X \times 10^2$ ( $\text{mol l}^{-1}$ )
252	4.76	0.11	7.97	4.56
415	5.50	1.31	7.96	4.70

$RTl_-/\phi X$ , determined from Figure 4 are shown in Table 1. The mobility of the coion,  $l_-$ , in the swollen membrane is related to the mobility,  $l_-^0$ , in an aqueous solution with the same concentration in the membrane by equation (4):

$$l_- = fl_-^0 \quad (4)$$

where  $f$  is a tortuosity factor. In homogeneous membranes without fixed channels and pores, the tortuosity factor may be thought of as an interference factor<sup>10</sup>. The slope of the straight line,  $RTl_-/\phi X$ , can be converted to the form  $RTfl_-^0/\phi X$  using the tortuosity factor. The following factors were then determined. First, the co-ion concentration in the swollen membrane,  $\bar{C}_-$ , was measured. An average value was determined in potassium chloride aqueous solutions with the same concentration as  $C''$  ( $0.1 \text{ mol l}^{-1}$ ) and  $C'$  ( $0.5 \text{ mol l}^{-1}$ ). The factor  $l_-^0$  was determined as the mobility in aqueous solution<sup>11</sup> with the same concentration as  $\bar{C}_-$ . The tortuosity factor which can be regarded as an inherent value for the grafted membrane, was estimated from the point of convergence in Figure 2, and the value of  $l_-^0$  by using equations (3) and (4). Subsequently, the effective concentration of the fixed charge,  $\phi X$ , was calculated from the slope by using the  $f$  value and a value of  $l_-^0$  which was estimated from the co-ion concentration in the swollen membrane (measured at  $C'' = 5 \times 10^{-3} \text{ mol l}^{-1}$ ).

The results on both grafted membranes (252% and 415%) are shown in Table 1. The tortuosity factor,  $f$ , gives values of  $0.11 \times 10^{-2}$  and  $1.31 \times 10^{-2}$  for the membranes with 252% and 415% grafting, respectively. The  $f$  value for the membrane with 415% grafting is about twelve times as large as that for the membrane with 252% grafting. There was little or no difference for the values of the coion mobility  $l_{-}^0$ , and the fixed charge  $\phi X$  between the membranes. Details of  $\phi X$  will be discussed later.

Since  $l_{-}^0$  and  $\phi X$  have similar values for both membranes, the tortuosity factor seems to be the value producing the difference in the permeability of potassium chloride through the grafted membranes. It is reasonable to consider<sup>10</sup> that the tortuosity factor for homogeneously swollen membranes is dependent on (i) the actual distance the diffusing co-ion must move, from one side of the membrane to the other, (ii) the contribution of the electric interaction between the co-ion and the counterion in the membrane, and (iii) the degree of hydration of the swollen membrane, which is related to the fine structure of the membrane. Accordingly, the membrane with 415% grafting seems to have a looser fine structure than the membrane with 215% grafting permitting potassium chloride to permeate to a greater extent.

In order to examine in more detail, the value of  $\phi X$  obtained by the permeation of potassium chloride, the values of  $\phi X$  for AA-grafted membranes with high percentages of grafting were determined from the Donnan membrane equilibrium in aqueous potassium chloride solutions. It has been reported<sup>12,13</sup> that the concentration of electrolyte in the membrane is determined by the Donnan membrane equilibrium of the membrane phase and the feed solution. Tasaka and Nagasawa *et al.*<sup>7</sup> proposed the following equation with a parameter,  $\phi$ , expressing the nonideality of the solution when a membrane is treated as a homogeneous polyelectrolyte solution.

$$(y_{\pm} C)^2 = \bar{y}_{\pm}^2 \bar{C}_{-} (\bar{C}_{-} + \phi X) \quad (5)$$

where  $y_{\pm}$  and  $\bar{y}_{\pm}$  are the mean activity coefficients of electrolyte in solution, and in the membrane respectively;  $C$  and  $\bar{C}$  are the concentrations of electrolyte in the solution, and the membrane, respectively.

It was assumed that equation (5) is applicable to the AA-grafted membranes with high levels of hydration, and the effective concentration of the fixed charge was measured at  $C = 0.1 \text{ mol l}^{-1}$ . The relationship between  $\phi X$  and grafting percentage is shown in Figure 5.  $\phi X$  slightly increased with increase of percent grafting. No differences in  $\phi X$  were found in the grafted membranes. It is difficult to compare the value of  $\phi X$  with that determined from transport parameters directly because of the concentration dependence of  $\phi$ . However,  $\phi X$  determined from thermodynamic and transport parameters shows similar behaviour to the grafting percentage of the membrane. In order to investigate the parameter,  $\phi$ , in more detail, we measured the concentration of fixed charge of the grafted membranes. The plot of the concentration of fixed charge,  $X$ , against the levels of grafting is illustrated in Figure 6. The concentration of fixed charge increased linearly with increasing levels of grafting. Figure 7 shows the relationship between the parameter,  $\phi$ , and the concentration of fixed charge,  $X$ . The value of  $\phi$  decreased with increases of the concentration of the fixed

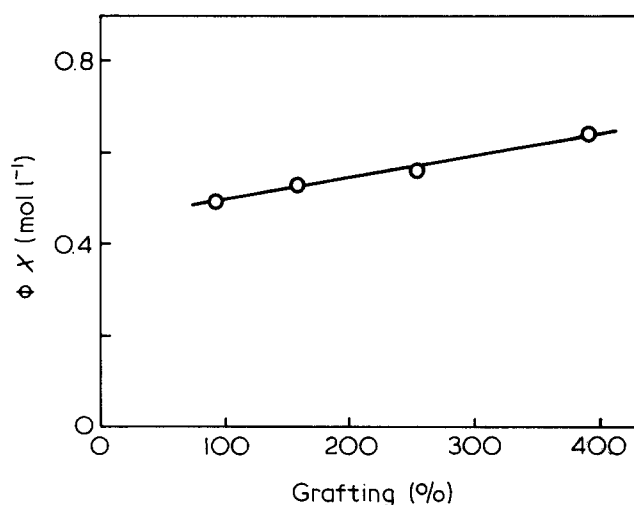


Figure 5 Relationship between the effective concentration of fixed charge and the grafting percentage for AA-grafted nylon-6 membrane

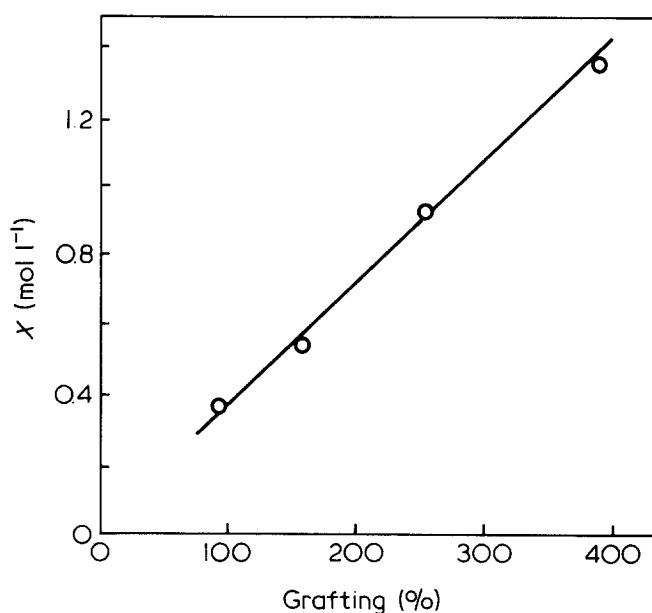


Figure 6 Concentration of the fixed charge versus grafting percentage for AA-grafted nylon-6 membrane

charge. The parameter,  $\phi$ , is defined as  $\bar{y}_p / \bar{y}_{\pm}$ . The mean activity coefficient of electrolyte in the membrane,  $\bar{y}_{\pm}$ , showed almost the same value for the grafted membranes (regardless of percent grafting). Therefore, it is inferred that the decrease of  $\phi$  is due to the change of  $\bar{y}_p$ . It is reasonable to assume that the activity coefficient of the counterion in the membrane,  $\bar{y}_p$ , decreases with increases in the concentration of the counterion in the membrane (i.e.  $X$ ). The parameter  $\phi$  has been investigated by Kobatake *et al.*<sup>14-17</sup>, and Nagasawa *et al.*<sup>7</sup>;  $\phi$  represents the fraction of free counterion which is not bound in the vicinity of the polyions. Accordingly, it is considered that the fraction of counterion bound around carboxyl groups may be increased with increases in the level of grafting; and the grafted membrane with high levels of grafting can be regarded as an ionic membrane with a similar effective concentration of fixed charge.

In conclusion, the permeation of potassium chloride through AA-grafted membranes is increased with increases in the levels of grafting. It was found that the

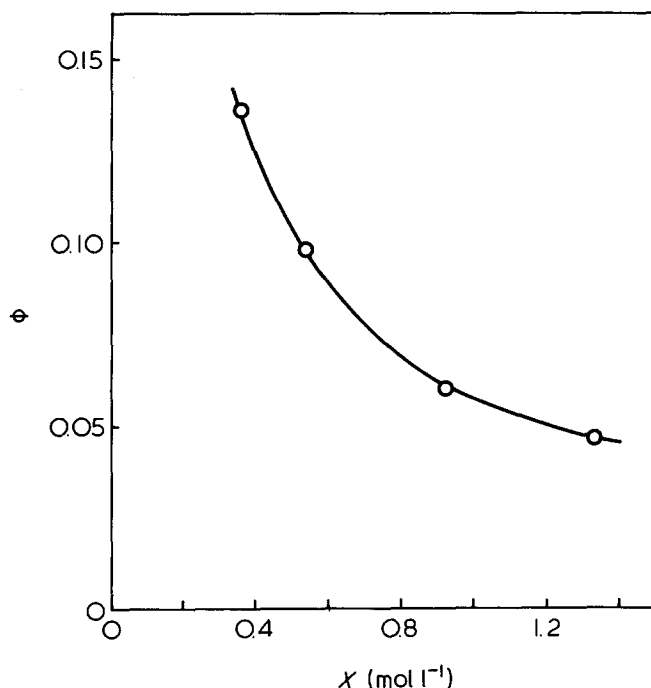


Figure 7 Relationship between parameter,  $\phi$ , and concentration of fixed charge for AA-grafted nylon-6 membrane

theory of permeation of electrolyte through ionic membranes (derived from phenomenological equations) is applicable to the permeation of potassium chloride through AA-grafted membranes with high levels of grafting. The effective concentration of fixed charge for the membrane (with more than about 100% grafting) gives almost the same value regardless of the level of grafting. But, the tortuosity factor increases with increasing levels of grafting. Accordingly, it is considered that the tor-

tuosity factor is the most important factor determining the permeation of potassium chloride through membranes grafted with acrylic acid.

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#### REFERENCES

- 1 Takigami, S., Nakamura, M. and Nakamura, Y. *Polymer* 1984, **25**, 963
- 2 Cohen, M. H. and Turnbull, D. *J. Chem. Phys.* 1959, **31**, 1164
- 3 Yasuda, H., Lamaze, C. E. and Ikenberry, L. D. *Makromol. Chem.* 1968, **118**, 19
- 4 Yasuda, H., Ikenberry, L. D. and Lamaze, C. E. *Makromol. Chem.* 1969, **125**, 108
- 5 Yasuda, H., Peterlin, A., Colton, C. K., Smith, K. A. and Merrill, E. A. *Makromol. Chem.* 1969, **126**, 177
- 6 Yasuda, H. and Lamaze, C. E. *J. Macromol. Sci.-Phys.* 1971 B, **B(1)**, 111
- 7 Tasaka, M., Aoki, N., Kondo, Y. and Nagasawa, M. *J. Phys. Chem.* 1975, **79**, 1307
- 8 Shimada, M., Kuribara, H., Matsumoto, I. and Nakamura, Y. *J. Appl. Polym. Sci.* 1979, **24**, 1017
- 9 Utsumi, S. *Nippon Kagaku Kaishi.* 1952, **73**, 835
- 10 Takigami, S., Maeda, Y. and Nakamura, Y. *J. Appl. Polym. Sci.*, 1979, **24**, 1419
- 11 Kagaku Binran (The Chemical Handbook), Kisohen (Basik) II, Nippon Kagakukai (Japan Chemical Society). Muruzen, Tokyo, 1975, p 1191
- 12 Hoffer, E. and Kedem, O. *Desalination* 1967, **2**, 25
- 13 Hoffer, E. and Kedem, O. *J. Phys. Chem.* 1972, **76**, 3638
- 14 Kamo, N., Toyoshima, Y., Nozaki, H. and Kobatake, Y. *Kolloid. Z. Z. Polym.* 1971, **248**, 914
- 15 Ueda, T., Kamo, N., Ishida, N. and Kobatake, Y. *J. Phys. Chem.* 1972, **76**, 2447
- 16 Kamo, N., Oikawa, M. and Kobatake, Y. *J. Phys. Chem.* 1973, **77**, 92
- 17 Ueda, T. and Kobatake, Y. *J. Phys. Chem.* 1973, **77**, 2995