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Characterization of hydrophilic hollow fiber membranes prepared from poly(vinyl alcohol)

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ABSTRACT

Hydrophilic hollow fiber membranes were prepared from a aqueous solution of poly(vinyl alcohol) (PVA) by a gel fiber spinning method. In order to control the water content of the hollow fiber membranes, the membranes were cross-linked physically by annealing, and then cross-linked chemically using glutaraldehyde (GA) solutions changing GA concentration. The diameter of the membranes was ca. 1.0 mm and the thickness of the membranes was ca. 100 µm. Permeation experiments were carried out in a diffusion dialysis system: $NaNO_3$ solution/membrane/mixed $NaNO_3$ and NaCl solution to examine ionic permselectivity of the membranes. The flux of both nitrate ions and chloride ions through the membranes decreases with increasing GA concentration. This is due to the fact that membrane water content decreases with increasing GA content. The selectivity coefficient for nitrate ions through the membranes increases with GA content because of the decreasing in the water content. The hollow fiber membrane prepared in this study will have potential application to separation of trace ions in ground water.

Keywords: Poly(vinyl alcohol); Hollow fiber membrane; Permselectivity; Diffusion dialysis

1. Introduction

Hollow fiber membranes have been widely used for various fields such as medical use for hemodialysis, water treatment for purification of wastewater and seawater desalination, etc. [1–5]. There have been many reports on preparation of hollow fiber membranes having high ionic separation performance by changing the hydrophilicity and pore-size of the membranes. However, almost all of hollow fiber membranes have hydrophobic matrix such as polysulufone, polyethersulfone, polyacrylonitrile, polyvinyldene fluoride, etc. It is well known that hydrophilicity of membrane surfaces crucial to reduce membrane fouling [6–14].

Poly(vinyl alcohol) (PVA) is one of the most popular polymers that have been used as a membrane matrix. Since PVA is a crystalline polymer, its crystalline region becomes a possible physical cross-linking point. The cross-linking can be controlled by the annealing conditions, because the number of cross-link points increases with increasing annealing temperature. PVA chains can also be chemically cross-inked using cross-linking agents such as glutaraldehyde (GA). Hence, the water content of the membrane can be easily controlled by changing the conditions of the cross-linking processes. Furthermore, PVA is a hydrophilic polymer. Hence, a hollow fiber membrane prepared from PVA will have anti-fouling property.

Recently, the concentration of harmful ions such as nitrate ions has been greatly increasing in the ground

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water of some parts of European countries and also in Japan due to excessive use of artificial fertilizers and for other reasons [15]. Nitrate ions affect human health e.g. methemoglobinemias, blue baby syndrome and cancer. One of the methods to solve this problem is to remove the anions from groundwater using membrane technologies.

The aim of this study is to prepare a non-porous hydrophilic hollow fiber membranes from PVA. Under various concentrations of GA solution, and to investigate the effect of the GA concentration on the ionic flux and selectivity for nitrate ions in a diffusion dialysis system consisting of PVA hollow fiber membrane and mixed NaCl–$NaNO_3$ solutions.

2. Experimental

2.1. Preparation of hydrophilic hollow fiber membranes

A hydrophilic hollow fiber membrane was prepared from an aqueous solution of a mixture of PVA-124 [poly(vinyl alcohol), Kuraray Co. Ltd.], boric acid [ISHIZUSEIYAKU Ltd] and acetic acid [ISHIZU SEIYAKU Ltd] by a gel spinning method. The hollow fiber membrane obtained was annealed at 160°C for 1010 min. and then cross-linked in an mixed solution of glutaraldehydeGA, 0.1 mol/dm^3 H_2SO_4, and 2.0 mol/dm^3 Na_2SO_4 at 25°C for 24 h. The hollow fiber membrane was immersed in deionized water at 25°C for 7 days.

2.2. Membrane thickness of the hollow fiber membrane

A hollow fiber membrane in swelling state was observed with a laser microscope (KEYENCE, VK-9700). The membrane thickness, inside diameter and outside diameter were measured by the image of the laser microscope. After immersing a sample membrane in deionized water, the sample was fractured in liquid nitrogen and sputtered with gold. The sample membrane in dry state was observed with a scanning electron microscope (SEM) (JEOL JSM-T300) to investigate the membrane morphology.

2.3. Ion permeation experiments

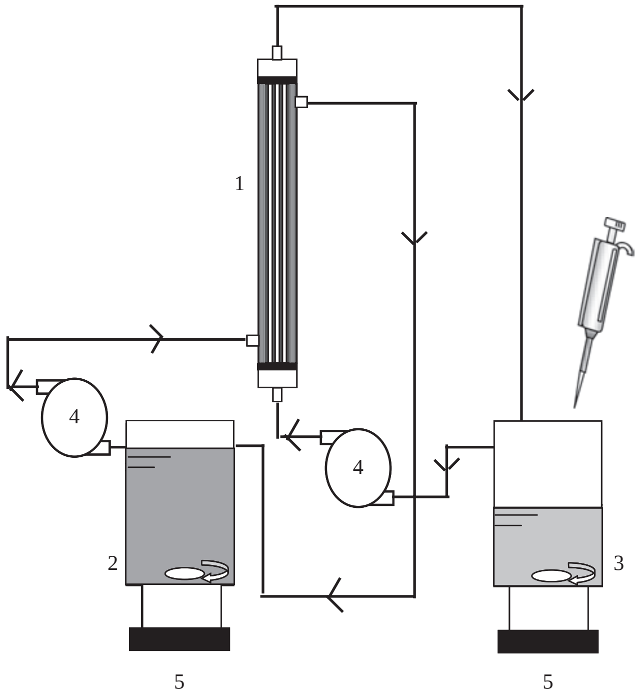


Fig. 1. Apparatus for ion permeation experiments. 1, hollow fiber membrane module; 2, shell solution tank; 3, lumen solution tank; 4, pump; 5, magnetic stirrer. The volume of the lumen side and the shell are 200 and 800 cm^3, respectively.

Ion permeation experiments using an apparatus shown in Fig. 1 were carried out in a diffusion dialysis systems: 3×10^{-4} M $NaNO_3$ (lumen side) / membrane / mixed 3×10^{-4} M $NaNO_3$ and 0.1 M NaCl (shell side). The volume of the lumen solution and the shell solution were 200 cm^3 and 800 cm^3, respectively. The solution in the lumen side was sampled to measure the concentration of nitrate ions and chloride ions with an ion chromatograph (TOHSO CO. IC-8010). The ionic flux of these ions, J_i, was obtained from the slope of their time-concentration curves. The flux of i species ion J_i and selectivity coefficient α were calculated in terms of the following equations:.

$$J_i = (V/S) \times (\Delta C_i/\Delta t), \qquad (1)$$

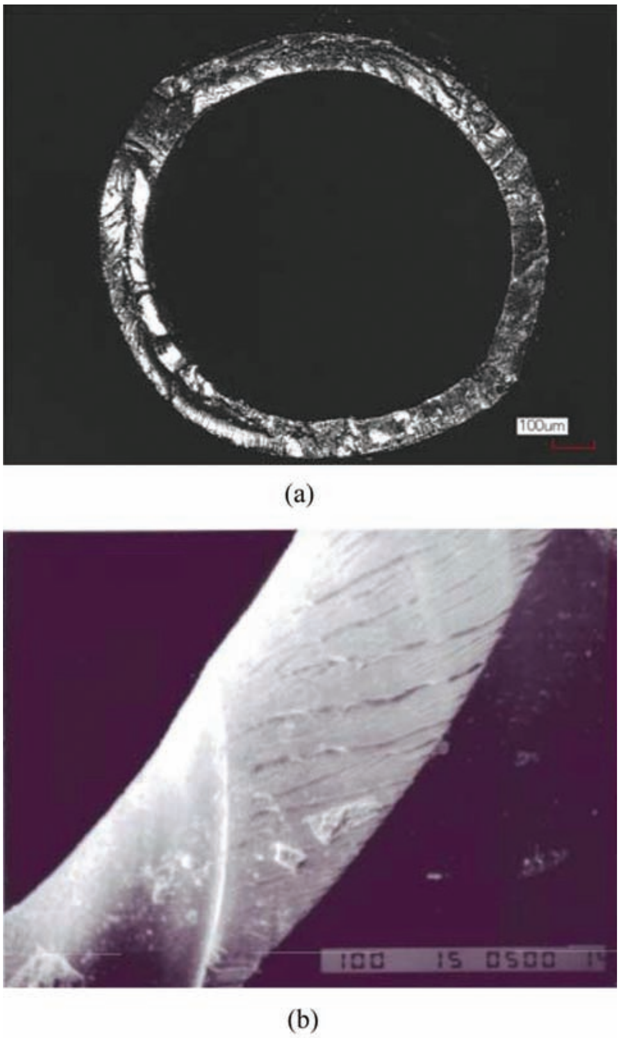
$$\alpha = \frac{J_{NO_3}}{J_{Cl}}, \qquad (2)$$

where V, S, d, $\Delta C/\Delta t$ are the volume of the lumen side solution, the effective area and thickness of the membrane, the initial slope of their time-concentration curves, respectively. Commercially available anion-exchange membrane, AM-1 (ASTOM Co.), was used to be compared with the PVA hollow fiber membrane.

3. Results and discussion

3.1. Morphology of the hollow fiber membrane

Fig. 2 shows the photographs of the hollow fiber membrane obtained by the laser microscope (a) and SEM (b). The inner and outer diameter, and thickness of the membrane determined by the cross-sectional image of the laser microscope were 885, 1070 and



(a)

(b)

Fig. 2. Cross-sectional image of the hollow fiber membrane. (a) laser microscope (b) SEM. Membrane thickness, 96 µm; Inside diameter, 885 µm; Outside diameter, 1.07 mm.

96 µm, respectively. Non-porous structure was shown from the cross sectional image of SEM. The hollow fiber membrane was formed by dehydration and coagulation process, and by cross-linking with hydrogen bond between boric acid and hydroxyl group of PVA. Thus, the membrane matrix has non-porous structure.

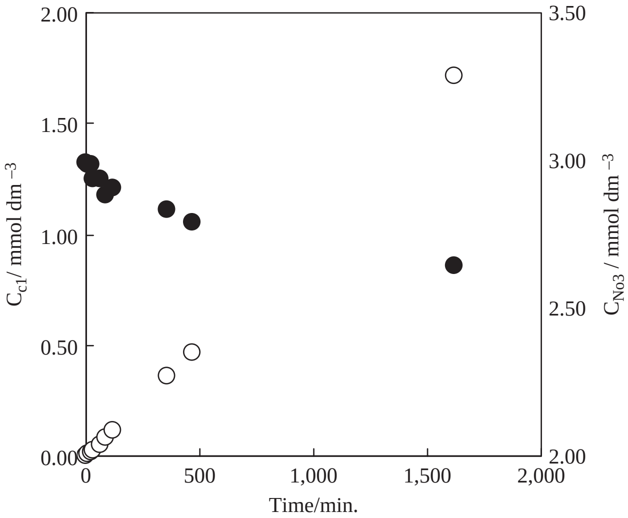


Fig. 3. Time–concentration curves of chloride and nitrate ions in the lumen side of the dialysis system with the membrane cross-linked with 0.01 vol.% GA solution. ●: nitrate ions, ○: chloride ions.

3.2. Ionic transport through the hollow fiber membrane

Fig. 3 shows the time–concentration curves of chloride and nitrate ions in the lumen side of the dialysis system with the membrane cross-linked with 0.01 vol.% GA solution. The concentration of nitrate ions decreases with time while that of chloride ions increases. The mobility of chloride and sodium ions in a aqueous solution are 5.4×10^{-13} mol m^2/(J s), 8.2×10^{-13} mol m^2/(J s), respectively. Hence, the diffusion potential generates between the membrane surfaces when NaCl diffuses from the shell side to the lumen side. The electric potential at the shell side is higher than that at the lumen side. Therefore, nitrate ions are transported against their concentration gradient from the lumen side to the shell side driven by the diffusion potential. Hence, the concentration of nitrate ions at the lumen side decreases with time. This means that ''uphill transport'' of nitrate ions occurs driven by the diffusion of NaCl. In the diffusion dialysis system, the electric current, *I*, should be zero:

$$I = FS\sum z_i J_i = FS(J_{\mathrm{Na}} - J_{\mathrm{Cl}} - J_{\mathrm{NO3}}) = 0, \tag{3}$$

where *F* and *S* are the Faraday constant and the membrane area, respectively. Eq. (3) can be rewritten as

$$J_{\mathrm{Cl}} - J_{\mathrm{Na}} = -J_{\mathrm{NO3}} \tag{4}$$

Eq. (4) indicates that nitrate ions are transported in the opposite direction to the diffusion of chloride ions. In this paper, we called chloride ions as ''driving ions'' of uphill transport, and nitrate ions as ''uphill transported ions''. The flux of the two anions was calculated from the initial slope of the time–concentration curves.

Fig. 4 shows the flux of nitrate and chloride ions as a function of GA concentration. The flux of the driving ion decreases with increasing GA concentration while the flux of uphill transported ions is almost independent of GA concentration. The decrease in the flux of

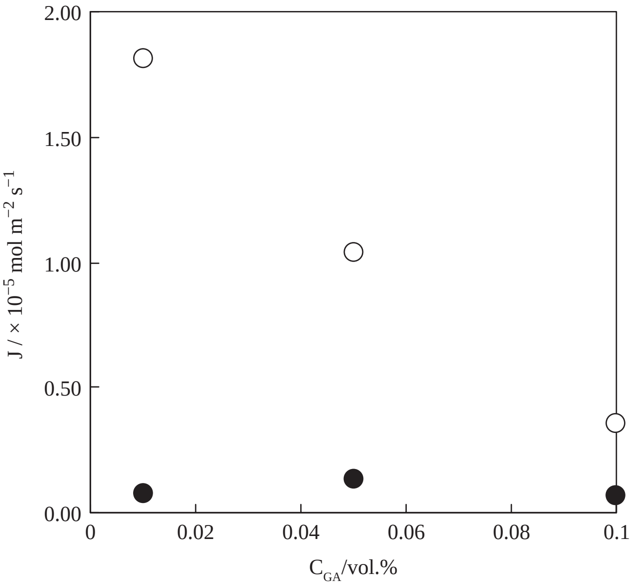


Fig. 4. Ionic flux J_i, as a function of GA concentration in the chemical cross-linking process. ●: nitrate ions, ○: chloride ions.

the driving ions is due to the decrease in the water content of the hollow fiber membrane with increasing GA concentration, whose data are not shown here.

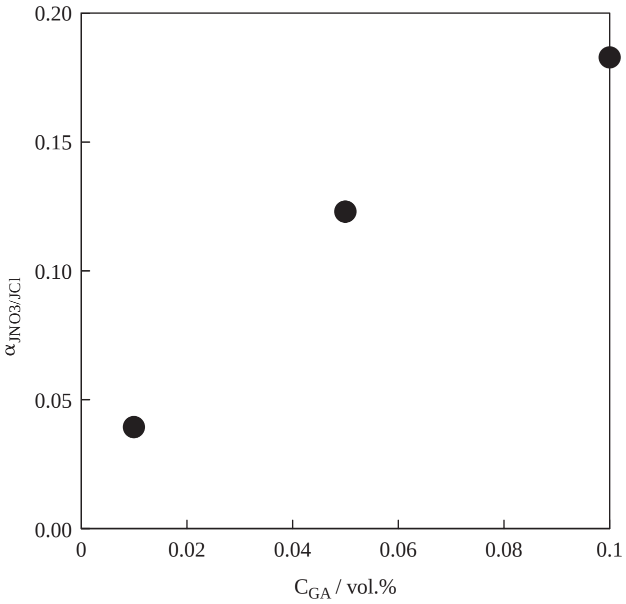


Fig. 5. Selectivity coefficient α, as a function of GA concentration in the chemical cross-linking process.

Table.1. The flux of ions J_i, selectivity coefficient, α, thickness, d, ion-exchange capacity, IEC, water content, H, and dynamic state transport number, t_{d-}, of AM-1.

Sample	α	d^a	IEC^b	H	t_{d-}	J_i ^{c}	
						Cl^-	NO_3^-
AM-1	0.89	150	2	0.30	0.98	4.48	4.00

a: d: μm, b: IEC: meq/g dry membrane, c: J_i: × 10^{-5} mol/m^2 s

Fig. 5 shows the selectivity coefficient, α, as a function of GA concentration. α increases with increasing with GA concentration. The increase in α occurs due to the following factors: The water content of the membrane decreases with increasing GA concentration. The flux of sodium ions will decrease more steeply than that of chloride ions with decreasing water content because the stokes radius of sodium ions is larger than that of chloride ions. Hence, the difference in the flux between chloride ions and sodium ions increases with decreasing water content. Therefore, Eq. (4) gives the increase in the flux of nitrate ions when the difference in the flux of the two ions increases. The maximum value of the selectivity coefficient of the hollow fiber membrane is 0.18 at 0.1 vol.% of GA concentration.

The flux of chloride ions and nitrate ions through the commercially available membranes, AM-1, measured under the same conditions are listed in Table 1. The flux of nitrate ions through AM-1 is almost 20 times higher than that of the PVA hollow fiber membrane although the membrane thickness of the former is larger than that of the latter. AM-1 has high ion-exchange capacity and low water content; hence, the membrane has high charge density. This means that the concentration of the counter-ions (anions) in the membrane is much higher than those in external solution. The flux of ions is almost proportional to their concentration. Hence, AM-1 has high flux for anions. The selectivity coefficient between nitrate and chloride ions of AM-1 is also listed in Table 1. The coefficient of AM-1 is 0.89 and about five times higher than that of the PVA hollow fiber membrane. AM-1 has much high value of dynamic state transport number: $t_{d-} = 0.98$. This means the flux of the co-ions (cations) through the membrane is almost equal to zero. Hence, Eq. (3) can be rewritten as:

$$J_{\mathrm{Cl}} \approx -J_{\mathrm{NO3}}. \tag{5}$$

This is the reason why AM-1 has high selectivity coefficient for anions.

The selectivity coefficient of PVA hollow fiber membrane increases with decreasing water content as shown in Fig. 5. Hence, the selectivity coefficient will be improved by changing the cross-linking conditions. Although the hollow fiber membrane has lower flux than the commercially available anion-exchange membranes, the membrane surface area per unit volume in a hollow fiber module is much higher than that of a diffusion dialysis system with commercially available anion-exchange membranes. Moreover, PVA hollow fiber membrane can be prepared with low cost by one-step process. Hence, the membranes in this study will have potential application in removal of trace ions in the wastewater and groundwater.

4. Conclusions

In this paper, hydrophilic hollow fiber membrane with non-porous structure is prepared from an aqueous solution of PVA by a gel spinning method, and changing the concentration of cross-linking agent.

From the cross-sectional image of the laser microscope, the thickness, inside diameter and outside diameter of the membrane were 96 μm, 885 μm and 1.07 mm, respectively. Non-porous structure was shown from the cross-sectional image of SEM.

Ion permeation experiments show that nitrate ions are transport against their concentration gradient driven by the diffusion potential, which was generated by the difference in the flux between chloride and sodium ions. The flux of driving ions decreases with increasing with GA concentration, and selectivity coefficient increases because the water content of the PVA hollow fiber membrane decreases. Although the flux of nitrate ions and selectivity coefficient of the PVA hollow fiber membrane is lower than those of the commercially available anion-exchange membrane, the flux per unit volume of a hollow fiber module with the PVA hollow fiber membrane will be larger than a diffusion dialysis system with commercially available anion-exchange membrane. The membranes will have potential application in removal of trace ions in the wastewater and groundwater.

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Symbols

C	Ionic concentration, mmol/dm^3
I	Electric current, C/s
F	Faraday's constant, C/mol
J_i	Ionic flux, mol/m^2 s
V	Solution volume, cm^3
S	Effective membrane area, cm^2
d	Membrane thickness, μm
T	Permeation time, s
$t_{\mathrm{d}-}$	Dynamic state transport number
z	Valence of ion

Greek symbols

α	Selectivity coefficient

Subscripts

i	ith ion
Cl	Chloride ion
GA	Glutaraldehyde
NO_3	Nitrate ion
Na	Sodium ion

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