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Electrodialytic transport properties of cation exchange membranes prepared from poly(vinyl alcohol) and poly(vinyl alcohol-*co*-2-acrylamido-2-methylpropane sulfonic acid)

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ABSTRACT

In this study, cation exchange membranes with an interpenetrating network structure were prepared by blending poly(vinyl alcohol) (PVA) and a polyanion, poly(vinyl alcohol-*co*-2-acrylamido-2-methylpropane sulfonic acid). The membranes obtained were physically cross-linked by annealing them and chemically cross-linked by reaction with various concentrations of glutaraldehyde (GA) aqueous solutions. The effect of the cross-linking conditions and polyanion content on the ionic transport properties through the membranes was investigated. The water content of the membranes increases with increasing polyanion content and with decreasing GA concentration. The charge density of the membranes increases with increasing polyanion content and have a maximum value. The maximum value increases with increasing GA concentration. The dynamic transport number of the membranes increases with increasing polyanion content and with increasing GA concentration while the membrane resistance increases with increasing GA concentration. These results indicate the transport properties of the PVA-based cation exchange membranes can be controlled by changing the polyanion content and the cross-linking conditions. The membranes will have potential application in the desalination of salt water.

Keywords: Poly(vinyl alcohol); Cation exchange membrane; Cross-linking conditions; Ionic transport property

1. Introduction

Ion exchange membranes for electrodialysis have been applied to various industrial fields [1]: the separation of environmental polluting metal ions from hard water [2], a separator for electrolysis such as in chlor-alkali production [3], solid polymer electrolytes for fuel cells, and the electrodialytic concentration or desalination of electrolyte solutions [4], etc. Demands of ion exchange membranes for electrodialysis are high counter-ion permselectivity, low membrane resistance, and low cost. At present, almost all of the commercially-available cation exchange membranes for electrodialysis have styrene-*co*-divinylbenzene matrices. The drawbacks of this type of membrane are that it is difficult to control the membrane structure because its copolymerization and cross-linking processes occur at same time, and the high cost of preparing the membranes. Recently, a lot of study on preparation of novel ion exchange membranes has

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been reported to overcome these problems. For example, Choi et al. [5] controlled the fixed charge distribution of an ion exchange membrane by plasma-induced graft polymerization onto glycidylmethacrylate-*g*-polypropylene membranes. Miyazawa et al. prepared cation exchange membrane with one-step reaction by means of electron-beam induced graft polymerization of sodium styrene sulfonate onto a nylon-6-film [6].

Another method of preparing an ion exchange membrane is to mix water-soluble base polymers and a polyelectrolyte, and then cross-link the base polymer. The membrane obtained has a semi-interpenetrating network (semi-IPN) structure in which polyelectrolyte chains are immobilized in a polymer cross-linked network matrix. The ion exchange capacity of the membranes can be controlled easily by changing the polymer ratio of water-swollen base polymer to polyelectrolyte. Poly(vinyl alcohol) (PVA) is one of the most popular polymers that have been used as a membrane matrix. PVA is a polyhydroxy polymer that has been studied intensively because of its good film forming and physical properties, high hydrophilicity, processability, biocompatibility, and good chemical resistance [7–10]. Since PVA is a crystalline polymer, its crystalline region becomes a possible physical cross-link point. Hence, self-standing membranes can be easily prepared by casting PVA solution on a glass plate. The degree of cross-linking can be controlled easily by annealing conditions, because the number of cross-link points increases with increasing annealing temperature [11]. PVA chains can also be chemically cross-linked using cross-linking agents such as glutaraldehyde (GA). Hence, the water content of the membrane, which plays an important role in permselectivity in an ion exchange membrane, can be easily controlled by annealing an as-cast membrane and/or cross-linking it by using cross-linking agents. Cation exchange membranes with a semi-IPN structure have been prepared by blending PVA and a polyanion such as poly(styrene sulfonic acid) [12], poly(acrylic acid) [13], poly-(styrene sulfonic acid-*co*-maleic acid) [14], poly (vinyl alcohol-*co*-2-acrylamido-2-methylpropane sulfonic acid) [15,16], and by using PVA, sulfosuccinic acid [17], etc.

In this paper, cation exchange membranes with a semi-IPN structure have been prepared by blending PVA and poly (vinyl alcohol-*co*-2-acrylamido-2-methylpropane sulfonic acid) with changing polyanion content, and by cross-linking PVA chains under various conditions with GA. We have investigated the effect of the cross-linking conditions and polyanion content on the membrane ionic transport properties: the charge density, membrane resistance and the transport number.

2. Experimental

2.1. Preparation of cation exchange membranes

An aqueous solution of a mixture of PVA (Kuraray Co., Ltd.) and poly (vinyl alcohol-*co*-2-acrylamido-2-methyl propane sulfonic acid) (AP-4: Kuraray Co., Ltd.) was cast on a plastic plate and dried over a hot stage (NISSIN, NH-45N) at 50°C for overnight to afford a self-standing membrane (thickness ca. 0.1 mm). The weight percentage of AP-4 to PVA in the resulting dried membranes was modified to control the ion exchange capacity of the membranes. The membranes were annealed at 180°C for 30 min. under vacuum to induce physical cross-linking between PVA chains. The membranes were chemically cross-linked by immersing the membranes in an aqueous solution of various concentrations of GA, 0.05 mol/dm^3 H_2SO_4 (pH 1), and 2.0 mol/dm^3 Na_2SO_4 at 25°C for 24 h.

2.2 Measurement of membrane water content

The water content, H, was measured as follows. Membranes were weighed in the dry state after the annealing treatment, and cross-linked chemically. The cross-linked membranes were immersed in deionized water at 25°C for 7 d. The membranes were removed from the water, dabbed with filter paper to remove excess water on the membrane surfaces, and weighed in the wet state. The volumetric water content is calculated from the weights in the wet state, W_w, and in the dry state, W_d, as:

$$H \equiv (W_w - W_d)/1.0/((W_w - W_d)/1.0 + W_d/1.3), \tag{1}$$

where 1.0 and 1.3 are the densities of water and PVA [18], respectively.

2.3. Determination of membrane charge density

Membrane charge density is one of the most important factors for estimating the permselectivity between ions with different sign and valence through an ion exchange membrane. In order to estimate the charge density, the membrane potentials, $\Delta\phi$, were measured by using an acrylic plastic cell of two parts separated by a membrane, as shown in Fig. 1. One chamber of the cell was filled with KCl solution of various concentrations, C_o, while the other chamber was filled with KCl solutions with concentration, C_d, which is five times higher than those in the first chamber ($r = C_d/C_o = 5$). The membrane potential between the solutions in the two chambers was measured at 25.0 ± 0.5°C using Ag/AgCl electrodes (TOA HS-205C) with a salt bridge (3.0 mol/dm^3 KCl) and a voltmeter. The membrane charge density, C_x, was calculated from the measured membrane potential using the following equation [18,19]:

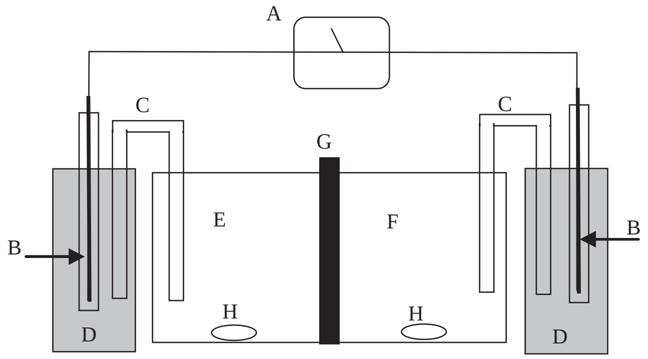

Fig. 1. Apparatus for membrane potential measurement. A, voltmeter; B, Ag/AgCl electrode; C, KCl salt bridge; D, saturated KCl solution; E, high concentration of KCl solution; F, low concentration of KCl solution; G, sample membrane; H, magnetic stirrer tip. The effective area of the cell is 7.06 cm^2.

$$\Delta\varphi = -\frac{RT}{F}\ln\left(r\cdot\frac{\sqrt{C_x^2+(2C_0)^2}-C_x}{\sqrt{C_x^2+(2rC_0)^2}-C_x}\right) - \frac{RT}{F}W\ln\left(\frac{\sqrt{C_x^2+(2rC_0)^2}-C_xW}{\sqrt{C_x^2+(2C_0)^2}-C_xW}\right), \tag{2}$$

where $W \equiv (\omega_K - \omega_{Cl})/(\omega_K + \omega_{Cl})$; ω_K and ω_{Cl} are the K^+ and Cl^- ion mobilities in a membrane, respectively; F, R and T are the Faraday constant, the gas constant and the absolute temperature, respectively. Parameters W and C_x are adjusted so that the left-hand side of Eq. (2) fits the experimental data of $\Delta\phi$ at various KCl concentrations.

2.4. Measurement of membrane resistance

The electric resistance through the membranes was measured by using a hand-made acrylic plastic cell of two parts separated by a membrane, as shown in Fig. 2, with a LCR meter at 10 KHz AC (A&D corp. Ltd. AD-5827). After 0.5 mol/dm^3 NaCl solution was poured into the two cell compartments, the electrical resistance, R_o, was measured at 25.0 ± 0.5°C with a water bath. And then, after a sample membrane was set in the cell, the resistance, R_s, was measured again under the same conditions. The difference between R_s and R_o gives the membrane resistance, R_m.

2.5. Measurement of transport number

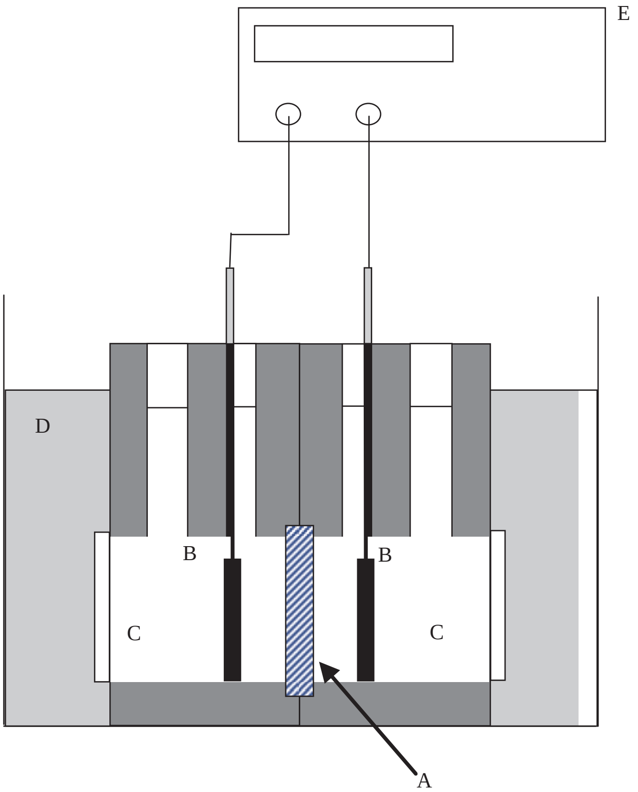

Fig. 2. Apparatus for membrane resistance. A, sample membrane; B, Pt electrodes; C, NaCl solution; D, water bath; E, LCR meter. The effective area of the cell is 1.0 cm^2.

There are two types of transport numbers; one is so-called static state transport number and the other dynamic state transport number. The static state transport number of the counter-ion in the membranes is calculated from membrane potential data in a diffusion dialysis system. The membrane potentials were measured by using the same apparatus as the measurement of the charge density. 0.5 and 2.5 mol/dm^3 NaCl were used as the measurement solutions. The static state transport number, t_{s+}, for each membrane was calculated by the following equation:

$$E_m = RT/F/(2t_{s+} - 1)\ln(a_1/a_2), \tag{3}$$

where E_m, a_1 and a_2 are the membrane potential, the activity of the dilute and concentrated side solutions in cell compartments, respectively.

To determine the dynamic state transport number, t_{d+}, of the membrane, electrodialysis was carried out by using a hand-made acrylic plastic cell of two parts separated by a membrane, as shown in Fig. 3 at a current density of 10 mA/cm at 25°C for 75 min. (360°C). The amount of transported ions passed through the membrane during the electrodialysis was measured with using a conductivity meter (HORIBA 3552-10D). The dynamic state transport number was obtained in terms of the following equation:

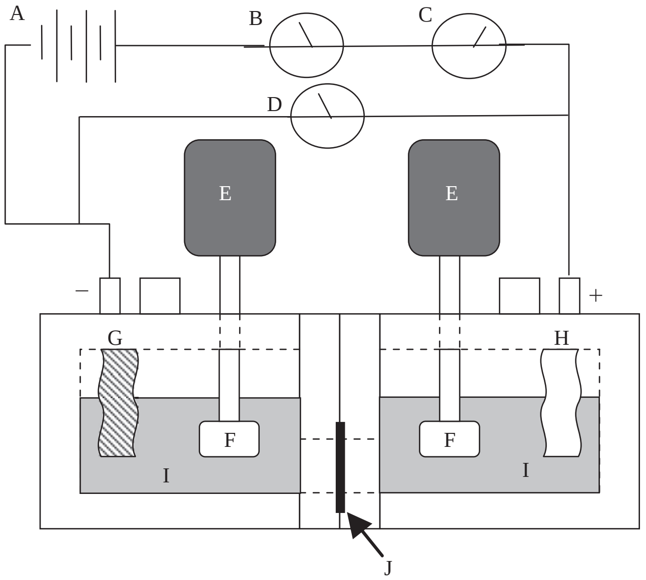

Fig. 3. Apparatus for measuring dynamic state transport number. A, power supply; B, ampere meter; C, coulomb meter; D, voltmeter; E, motor; F, stirrer; G, cathode electrode; H, anode electrode; I, 0.5 mol/dm^3 NaCl solution; J, sample membrane. The effective area of the cell is 8.0 cm^2.

$$t_{d+} = \Delta CVF/Q \tag{4}$$

where ΔC, V, Q are the concentration change of transported ions, the amount of electricity passed through the membrane during the electrodialysis and the volume of the measurement solution, respectively.

3. Results and discussion

3.1. Water content as a function of polyanion content

The water content of an ion exchange membrane is an important property of the membrane because both the charge density and electric resistance of the membrane depend on the water content. Fig. 4 shows the water content of the cation exchange membranes as a function of polyanion content. The water content increases with increasing polyanion content because the osmotic pressure in the membranes increases with increasing number of charged groups in the membranes. The water content decreased with increasing GA concentration because the membrane has much dense structure after cross-linked with high concentration of GA solution.

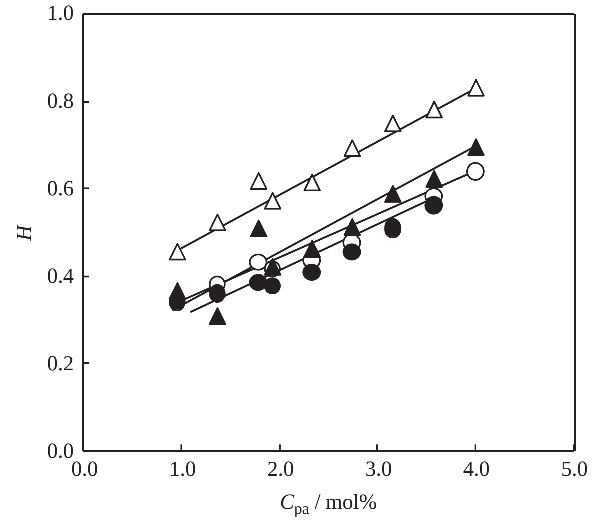

Fig. 4. Water content, H, of the cation exchange membranes as a function of polyanion content, C_{pa}. Annealing temperature: 180°C. Concentration of GA solution: open triangles, 0.01 vol.%; closed triangles, 0.05 vol.%, open circles, 0.075 vol.%, and closed circles, 0.15 vol.%, respectively.

3.2. The charge density of the membranes as a function of polyanion content

The charge density is also one of the important properties of an ion exchange membrane. The higher charge density a membrane has, the higher counter-ion permselectivity it has. Fig. 5 shows the charge density of the membranes as a function of polyanion content. The charge density increases with polyanion content, and has a maximum value. The charge density is proportional to the division of ion exchange capacity, IEC, by water content, H:

$$C_x \propto \mathrm{IEC}/H \tag{5}$$

The ion exchange capacity is proportional to polyanion content. Hence, at the first stage of charge

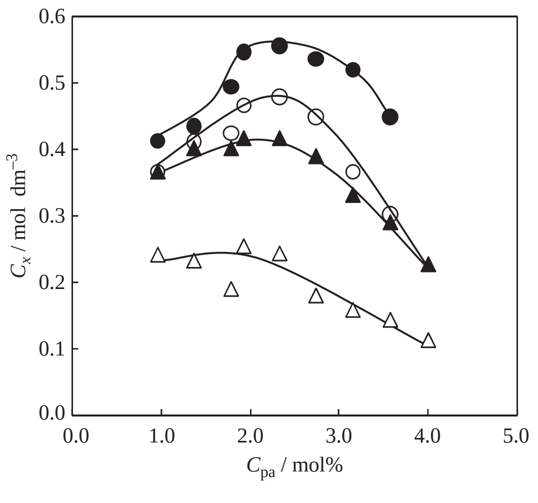

Fig. 5. Charge density, C_x, of the cation exchange membranes as a function of polyanion content, C_{pa}. Markers in this figure are the same as those in Fig. 4.

density–polyanion content curves, the charge density increases with increasing polyanion content because of the increase in the ion exchange capacity. At the region of high polyanion content (more than 2.3 mol%), the effect of the increase in the water content on the charge density is larger than that of the increase in the ion exchange capacity. Hence, the charge density decreases after it reached a maximum value. The maximum value of the charge density increases with increasing GA concentration because the water content decreases with increasing GA concentration. The highest value of the charge density is 0.56 mol/dm^3 at the membrane of polyanion content = 2.3 mol% and GA concentration = 0.15 vol.%.

3.3. Membrane resistance as a function of polyanion content

The membrane resistance is an important parameter for an energy-saving electrodialysis process. Fig. 6 shows the membrane resistance as a function of polyanion content. The membrane resistance decreases with increasing polyanion content, because the water content increases with increasing polyanion content. The resistance increases with increasing GA concentration because of the decrease in the water content. This means that the membrane resistance in this study can be controlled by changing the water content. The membrane of polyanion content = 4.0 mol% and GA concentration = 0.01 vol.% has the lowest membrane resistance (1.0 Ω cm^2) in all the membranes.

3.4. Relationship between dynamic state transport number and polyanion content

The dynamic state transport number relates to the counter-ion permselectivity of an ion exchange membrane in a practical electrodialysis process. A membrane with 1.0 of the transport number can permeate only the counter-ions in an electrodialysis system. Fig. 7 shows the dynamic state transport number of the cation exchange membranes as a function of the polyanion content. The transport number increases with increasing polyanion content, and then decreases after it has reached a maximum value when polyanion content is almost equal to 2.3 mol%. As mentioned above, it is because the charge density has a maximum value at the same value of polyanion content. These results indicate that the transport number of the membranes can be controlled by changing the cross-linking conditions.

3.5. Relationship between dynamic state transport number and static state transport number

The transport number depends on the ratio of the concentration of ion exchange group in the membrane (charge density of the fixed charged groups) to the concentration of outer electrolyte solution. There are two methods to measure the transport number: calculation from the membrane potential (static state transport number) in a diffusion dialysis system and direct measurement in electrodialysis system (dynamic state

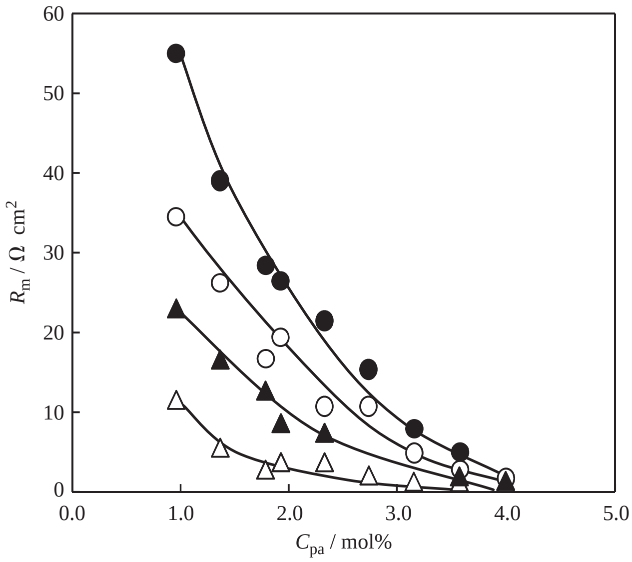

Fig. 6. Membrane resistance, R_m, of the cation exchange membranes as a function of polyanion content, C_{pa}. Markers in this figure are the same as those in Fig. 4.

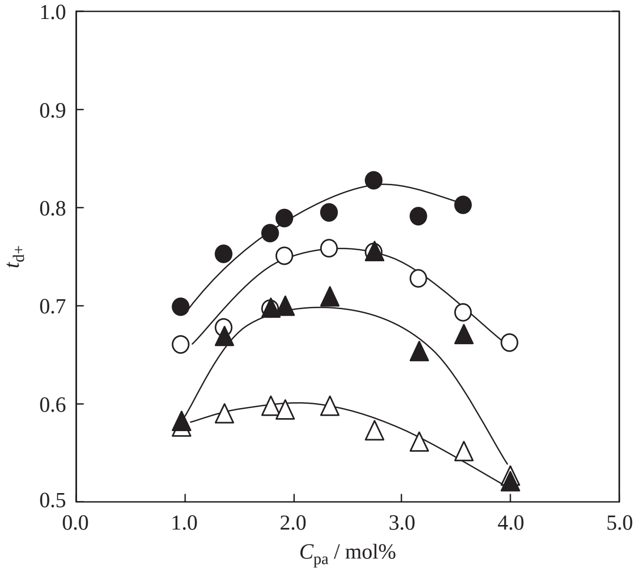

Fig. 7. Dynamic state transport number, t_{d+}, of the cation exchange membranes as a function of polyanion content, C_{pa}. Markers in this figure are the same as those in Fig. 4.

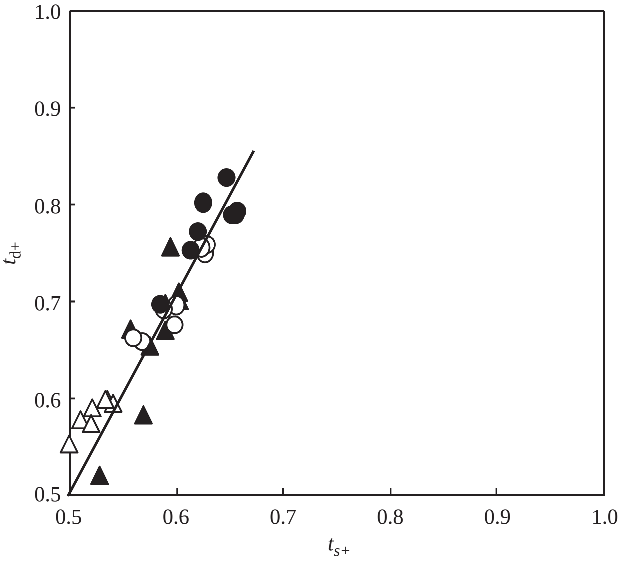

Fig. 8. Dynamic state transport number, t_{d+}, of the cation exchange membranes as a function of static state transport number, t_{s+}. Markers in this figure are the same as those in Fig. 4.

transport number). The former is an easy method to measure. The later will give a more practical value. Fig. 8 shows the dynamic state transport number as a function of the static state transport number of the membranes. The dynamic state transport number of all the membranes is larger than the static state transport number. This is due to the fact that the static state transport number measured by membrane potential [1] neglects water transport through the membrane. The value of dynamic state transport number will be able to estimate from that of static state transport number.

3.6. Relationship between membrane resistance and dynamic state transport number

An ion exchange membrane having both high ion permselectivity and low membrane resistance is desirable in electrodialysis processes. Fig. 9 shows the relationship between the membrane resistance and dynamic state transport number of the membranes. A membrane located on the upper left-hand side has high performance for electrodialysis processes. The membrane resistance decreases and the dynamic state transport number increases with increasing polyanion content of the membranes. The transport number of the membrane increased with increasing GA concentration. The dynamic transport number of a commercially-available cation exchange membrane [Neosepta CMX: manufactured by ASTOM Co.] is 0.98 under the same conditions. This means that the PVA-based cation exchange membranes have lower ionic selectivity than CMX membrane at high concentrations of salt solutions.

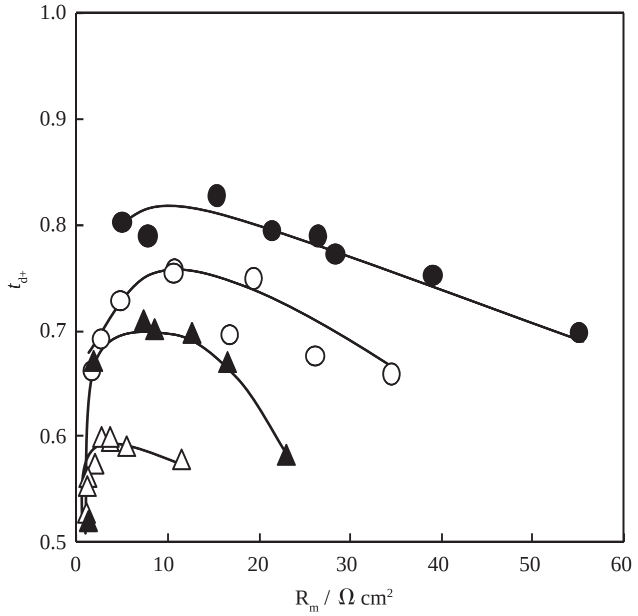

Fig. 9. Dynamic state transport number, t_{d+} of the cation exchange membranes as a function of membrane resistance, R_m. Markers in this figure are the same as those in Fig. 4.

4. Conclusions

In this paper, cation exchange membranes with a semi-IPN structure are prepared by blending PVA and poly (vinyl alcohol-*co*-2-acrylamido-2-methylpropane sulfonic acid: AP-4) with changing AP-4 content, and by cross-linking them under various concentrations of the cross-linker.

The water content of the membranes increases with increasing polyanion content and with decreasing cross-linker concentrations. The charge density of obtained membranes increases with increasing polyanion content of the membranes and have a maximum value. The maximum value of the charge density increases with increasing cross-linker concentration. This means that the charge density of the membranes in this study can be controlled by changing the cross-linking conditions.

The membrane resistances of all the membranes decrease in almost the same trend with increasing water content, which means that the resistance will be estimated from the value of the water content.

The dynamic state transport number increases with increasing polyanion content, and have a maximum value. The dynamic transport number of all the membranes is larger than the static state transport number.

The PVA-based cation exchange membranes can be prepared more cheaply and have higher mechanical strength than commercially-available cation exchange membranes. Although their ionic selectivity at high salt concentrations is inferior to commercial ion exchange membranes, the membranes will have potential application in the desalination of salt water at low concentrations.

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Symbols

a_1, a_2	Activity, mol dm^{-3}
C	Ionic concentration in a solution, mol dm^{-3}
C_{GA}	Concentration of GA solution, vol.%
C_0	KCl concentration in the low-concentration chamber, mol dm^{-3}
C_{pa}	Polyanion content in the membrane, wt.%
C_x	Charge density, mol dm^{-3}
ΔC	The concentration of transported ions passed through the membrane during the electrodialysis, mol dm^{-3}
E_m	Membrane potential, V
F	Faraday's constant, $F = 96484.6$°C/mol
H	Water content
IEC	Ion exchange capacity, meq./g dry membrane
K	Temperature, K
Q	The amount of electricity, C
R	Gas constant, $R = 8.31442$ J/K mol
R_m	Membrane resistance, Ω cm^2, $R_m = R_s - R_o$ Ω cm^2
R_o	Measured resistance without a sample membrane, Ω cm^2
R_s	Measured resistance with a sample membrane, Ω cm^2
r	KCl concentration ratio between the high and low-concentration chambers
T	Absolute temperature, K
t_{d+}	Dynamic state transport number
t_{s+}	Static state transport number
V	The volume of measurement solution, dm^3
W	Mobility difference, $W = (\omega_K - \omega_{Cl})/(\omega_K + \omega_{Cl})$
W_d	Weight in dry state, g
W_w	Weight in wet state, g

Greek symbols

$\Delta\phi$	Membrane potential, V
ω	Ionic mobility, mol m^2/J s

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