

# Selective permeability of grafted nylon-6 membranes: 1. Permeability of urea and potassium chloride in acrylamide and acrylic acid grafted membranes

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The permeability of urea and potassium chloride through  $\gamma$ -irradiated nylon-6 membranes grafted with acrylamide (AM) and acrylic acid (AA) was investigated. The permeability of urea and potassium chloride through both AM and AA grafted membranes increased with increases in the levels of grafting. The diffusion of urea and potassium chloride through AA and AM grafted membranes (with more than 100% grafting) can be explained by the free volume concept. However, this explanation does not apply to potassium chloride permeating through AA-grafted membranes. The diffusion of potassium chloride through highly swollen AA-grafted membrane obeys the free volume concept outwardly, however the diffusion is modified by the concentration dependence of the permeant.

(Keywords: graft copolymerization; diffusion coefficient; free volume; effective cross-section; sieve effect)

## INTRODUCTION

Recent work, with grafted membranes has been concerned with their physical properties, such as the permeation of solutes<sup>1</sup> and gases<sup>2</sup>, reverse osmosis<sup>3-5</sup>, and pervaporation<sup>6</sup>. In previous papers<sup>7-8</sup>, the diffusive permeability of urea, uric acid, and potassium chloride through cellophanes grafted with various monomers has been reported. It was found (except for the permeability of potassium chloride through the membrane grafted with acrylic acid), that the permeation of solutes through the grafted cellophanes, was explained by the free volume concept of homogeneously water-swollen membranes<sup>9-13</sup>. With grafted cellophanes, however, the graft copolymerization did not improve the permeability of the solutes because the original cellophane was easily permeable to solutes. However, nylon-6 films are only slightly permeable to the solutes. In the paper presented here, acrylamide and acrylic acid were grafted onto nylon-6 films, using a  $\gamma$ -ray post-irradiation method, and the permeation of urea and potassium chloride through the grafted nylon-6 membranes was measured. The influence of monomer types and the level of grafting on the permeation of the solutes was studied, and the behaviour of the diffusion coefficient of the solutes is discussed in relation to the concept of the 'free volume' theory of diffusion.

## EXPERIMENTAL

### Materials

Nylon-6 film ( $1.5 \times 10^{-3}$  cm in thickness) produced by Unitika Co. Ltd. was used as a starting material. The viscosity-average molecular weight<sup>14</sup> of the nylon-6 film

measured in 85% formic acid was found to be  $2.5 \times 10^4$ . The film used was biaxially stretched with a degree of crystallinity of 45.7% as determined by X-ray diffraction<sup>15</sup>. The sample was washed with 0.1% non-ionic surfactant aqueous solution and rinsed with distilled water prior to air-drying. Acrylamide (AM) was purified by recrystallization from benzene, and acrylic acid (AA) was distilled under reduced pressure before use. Potassium chloride, urea, and other chemicals of analytical grade were used and needed no further purification.

### Graft copolymerization.

After nylon-6 film (ca. 0.5 g) had been dried under reduced pressure at 50°C for 20 h, it was irradiated 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 under nitrogen atmosphere. Graft copolymerization onto the irradiated nylon-6 film was carried out in reaction systems consisting of AM-water (5:95 wt%) and AA-water (20:80 wt%) (under nitrogen atmosphere at 30°C). The liquor-to-material ratio was maintained at 400:1. After graft copolymerization, the nylon-6 membranes (grafted with AM and AA) were washed with distilled water and extracted in hot water to remove the homopolymer. The grafting percentage was expressed as weight percent increase compared to the original weight of the sample. The membranes grafted with AM and AA, were stored in distilled water, and in 0.1% potassium chloride aqueous solution, respectively, in the dark.

### Water incorporation

After the weighed samples had been immersed in

distilled water for one day at room temperature, they were placed between sheets of filter paper (thus removing the excess water), and then weighed. The same procedure was repeated several times. Weight increase by water was then plotted against blotting times. Finally, the weight increase at time zero was obtained by extrapolation, thus giving the percentage water incorporation<sup>16</sup>.

*Diffusive permeability*

The diffusive permeability of urea and potassium chloride was measured by using a two compartment dialysis cell; the upper and the lower compartments were filled with aqueous solution of concentration  $C''$  and  $C'$  (in  $\text{mol l}^{-1}$ ,  $C'' < C'$ ), respectively. The ratio of the higher concentration  $C'$  to the lower one  $C''$ ,  $r$  was maintained at 20. The membrane was equilibrated in the same solution as that in the upper compartment before attachment to the dialysis cell. The cell was placed in a water bath at  $25 \pm 0.1^\circ\text{C}$ , and both solutions were magnetically stirred at 50 rpm. The concentration of solute permeated from the lower compartment to the upper one was determined by picking up 1 ml of solution from the upper compartment at regular intervals.

The permeability coefficient,  $P$  (in  $\text{cm}^2 \text{s}^{-1}$ ), was calculated according to the equation,

$$\ln \frac{C' - C''}{C' - C'' - 2C_t} = \frac{2PA t}{\delta V} \quad (1)$$

where  $C''$  and  $C'$  are the initial concentrations of the solutions (in the upper and the lower compartments, respectively),  $C_t$  is the increment of the concentration of the solute transported from the lower compartment to the upper one at time  $t$  (in sec),  $\delta$  is the membrane thickness (in cm), and  $V$  is the volume of each compartment of the cell (in  $\text{cm}^3$ ). The concentrations of urea<sup>17</sup> and potassium chloride<sup>18</sup> were determined colorimetrically.

*Membrane thickness*

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

*Hydration*

The weighted sample was immersed in the solution from the upper compartment, and after equilibrium, the sample was dried between sheets of filter paper and reweighed. By extrapolation of the linear part of the curve to time zero, the weight of the swollen sample at time zero was determined; and subsequently, weight was converted into the volume of the swollen membrane. The degree of hydration of the sample,  $H$ , was calculated from the following equation:

$$H = \frac{\text{volume of water in swollen membrane}}{\text{volume of swollen membrane}} \quad (2)$$

*Partition coefficient*

The weighed sample was then equilibrated in the solution from the lower compartment. The sample was then dried between sheets of filter paper until the sample had attained the same weight increase and degree of hydration described above. The sample was then placed in a known amount of distilled water, and the solute

extracted by ultrasonic irradiation for 2 h. The concentration of urea and potassium chloride was determined colorimetrically. The partition coefficient,  $K_2$ , was calculated from the following equation:

$$K_2 = \frac{\text{grams of solute per } 1 \text{ cm}^3 \text{ swollen membrane}}{\text{grams of solute per } 1 \text{ cm}^3 \text{ solution}} \quad (3)$$

*Diffusion coefficient in swollen membrane*

The diffusion coefficient,  $D_{2,13}$ , of a solute in a swollen membrane can be related to the permeability coefficient,  $K_2$ , by the following relationship:

$$P_{2,13} = K_2 D_{2,13} \quad (4)$$

Using the value of  $P_{2,13}$  and  $K_2$ ,  $D_{2,13}$  was determined from equation (4).

RESULTS AND DISCUSSION

*Graft copolymerization*

The relationship between the level of grafting and the reaction time in AM- and AA-grafted membranes is shown in Figure 1. The level of grafting of AM-grafted membranes increased with the reaction time until 8 h, and thereafter, increased rapidly. A similar tendency was observed with AA-grafted membranes. The level of grafting of AA-grafted membranes showed larger values than that of AM-grafted membranes; the differences in these values between AA- and AM-grafted membranes may be attributed to the amount of monomer in the reaction solution. The rapid increase in the level of grafting observed after 8 h for both systems is probably due to the Trommsdorff effect<sup>19</sup>, while termination of the growing polymer radicals, is decreased as the viscosity of the solution increases with reaction time.

*Water incorporation*

The relationship between the level of grafting and water incorporation is shown in Figures 2a and 2b on AM- and AA-grafted nylon-6 membranes, respectively. The incorporation of water into the AM-grafted membranes

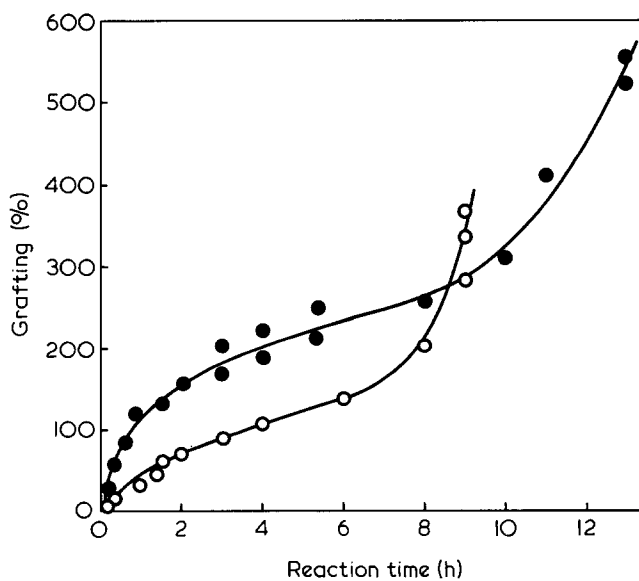
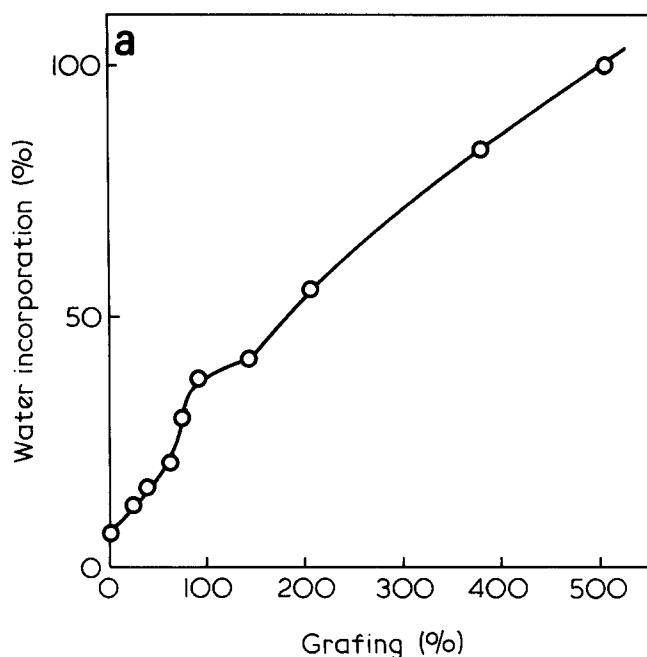
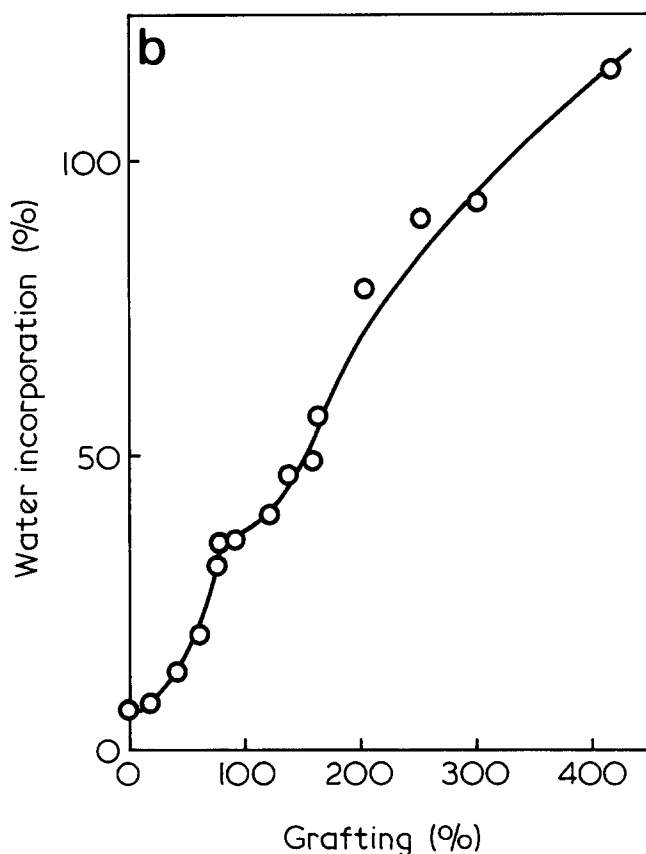


Figure 1 Percentage grafting versus reaction time. (○) acrylamide; (●) acrylic acid



**Figure 2a** Relationship between water incorporation and percentage grafting for AM-grafted membrane



**Figure 2b** Relationship between water incorporation and percentage grafting for AA-grafted membrane

increased with increases in the levels of grafting. The incorporation of water is a quantity reflected by the fine structure of polymer. If water is adsorbed independently by trunk polymers and branch polymers, the water incorporation must increase linearly with the level of grafting. The increase of water incorporation, however, is not linear; as it increases markedly in the range of about 50% to 100% grafting. The increase of water

incorporation can be attributed to the changes in the fine structure of the grafted nylon-6 membrane. Branch polymers probably deposit more homogeneously in membranes with more than 100% grafting. In Figure 2b, a similar relationship between the level of grafting and water incorporation was obtained for AA-grafted membranes.

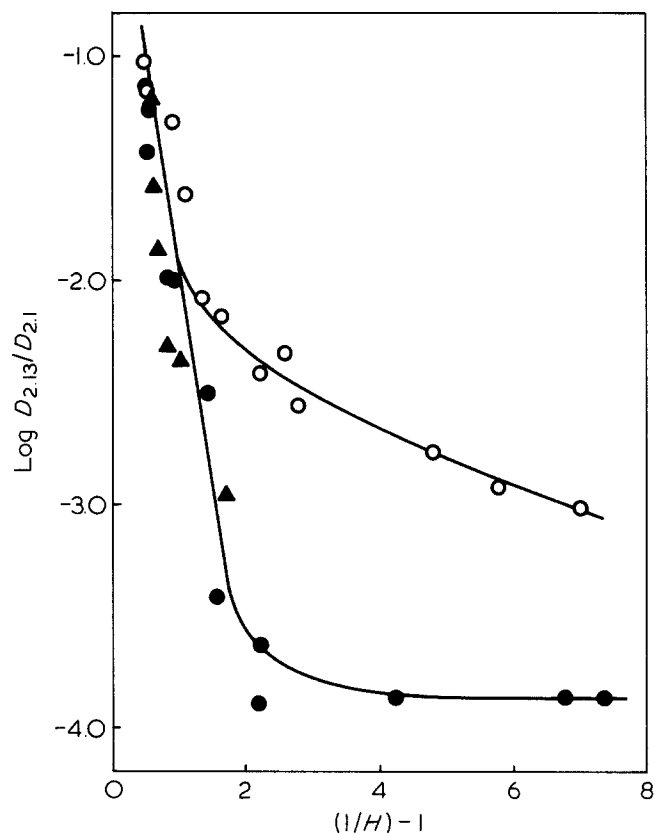
#### Permeation of urea through AM- and AA-grafted membranes

The diffusion coefficient,  $D_{2,13}$ , for solute diffusing through homogeneously water-swollen membranes; based on the concept of the free volume theory, is expressed in the following equation<sup>12,13</sup>:

$$\log D_{2,13}/D_{2,1} = \log \phi(q_2) - \frac{1}{2.303} \left( \frac{V^*}{V_{f,1}} \right) \left( \frac{1}{H} - 1 \right) \quad (5)$$

where  $D_{2,1}$  is the diffusion coefficient of the solute in pure water;  $\phi(q_2)$  is the probability describing the sieve mechanism of the membrane;  $V^*$  is the critical volume of the permeant;  $V_{f,1}$  is the free volume fraction of pure water; and  $H$  is the degree of hydration. It was reported in a previous paper by these authors<sup>7</sup>, that the permeation of solutes through grafted cellophanes (with various monomers) could be explained by the free volume concept of homogeneously water-swollen membrane.

The relationship between the diffusion coefficient,  $D_{2,13}$ , of urea through AM- and AA-grafted membranes (measured at  $C'' = 1.0 \times 10^{-2} \text{ mol l}^{-1}$ ) and degree of hydration,  $H$ , is shown in Figure 3. The value of



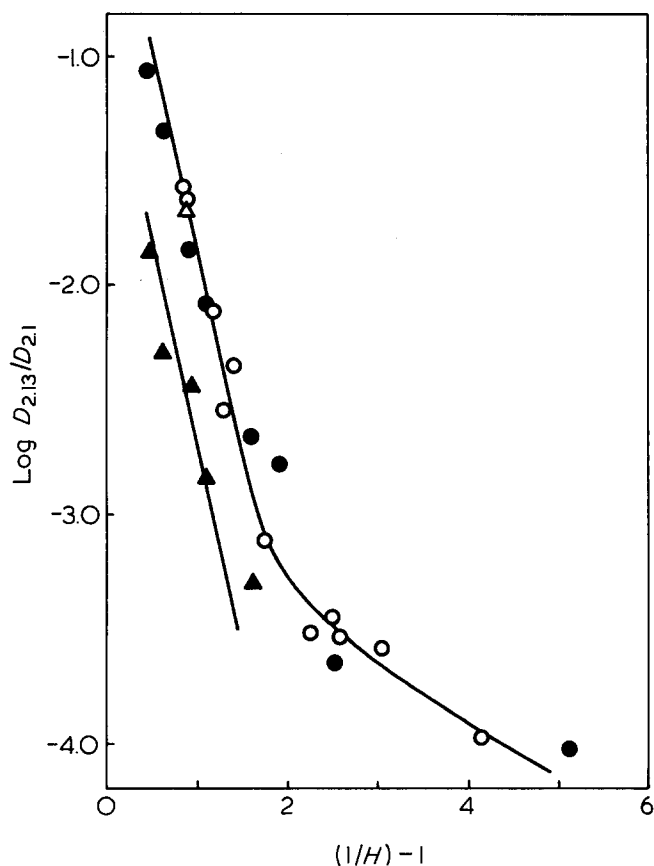
**Figure 3** Relationship between  $\log D_{2,13}/D_{2,1}$  and  $(1/H) - 1$  for urea. (○) AM-grafted nylon-6 at  $C'' = 1 \times 10^{-2} \text{ mol l}^{-1}$ ; (●) AA-grafted nylon-6 at  $C'' = 1 \times 10^{-2} \text{ mol l}^{-1}$ ; (▲) AA-grafted nylon-6 at  $C'' = 1 \times 10^{-3} \text{ mol l}^{-1}$

$\log D_{2,13}/D_{2,1}$  for AM-grafted membranes decreased linearly in the range of higher hydration, and then decreased gradually with lower values of hydration. In the case of AA-grafted membranes, the relationship  $\log D_{2,13}/D_{2,1}$  and hydration showed a similar tendency. However, the AM-grafted membranes with lower values of hydration had smaller values of  $D_{2,13}/D_{2,1}$ .  $D_{2,13}$  was measured at  $C'' = 1.0 \times 10^{-3} \text{ mol l}^{-1}$ , to investigate the dependence of the concentration of permeant on the diffusion of urea through AA-grafted membrane. The value of  $\log D_{2,13}/D_{2,1}$  at  $C'' = 1 \times 10^{-3} \text{ mol l}^{-1}$  is also shown in Figure 3. The value measured at  $C'' = 1.0 \times 10^{-3} \text{ mol l}^{-1}$  was almost the same as that at  $C'' = 1 \times 10^{-2} \text{ mol l}^{-1}$ . Since the plot of  $\log D_{2,13}/D_{2,1}$  vs.  $(1/H) - 1$  gives a straight line regardless of the type of branch polymer, and concentration of the permeant used, the permeation of urea through AM- and AA-grafted membranes may be explained by the free volume concept of homogeneously water-swollen membrane in highly hydrated regions, i.e.  $\{(1/H) - 1\} < 2$ . The slope,  $V^*/V_{f1}$ , and the intercept,  $\log \phi(q_2)$ , of the straight line are determined from Figure 3.  $V^*/V_{f1}$  is a value closely related to the effective cross section of solute, and for urea gives a value of 4.56. On the other hand,  $\phi(q_2)$  is a parameter for the sieve mechanism of the membrane, and for urea gives a value of 0.93. When  $\phi(q_2) = 1$ , the permeant is not effected by the presence of the membrane. Therefore, these highly swollen grafted membranes hardly exert a sieve-effect on the diffusion of urea.

The values of  $\log D_{2,13}/D_{2,1}$  measured for both grafted membranes in the lower hydration region deviates from the straight line obtained in the highly hydrated region. The deviation is due to the non-uniformity of the fine structure of grafted membrane. As mentioned, for the incorporation of water, it is considered that the branch polymers in the membrane with less than 100% grafting do not distribute homogeneously through the membrane. It is difficult to apply equation (5) to the diffusion of urea through the membrane with lower levels of hydration. The disparity between the values of  $\log D_{2,13}/D_{2,1}$  for AM- and AA-grafted membranes observed in the lower hydration region may be attributable to an affinity between urea and the branch polymers.

#### Permeation of potassium chloride through AM- and AA-grafted membranes

The diffusion coefficient,  $D_{2,13}$ , of potassium chloride through AM- and AA-grafted nylon-6 membranes was determined (keeping  $C'' = 1.0 \times 10^{-2} \text{ mol l}^{-1}$  and  $C' = 2.0 \times 10^{-1} \text{ mol l}^{-1}$ ). It was found that below a threshold level of 30% grafting (for AM grafted membranes), no diffusion of potassium chloride took place, while above this level the diffusion increased with increases in the level of grafting. The relationship between  $\log D_{2,13}/D_{2,1}$  and  $(1/H) - 1$  for AM-grafted membranes gave a straight line in the higher hydration region (Figure 4) (similar to that for urea). The slope,  $V^*/V_{f1}$ , and the intercept,  $\log \phi(q_2)$ , of the straight line (determined from Figure 4), are 4.10 and 0.93, respectively. The value of  $V^*/V_{f1}$  for potassium chloride is slightly smaller than that for urea, but  $\phi(q_2)$  for potassium chloride shows the same value as that for urea. These results mean that the effective cross section for potassium chloride is only slightly smaller than that for urea, and the sieve effect of the membrane hardly influences the diffusion of potassium



**Figure 4** Relationship between  $\log D_{2,13}/D_{2,1}$  and  $(1/H) - 1$  for potassium chloride. (○) AM-grafted nylon-6 at  $C'' = 1 \times 10^{-2} \text{ mol l}^{-1}$ ; (△) AM-grafted nylon-6 at  $C'' = 1 \times 10^{-3} \text{ mol l}^{-1}$ ; (●) AA-grafted nylon-6 at  $C'' = 1 \times 10^{-2} \text{ mol l}^{-1}$ ; (▲) AA-grafted nylon-6 at  $C'' = 1 \times 10^{-3} \text{ mol l}^{-1}$

chloride and urea through AM-grafted membranes. Potassium chloride could not permeate through AA-grafted nylon-6 membranes with less than 60% grafting. The relationship between  $\log D_{2,13}/D_{2,1}$  (measured at  $C'' = 1.0 \times 10^{-2} \text{ mol l}^{-1}$ ) and  $(1/H) - 1$  gave a similar straight line as urea (Figure 4). It is known that the permeation of electrolytes through ionic membranes depends on the concentration of the permeant<sup>20</sup>.  $D_{2,13}$  was measured at  $C'' = 1.0 \times 10^{-3} \text{ mol l}^{-1}$  and  $C' = 2.0 \times 10^{-2} \text{ mol l}^{-1}$  in AM- and AA-grafted membranes, and the influence of the concentration on  $D_{2,13}$  investigated. The results are shown in Figure 4. The permeation of KCl through AM-grafted membranes were found to be independent of concentration. However, in AA-grafted membranes at  $C'' = 1.0 \times 10^{-3} \text{ mol l}^{-1}$ , the plot of  $\log D_{2,13}/D_{2,1}$  vs.  $(1/H) - 1$  gave another straight line with the same slope but a different intercept. (c.f. straight line at  $C'' = 1.0 \times 10^{-2} \text{ mol l}^{-1}$ ). The  $D_{2,13}$  of potassium chloride diffusing through AA-grafted membranes, shows a marked concentration dependence. These effects may be due to inapplicability of equation (4) to the diffusion of salt through ionic membranes. For the conversion of the permeability coefficient into the diffusion coefficient, it is necessary to consider other factors such as the influence of membrane charge, and concentration of solution, in addition to  $K_2$ . In general, equation (5) is applicable to homogeneously water-swollen membranes, lacking fixed charge. Nevertheless, equation (5) can be outwardly applied to the diffusion of potassium chloride through the AA-grafted membrane

with high hydration. However, equation (5) does not explain the dependence of diffusion on the concentration of potassium chloride. Details of the permeation of potassium chloride through AA-grafted membrane will be discussed in our next paper<sup>21</sup>.

## CONCLUSION

The permeability of urea and potassium chloride through AM- and AA-grafted membranes increased with increases in the levels of grafting. The diffusion of urea and potassium chloride through AA- and AM-grafted membranes with more than 100% grafting, can be explained by the free volume concept of homogeneously water-swollen membrane. However, this explanation does not apply to potassium chloride permeating through AA-grafting membranes. It is found that potassium chloride has a slightly larger effective cross sectional area than urea; the sieve effect of the grafted membranes hardly influences the diffusion of both permeants.

However, the diffusion of potassium chloride through AA-grafted membranes shows a marked dependence on the concentration. However, by making allowances for the concentration dependence, the free volume concept can be applied to the diffusion of potassium chloride through AA-grafted membranes, which have high levels of hydration.

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