Preparation and Characterization of High-Performance Dehydrating Pervaporation Alginate Membranes

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ABSTRACT: In a previous work, sodium alginate dense membranes demonstrated a good combination of selectivity and permeation flux for dehydrating organic solvents by pervaporation. In this article, the pervaporation performances of alginate composite membranes has been investigated to find out the best condition of membrane formation and the optimum operating conditions. Some ultrafiltration membranes made of poly-(vinylidene fluoride), polyacrylonitrile, and hydrolyzed polyacrylonitrile—either commercially available or prepared in our laboratories—were used as supports for the composite membranes. Sodium alginate dense membranes, modified through ion exchange of sodium with multivalent metal ions (such as Al^{3+}, Cr^{3+}, Fe^{3+}, and Mg^{2+}) have also been prepared, and their permselectivities have been tested for the water–ethanol mixture. An interesting stability of the modified membranes in long-term operation is expected. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 959–968, 1998

Key words: pervaporation; alginate composite membranes; multivalent ions crosslinking; dehydration of organic solvents

INTRODUCTION

Pervaporation (PV) is a recently developed membrane operation for separation in chemical and biochemical engineering. The potentiality of this membrane process has been demonstrated by considering energy and cost savings, easier operation, and lower environmental pollution with respect to conventional techniques.[1] The build-up of a PV separation involves the development of membrane materials, design of membrane modules, assemblage of the total system as a basic separation unit, and eventually integration with other processes. Therefore, besides optimization of the engineering design, membrane materials with good separating performances, chemical/physical resistance, and long-term durability should be prepared. The latter is the basic starting point, because the membrane material performances are intrinsic properties for engineering design.

The materials for PV membrane through which actual liquid mixtures can be treated are generally classified into three types: 1) water preferentially permeating membranes, 2) membranes used to concentrate organic compounds from their dilute aqueous solution, and 3) those specified for separating organic binary or multiple components systems. From the view point of engi-

neering and the actual operating process, a PV membrane, when used to dehydrate an organic solvent, is ideal if it possesses both selectivity higher than 1000 for water over the organic component, and the overall permeation flux exceeding $1000 \ g \ m^{-2} \ h^{-1}$.

Alginic acid, which is a highly hydrophilic polysaccharide present in some seaweeds—used mainly in biotechnology, pharmaceutical, and cosmetic industries for a market of 125 million U.S. dollars worldwide, with a total consumption of 23 kT per year[2]—attracted researchers' attention among various candidate polymers. Although alginic acid can hardly dissolve into commercially available solvents, its alkali metal salt form (alginate), obtained by neutralizing the acidic functional groups with strong alkalis, is well soluble in water. Thus, a membrane can be easily prepared from an alginate aqueous solution. Concerning the PV characteristics of sodium alginate dense membrane, some data were reported in the literature.[3,4] Good separating performances (virtually infinite selectivity and flux of about $900 \ g \ m^{-2} \ h^{-1}$) for separating water–ethanol binary mixtures, have also been found in our laboratory through homogeneous dense membranes.[5] It means that sodium alginate is a potential separating material for PV membranes. Because the permeation flux is inversely proportional to the membrane thickness, it is interesting to prepare and study composite sodium alginate membranes, and to find the optimal microporous support for enhancing membrane performance.

In this article, composite sodium alginate membranes have been prepared on different ultrafiltration (UF) membranes and then characterized for the PV dehydration of organic solvents. We also tried to crosslink membranes by ion exchange of the sodium ions with divalent or trivalent metal ions, partially or completely. The probability of ion loss, compared with sodium alginate, will be decreased. Thus, various multivalent ion crosslinked membranes have been investigated for their PV performances and long-term stability. In addition, the sorption behavior, solubility, and the crosslinking degree of the membranes under different temperature and different reaction times have been studied.

EXPERIMENTAL

Hydrolytic Reaction of Polyacrylonitrile (PAN) UF Membrane in NaOH Aqueous Solution

A PAN UF membrane prepared in China was hydrolyzed in $1M$ NaOH aqueous solution for differ-

ent times, and then transferred into deionized water to continue the hydrolytic reaction until the brown color disappeared. This hydrolyzed support will be called H-PAN-C in the following.

Preparation of Composite Membranes with Different Supports

Three types of UF membranes, including hydrolyzed PAN (H-PAN-C), PAN from GKSS GmbH (Germany) (named PAN-G), and poly(vinylidene fluoride) (PVDF) UF membranes, were used as supports for the alginate composite membranes. A 2.5–2.7 wt % sodium alginate aqueous solution was carefully cast onto the support, which was fixed on a flat glass plate, with a blade at a knife gap of 0.245 mm. The solvent was allowed to evaporate completely at room temperature.

PV Characteristics of Composite Membrane for Separating Organic Water Mixtures

The experimental apparatus for PV has been described in the literature[5]; it is composed of a magnetically stirred testing cell with an effective permeating area of 28.3 cm^2, a permeate collection condenser (with the cooling finger dipped in liquid nitrogen), and a vacuum system.

Composition of the feed and of the permeate was determined by gas chromatography (GC-8810, Kechuang Instruments Ltd., Shanghai, People's Republic of China). The selectivity of water against organic component, $\alpha_{w/\mathrm{org}}$, is defined as:

$$\alpha_{w/\mathrm{org}} = \frac{C_w^p/C_{\mathrm{org}}^p}{C_w^f/C_{\mathrm{org}}^f} \quad (1)$$

where C is the concentration, subscripts w and org are the water and organic components, and superscripts f and p are the feed and permeate stream, respectively.

Acetone, ethanol, 2-propanol (i-PrOH), and 1-butanol (n-BuOH) aqueous solutions were fed to the PV apparatus for testing the membranes.

Crosslinking Reaction of Sodium Alginate Dense Membrane

Considering the ion exchangeability of the carboxyl groups in the alginate, Na$^+$, a univalent cation, should be easily replaced by divalent or

trivalent species. We believe that the replacement of Na^+ with multivalent cations actually leads to a crosslinked network among the alginic chains in the membrane, similarly to what is found in calcium alginate.[6] Solutions of Mg^{2+}, Al^{3+}, Cr^{3+}, and Fe^{3+} salts were chosen to crosslink the membranes. Nitrates were considered because of their good solubility in organic aqueous solutions where sodium alginate membrane will not dissolve but swell well. The extent of ion exchange was checked by atomic absorption spectroscopy.

Swelling Properties Investigation

To determine crosslinking ability of the different cations, the metal ion-crosslinked dense membranes were characterized by measuring the sorption capacity of water vapor in the membranes. An isolated glass system was filled with pure water on the bottom and, on the surface, a series of small plastic vessels loading membrane strip samples were set. Because the ambient in this isolated system was saturated with water vapor, water sorption occurred in the membrane. The direct contact with liquid water was avoided to prevent any dissolution of the membrane samples. After 24 h at 25°C, a sorption equilibrium was established, and the swollen samples were weighted. The weight ratio of water dissolved in the crosslinked membranes was calculated in terms of the following formula:

$$S = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \qquad (2)$$

Desorption Kinetics Investigation

For understanding the mass transport during the PV process, diffusion also needs to be determined. The desorption behavior, which is controlled by the same mechanism of sorption, was conducted by weighing the swollen samples continuously and by allowing adsorbed water to evaporate freely to the drier environment until no variation of mass could be observed. The latter measurements were conducted at room temperature.

RESULTS AND DISCUSSION

Separation Performances of Composite Membranes

Composite sodium alginate membranes with different supports have been evaluated for the separation of organic aqueous solutions. A high content of water in the feed results in the dissolution of the selective layer; therefore, the content of water in the feed was limited to less than 30 wt %.

When treated with sodium hydroxide aqueous solution, part of the cyano groups of PAN hydrolyses forming carboxyl groups ($-COO^-$) whose amount on the PAN surface increases with hydrolyzing time.[7] Thus, the hydrophilicity and binding ability of PAN supports are improved for

Table I PV Characteristics of Sodium Alginate Composite Membranes with Different Supports for the Dehydration of Ethanol–Water Mixtures

Membrane	Hydrolyzing Time of the Support (min)	Ethanol Content in Feed (wt %)	Temperature (°C)	Flux (g m^{-2} h^{-1})	$\alpha_{w/\text{org}}$
Sodium alginate H-PAN-C	5	95	70	91	1538
	15	95	70	128	8532
	25	95	70	101	4761
	35	95	70	95	4460
	45	95	70	115	1304
Sodium alginate PAN-G	0	95.1	70	357	1940
		95.2	70	342	2905
GFT-1000 PVA	—	95	80	225	361
GFT-1001 PVA	—	95	80	350	608

Table II   PV Characteristics of Sodium Alginate Composite Membranes with Different UF Supports for the Dehydration of Organic Liquids

Support Type	Organic Component	Temperature (°C)	Organic in Feed (wt %)	Flux (g m^{-2} h^{-1})	$\alpha_{w/org}$[a]
H-PAN-C	Acetone	50	88.0	1184	∞
			92.0	751	∞
			95.0	592	∞
	Ethanol	70	79.7	1365	2370
			84.5	618	∞
			91.0	218	∞
			95.0	101	4761
	i-PrOH	70	95	343	2514
			90	741	∞
			85	1224	∞
			80	17006	∞
	n-BuOH	70	95	730	> 7580[b]
			90	1862	> 3990[b]
			84	3698	> 2090[b]
			80	6467	> 1590[b]
PAN-G	Ethanol	70	95.1	357	1969
			95.9	255	2367
			90.0	942	2750
			90.8	758	3114
			92.2	595	3585
			94.7	402	2512
			95.2	342	2905
			95.5	296	3386
			95.8	271	3330
			96.0	246	3434
	i-PrOH	70	72.8	4171	∞
			78.3	3235	∞
			82.9	2331	∞
			89.4	2815	4521
			91.1	2096	5853
			94.8	998	4597
			96.3	587	3630
			97.3	327	2761
PVDF	Ethanol	70	91.2	231	618

[a] Infinite selectivity means that the organic amount in permeate was below the detection limit of the gas chromatograph.

[b] The content of n-BuOH in all permeate was lower than 0.25 wt %.

the preparation of composite membranes with better affinity and adhesion between the selective layer and the support. The PV results obtained so far are listed in Table I with PAN [both hydrolyzed (H-PAN-C) and unhydrolyzed (PAN-G)] supported sodium alginate composite membrane for the water–ethanol mixture. It is found that the sodium alginate membranes show much higher water/ethanol selectivity in comparison with those of commercial poly(vinyl alcohol) (PVA) products.

For dehydrating organic solvents, as shown in Table II, H-PAN-C supported composite membrane shows excellent selectivity of water against the organic penetrant, whereas unhydrolyzed PAN supports (PAN-G) yield enhanced flux composite membranes with good selectivity. For example, no acetone in permeate is detected while the flux exceeds 500 g m^{-2} h^{-1} in a wide range of feed composition of the water–acetone mixture. As for dehydrating ethanol containing 20 wt % water, it is interesting that both selectivity and

flux are very high. The PVDF-supported sodium alginate membrane, when compared with PAN-supported ones, shows a decrease in both flux and selectivity for the separation of the water–ethanol mixture. When comparing the composite membranes obtained with different PAN supports [the hydrolyzed one (from the People's Republic of China, H-PAN-C) and the nonhydrolyzed one (from GKSS, PAN-G)], it is noted that the water/organic selectivity is in favor of the membranes obtained with hydrolyzed supports, but the best combination between permeation flux and selectivity comes from the unhydrolyzed PAN supports. These phenomena confirm that the supports, even from the same polymer (although for some of them, carboxyl groups have been introduced by hydrolysis), have a great influence on the final separating performances of the composite membranes. It can be assumed that the flux and selectivity decrease of membranes cast on PVDF supports results from the low hydrophilicity of the fluorinated polymer, which leads to a low affinity between the support and the membrane-forming polymer, and from the thicker separating layer necessary to cover the support completely.

Table II shows the performances of the unhydrolyzed PAN (PAN-G) supported sodium alginate composite membrane in water/ethanol separation in a range of concentrations between 90 and 96 wt % ethanol. The measurements were performed in the order listed in Table II. It is evident that permeation fluxes were reproducible. They ranged from 950 to 260 g m^{-2} h^{-1} at 90 and 96 wt % ethanol feed, respectively. The comparison with the data in ref. 5 leads to an estimated average thickness of the separating layer of the composite membrane of about 4 μm.

An increase in selectivity was found when previous measurements were repeated, and also during the course of the measurements when the water content in the feed was reduced. With a feed composition around 95–96 wt % ethanol, the water–ethanol selectivity values change from about 2000–2500 (first runs of measurement) to 2500–3000 (second runs).

Comparing the above data at about 95 wt % ethanol with the correspondent ones reported for dense sodium alginate membranes,[5] we observed an increase of about 370% in selectivity and permeation fluxes eight times higher for the PAN-G supported sodium alginate membrane. Fluxes are doubled with respect to H-PAN-C sodium alginate composite membranes (Table II), but selectivity instead is decreased (about 50%). The performances of the membrane cast on the PAN-G support is better than the one of a composite PVA/PAN membrane[8] for both flux and selectivity.

The flux and selectivity performances of the composite membrane obtained with the PAN-G support in water/*i*-PrOH separations, in the feed composition range of 73–97 wt % of *i*-PrOH, is reported in Table II as well. From 73 to 83 *i*-PrOH wt % at 70°C, the permeation flux decreases linearly from 4200 to 2300 g m^{-2} h^{-1}, better than in the case of commercial composite PVA/PAN membranes at 75°C. As *i*-PrOH concentration increases in feed from 89 to 97.3 wt %, the permeation flux decays steadily from 2815 to 327 g m^{-2} h^{-1}. The water/isopropanol selectivity instead rises from about 4500 to a value of about 6100 at feed of 92.5% *i*-PrOH, then falls to about 2760 at the end of the testing. The PV tests were not repeated with the same feed composition; however, as in the case with the ethanol solution feed, an increase of selectivity is observed at the beginning of the experiment.

Separating Performances of Crosslinked Dense Membranes

A sodium alginate dense membrane, when used in continuous permeation experiments, shows a declining trend for both flux and selectivity. Yeom and coworkers[3] also reported the flux decline of the dense sodium alginate membrane in PV and attributed the phenomenon to the relaxation of the polymer. Another reason might be that sodium ions are lost during PV operation, because the ionic bond RCOO$^-$—Na$^+$ is weakened in an aqueous environment. This phenomenon takes place also in the composite alginate membranes and, to minimize it, the polymer structure can be modified in three ways: (1) synthesizing a polymeric material that contains both negative and positive charges on groups covalently linked; (2) substituting univalent ions with divalent or trivalent ion species, in other words, crosslinking membranes with multivalent ions; and (3) using a polyelectrolyte with a fixed opposite charge as a crosslinking agent to form a polyion complex that shows very good separating performances as reported by Karakane and coworkers.[9] To stabilize the membrane, fixed counter ions (bigger and/or multivalent ones) should be introduced to replace the smaller and/or monovalent mobile ions.
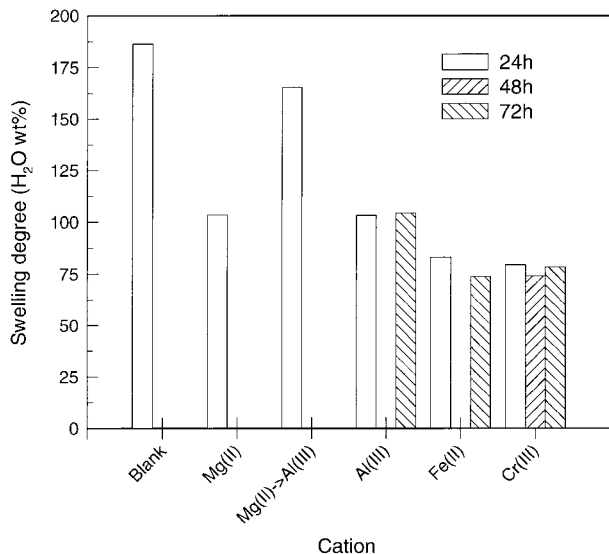
Figure 1 Water sorption of various metal ion-crosslinked dense alginate membranes with different crosslinking time in saturated water vapor at 25°C (sorption time: 24 h).

In this study, the second method has been used to stabilize the alginate membrane. Thus, multivalent metal ions like Mg^{2+}, Al^{3+}, Cr^{3+}, and Fe^{3+} —with higher charge densities in aqueous solutions—were used to crosslink sodium alginate membranes. The X-ray diffraction runs performed on the membranes as made or exchanged with Mg^{2+}, Al^{3+}, and Cr^{3+} do not show any sharp peak, indicating the absence of large, well-structured crystalline domains in appreciable amounts. Three amorphous halos are centered around 5.6–6.4 Å, 3.9–4.4 Å, and 2.3–2.4 Å. Before characterizing the separating performances, the swelling behavior of modified membranes (Fig. 1) indicates that the sodium alginate membrane presents the maximum value of sorption ratio, followed by those crosslinked with Mg^{2+} and Al^{3+}, which are located in the same period as sodium ions. Cr^{3+} and Fe^{3+} alginates, as expected, show partial covalent characteristics, and these membranes cannot be regarded as made of pure polyelectrolytes. Thus, their hydrophilicity decreases.

Swelling properties in a feed containing 8.8 wt % water in ethanol were also investigated at different temperatures (Fig. 2). Basically, no significant change is observed with rising temperature for Al^{3+}, Cr^{3+}, and Fe^{3+} crosslinked membrane; for Mg^{2+} and sodium and alginates, the swelling capacity decreases.

The extent of ion exchange of the membranes can be determined by atomic absorption analysis. The extent of ion exchange of Cr^{3+} crosslinked membranes as a function of time is shown in Figure 3. Within 8 h, the exchange degree reaches 96%. At longer times, sodium ions in the membrane tend to be replaced completely with Cr^{3+}.

The water vapor desorption curves (as plotted in Fig. 4) can be used to calculate the diffusion coefficient of water in membranes. It is found that Al^{3+}, Fe^{3+}, and Cr^{3+} crosslinked membranes have a higher diffusion rate, compared with the Mg^{2+}-crosslinked membrane.

Magnesium decreases water diffusion across the membrane. Hydrated bivalent metal ions with larger activity and strong charge density, when exchanging sodium ion, caused compact structure of the polymer because of high crosslinking degree, compared with those crosslinked by trivalent ions. The water diffusivity in the crosslinked membranes, calculated from the desorption kinetics, is listed in Table III. It is interesting to note that, despite the different experimental conditions (sorption and desorption of water vapor versus real PV experiments with liquid water), by combining diffusion and solubility data according to the simple relationship $P = DS$ (solution-diffusion transport mechanism), the same trend is found than in real PV experiments (see the last column in Table III).

PV Characterization of Crosslinked Membranes

PV characteristics were tested and compared for the separation of 91.2% ethanol aqueous solutions through Cr^{3+} and Al^{3+} crosslinked membranes at 70°C. As shown in Figure 5(b,c), Al^{3+}-crosslinked samples yield better selectivity, but lower fluxes than the Cr^{3+}-exchanged membrane. A preliminary conclusion might be that the Cr^{3+}-crosslinked membrane rapidly reaches the stable operating condition within 3 h, whereas the Al^{3+}-crosslinked membrane takes at least 6 h. This is in agreement with the sorption-desorption behavior of water vapor. Concerning long-term operations (Fig. 5), 20 h are necessary for crosslinked membranes to reach the steady state. The tested results, in initial operation, is in agreement with simulated results. However, if we raise the hypothesis that crystallization takes place in membrane during PV operation, the effective area suitable for mass transfer decreases and thus the flux decreases with time until equilibrium is reached.
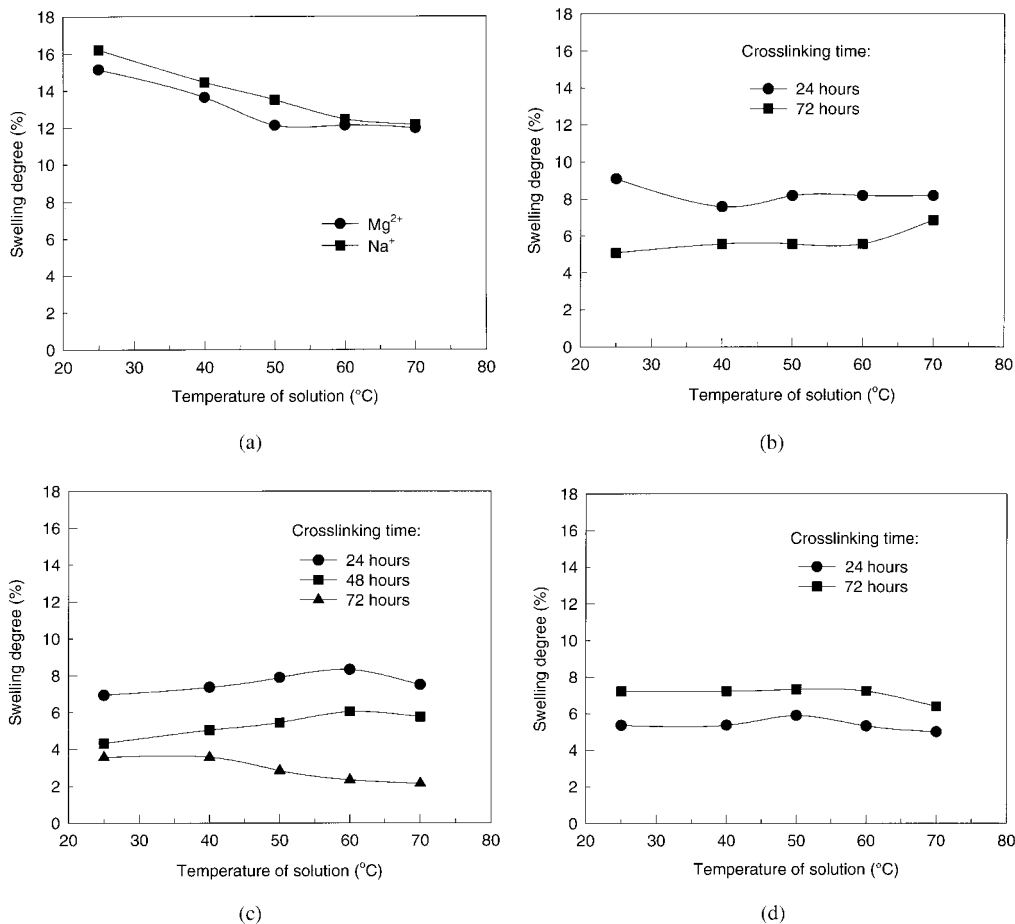
Figure 2 Effect of temperature on swelling degree of metal ion-crosslinked and sodium alginate dense membranes in 91.2% ethanol aqueous solution. Crosslinking metal ions: (a) Mg^{2+} and Na^+; (b) Al^{3+}; (c) Cr^{3+}; and (d) Fe^{3+}.

CONCLUSIONS

Different UF supports (including PAN from different sources, hydrolyzed PAN, and PVDF) were
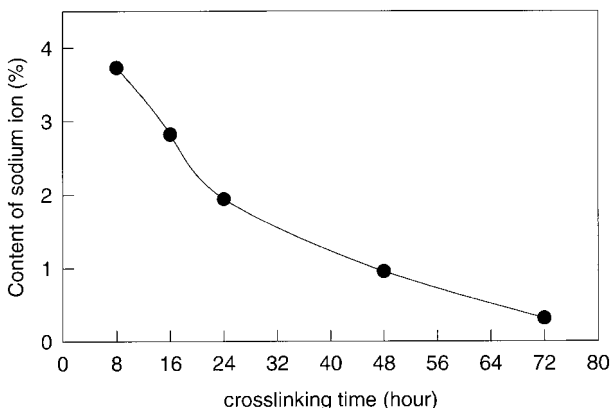

Figure 3 Effect of crosslinking time on Na^+ content in sodium alginate membrane in exchange with Cr^{3+}.

used to cast sodium alginate aqueous solutions to prepare composite PV membranes. The PV characteristics were evaluated for dehydrating organic liquids (acetone, ethanol, i-PrOH, and n-BuOH). Compared with commercial PVA membranes, the selectivity of hydrolyzed PAN-supported alginate membranes is improved from less than 540 to more than 4000, albeit the flux decreased a little for separating 95 wt % water–ethanol mixtures. The performance of the GKSS PAN-supported sodium alginate composite membranes are instead better than commercial PVA membranes for both flux and selectivity. The PAN supports from GKSS were not hydrolyzed and were used as made. This fact also demonstrates that the quality of the sodium alginate coating may still be improved, thus enabling the preparation of higher quality, thinner separating layers with enhanced permeability, in case good quality PAN supports are hydrolyzed before membrane casting.
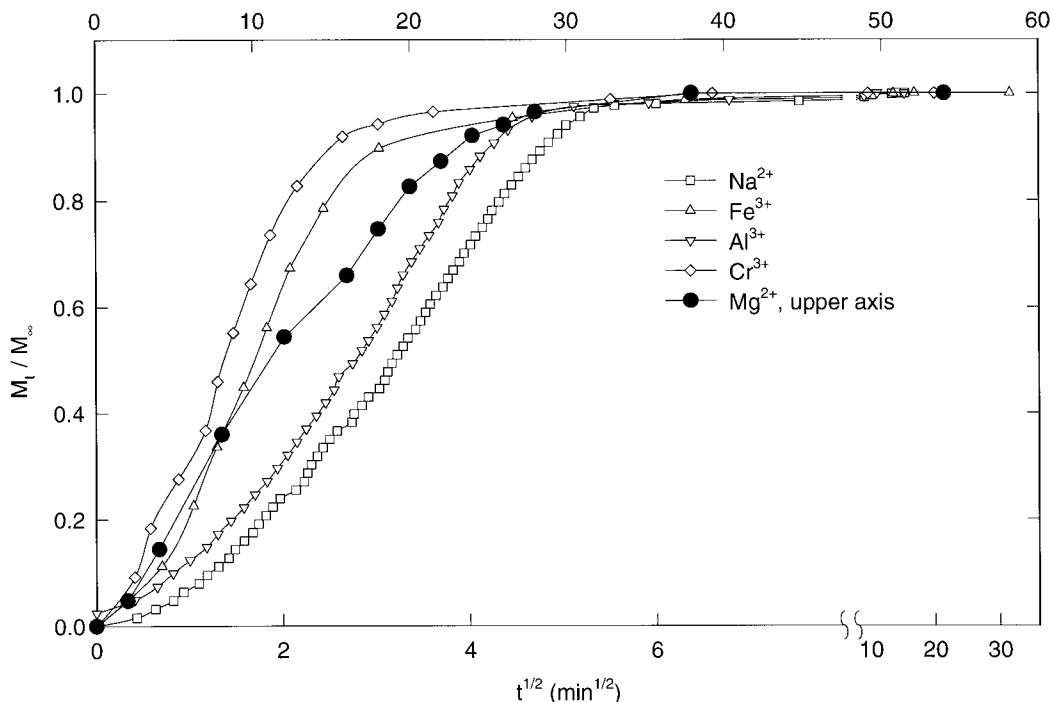
Figure 4 Desorption behavior of water vapor in various metal ion-crosslinked alginate dense membranes at room temperature.

For the dehydration of acetone and n-BuOH, the hydrolyzed PAN-supported sodium alginate membrane seems to give better permselective performances than commercial PVA membranes in all cases. PVDF composite membrane also showed a good compromise between selectivity (685) and flux (231 g m^{-2} h^{-1}).

Multivalent metal ions (such as Mg^{2+}, Al^{3+}, Cr^{3+}, and Fe^{3+}) were chosen to crosslink sodium alginate dense membrane. Atomic absorption spectroscopy confirmed that longer ion-exchange times

increase the extent of ion exchange. Mg^{2+} and Al^{3+} crosslinked membranes are more swellable, but show lower diffusion coefficient of water in comparison with Fe^{3+} or Cr^{3+} exchanged membranes. The results indicate that stabilization of PV performances is attained within 2 h for membranes treated with Cr^{3+} ion; in that case, flux fluctuated between 45 and 52 g m^{-2} h^{-1}, and a water/ethanol separation factor of more than 2000 remains constant for a 91.2 wt % of ethanol aqueous solution. Dense membranes treated with Al^{3+}, however,

Table III Diffusivity, Sollubility, and Flux of Pure Water in Crosslinked Alginate Membranes by the Sorption–Desorption Method

Crosslinking Species	Diffusivity[a] (cm^2 sec^{-1})	Solubility[b] [g (solvent)/g (polymer)]	Flux[c] (g m^{-2} h^{-1})
Mg^{2+}	1.5×10^{-9}	1.03	29.5
Al^{3+}	2.6×10^{-8}	1.03	42.9
Fe^{3+}	1.0×10^{-7}	0.83	40.8
Cr^{3+}	1.1×10^{-7}	0.79	54.3
Na^+	2.0×10^{-8}	1.86	

[a] Measured at room temperature, membrane thickness ca. 20 μm.
[b] From sorption, 100% relative humidity at 25°C.
[c] PV experiments at 25°C.

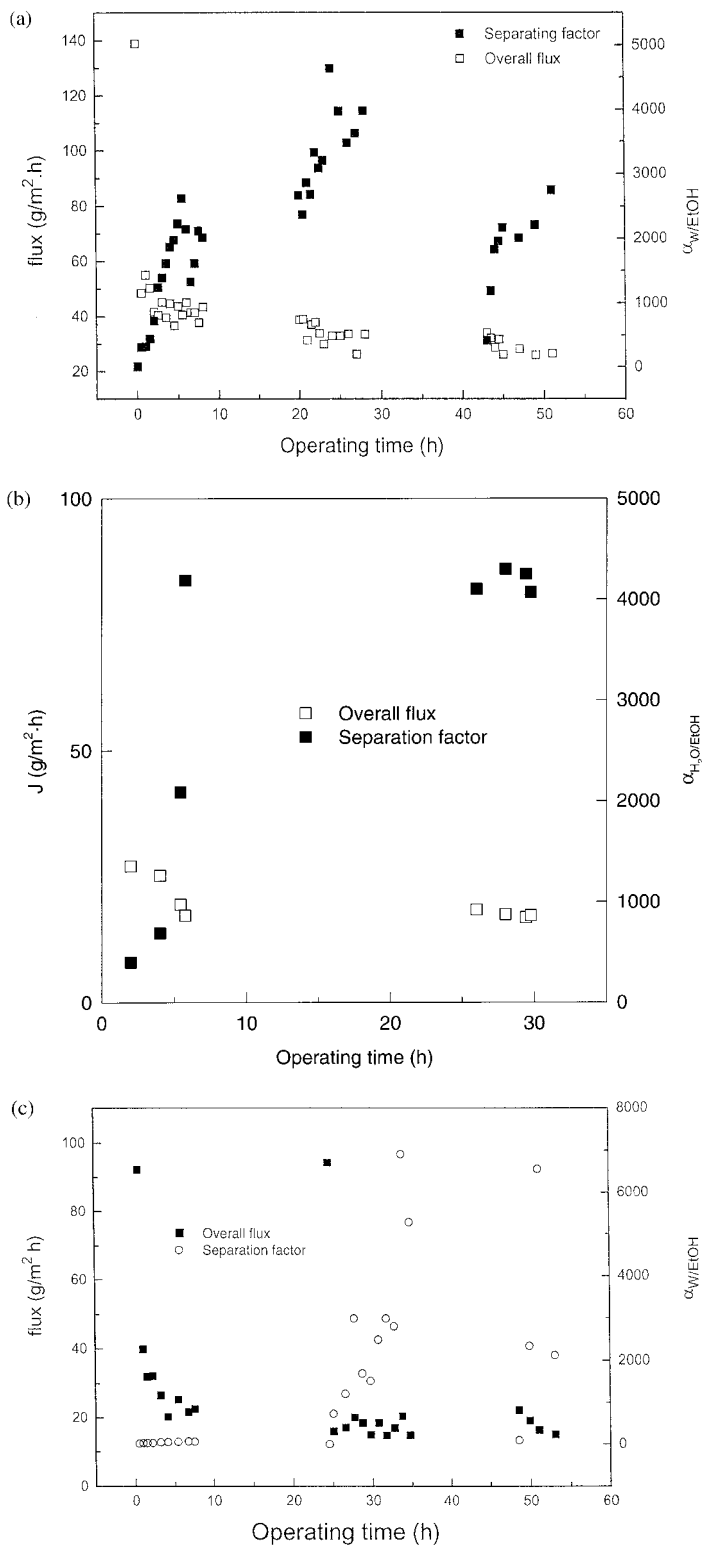**Figure 5** PV performance metal ion-crosslinked alginate dense membranes versus operation time at 70°C. Crosslinking metal ions: (a) Mg^{2+}; (b) Al^{3+}; and (c) Cr^{3+}. EtOH, ethanol.

need longer time to reach the steady state; the selectivity of water against ethanol is high.

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