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Anion exchange membranes prepared by amination of cross-linked membranes having chloromethyl groups with 4-vinylpyridine and trimethylamine

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Abstract

Copolymer membranes composed of chloromethylstyrene and divinylbenzene were reacted with 4-vinylpyridine and then trimethylamine to prepare highly tight anion exchange membranes. When 4-vinylpyridine reacted with chloromethyl groups of the copolymer membranes, 4-vinylpyridine polymerized in the membrane matrix to form a ladder-like polymer, of which one polymer was cross-linked. Consequently, relationships of ion exchange capacity and water content to electrical resistance of the obtained membranes were completely different from those of the anion exchange membranes with benzyl trimethylammonium groups cross-linked with divinylbenzene. With increasing reaction time of the copolymer membranes with 4-vinylpyridine, the electrical resistance of the membranes markedly increased with a small decrease in ion exchange capacity and with the decrease in water content. And fixed ion concentration of the membranes reacted with 4-vinylpyridine and then trimethylamine was higher than that of the membranes with benzyl trimethylammonium groups. These are thought to be because of the formation of a ladder-like polymer in the membrane matrix and the introduction of pyridine unit, which is more hydrophobic and bulkier than trimethylamine. The remarkable decrease in the pore size of the membranes was confirmed by the measurement of the diffusion coefficient of neutral molecules, urea and glucose, through the membranes. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Anion exchange membranes; 4-vinylpyridine; Matrix polymerization in cross-linked membranes

1. Introduction

Ion exchange membranes have been widely used in various industries: in electrodialysis to concentrate or desalinate salt solutions; in diffusion dialysis to recover acids or alkalis from waste acids or alkalis [1,2]; in the electrolysis of solutions such as chlor-alkali production as a separator [3,4]; in the pervaporation for dehydration of solvents [5–7]; in the separation of acidic gas such as carbon dioxide by carrier transport [8–10]; in the dehumidification of gases [11]; in sensing materials such as humidity sensor [12,13], carbon monoxide sensor [14], etc. The utilization of the ion exchange membranes is diverse, as not only separation membranes but also functional charged membranous materials. Among these, separation of salts from mixed salt and neutral solute solutions is one of the important utilizations in electrodialysis using the ion exchange membranes, such as demineralization of sugar solution, amino acid solution, etc. High current efficiency of salt removal and low leakage of neutral molecules through the membranes are required. To achieve these, the ion exchange membranes having tight structure should be prepared by the increase in the cross-linkage of the membranes. And further requirements for the ion exchange membranes have arisen in this field.

Quaternization of 4-vinylpyridine with alkyl halide in an organic solvent was reported to result in spontaneous polymerization, forming the corresponding poly(*N*-alkyl 4-vinylpyridinium) halide [15,16]. Similar effects were also reported when 4-vinylpyridine reacted with polyacids such as poly(styrene sulfonic acid), polyacrylic acid, carboxymethyl cellulose, etc. or strong mineral acids in aqueous or organic solutions [17,18]. In these cases, so-called matrix polymerization occurs. The initiation of polymerization in these reactions was suggested to be the attack of the counter ions (X^-) on the β-position of the double bond of the 4-vinylpyridinium salt to give a zwitterion and to be initiated by the zwitterion by addition to a 4-vinylpyridinium double bond [19]. Though the polymerization were carried out in aqueous and organic solvents, the polymerization in the polymeric membranes cross-linked with divinylbenzene, which are rigid and hydrophobic, should be different from

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that in the solutions. It was reported that 4-vinylpyridine reacted with chloromethyl groups on the surfaces of a cross-linked membrane and sulfate ions permeated through the obtained membrane with difficulty compared to chloride ions [20]. When 4-vinylpyridine underwent reaction throughout the cross-linked membranes having chloromethyl groups to aminate the membranes and polymerized in the membrane matrix, the obtained membranes should have a ladder-like polymer structure of which one polymer is cross-linked. Thus, the anion exchange membranes aminated with 4-vinylpyridine are thought to have a tight structure and show interesting properties. Though the preparation of anion exchange membranes is reported by the polymerization of chloromethylstyrene and 2-methyl-5-vinylpyridine in the presence of an inert polymer and a woven cloth, the membranes did not have a ladder-like polymer structure [21].

In this study, to prepare the anion exchange membranes having a tight structure, the copolymer membranes with different crosslinkages prepared from chloromethylstyrene and divinylbenzene were reacted with 4-vinylpyridine and then trimethylamine, and their electrochemical properties were evaluated.

2. Experimental

2.1. Materials

Vinyl monomers for membrane preparation, chloromethylstyrene, obtained from Seimi Chemical Co. Ltd. and divinylbenzene from Sankyo Kasei Kogyo Co., Ltd. were used without further purification (the purity of divinylbenzene was 55%: a mixture of *m*-, *p*-divinylbenzene, ethylvinylbenzenes and diethylbenzenes). Acrylonitrile–butadiene rubber (NBR) was obtained from Japan Synthetic Rubber Co., Ltd. 4-vinylpyridine was supplied by Koei Chemical Co., Ltd. which was distilled under reduced pressure before use. Sodium chloride, methyl alcohol, benzoyl peroxide (an initiator of radical polymerization), glucose, urea, hydrochloric acid (36%), ammonia solution (29%) and other reagents, obtained from Ishizu Seiyaku Co. Ltd. were of reagent grade. Deionized water was used in all experiments.

2.2. Preparation of the cross-linked membranes with different crosslinkage

The cross-linked membranes were prepared by copolymerizing chloromethylstyrene and divinylbenzene in the presence of benzoyl peroxide, acrylonitrile–butadiene rubber and backing fabric with the same method as the paste method [22,23]. Chloromethylstyrene and divinylbenzene were mixed, and 5 wt.% of acrylonitrile–butadiene rubber was dissolved in the vinyl monomer mixture to impart mechanical strength to the membrane. The content of divinylbenzene to total vinyl monomers, [0.55 × divinylbenzene/(chloromethylstyrene + divinylbenzene)] × 100, was changed: 10.0, 14.0 and 20.0. After 3 wt.% of benzoyl peroxide (with respect to total vinyl monomers) had been dissolved in the mixture, the obtained pasty mixtures were coated on woven fabric made of poly(vinyl chloride), Teviron cloth, Teijin Co., Ltd., respectively, and polymerized at 80°C for 16 h under nitrogen atmosphere after covering the composite with a polyester film on both sides. Thickness of the obtained copolymer membranes was about 100 μm.

2.3. Polymerization of 4-vinylpyridine in the cross-linked membrane matrix

After examining the ratio of 4-vinylpyridine to methyl alcohol to determine the concentration of 4-vinylpyridine in a reaction bath, 30 wt.% of 4-vinylpyridine methyl alcohol solution was selected as the reaction bath. The cross-linked membranes swelled abnormally in higher concentration than 30 wt.% of 4-vinylpyridine in methyl alcohol solution and the reaction speed was almost constant in the solution of higher concentration than 30 wt.% (the reaction speed was measured by the decrease in electrical resistance of the copolymer membrane measured in 0.5 N sodium chloride solution). A 7.0 cm × 7.0 cm of the cross-linked membrane was immersed in the reaction bath at 25.0°C with stirring for various periods: 2, 4, 8, 16, 24 and 48 h. After the reaction, the membranes were washed with methyl alcohol and then immersed in 1.0 N trimethylamine acetone (25%) and water (75%) mixed solution to react the remaining chloromethyl groups of the membranes with trimethylamine. The obtained anion exchange membranes were equilibrated with 1.0 N hydrochloric acid solution and 0.5 N ammonia solution alternately several times and then equilibrated with 0.5 N sodium chloride solution.

2.4. Measurements

Electrical resistance of the anion exchange membranes was measured by 1000 Hz AC, Hewlett Packard LCR meter, model 4263A, at 25.0°C, after equilibration with a 0.5 N sodium chloride solution. Ion exchange capacity and water content of the membranes were measured according to conventional methods (based on Cl^- form dry membrane) [24]. Transport number of counter ions was determined by electrodialyzing a 0.5 N sodium chloride solution at 10 mA/cm^2 at 25.0°C for 1 h. The transport number was calculated from the transported chloride ions, which was determined by the Mohr method, and electrical current passed through the membrane, which was measured by a digital coulometer, NDCM-4, Nikko Keisoku Ltd.

The IR spectra of the cross-linked membrane and the membrane reacted with 4-vinylpyridine were measured by the ATR method using FTIR spectrophotometer, Shimadzu FT-IR-8100A, Shimadzu Corp. to confirm the formation of pyridinium groups in the membrane and polymerization of 4-vinylpyridine.

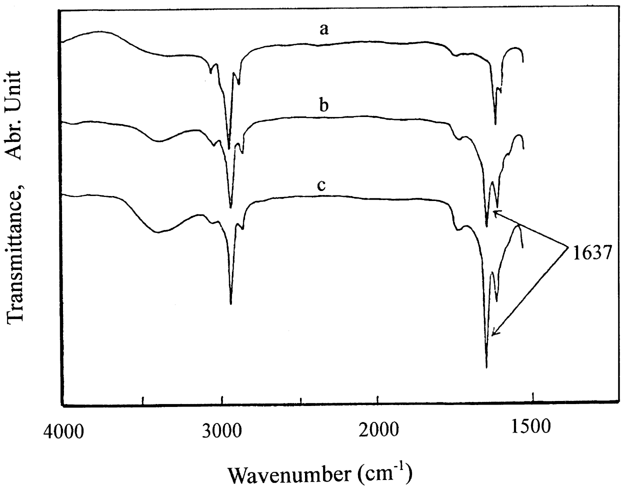

Fig. 1. ATR spectra of the copolymer membrane and the membrane aminated with 4-vinylpyridine. (a) Cross-linked membrane (crosslinkage: 10%) (b) aminated for 4 h (c) aminated for 48 h. The cross-linked membrane was immersed in a 30 wt.% 4-vinylpyridine methyl alcohol solution at 25.0° for different periods.

2.5. Measurements of diffusion coefficients of glucose and urea

To estimate the change in pore size of the membranes by amination with 4-vinylpyridine and polymerization of 4-vinylpyridine, the diffusion coefficients of glucose and urea, which are neutral molecules, were measured using a two compartment cell at 25.0°C. After an aqueous 2.0 mol/l glucose or urea solution had filled the concentrated compartment ($250\ \mathrm{cm}^2$) and pure water ($120\ \mathrm{cm}^2$) the dilute compartment, diffusion dialysis of the solutes was carried out for 24 h and more under vigorous agitation (1500 ± 100 rpm). The permeated glucose or urea into the pure water was analyzed by HPLC (Hitachi L-6000) and the diffusion coefficient, D, was calculated by the following equation:

$$D = \frac{\Delta m}{At\delta(C_C - C_D)},$$

where Δm is the permeated equivalent of glucose or urea, A the effective membrane area (20 cm), t the diffusion time (sec), C_C the average concentration of the concentrated compartment ($\mathrm{eq./cm}^3$), C_D the average concentration of the dilute compartment ($\mathrm{eq./cm}^3$) and δ thickness of the membrane (cm).

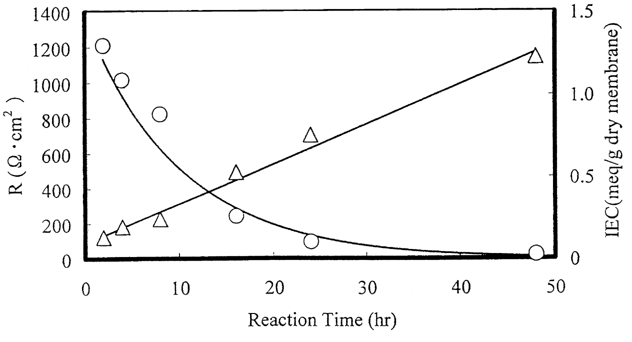

Fig. 2. Change in ion exchange capacity and electrical resistance of the copolymer membrane (crosslinkage: 10%) with reaction time of 4-vinylpyridine. ○: electrical resistance; △: ion exchange capacity. The copolymer membrane was immersed in a 30 wt.% 4-vinylpyridine methyl alcohol solution at 25.0° for different period. Electrical resistance was measured after equilibration with 0.5 N sodium chloride solution.

3. Results and discussion

3.1. Amination of the cross-linked membranes with 4-vinylpyridine

The amination of chloromethyl groups in cross-linked membranes with 4-vinylpyridine is thought to be restricted compared to the reaction of 4-vinylpyridine with alkyl halide in solution. Fig. 1 shows the ATR spectra of the surface of the cross-linked membrane (crosslinkage: 10%) and the same membrane reacted with 4-vinylpyridine. A characteristic peak at $1637\ \mathrm{cm}^{-1}$ was attributed to quaternized 4-vinylpyridine groups and probably arises from stretching vibration of C=C and C=N bonds in pyridine ring. The absorbance at $1637\ \mathrm{cm}^{-1}$ increased with an incremental increase in the 4-vinylpyridine reaction time. However, the pendant vinyl groups in 4-vinylpyridine could not be assigned by the ATR. From these measurements, it can be seen that 4-vinylpyridine reacted with the chloromethyl groups of the cross-linked membrane and polymerized in the membrane matrix.

First of all, the effect of an inhibitor, *p*-*t*-butyl catechol, which was contained in 4-vinylpyridine, on the membrane properties upon the polymerization of 4-vinylpyridine was examined though the presence of the inhibitor is thought not to affect polymerization as a result of the ionic reaction. The anion exchange membranes were prepared using distilled 4-vinylpyridine and without distillation, which contained 3000 ppm of the inhibitor (the membranes were immersed in a 30 wt.% 4-vinylpyridine methyl alcohol solution for various periods and then immersed in 1.0 N trimethylamine solution). There was no appreciable difference between electrical resistance of the membranes prepared with the distilled monomer and that without distillation when the reaction time was changed from 2 to 48 h.

Fig. 2 shows the changes in electrical resistance and ion exchange capacity of the cross-linked membranes (crosslinkage: 10%) with reaction time of 4-vinylpyridine (the membranes did not react with trimethylamine). The ion exchange capacity of the membranes increased linearly and electrical resistance decreased steeply with increasing reaction time. Even in 2 h reaction, electrical resistance decreased by about $1200\ \Omega\ \mathrm{cm}^2$ from an insulator though ion exchange capacity was extremely low. This suggests

Table 1
Characteristics of anion exchange membranes prepared in this work

Name	A-1[a]	A′-1[b]	A-2[a]	A′-2[b]	A-3[a]	A′-3[b]
Crosslinkage(%)[c]	10	10	14	14	20	20
Electrical Resistance (Ω cm^2)[d]	1.5	15.5	2.5	162.8	3.2	458.5
Transport Number[e]	>0.98	>0.98	>0.98	>0.98	>0.98	>0.98
Ion Exchange Capacity[f]	2.20	1.22	1.95	0.64	1.73	0.42
Water Content[g]	29.1	10.5	22.8	7.1	17.9	5.5
Thickness (mm)	0.132		0.127		0.111	

[a] Cross-linked copolymer membranes were reacted with trimethylamine by immersing the membranes in 1.0 N trimethylamine acetone (25 wt.%) and water (75 wt.%) mixed solution for 24 h at 25.0°C.

[b] 4-vinylpyridine was reacted with the cross-linked copolymer membranes by immersing the membranes in 30% 4-vinylpyridine methyl alcohol solution for 48 h at 25.0°C.

[c] Crosslinkage of the membranes: [0.55 × (divinylbenzene/(chloromethylstyrene + divinylbenzene)] × 100.

[d] Ω cm^2, measured with 1000 Hz AC at 25.0°C after equilibration with 0.5 N sodium chloride solution.

[e] Measured by electrodialysis of 0.5 N sodium chloride solution at 10 mA/cm^2 for 1 h.

[f] In meq/g-Cl$^-$ form dry membrane.

[g] In (g H_2O/g-Cl$^-$ form dry membrane) × 100.

that the cross-linked membrane swelled with methyl alcohol and then 4-vinylpyridine penetrated in the membrane matrix and reacted with chloromethyl groups of not only membrane surfaces but also those of the inner part of the membrane. About 56% of the chloromethyl groups of the cross-linked membrane were aminated with 4-vinylpyridine for 48 h reaction. Table 1 shows the characteristics of the anion exchange membranes with different crosslinkage when the copolymer membranes were aminated with trimethylamine (A-1, A-2 and A-3 membranes) or the membranes did with only 4-vinylpyridine (A′-1, A′-2 and A′-3 membranes). In general, because trimethylamine reacts quantitatively with chloromethyl groups of the cross-linked polymer, the ion exchange capacity of the A-1, A-2 and A-3 membranes agreed with the amount of chloromethyl groups in the membranes (calculated from the monomer ratio in the membranes). However, amination of chloromethyl groups with 4-vinylpyridine became difficult with increasing crosslinkage of the membranes because of the increase in difficulty in penetrating the monomer through highly cross-linked polymer network. In this reaction, the copolymer membrane is thought to change a ladder-like polymer, of which one polymer was cross-linked. The formed ladder-like polymer network on the membrane surfaces is thought to disturb migration of 4-vinylpyridine in the inner part of the cross-linked membrane. At the same time, it was reported that when 4-ethylpyridine reacted with chloromethyl groups of the copolymer membrane (crosslinkage: 10%) for severe conditions, the ion exchange capacity attained 1.82 meq./g-dry membrane (though ion exchange capacity of the same membrane reacted with trimethylamine was 2.25 meq./g-dry membrane) [25]. Bulky tertiary amines are difficult to react with chloromethyl groups of the cross-linked membranes. Ion exchange capacity of the membranes aminated with 4-vinylpyridine was therefore low and the electrical resistance of the membranes was extremely high in the highly cross-linked membranes in spite of 48 h reaction. It is well known that the copolymer of chloromethylstyrene and divinylbenzene distributes in the membranes forming micro-domain as a result of less compatibility with added polymers such as acrylonitrile–butadiene rubber and poly(vinyl chloride) fabric [26]. This means that the ladder-like polymer was formed in the domain after migrating through the membrane matrix.

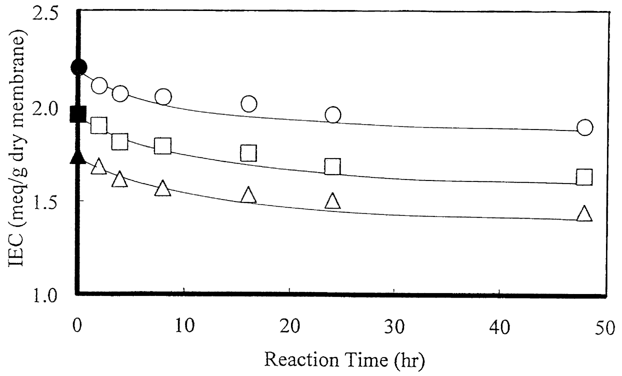

Fig. 3. Change in ion exchange capacity of the anion exchange membranes with reaction time. ○: crosslinkage, 10%; □: crosslinkage, 14%; △: crosslinkage: 20%. After the copolymer membranes had been immersed in a 30 wt.% 4-vinylpyridine methyl alcohol solution for various periods, the membranes were reacted with trimethylamine (24 h, at 25.0°C). Closed marks: anion exchange membranes reacted with only trimethylamine.

Fig. 3 shows the change in the ion exchange capacity of the anion exchange membranes with reaction time when the membranes with different crosslinkage were reacted with 4-vinylpyridine for various periods and then immersed in trimethylamine solution for 24 h. The ion exchange capacity of the membranes reacted with 4-vinylpyridine decreased with increasing reaction time with 4-vinylpyridine after the reaction with trimethylamine though the ion exchange capacity of the membranes increased remarkably compared with A′-1, A′-2 and A′-3 membranes. As 4-vinylpyridine is a bulky amine and the polymer structure of the membranes

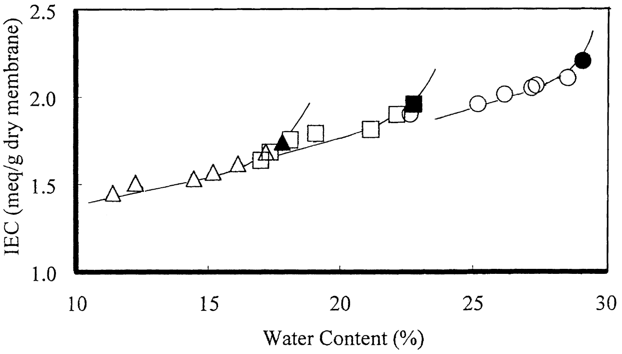

Fig. 4. Relationship between ion exchange capacity and water content of the anion exchange membranes. ○: crosslinkage, 10%; □: crosslinkage, 14%; △: crosslinkage: 20%. After the copolymer membranes had been immersed in a 30 wt.% 4-vinylpyridine methyl alcohol solution for various periods, the membranes were reacted with trimethylamine (24 h, at 25.0°C). Closed marks: anion exchange membranes reacted with only trimethylamine.

changed into the ladder-like polymer by the amination, the reaction of trimethylamine with the remaining chloromethyl groups in the membranes would be sterically restricted.

Fig. 4 shows relationship between ion exchange capacity and water content of the anion exchange membranes when the copolymer membranes with different crosslinkage were reacted with 4-vinylpyridine and then trimethylamine. Though water content of the membranes decreased with decreasing ion exchange capacity, the magnitude of decrease was more than the decrease in the ion exchange capacity in the reaction with 4-vinylpyridine (closed marks show the value of the membrane reacted with only trimethylamine). This provided the increase in the fixed ion concentration (ion exchange capacity/water content) to the membranes. For example, the fixed ion concentration of the A-2 membrane was 8.47 m and that of the A′-2 membrane after reaction with trimethylamine was 9.52 m, and also those of the A-3 membrane and the A′-3 membrane reacted with trimethylamine were 9.72 and 12.50 m, respectively. The formation of the ladder-like polymer in the cross-linked membranes caused water content of the membrane to decrease. This is thought to be because of the introduction of 4-vinylpyridine unit, which is more hydrophobic than trimethylamine, into the membrane.

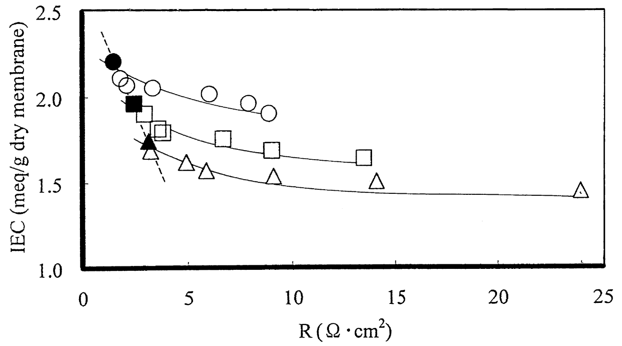

Fig. 5. Relationship between ion exchange capacity and electrical resistance of the anion exchange membranes. ○: crosslinkage, 10%; □: crosslinkage, 14%; △: crosslinkage: 20%. After the copolymer membranes had been immersed in a 30 wt.% 4-vinylpyridine methyl alcohol solution for various period, the membranes reacted with trimethylamine. Electrical resistance was measured using 0.5 N sodium chloride solution at 25.0°C. Closed marks: anion exchange membranes reacted with only trimethylamine.

Basically, conductivity of the ion exchange membrane increases with increasing ion exchange capacity of the membranes [27,28]. Fig. 5 shows relationship between the electrical resistance of the anion exchange membranes and their ion exchange capacity when copolymer membranes with different crosslinkage reacted with 4-vinylpyridine and then trimethylamine. Dotted line (closed marks) is the relationship of the membranes reacted with only trimethylamine (the ion exchange capacity decreased with increasing content of divinylbenzene because the ratio of chloromethylstyrene to total vinyl monomers decreased in the membrane). Naturally electrical resistance of the membranes linearly increased with decreasing ion exchange capacity. However, the electrical resistance increased remarkably in the membranes aminated with 4-vinylpyridine and then trimethylamine in spite of minute decrease in the ion exchange capacity (in the membranes reacted with 4-vinylpyridine for longer period). It should be noted that the electrical resistance of the membrane in which the crosslinkage is 20% markedly increased by amination with both 4-vinylpyridine and trimethylamine (increased from 3.2 to 24.1 Ω cm^2 with the decrease from 1.73 meq/g Cl$^-$ form dry membrane to 1.44 meq/g Cl$^-$ dry membrane). Similarly, the relationship between water content of the anion exchange membranes and electrical resistance of the membranes is shown in Fig. 6. Naturally, electrical resistance increases with decreasing water content because ions become difficult to migrate through the membrane. Dotted line shows the change in electrical resistance of the anion exchange membranes aminated with only trimethylamine with water content. Electrical resistance increased only to a smaller extent with decreasing water content. The anion exchange membranes reacted with both 4-vinylpyridine and trimethylamine showed extremely high electrical resistance with a small change in water content. These results suggest that migration of chloride ions through the membrane was extremely restricted by the formation of the ladder-like polymer in the membranes. The effect of the ladder-like polymer in the membrane on the electrical resistance was remarkable with increasing content of divinylbenzene in the membranes as shown in Fig. 6. It was reported that when the copolymer membranes of chloromethylstyrene and divinylbenzene were reacted with 4,4′-bipyridine, both pyridine units reacted with chloromethyl groups with increasing crosslinkage of the copolymer membranes (ratio of quaternary ammonium groups to total anion exchange capacity increased with increasing crosslinkage) [29]. The crosslinking degree of the micro-domain in the membranes is thought to markedly affect the reaction with 4-vinylpyridine and therefore electrical resistance of the membranes. In

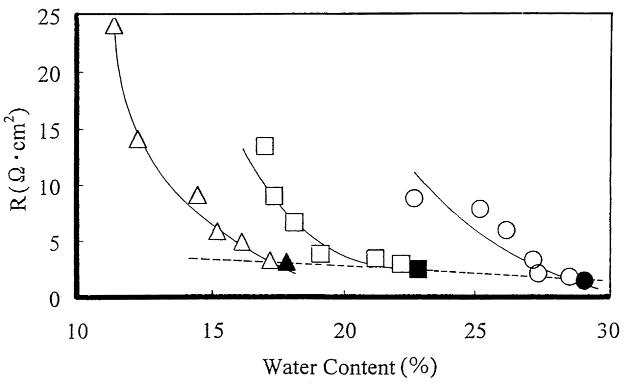

Fig. 6. Change in electrical resistance of the anion exchange membranes with their water content. ○: crosslinkage, 10%; □: crosslinkage, 14%; △: crosslinkage: 20%. After the copolymer membranes had been immersed in a 30 wt.% 4-vinylpyridine methyl alcohol solution for various period, the membranes were reacted with trimethylamine. Water content and electrical resistance were measured after equilibration with 0.5 N sodium chloride solution. Closed marks: anion exchange membranes reacted with only trimethylamine.

highly cross-linked membrane, much ladder-like polymer would be formed in the domain.

The obtained anion exchange membranes are thought to have tight structure from abnormal behavior in the relationship among ion exchange capacity, water content and electrical resistance compared with anion exchange membranes aminated with trimethylamine. Thus, diffusion coefficients of neutral molecules, urea and glucose, were evaluated. The diffusion coefficients of glucose through the A-1, A-2 and A-3 membranes were 5.75×10^{-7}, 1.02×10^{-7} and 0.57×10^{-7} cm/sec, respectively. However, glucose was not detected in dialysate (in pure water) even in diffusion dialysis for 168 h using the anion exchange membranes (A″-1, A″-2 and A″-3) prepared by the reaction of the A′-1, A′-2 and A′-3 membranes with trimethylamine. Diffusion coefficient of urea (Stokes radius: 3.3 Å) was then measured using the A-1, A-2 and A-3 membranes and the membranes reacted with 4-vinylpyridine and then trimethylamine (Fig. 7). The diffusion coefficients through the A-1, A-2 and A-3 membranes naturally decreased with increasing crosslinkage of the membranes and those of the membranes reacted with 4-vinylpyridine and then trimethylamine were extremely low, which could not be attained by the increase in crosslinkage of the membranes.

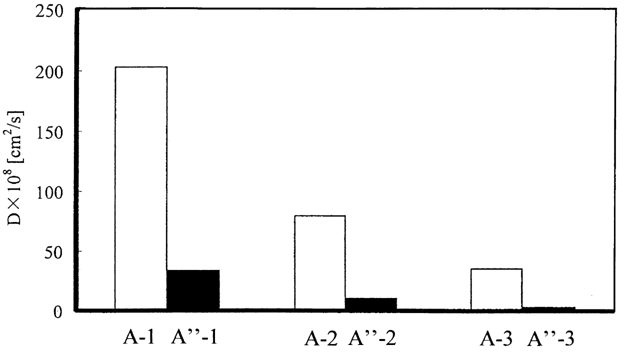

Fig. 7. Diffusion coefficient of urea through the anion exchange membranes reacted with 4-vinylpyridine and that of the membranes without 4-vinylpyridine. □: A-1, A-2, A-3 (immersed in 1.0 N trimethylamine acetone (25%) and water (75%) mixed solution for 24 h at 25.0°C). ■: A″-1, A″-2, A″-3 (after immersed in 30 wt.% 4-vinylpyridine methyl alcohol solution for 48 h, the membranes were reacted with trimethylamine). Diffusion coefficient of urea was measured using 2.0 N urea solution and pure water for 24 h at 25.0°C.

The electrical resistance of the obtained membranes showed different behavior of the anion exchange membranes aminated with trimethylamine with respect to ion exchange capacity and water content, which means that the migration behavior of chloride ions through the membranes would be different from the anion exchange membranes aminated with trimethylamine. It is expected that the transport numbers of various anions relative to chloride ions is different from those of the anion exchange membranes aminated with trimethylamine. Transport properties of the membranes will be reported in the following article.

4. Conclusions

The membranes prepared from chloromethylstyrene and divinylbenzene could be aminated with 4-vinylpyridine though the reaction speed was slow and 4-vinylpyridine polymerized in the membrane matrix to form a ladder-like polymer. After the amination of the membranes with 4-vinylpyridine, the membranes reacted with trimethyamine to aminate remaining chloromethyl groups. The obtained anion exchange membranes showed different behavior from anion exchange membranes aminated with trimethylamine with respect to relationship among electrical resistance, water content and ion exchange capacity. Permeation of chloride ions through the membranes became remarkably difficult with a small decrease in ion exchange capacity and water content. This is thought to be because of the formation of the ladder-like polymer in the membrane matrix and the introduction of pyridine unit in the membrane. Thus, membrane structure became tight.

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