



Dehydration of an ethanol/water azeotrope through alginate-DNA membranes cross-linked with metal ions by pervaporation



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ABSTRACT

To obtain high dehydration membranes for an ethanol/water azeotrope, dried blend membranes prepared from mixtures of sodium alginate (Alg-Na) and sodium deoxyribonucleate (DNA-Na) were cross-linked by immersing in a methanol solution of CaCl₂ or MgCl₂. In the dehydration of an ethanol/water azeotropic mixture by pervaporation, the effects of immersion time in methanol solution of CaCl₂ or MgCl₂ on the permeation rate and water/ethanol selectivity through Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes were investigated. Alg-DNA/Mg²⁺ cross-linked membrane immersed for 12 h in methanol solution of MgCl₂ exhibited the highest water/ethanol selectivity. This results from depressed swelling of the membranes by formation of a cross-linked structure. However, excess immersion in solution containing cross-linker led to an increase in the hydrophobicity of cross-linked membrane. Therefore, the water/ethanol selectivity of Alg-DNA/Mg²⁺ cross-linked membranes with an excess immersion in cross-linking solution was lowered. The relationship between the structure of Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes and their permeation and separation characteristics during pervaporation of an ethanol/water azeotropic mixture is discussed in detail.

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1. Introduction

Polysaccharides such as alginate, cellulose, chitin, chitosan and their derivatives are getting attention in various membrane separation areas (Uragami, 1998, 2005, 2006, 2011). Alginate is mainly obtained from kelp and has a high solvent stability. In particular, alginate membranes can be easily prepared by casting aqueous solutions. The obtained membranes have a high hydrophilicity (Uragami & Saito, 1989). To make use of such character of alginate a lot of blended membranes consisted of sodium alginate and other polymers and cross-linked alginate membranes have been prepared and the dehydration of organic solvents was actively investigated by those membranes (Yeom & Lee, 1998; Wang, Khor, & Lim, 2001; Wang, 2000; Kanti, Srigowri, Madhuri, Smitha, & Sridhar, 2004; Kalyani, Smitha, Sridhar, & Krishnaiah, 2006; Veerapur et al., 2006; Bhat & Aminabhavi, 2006, 2007; Adoor, Manjeshwar, Bhat, & Aminabha, 2008; Kalyani, Smitha, Sridhar, & Krishnaiah, 2008; Rao, Lokesh, Rao, & Rao, 2008; Patil, Veerapura,

Bhata, Madhusoodanab, & Aminabhavi, 2009; Chen, Gao, Wang, Wang, & Gao, 2010; Suhas, Raghu, Jeong, & Aminabhavi, 2013; Nigiz & Hilmioglu, 2013; Gao et al., 2014; Rao, Sekharnath, Sudhakar, Rao, & Subha, 2014).

Recently, DNA could be readily purified from salmon milts and shellfish gonads which were discarded as a fish industrial waste and is very cheap (Yamada, Kato, Ohkawa, Yamamoto, & Nishi, 2002). In this opportunity DNA studies as functional biopolymer materials are begun in various fields. We noticed a very high hydrophilic character of DNA for the dehydration of organic solvents, in particular as membrane material for the dehydration of an ethanol/water azeotrope.

Membrane separation techniques attract much attention in many fields, since they have high efficiency with energy savings. Pervaporation (PV) is one of the membrane separation techniques for multicomponent solutions (Huang, 1991; Yamaguchi, Nakao, & Kimura, 1991; Feng & Huang, 1997; Uragami, Takuno, & Miyata, 2002). Especially, PV is a promising technique for separation of organic liquid mixtures such as azeotropic mixtures (Baker et al., 1991; Psaume, Aurell, Mora, & Bersillon, 1988) or close-boiling point mixtures (Blume, Wijmans, & Baker, 1990; Fang, Pham, Matuura, Santerre, & Narbaitz, 1994).

Many materials have been investigated as PV membranes for separation of azeotrope of ethanol/water to develop dehydration

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systems with high performance (Huang & Yeom, 1990; Liang & Ruckenstein, 1995; Uragami, Yamamoto, & Miyata, 2003; Uragami et al., 2004).

In this study, to obtain highly water permselective membranes for an ethanol/water azeotrope in PV, Alg-DNA blends were selected as membrane materials. Alg-DNA blend membrane was cross-linked with Ca^{2+} or Mg^{2+} ion. The permeation and separation characteristics for an ethanol/water azeotrope during PV were studied using Alg-DNA/ Ca^{2+} and Mg^{2+} cross-linked membranes with different degrees of cross-linking. The separation mechanism for the water permselectivity of an azeotropic mixture of ethanol/water was discussed by analyzing the permeation data on the basis of the solution-diffusion model (Binning, Lee, Jennings, & Mertin, 1961; Aptel, Cuny, Jozefonvicz, Morel, & Neel, 1974).

2. Experimental

2.1. Materials and reagents

Sodium alginate (Alg-Na) was supplied from Wako Pure Chemical Industries, Ltd., Japan. Sodium deoxyribonucleate (DNA-Na) which is a single strand without almost double spiral structure whose molecular weight is 500,000–660,000 was supplied from Sandel Chemical Agents, Japan. All other solvents and reagents were of analytical grade, and were obtained from commercial sources and without further purification.

2.2. Preparation of Alg-DNA blend membranes and Alg-DNA cross-linked membranes

Each Alg-Na and DNA-Na powder was dissolved in pure water to make a 3 wt% casting solution. After removal of the insoluble impurities using a glass filter, they were stirred for 1 h at 30 °C. Alg-DNA blend membranes with different blend ratio of Alg/DNA were prepared by pouring casting solutions onto glass plates treated with silicone oil and then allowing the water to evaporate completely at 50 °C for 24 h. An Alg-DNA blend membrane was cross-linked by immersing in 1 M CaCl_2 or MgCl_2 methanol solution to prepare Alg-DNA/ Ca^{2+} and Alg-DNA/ Mg^{2+} cross-linked membranes.

2.3. Permeation measurements

PV experiments were carried out using the apparatus described in previous studies (Uragami, Doi, & Miyata, 1999; Uragami, Yamada, & Miyata, 2001; Uragami, Meotoiwa, & Miyata, 2001; Uragami, Wakita, & Miyata, 2001) under the following conditions: permeation temperature: 40 °C; permeate-side pressure: 1.33 Pa. The effective membrane area was 13.8 cm². An aqueous solution of 96 wt% ethanol was used as the feed solution. The permeate was collected in a U-tube at liquid nitrogen temperature. The permeation rates ([kg/(m²h)]) of an ethanol/water azeotrope during PV were determined from the weight of the permeate collected in the U-tube, the permeation time, and the effective membrane area. The compositions of the feed solution and permeate were determined using a gas chromatograph (Shimadzu GC-9A) equipped with a flame ionization detector (FID) and a capillary column (Shimadzu Co., Ltd.; Shimalite F) heated to 200 °C. The permeation results were reproducible, and the errors inherent in the permeation measurements were on the order of a few percent.

The PV separation factor, $\alpha_{\text{sepa.H}_2\text{O}/\text{EtOH}}$, was calculated from Eq. (1):

$$\alpha_{\text{sepa.H}_2\text{O}/\text{EtOH}} = \frac{(P_{\text{H}_2\text{O}}/P_{\text{EtOH}})}{(F_{\text{H}_2\text{O}}/F_{\text{EtOH}})} \quad (1)$$

where $F_{\text{H}_2\text{O}}$ and F_{EtOH} , $P_{\text{H}_2\text{O}}$ and P_{EtOH} are the weight fractions of water and ethanol in the feed solution and the permeate, respec-

tively. It is assumed that the separation factor for each membrane is not dependent on the membrane thickness.

2.4. Contact angle measurements

The contact angles for methylene iodide on the surface of the sodium alginate and Alg-DNA membranes cross-linked with metal ion were measured using a contact angle meter (Erma, Model G-1) at 25 °C. The contact angles, θ , were determined by Eq. (2),

$$\theta = \cos^{-1}\{(\cos\theta_a + \cos\theta_r)/2\} \quad (2)$$

where θ_a and θ_r are the advancing contact angle and the receding contact angle, respectively.

2.5. Composition of the solution absorbed in Alg-DNA blend membrane and Alg-DNA membranes cross-linked with metal ion membranes

The Alg-DNA membranes cross-linked with metal ion were dried completely under reduced pressure at room temperature and weighed. The dried membranes were immersed into an azeotropic mixture of ethanol/water in a sealed vessel at 40 °C until equilibrium was reached. A large amount of the swollen Alg-DNA blend membrane and Alg-DNA membrane cross-linked with metal ion was placed in a container, as shown in a previous paper (Uragami et al., 2004). This system was evacuated, and the container with the swollen membranes was heated. The solution sorbed into the swollen membranes was completely desorbed under reduced pressure and was collected in a U-tube cooled with liquid nitrogen. The composition of the solutions sorbed in the membranes was then determined by measuring the ethanol concentration in the collected solution by gas chromatography (Shimadzu GC-14A). The ethanol/water composition in the DNA-Alg membranes and that in the feed solution yielded the sorption selectivity, $\alpha_{\text{sorp.H}_2\text{O}/\text{EtOH}}$, as expressed in Eq. (3)

$$\alpha_{\text{sorp.H}_2\text{O}/\text{EtOH}} = \frac{(M_{\text{H}_2\text{O}}/M_{\text{EtOH}})}{(F_{\text{H}_2\text{O}}/F_{\text{EtOH}})} \quad (3)$$

where $F_{\text{H}_2\text{O}}$ and F_{EtOH} are the weight fractions of water and ethanol in the feed solution and $M_{\text{H}_2\text{O}}$ and M_{EtOH} are those sorbed in the membrane, respectively.

2.6. Membrane density

The density of the membranes was measured by the floatation method (Nakamae, Nishino, & Okubo, 1991) using a mixed solution of benzene and carbon tetrachloride at 40 °C.

2.7. Degree of swelling of membranes

The Alg-DNA blend membrane and Alg-DNA membrane cross-linked with metal ion were dried completely under reduced pressure at 40 °C and weighed. Thereafter, the membranes were immersed into an aqueous solution containing 96 wt% ethanol in a sealed vessel at 40 °C. After the weight of the membranes became constant, they were taken out of the vessel, wiped quickly with filter paper and weighed. The degree of swelling (DS) of the membrane was determined by Eq. (4):

$$\text{DS} = \frac{W_s}{W_d} \quad (4)$$

where W_s is the weight of the membrane swollen in an aqueous solution of 96 wt% ethanol and W_d is the weight of the dried membrane.

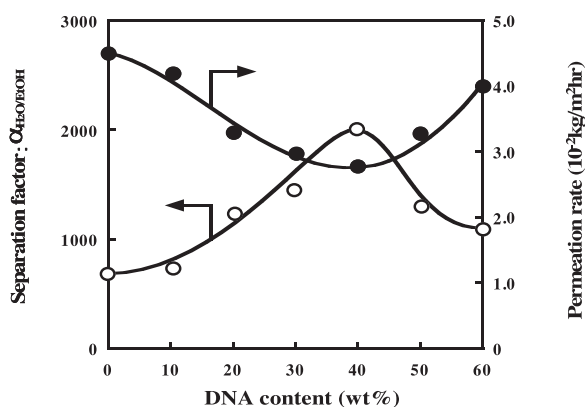


Fig. 1. Effects of the DNA content on the permeation rate (●) and separation factor (○) for an azeotropic mixture of ethanol/water through the Alg-DNA membranes during PV.

2.8. X-ray photoelectron spectroscopy (XPS)

Surfaces of the Alg-DNA blend membrane and Alg-DNA membranes cross-linked with metal ion were characterized with X-ray photoelectron spectroscope (JEOL, JPS-9000MX). Typical operation conditions were as follows: Mg K α radiation with 10 kV and 10 mA. The pressure in the instrumental chamber was less than 1×10^{-5} Pa. No radiation damage was observed during the data collection time. The charge correction in the binding energy scale was done by setting the $-\text{CH}_2-$ peak in the carbon spectra to 280.5 eV. Overlapping peaks were resolved into their individual components of the core-level spectra, which were well described by Gaussians. The full width at half-maximum (fwhm) of each individual peak was less than 2.0 eV.

3. Results and discussion

3.1. Effect of DNA content on permeation and separation characteristics of Alg-DNA blend membranes

Fig. 1 shows the effects of DNA content in the Alg-DNA blend membranes on the permeation rate and separation factor for the H₂O/EtOH selectivity for an ethanol/water azeotrope during PV. The separation factors for the H₂O/EtOH selectivity of all Alg-DNA blend membranes were very high. These results suggest that the Alg-DNA blend membranes showed high H₂O/EtOH selectivity. Up to 40 wt% DNA with increasing DNA content, the H₂O/EtOH selectivity increased; however, its selectivity decreased when the DNA content was further increased. The best performance was observed for the Alg-DNA blend membrane with 40 wt% DNA content and the separation factor for the H₂O/EtOH selectivity was 2000. The permeation rate gradually decreased by increasing the DNA content up to 40 wt% but then increased at higher DNA contents. These results can be attributed to the degree of entanglement between the DNA and alginate molecules. This discussion is supported by the fact that the degree of swelling of Alg-DNA membranes more than 40 wt% DNA remarkably increased. From the above results, the Alg-DNA blend membrane at 40 wt% DNA content was selected as a base membrane in this paper.

3.2. Permeation and separation characteristics of Alg-DNA membranes cross-linked with bivalent metal cation

In **Fig. 2**, the permeation rate and separation factor for an ethanol/water azeotrope through the Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes during PV are as a function

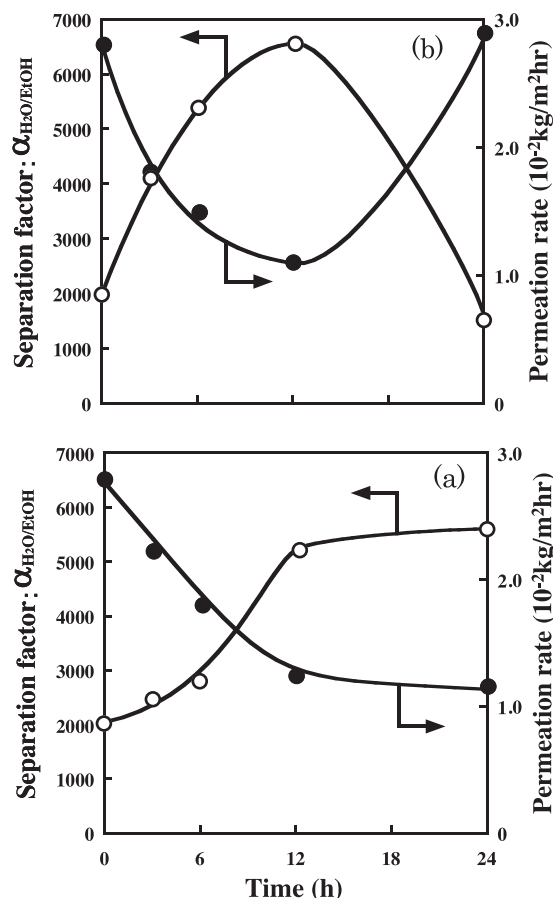


Fig. 2. Effects of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂ on the permeation rate (●) and separation factor (○) for an azeotropic mixture of ethanol/water through Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes during PV. The DNA content in the each membrane is 40 wt%.

of the immersion time in the CH₃OH solutions of CaCl₂ and MgCl₂. In Alg-DNA/Ca²⁺ cross-linked membranes in **Fig. 2**(a), with increasing the immersion time the separation factor increased and the permeation rate decreased. All separation factors were much higher than those in the Alg-DNA blend membrane without the cross-linking. These results suggest that the Alg-DNA/Ca²⁺ cross-linked membranes showed much higher H₂O/EtOH selectivity.

The difference in the permeation and separation characteristics for an ethanol/water azeotrope through the Alg-DNA blend membrane and Alg-DNA/Ca²⁺ cross-linked membranes can be explained by illustrations in **Fig. 3**. The Alg-DNA blend membranes are very high hydrophilic but have not the cross-linking. On the other hand, the Alg-DNA/Ca²⁺ membranes can form the cross-linking structure but their hydrophilicity is decreased. The differences in the membrane characteristics in the chemical and physical structure of the membrane are significantly influenced the difference in the permeation and separation characteristics. Consequently, the Alg-DNA blend membranes show a high permeability and low water-permeability and Alg-DNA/Ca²⁺ cross-linked membranes show a high water-permeability and low permeability.

On the other hand, in Alg-DNA/Mg²⁺ cross-linked membranes in **Fig. 2**(b), at 12 h of the immersion time, the separation was maximum and the permeation rate was minimum. The separation factors up to for 12 h were higher than those of the Alg-DNA/Ca²⁺ cross-linked membranes and that at 12 h was the highest.

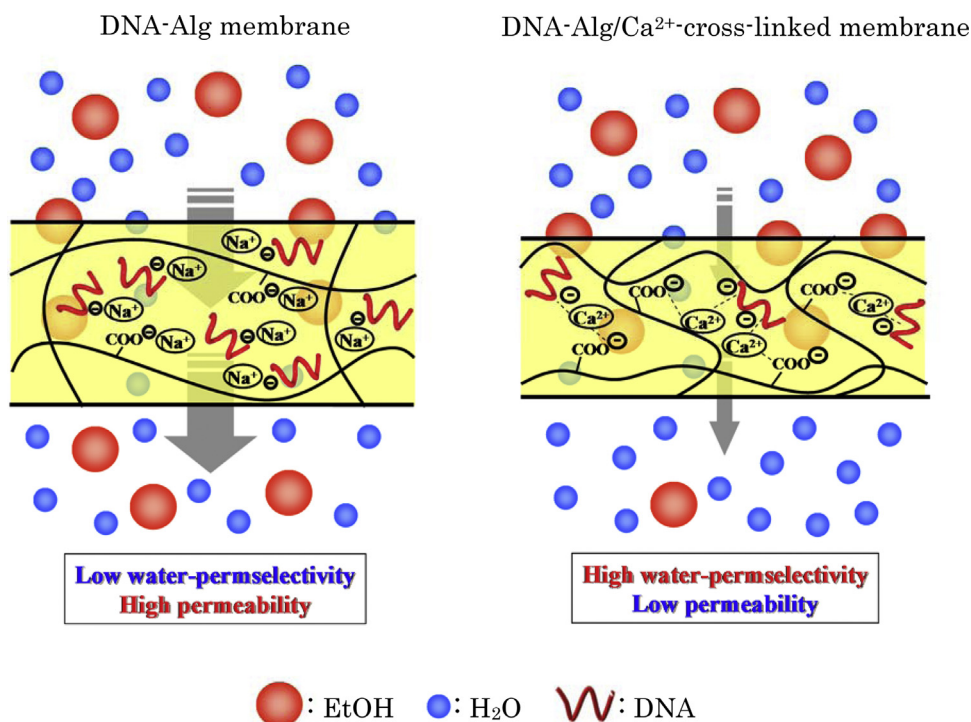


Fig. 3. Tentative model structures of the permeation and separation for an aqueous ethanol solution through Alg-DN and Alg-DNA/Ca²⁺ membranes.

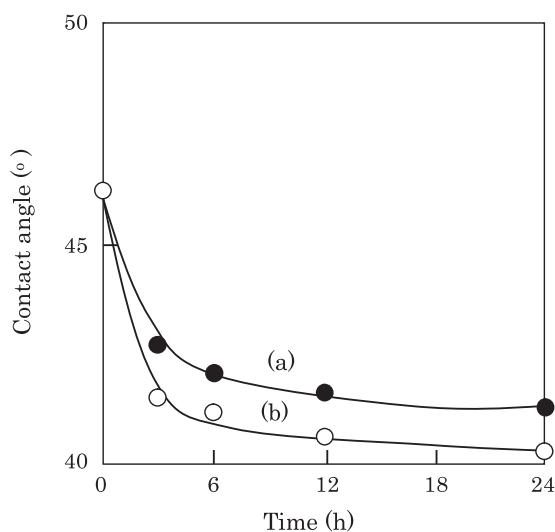


Fig. 4. The contact angle for methylene iodide of the surface of Alg-DNA/Ca²⁺ (a) and Alg-DN/Mg²⁺ (b) cross-linked membranes as a function of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂. The DNA content in the each membrane is 40 wt%.

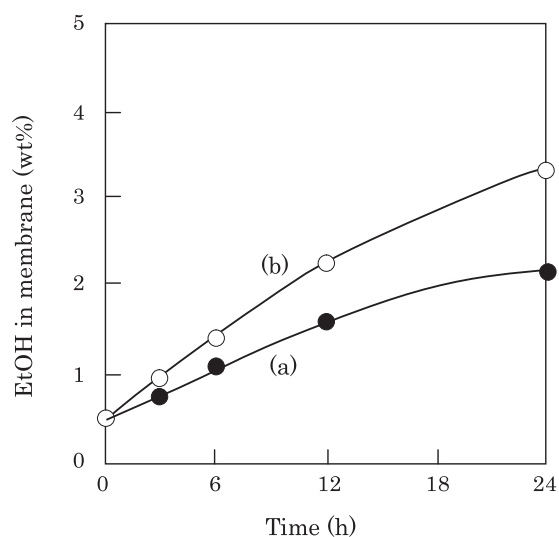


Fig. 5. Effects of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂ on the ethanol concentration sorbed in Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes. The DNA content in the each membrane is 40 wt%.

3.3. Chemical structure of Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes

In general, the selectivity of polymer membranes depends upon their chemical and physical structures, influence the solubility of permeants in the membrane and the diffusivity of permeants through the membrane. Therefore, we investigated the chemical and physical structures of the Alg-DNA cross-linked with metal ions to their permeation and separation characteristics, as shown in Fig. 2. Fig. 4 shows the effect of the immersion time on the contact angle for methylene iodide of the surface of Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes. As can be seen from Fig. 4, the contact angles of the surface of Alg-DNA/Ca²⁺ (a)

and Alg-DNA/Mg²⁺ (b) cross-linked membranes were lower than that of the Alg-DNA membrane. These results suggest that when the Alg-DNA blend membrane was cross-linked by Ca²⁺ and Mg²⁺ ion, the formed membranes became hydrophobic. The degree of hydrophobicity of the Alg-DNA/Mg²⁺ cross-linked membrane was higher than that of the Alg-DNA/Ca²⁺ cross-linked membrane.

In Fig. 5, the ethanol concentrations sorbed in Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes are shown as a function of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂. With increasing the immersion time, the ethanol concentrations sorbed in Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes increased. Those in Alg-DNA/Mg²⁺ (b) cross-linked membranes were higher than those in Alg-DNA/Ca²⁺

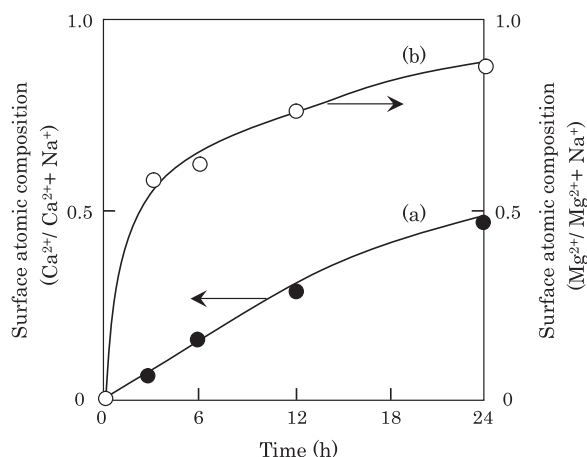


Fig. 6. The atomic composition of the surface of Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes as a function of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂. The DNA content in the each membrane is 40 wt%.

(a) cross-linked membranes. These results are supported by a higher hydrophobicity of the Alg-DNA/Mg²⁺ cross-linked membrane as discussed in Fig. 4.

Fig. 6 shows the effect of the immersion time on the surface atomic composition of Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes. As can be seen from Fig. 6, ion atomic ratios (Ca²⁺/Ca²⁺+Na⁺ and Mg²⁺/Mg²⁺+Na⁺) increased considerably with an increase of the immersion time and its increase in the Alg-DNA/Mg²⁺ cross-linked membrane was higher than that of Alg-DNA/Ca²⁺ cross-linked membrane. These results can be attributed to the fact that Mg²⁺ ions can easily go into the Alg-DNA blend membrane matrix because ionic radius of Mg²⁺ ion is smaller than that of Ca²⁺ ion.

As discussed in Fig. 4, in spite of the fact that the surface of the Alg-DNA/Mg²⁺ cross-linked membranes were hydrophobic compared with that of Alg-DNA/Ca²⁺ cross-linked membranes, the H₂O/EtOH selectivity of the former membranes was higher. From these facts, it is presumed that the effect of ion cross-linking cannot be attributed to only a change of solubility of the permeant into the membrane.

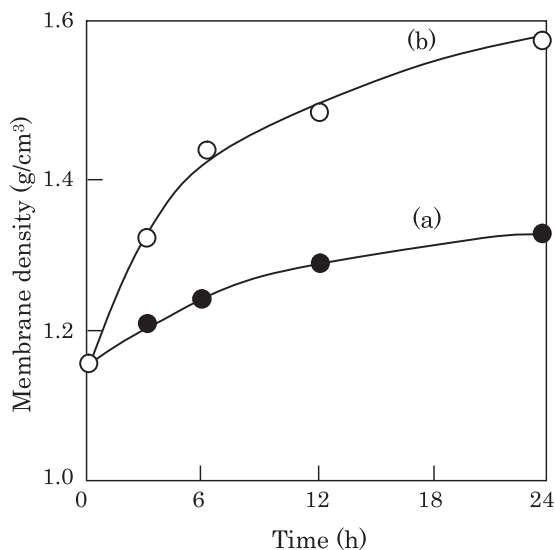


Fig. 7. Effects of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂ on the membrane density of Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes. The DNA content in the each membrane is 40 wt%.

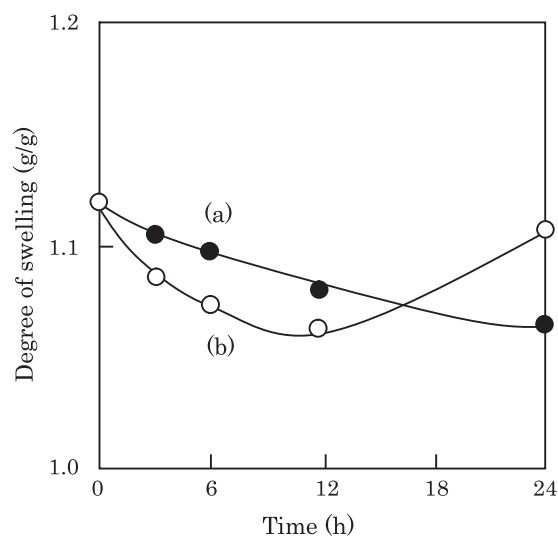


Fig. 8. The degree of swelling of Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes as a function of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂. The DNA content in the each membrane is 40 wt%.

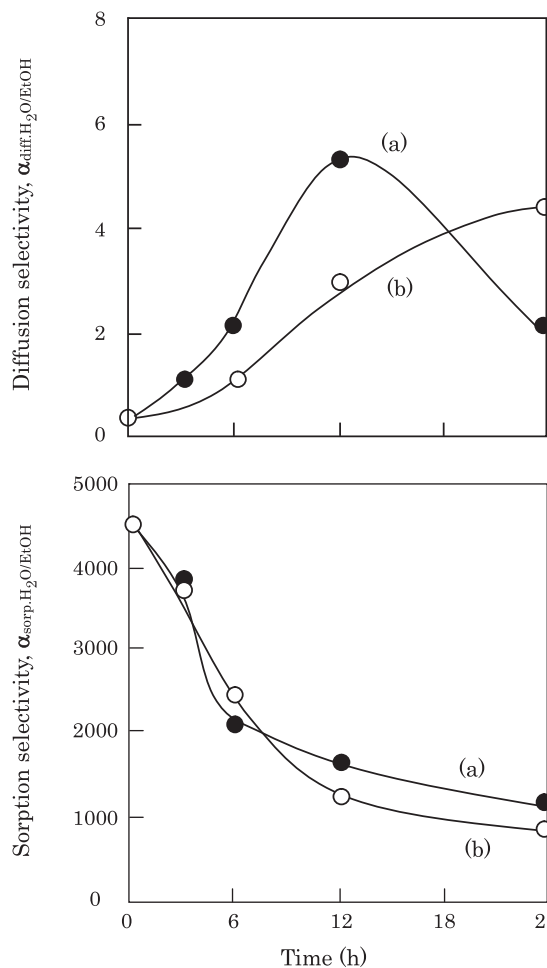


Fig. 9. The sorption selectivity and diffusion selectivity of Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes as a function of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂. The DNA content in the each membrane is 40 wt%.

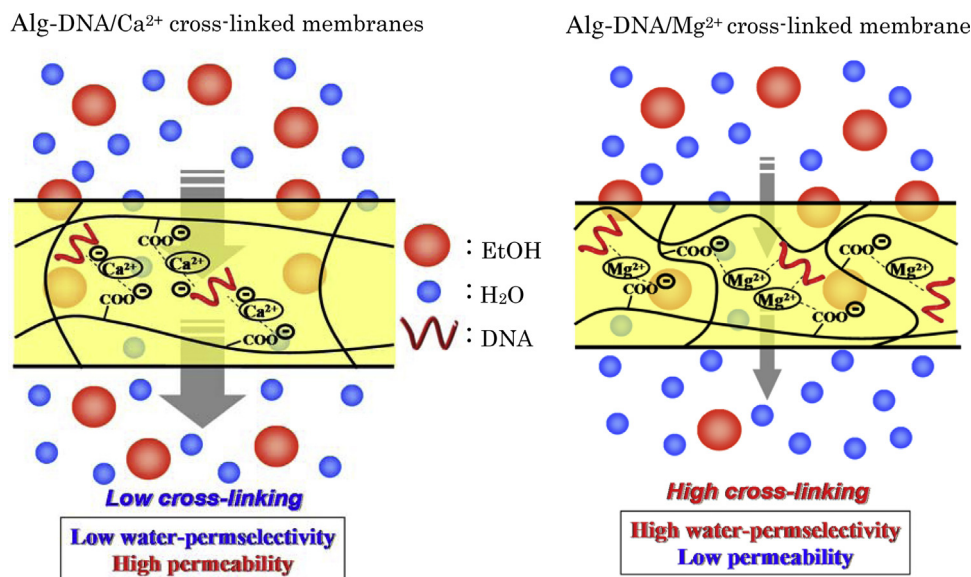


Fig. 10. Tentative model structures of the permeation and separation for an aqueous ethanol solution through Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes.

3.4. Physical structure of DNA-Alg/Ca²⁺ and DNA-Alg/Mg²⁺ cross-linked membranes

To characterize the cross-linked structure of the Alg-DNA/Ca²⁺ and DNA-Alg/Mg²⁺ cross-linked membranes, the membrane density and the degree of membrane swelling were measured.

Fig. 7 shows the membrane density of Alg-DNA/Ca²⁺ (a) and Alg-DNA/Mg²⁺ (b) cross-linked membranes as a function of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂. The membrane densities of Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes increased with an increasing of the immersion time. These results are due to the fact that with increasing the immersion time the cross-linking reactions proceeded smoothly. In particular, the increase in the membrane density of Alg-DNA/Mg²⁺ cross-linked membrane is significantly. This depends on active cross-linking reactions by Mg²⁺ ion with small ion radius.

Fig. 8 shows the effect of the immersion time in CH₃OH solutions of CaCl₂ and MgCl₂ on the degree of swelling of Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes. The degree of swelling of Alg-DNA/Mg²⁺ cross-linked membranes was minimum at for 12 h of the immersion time. The decrease in the degree of swelling up to for 12 h is due to the increase of the cross-linked structure by Mg²⁺ ions. The increase in the degree of swelling after for 12 h depends upon the swelling by ethanol in an azeotropic mixture of ethanol/water because the hydrophobicity of the Alg-DNA/Mg²⁺ cross-linked membrane during the long immersion time is increased.

3.5. Analysis of selectivity

It is well known that the separation mechanism of organic liquid mixtures through dense polymer membranes by PV results from differences in the (i) solubility of permeants into the polymer membrane and (ii) diffusivity of permeants through the membrane.

In the solution-diffusion model (Binning et al., 1961; Aptel et al., 1974) differences in the solubility of the permeants in the membranes and differences in the diffusivity of the permeants in the polymer membranes are very significantly related to their permselectivity (Uragami, Matsuda, Okuno, & Miyata, 1994).

The separation factors for the H₂O/EtOH selectivity of Alg-DNA blend, Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes

were very high, as shown in Fig. 1 and the ethanol concentrations in these membranes were much low than that in an azeotropic mixture of ethanol/water, as shown in Fig. 5. These facts indicate that the H₂O/EtOH selectivities of Alg-DNA blend, Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes depend on both the sorption and diffusion process as described by the solution-diffusion model. The Alg-DNA, Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes have a high affinity for water, which results in high solubility selectivity; in addition, the molecular size of water is smaller than that of ethanol, and, thereby, contributes positively to a high diffusion selectivity (Psaume et al., 1988). To elucidate the separation mechanism for an azeotropic mixture of ethanol/water through Alg-DNA blend, Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes by PV is very important to determine both the sorption and the diffusion selectivity. The sorption selectivity, $\alpha_{\text{sorp. H}_2\text{O}/\text{EtOH}}$, was determined by Eq. (3) using the data in Fig. 5 and the diffusion selectivity, $\alpha_{\text{diff. H}_2\text{O}/\text{EtOH}}$, was calculated from the separation factor, $\alpha_{\text{sep. H}_2\text{O}/\text{EtOH}}$, obtained by applying the results in Fig. 1 to Eq. (1), and the sorption selectivity by Eq. (3), using Eq. (5) (Binning et al., 1961; Uragami, Wakita, & Miyata, 2010)

$$\alpha_{\text{diff. H}_2\text{O}/\text{EtOH}} = \frac{\alpha_{\text{sep. H}_2\text{O}/\text{EtOH}}}{\alpha_{\text{sorp. H}_2\text{O}/\text{EtOH}}} \quad (5)$$

The effects of the immersion time on the sorption and diffusion selectivity are shown in Fig. 9. For all immersion times, the sorption selectivity was greater than the diffusion selectivity. This result suggests that the separation mechanism for the azeotropic mixture of ethanol/water through Alg-DNA blend, Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes is more governed by the sorption than the diffusion process. Previous works indicated that the sorption selectivity mainly determined the separation of organic liquid mixtures for dehydration of organic solvents by PV (Uragami, Matsuda, Okuno, Miyata, 1994; Uragami et al., 2004). The fact that the water concentrations in the permeate were higher than those in Alg-DNA blend, Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes, as shown in Fig. 5, can be explained by the above discussion, that is, the sorption selectivity and the diffusion selectivity significantly influence the H₂O/EtOH selectivity.

Table 1
Comparison of permeation and separation characteristics for dehydration.

Membrane ^a	Feed composition		Separation factor $\alpha_{\text{sep.H}_2\text{O}/\text{EtOH}}$	Permeation rate (kg/m ² h)	Ref.
	Water (wt%)	Ethanol (wt%)			
PVA/PAAM	5.0	95.0	1300	0.80	1
Alg	10.0	90.0	120	0.29	2
CS/Alg	5.0	95.0	1110	0.07	3
Alg-Ca ²⁺	5.0	95.0	560	0.10	4
Alg/HDA	10.0	90.0	891	0.59	5
Zeolite NaA	30.0	70.0	2140	2.10	6
PVA	30.0	70.0	6.4	1.20	6
PVA/PSA	6.2	93.8	700	0.50	7
CS/Alg	13.5	86.4	436	0.22	8
CTSN/BCM	5.0	95.0	10	42.8	9
CTSN/PVA	5.0	95.0	22.0	1.7	9
P-Alg/PVP	4.6	95.4	364	0.09	10
Alg	5.0	95.0	73	0.17	11
Alg/HEMA	5.0	95.0	571	0.13	11
Alg/PA	5.2	94.8	2200	0.28	12
Alg-PVA/PSF	5.0	95.0	886	0.13	13
Alg/HA/PAN	10.0	90.0	43	0.99	14
HA/Alg/PAN	10.0	90.0	45	1.00	14
Alg/DNA-Ca ²⁺	3.5	96.5	5500	0.01	Present work
Alg/DNA-Mg ²⁺	3.5	96.5	6500	0.01	Present work

PVA/PAAM: poly(vinyl alcohol)/poly(acrylamide), Alg: alginate, CS/Alg: chitosan/alginate, Alg-Ca²⁺: alginate-Ca²⁺, Alg/HDA: alginate/1,6-hexanediamine, PVA: poly(vinyl alcohol), PVA/PSA: poly(vinyl alcohol)/poly(styrene sulfonic acid), CTSN-BCM: bacteria cellulose membrane impregnated with chitosan, CTSN-PVA: CTSN-PVA blend, P-Alg/PVP: phosphorylated alginate/poly(vinyl pyrrolidone), Alg/PHEMA: alginate/poly(hydroxyethylmethacrylate), Alg/PA: alginate/phosphoric acid, Alg/PVA/PSF: alginate/poly(vinyl alcohol)/poly(sulfone), Alg/HA/PAN: alginate/hyaluronic acid/poly(acrylonitrile), HA/Alg/PAN: hyaluronic acid/alginate/poly(acrylonitrile), Alg/DNA-Ca²⁺: alginate/deoxyribonucleate-Ca²⁺ ion, Alg/DNA-Mg²⁺: alginate/deoxyribonucleate-Mg²⁺ ion. 1. Ruckenstein and Liang (1996). 2. Yeom, Jegal, & Lee (1996). 3. Moon, Pal, & Huang (1999). 4. Huang et al. (1999). 5. Wang (2000). 6. Shah, Kissi, Ghorpade, Hannah, & Bhattacharyya (2000). 7. Toutianoush, Krasemann, & Tieke (2002). 8. Kanti et al. (2004). 9. Dubey, Pandey, & Saxena (2005). 10. Kalyani et al. (2006). 11. Veerapur et al. (2006). 12. Kalyani et al. (2008). 13. Kai, Zhen-liang, & Young-ming (2008). 14. Gao et al. (2014).

3.6. Comparison of membrane performance between Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes

The PV membrane performances of the dehydration for an azeotropic mixture of ethanol/water through Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes were higher than that of a Alg-DNA membrane. This result can be attributed to the fact that an adequate immersion of a Alg-DNA membrane in the CaCl₂/CH₃OH or MgCl₂/CH₃OH solution could form an efficient cross-linking structure and consequently the swelling of membrane could be depressed effectively.

The Alg-DNA/Mg²⁺ cross-linked membranes showed an excellent water permselectivity compared with Alg-DNA/Ca²⁺ cross-linked membranes as shown in Fig. 10. This fact was due to that since the ionic radius of Mg²⁺ ion is smaller than that of Ca²⁺ ion, the cross-linking structure with Mg²⁺ in the membrane could be smoothly constructed and the swelling of cross-linked membrane could be significantly depressed. To control the immersion time of a Alg-DNA blend membrane in the MgCl₂/CH₃OH solution could offer excellent water permselective membranes for the dehydration of aqueous organic solvents.

3.7. Rank of Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ Membranes in Pervaporation Performance for Dehydration of Ethanol/Water Mixture

In Table 1 the permeation and separation characteristics of Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ membranes are compared with those of other membranes previously reported. As can be seen from the table, the separation factors of Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ membranes prepared in this work are extremely high. In the near future the improvement in the permeation rate of those membranes is strongly required. To achieve this improvement the preparation of thinner membrane onto a porous support have to try.

4. Conclusions

Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked PV membranes were prepared using CaCl₂ and MgCl₂ as ionic cross-linker for the dehydration of an azeotropic mixture of ethanol/water. The permeation and separation characteristics for an ethanol/water azeotrope through Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes were significantly influenced by the immersion time for the cross-linking reaction of a Alg-DNA blend membrane in CaCl₂ or MgCl₂ methanol solution. The separation factors for H₂O/EtOH selectivity of those membranes were very high and the permeation rates also were high. However, those with the immersion time were considerably different by the cross-linking metal ion and could be well explained by the chemical and physical structure of Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes. The best permeation rates and separation factors in the dehydration for an ethanol/water azeotrope through Alg-DNA/Ca²⁺ and Alg-DNA/Mg²⁺ cross-linked membranes were 1.2×10^{-2} , 1.2×10^{-2} and 5500, 6500, respectively.

In this study, we demonstrated that membranes with high water/ethanol selectivity can be designed by selecting the blend ratio of Alg/DNA. Cross-linking with bivalent metal ions a Alg-DNA blend membrane offers potential for the improved selective separation of water/ethanol.

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