Carbohydrate Polymers 120 (2015) 1–6

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Pervaporative dehydration characteristics of an ethanol/water azeotrope through various chitosan membranes

Tadashi Uragami*, Tomoyuki Saito, Takashi Miyata

Department of Chemistry and Materials Engineering and Organization for Research and Development of Innovative Science and Technology, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Osaka, Japan

ARTICLE INFO

Article history:
Received 29 October 2012
Received in revised form 25 January 2014
Accepted 12 November 2014
Available online 27 November 2014

Keywords:
Chitosan
Molecular weight
Deacetylation
Membrane
Dehydration
Ethanol/water azeotrope

ABSTRACT

The permeation and separation characteristics of an ethanol/water azeotrope through chitosan membranes of different molecular weights and degrees of deacetylation during pervaporation were investigated. The normalized permeation rate decreased with increasing molecular weight up to 90 kDa, but at over 90 kDa, the rate increased. On the other hand, the water/ethanol selectivity increased with increasing molecular weight up to 90 kDa but decreased at over 90 kDa. With increasing degree of deacetylation, the water/ethanol permselectivity increased significantly, but the normalized permeation rate decreased. The characteristics of chitosan membranes are discussed based on their chemical and physical structures such as the contact angle, density, degree of swelling, and glass transition temperature.

1. Introduction

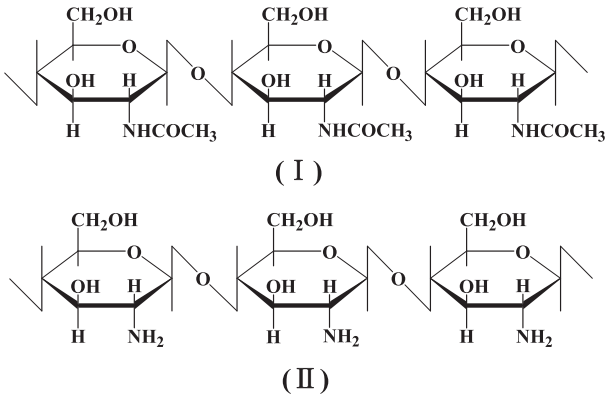
Recently, polysaccharides such as chitin and chitosan are getting much attention in a lot of difference areas (Uragami & Tokura, 2006). Chitin (**I**) is mainly obtained from crab and shrimp shell (Muzzarelli, 1977). Chitosan (**II**) is prepared by the deacetylation of chitin (Muzzarelli, 1973) (Scheme 1). Chitin and chitosan have high solvent-resistance. In particular, chitosan membranes can be easily prepared by casting a chitosan solution in dilute aqueous solutions of organic acids and neutralizing with an aqueous alkalaine solution. Since the chitosan membrane is highly hydrophilic, it is advantageous for the dehydration of organic solvents (Uragami, Saito, & Takigawa, 1988; Wang, Shen, & Zhang, 1996; Uragami & Takigawa, 1990; Lee, Park, Nam, Won, & Kim, 1998).

Bioethanol is produced by the fermentation of biomass is an aqueous solution of about 10 wt%. After distillation of the resulting aqueous ethanol solution, an azeotropic mixture of ethanol/water (96.5 wt% ethanol) is obtained. However, the distillation process is very difficult. In order to solve this problem, the use of pervaporation (PV), which is a membrane separation technique, is appropriate for the separation and concentration of azeotropic mixtures (Baker et al., 1991). In a previous study, we reported that chitosan and its derivative membranes such as chitosan membranes cross-linked with glutaraldehyde (Uragami, Matsuda, Okuno, & Miyata, 1994), as well as quaternized chitosan membranes cross-linked with glutaraldehyde (Uragami, Tanaka, & Nishida, 2002a), ethylene glycol diglycidyl ether (Uragami, Takuno, & Miyata, 2002b) and poly(ethylene oxydiglycolic acid) (Uragami, Yamamoto, & Miyata, 2003), were water permselective and advantageous for the dehydration of organic solvents.

The pervaporative dehydration of ethanol has been studied by sodium alginate/poly(hydroxyethylmethacrylate) interpenetrating polymeric network membranes (Patil, Gudasi, & Veerapur, 2006), sodium alginate-based inorganic–organic hybrid membranes (Magalad, Surapale, Maradur, Gavisidduppa, & Gokavi, 2010), mixed matrix blend membranes of poly(vinyl alcohol)-poly(vinyl pyrrolidone) loaded with phosphomolybdic acid (Veeresh, Gavisiddappa, Gokavi, & Raju, 2010), and organic–inorganic nanocomposite membranes (Mochizuki, Sato, Ogawara, & Yanashita, 2011). Furthermore, chitosan/gelatin blend (Shiranand et al., 2009), and mixed matrix blend of poly(vinyl alcohol)/poly(vinylpyrrolidone) loaded with phosphomolybdic acid (Anjali, Smitha, Sridhar, & Aminabhari, 2011), phosphorylated chitosan (Sunitha, Satyanarayana, Sridhar, 2012), chitosan/poly(acrylic acid) composite (Li, Lin, Zhu, Luo, Yu, 2012), hollow titanium spheres–chitosan hybrid (Liu, Jiang, Wang, Yang, 2013), chitosan/sulfonated polyethersulfone–polyethersulfone composite (Wu, Li, Zhao, Shen, Jiang, Wang, 2013), chemically cross-linked chitosan membrane by adipic acid (Cai, Gong, Cao,

* Corresponding author. Tel.: +81 6 6368 1111; fax: +81 6 6368 0080.
E-mail addresses: v701489@kansai-u.ac.jp, uragami@ipcku.kansai-u.ac.jp (T. Uragami).

http://dx.doi.org/10.1016/j.carbpol.2014.11.032
0144-8617/



Scheme 1. Structure of chitin and chitosan.

Chen, Luo, 2013) membranes have been reported. These are very interesting dehydration membranes for organic solvents.

Ethanol concentration produced by biofermentation is about 10 wt%. Therefore, to concentrate the resulting aqueous ethanol solution, it is distilled but the resulting solution is an azeotrope of ethanol/water. It is well known that PV method is effective for dehydrating this azeotopic mixture but the selection of dehydration membranes is a very important problem. An appropriate membrane material is chitosan. Chitosan is a typically hydrophilic material and can be prepared with different molecular weights and degrees of deacetylation.

In this study, the permeation and separation characteristics of an ethanol/water azeotrope through chitosan membranes with different molecular weights and degrees of deacetylation during PV were investigated. The characteristics of these chitosan membranes during PV are also discussed based on their chemical and physical structures.

2. Experimental

2.1. Materials and reagents

Six kinds of chitosans were used with molecular weights in the range of 1.3×10^5–2.0×10^6 and a degree of deacetylation (DAC) of 86% as shown in Table 1. Three kinds of chitosans with DACs in the range of 50–100% and a molecular weight of 5×10^4 were also used as shown in Table 2. They were kindly supplied by Kyowa Technos Co. Ltd. All other reagents and solvents were obtained from commercial sources.

Table 1
Molecular weight (*Mw*) of chitosan with a constant degree of decetylation (DAC).

Mw ($\times 10^2$ kDa)	*Mw*/*Mn*	DAC (%)
0.13	2.0	85.6
0.72	3.7	86.5
0.89	4.3	85.6
1.52	4.5	85.6
2.01	3.8	85.6

Table 2
Degree of deacetylation (DAC) of chitosan with a constant molecular weight (*Mw*).

Mw ($\times 10^2$ kDa)	*Mw*/*Mn*	DAC (%)
4.8	3.2	50
5.0	4.3	70
5.1	3.6	100

2.2. Preparation of chitosan membranes

Chitosan membranes were prepared by casting 2 wt% chitosans in aqueous acetic acid solutions on glass dishes, drying at 60 °C for 24 h, treating with an aqueous sodium hydroxide solution, washing thoroughly with pure water, and finally drying under a reduced pressure.

2.3. Pervaporation apparatus and experiments

The PV cell and PV apparatus were described in a previous paper (Inui, Miyata, & Uragami, 1996). The effective membrane area was about 13.8 cm^2. The PV experiments were carried out under the following conditions: permeation temperature, 40 °C, and pressure of the permeate side, 1.33 Pa. The feed solution, an aqueous solution of 96.5 wt% ethanol (an ethanol/water azeotrope), was circulated between the PV cell and the feed tank to maintain a constant concentration of feed solution in the cell. The permeation rate (kg/m^2 h) for the ethanol/water azeotrope during PV was determined from the weight (kg) of the permeate collected in the cold trap, the permeation time (h) and the effective membrane area (m^2). In order to compare the permeation rates of membranes of different thicknesses, the normalized permeation rate [kg m/(m^2 h)], which is the product of the permeation rate and the membrane thickness, was determined. The permeation results for the ethanol/water azeotrope by PV were reproducible, and the inherent errors of these permeation measurements were within a few percent of the permeation rates through the membranes. The permeation results in this study were determined after a steady-state flux.

The ethanol concentrations in the feed and permeate were determined by a gas chromatograph (Shimadzu GC-14A, Japan) with a flame ionization detector (FID) and a capillary column (Shimadzu Co. Ltd: PorapacQ, Japan) heated to 180 °C.

The selectivity, P_{H_2O}/P_{EtOH}, was calculated from the ratio of water and ethanol in the permeate, respectively.

2.4. Measurement of contact angle

The contact angle of methylene iodide on the surface of various chitosan membranes was measured by a contact angle meter (Dropmaster Kyouwa Sci. Co. Ltd.) at 25 °C. The contact angle, θ, was calculated from the following equation:

$$\theta = \cos^{-1}\left[\frac{(\cos\theta_a + \cos\theta_r)}{2}\right] \quad (1)$$

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

2.5. Membrane density

The densities of various chitosan membranes were determined by measuring their weights in air and *n*-hexane with an electric gravity meter (Mirage Boeki, SD-120L) at 25 °C.

2.6. Cross-linking density of various chitosan membranes

The cross-linking density, ρ, of the chitosan membranes was calculated from the network theory of rubber elasticity given in Eq. (2) (Tobolsky, Carlson, & Indictor, 1961):

$$\rho = \frac{E'}{3d\phi RT} \quad (2)$$

where E' was determined from measurements with a dynamic mechanical analyzer (Rheogel-E4000 F3, U.B.M) under the following conditions: frequency 1, 2, 4, 10 Hz and temperature 40 °C, d is

the membrane density, ϕ is the front factor (where $\phi = 1$), R is the gas constant and T is the absolute temperature.

2.7. Degree of swelling

The chitosan membranes were completely dried under a reduced pressure at 40 °C and then weighed. These dried membranes were immersed in an ethanol/water azeotrope (96.5 wt% ethanol) in a sealed vessel at 40 °C until equilibrium was reached. The membranes were removed from the vessel, wiped quickly with a filter paper, and weighed again. The degree of swelling (DS) of the membrane was determined from the following equation:

$$\mathrm{DS} = \frac{W_s}{W_d} \tag{3}$$

where W_d and W_s are the weights of the dried membrane and the swollen membrane in the feed, respectively.

2.8. Measurement of glass transition temperature (T_g)

The glass transition temperatures (T_gs) of dry chitosan membranes were determined by differential scanning calorimetry (DSC) (Rigaku, TAS-200). The specimens were heated from about−150 °C to +159 °C at a heating rate of 20 °C/min.

3. Results and discussion

3.1. Effect of molecular weight

Fig. 1 shows the effect of the molecular weight of chitosan on the water/ethanol selectivity and the normalized permeation rate for an aqueous solution of 96.5 wt% ethanol. The normalized permeation rate decreased with increasing molecular weight up to 90 kDa but at over 90 kDa, the rate increased. On the other hand, the water/ethanol selectivity increased with increasing molecular weight up to 90 kDa, but at over, the selectivity decreased. These permeation and separation characteristics may be 90 kDa attributed to the different structures of the resultant membrane due to different molecular weights of chitosan.

Fig. 2 shows the effect of the molecular weight of chitosan on the contact angle of methylene iodide on the surface of the chitosan membrane. As can be seen from this figure, the contact angles were not dependent on the molecular weight. This result suggests that the state of the hydrophilic functional groups, such as hydroxyl and amine groups on the surfaces of the various chitosan membranes were similar, and consequently the chemical characteristics of the membrane surfaces prepared from chitosans of the same degree of deacetylation were almost the same.

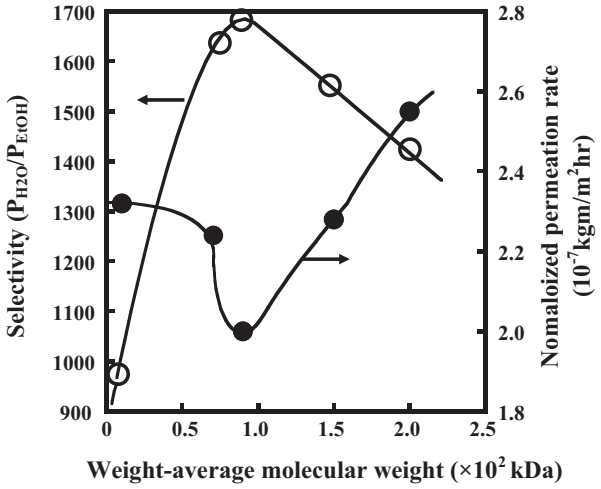


Fig. 1. Effects of the molecular weight of chitosan on the water/ethanol selectivity (○) and normalize permeation rate (●) for an aqueous solution of 96.5 wt% ethanol.

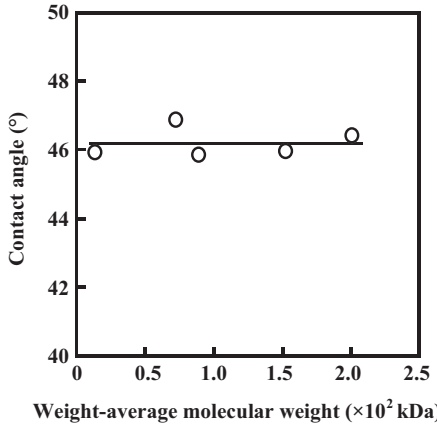


Fig. 2. Effect of the molecular weight of chitosan on the contact angle of methylene iodide on the surface of chitosan membrane.

In Fig. 3, the density and degree of swelling of the chitosan membranes as a function of the molecular weight of chitosan are shown. The membrane density increased with increasing molecular weight up to 90 kDa, but at over 90 kDa, the membrane density decreased. Consequently, the membrane density showed a maximum at a molecular weight of 90 kDa. This result suggests that the chitosan membrane with the highest density was formed at this molecular weight. In other words, at a molecular weight of 90 kDa, various entanglements and hydrogen bonds between the molecular chains of chitosan were effectively formed, and consequently the densification of the chitosan membrane could be accelerated. On the other hand, the degree of swelling of the chitosan membrane showed a minimum at a molecular weight of 90 kDa. This observation corresponds to the change in the membrane density with the molecular weight of chitosan.

To further investigate the physical structure of the chitosan membrane, the glass transition temperatures of the chitosan membranes were determined. In Fig. 4, the relationship between the glass transition temperature and the molecular weight of chitosan is shown. As can be seen from Fig. 4, the glass transition

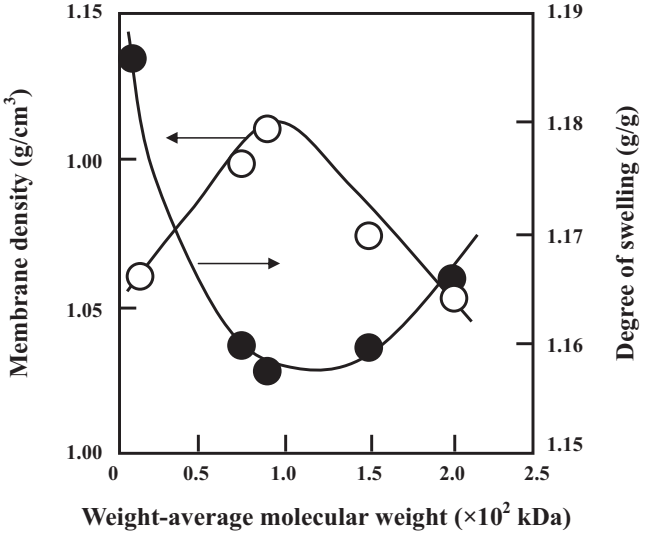


Fig. 3. Effects of the molecular weight of chitosan on the density (○) and degree of swelling (●) of chitosan membrane.

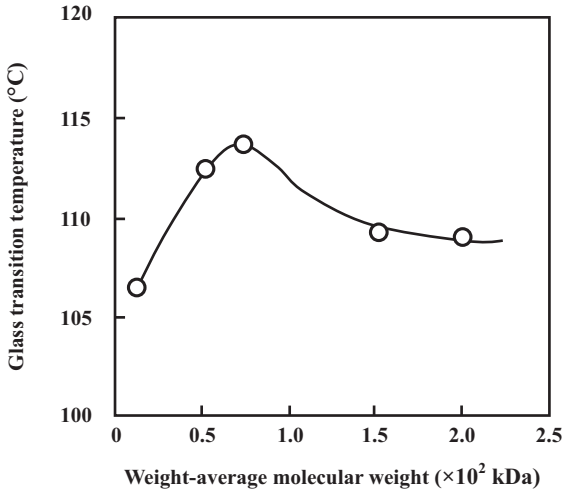


Fig. 4. Relationship between the glass transition temperature and the molecular weight of chitosan.

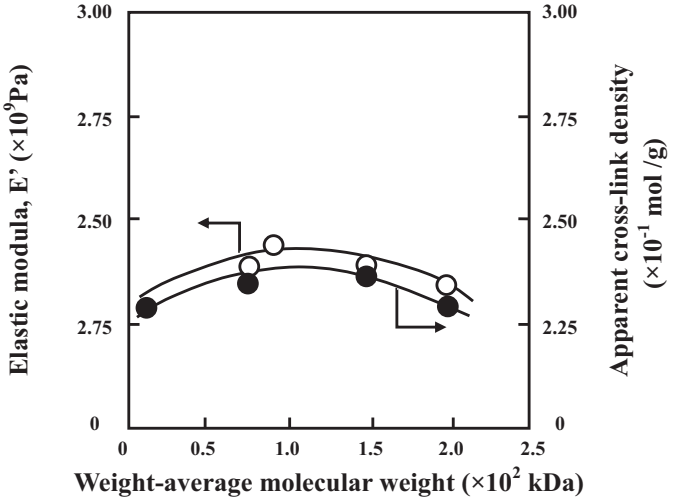


Fig. 6. Effect of the molecular weight of chitosan on the elastic modulus (○) and apparent cross-link density (●) of the chitosan membranes.

temperature of the membrane was highest at a molecular weight of 90 kDa. This suggests that the motion of the chitosan molecular chains in the membrane with chitosan at a molecular weight of 90 kDa was significantly suppressed. The results from Fig. 4 support the results in Fig. 3.

To investigate the above speculations raised in the discussion, above, the viscosity of casting solutions of chitosan with different molecular weight and the apparent cross-linking density of the chitosan membranes were determined.

In Fig. 5, the relationship between the molecular weight of chitosan and the viscosity of casting solutions of chitosan of different molecular weights is shown. As can be seen from Fig. 5, the viscosity of the casting solution was the highest at a molecular weight of 90 kDa, the same as the density and glass transition temperature of the chitosan membranes.

The apparent cross-linking density of the chitosan membranes expressed in Eq. (2) was determined using the elastic modulus obtained from measurements of the dynamic viscoelasticity, and the membrane density measured by the electric gravity meter. In Fig. 6, the effect of the molecular weight of the chitosan membranes on the apparent cross-linking density of the membranes is also shown. The cross-linking density also showed a maximum at a molecular weight of 90 kDa.

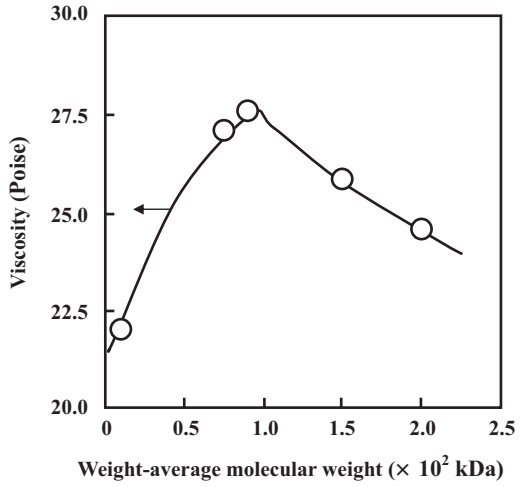


Fig. 5. Relationship between the viscosity of the casting solutions of various chitosans and the molecular weight of chitosan.

On the basis of the aforementioned results, the effects of the molecular weight of chitosan on the permeation and separation characteristics of the ethanol/water azeotrope through chitosan membranes with the same degree of deacetylation can be explained as follows. In the membrane prepared from chitosan with a low molecular weight, the entanglements between the chitosan molecules is poor because the molecular chains of chitosan are short, as can be understood from Fig. 5. Therefore, the membrane became a swollen state with the feed solution as shown in Fig. 3, causing a high permeation rate, but low water/ethanol selectivity.

In the membrane prepared from chitosan with a molecular weight of about 900,000, the entanglements and hydrogen bonds between the chitosan molecules are enhanced as can be understood from Figs. 4 and 5, and a dense chitosan membrane without swelling by the feed solution was formed as shown, in Fig. 3. Consequently, an excellent water–permselective chitosan membrane can be obtained because the diffusion of ethanol molecules through the chitosan membrane is suppressed. In this case, the permeation rate is low.

The membrane prepared using chitosan with a high molecular weight has a rough, open structure because the expansion of the chitosan molecular chains in the casting solution are insufficient, as can be seen in Fig. 5. Therefore, the ethanol molecules in the chitosan membrane can diffuse easily, causing low water/ethanol selectivity, but high permeability.

3.2. *Effect of the degree of deacetylation*

Fig. 7 shows the effects of deacetylation on the normalized permeation rate and the water/ethanol selectivity for an ethanol/water azeotrope through chitosan membranes with the same molecular weight during PV. With an increasing degree of deacetylation of chitosan, the water/ethanol selectivity increased significantly, but the normalized permeation rate decreased.

The relationship between the contact angle of methylene iodide on the surface of the chitosan membranes and their degree of deacetylation was investigated. Consequently, the contact angle increased significantly with an increasing degree of deacetylation. This result suggests that the surface of the chitosan membrane becomes hydrophilic with an increasing degree of deacetylation. This change in the chemical structure is due to a change from acetoamide groups to amino groups. The increase in the water/ethanol selectivity in Fig. 7 can be attributed to the fact that the membrane

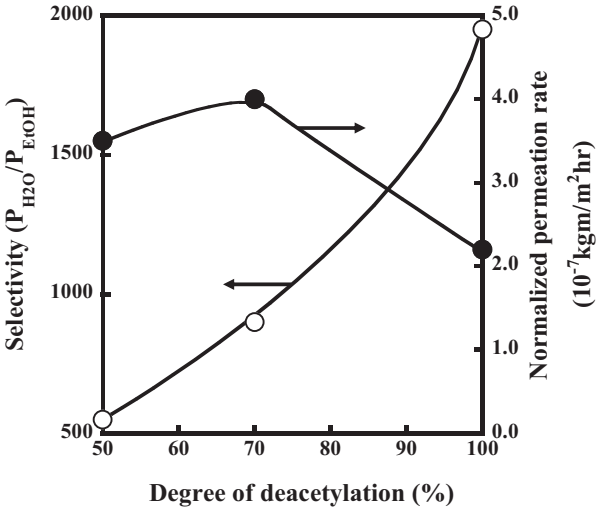


Fig. 7. Normalized permeation rate (●) and water selectivity (○) of an ethanol/water azeotrope through chitosan membranes with the same molecular weight during PV as a function of the degree of deacetylation of chitosan.

surface became hydrophilic with an increasing degree of deacetylation.

In Fig. 8, the effects of the degree of deacetylation on the density and degree of swelling of the chitosan membrane are shown. The membrane density increased with an increasing degree of deacetylation of chitosan. This increase in membrane density could be attributed to the fact that the number of amino groups which can form stronger hydrogen bonds than acetoamide groups, had increased. The degree of swelling of the chitosan membrane decreased with an increasing degree of deacetylation. This decrease in the degree of swelling was strongly correlated to the increase in hydrogen bonds between the amino groups, and between the amino and hydroxyl groups. The increases in both the membrane density and the degree of swelling support the decrease in the normalized permeation rate and increase in the water/ethanol selectivity as shown in Fig. 7.

The effect of degree of deacetylation on the glass transition temperature of the chitosan membranes was investigated by the DSC measurements. Consequently, the glass transition temperature increased significantly with an increase in the degree of deacetylation. This increase in the glass transition temperature could be due to the fact that the hydrogen bonds between the chitosan molecule

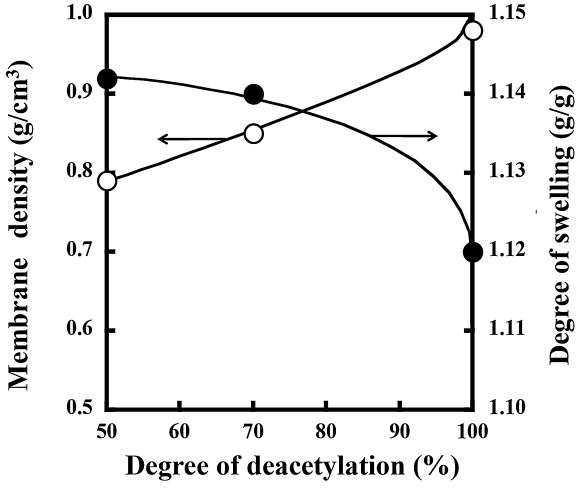


Fig. 8. Effects of the degree of deacetylation of chitosan on the density and degree of swelling of chitosan membranes.

chains were increased with an increase in the amino groups, and consequently the motion of the chitosan molecules became more limited.

Based on the results above, the effect of the degree of deacetylation on the permeation and separation characteristics for an ethanol/water azeotrope through the chitosan membranes with different degrees of deacetylation, but the same molecular weight, can be explained as follows. With an increasing degree of deacetylation, the acetoamido groups on the surface of the chitosan membrane are converted into amino groups. This conversion enhances the surface hydrophilicity of the chitosan membrane, and thus the selective absorption of water molecules in the ethanol/water azeotrope into the chitosan membrane is accelerated. On the other hand, the increase in the degree of deacetylation enhances the effective formation of hydrogen bonds between the amino and hydroxyl groups, and between the amino groups in the chitosan molecules, thus resulting in a dense chitosan membrane. Consequently, the diffusion of ethanol molecules in the chitosan membrane is prevented and an excellent water–permselective chitosan membrane can be realized.

4. Conclusions

The chemical and physical structures of chitosan membranes are strongly influenced by the structure of the chitosan molecule. Then some chitosan membranes with different molecular weights (*Mw*s) and degrees of deacetylation (DACs) were applied to dehydrate of an ethanol/water azeotrope during PV. In various chitosan membranes in which DAC is kept at ca. 86% and *Mw*s are 0.13–2.01 × 10^3 kDa, a chitosan membrane with *Mw* of 8.8 × 10 kDa showed the highest water/ethanol selectivity but the lowest permeation rate. On the other hand, in some chitosan membranes in which *Mw* of ca. 5 × 10 kDa and DAC is 50–100%, the water/ethanol selectivity of a chitosan membrane with DAC of 100% was the highest but the permeation rate was the lowest. These results depended upon the contact angle of the membrane surface, degree of swelling and density, glass transition temperature of chitosan membranes. Consequently, the permeation and separation characteristics of various chitosan membranes were governed by their chemically and physically structural characteristics.

In this study, we demonstrated that chitosan membranes with high permeability and high water/ethanol selectivity can be designed by selecting chitosan as a membrane material, and ensuring that the chitosan has a high degree of deacetylation and an adequate molecular weight. The selection of a membrane material, with an excellent chemical and physical structure offers the potential for the selective separation of water/ethanol.

References

Anjali, D., Smitha, B., Sridhar, S., & Aminabhari, T. M. (2011). Separation of isopropanol–water mixtures by pervaporation using mixed matrix blend membranes of poly(vinyl alcohol)/poly(vinyl pyrrolidone) loaded with phosphomolybdic acid. *Journal of Applied Polymer Science*, *121*, 711–719.

Baker, R. W., Cusssle, E. L., Eykamp, W., Koros, W. J., Riley, R. L., & Strathmann, H. (Eds.). (1991). Pervaporation membranes. In *Membrane separation system, recent developments and future directions* (pp. 151–177). New Jersey, USA: Noyes Data Corporation.

Cai, M. T., Gong, J., Cao, J., Chen, Y. W., & Luo, X. L. (2013). In situ chemically crosslinked chitosan membrane by adipic acid. *Journal of Applied Polymer Science*, *128*, 3308–3314.

Inui, K., Miyata, T., & Uragami, T. (1996). Permeation and separation of organic liquid mixtures through liquid-crystalline polymer networks. *Angewante Makromolekulare Chemie*, *240*, 241–250.

Lee, Y. M., Park, H. B., Nam, S. Y., Won, J. M., & Kim, H. (1998). Effect of deacetylation degree in chitosan composite membranes on pervaporation performance. *Separation Science and Technology*, *33*, 1255–1264.

Li, Q., Lin, W. H., Zhu, T. R., Luo, Y. B., & Yu, P. (2012). New chitosan/poly(acrylic acid) composite membrane for application in pervaporation dehydration of caprolactam solution. *Desalination and Water Treatment*, *43*, 43–51.

Liu, G. X., Jiang, Z. Y., Wang, Y. G., & Yang, D. (2013). Novel hollow titania spheres–chitosan hybrid membranes with high isopropanol dehydration performance. *Chemical Engineering & Technology*, *36*, 332–338.

Magalad, V. T., Surapale, A. R., Maradur, S. P., Gavisidduppa, S., & Gokavi, A. (2010). Preyssler type heteropolyacid-incorporated highly water-selective sodium alginate-based inorganic–organic hybrid membranes for pervaporation dehydration of ethanol. *Chemical Engineering Journal*, *159*, 75–83.

Mochizuki, A., Sato, Y., Ogawara, H., & Yanashita, S. (2011). Pervaporation separation of water–ethanol mixtures using organic–inorganic nanocomposite membranes. *Journal of Physical Chemistry*, *115*, 14731–14744.

Muzzarelli, R. A. A. (1977). *Chitin*. Oxford, UK: Pergamon Press.

Muzzarelli, R. A. A. (1973). *Natural chelating polymer*. New York, USA: Pergamon Press.

Patil, M. B., Gudasi, K. B., & Veerapur, R. S. (2006). Sodium alginate/poly(hydroxyethylmethacrylate) interpenetrating polymeric network membranes for the pervaporation dehydration of ethanol and tetrahydrofuran. *Journal of Applied Polymer Science*, *101*, 324–3329.

Shiranand, T., Gokavi, B., Gavisidduppa, S., Tea-Maan, T., Tejraj, M., & Winabhavio, A. (2009). Chitosan/gelatin blend membranes for pervaporation dehydration of 1,4-dioxane. *Separation Science and Technology*, *44*, 3202–3223.

Sunitha, K., Satyanarayana, S., & Sridhar, S. (2012). Phosphorylated chitosan membranes for the separation of ethanol-water mixtures by pervaporation. *Carbohydrate Polymers*, *87*, 1569–1574.

Tobolsky, A. V., Carlson, D. W., & Indictor, N. (1961). Rubber elasticity and chain configuration. *Journal of Polymer Science*, *54*, 175–192.

Uragami, T., Saito, M., & Takigawa, K. (1988). Comparison of permeation and separation characteristics for aqueous alocoholic solutions by pervaporation and new evapomeation methods through chitosan membranes. *Makromolekure Chemie. Rapid Communication*, *9*, 361–365.

Uragami, T., & Takigawa, K. (1990). Permeation and separation characteristics of ethanol–water mixtures through chitosan derivative membranes by pervaporation and evapomeation. *Polymer*, *31*, 668–672.

Uragami, T., Matsuda, T., Okuno, H., & Miyata, T. (1994). Structure of chemically modified chitosan membranes and their characteristics of permeation and separation of aqueous ethanol solutions. *Journal of Membrane Science*, *88*, 243–251.

Uragami, T., Tanaka, Y., & Nishida, S. (2002). Structure of chemically modified chitosan membranes and their characteristics of permeation and separation of aqueous ethanol solutions. *Desalination*, *147*, 449–454.

Uragami, T., Takuno, M., & Miyata, T. (2002). Evapomeation characteristics of cross-linked quaternized chitosan membranes for the separation of an ethanol/water azeotrope. *Macromolecular Chemistry & Physics*, *203*, 1162–1170.

Uragami, T., Yamamoto, S., & Miyata, T. (2003). Dehydration from alcohols by polyion complex cross-linked chitosan composite membranes during evapomeation. *Biomacromolecules*, *4*, 137–144.

Uragami, T., & Tokura, S. (Eds.). (2006). *Material science of chitin and chitosan*. Kodansha: Springer.

Veeresh, T., Gavisiddappa, S., Gokavi, B., & Raju, N. (2010). Mixed matrix blend membranes of poly(vinyl alcohol)–poly(vinyl pyrrolidone) loaded with phosphomolybdic acid used in pervaporation dehydration of ethanol. *Journal of Membrane Science*, *354*, 150–161.

Wang, X. P., Shen, Z.-Q., Zhang, F. Y., & Zhang, Y.-F. (1996). A novel composite chitosan membrane for the separation of alcohol–water mixtures. *Journal of Membrane Science*, *119*, 191–199.

Wu, H., Li, X. S., Zhao, C. H., Shen, X. H., Jiang, Z. Y., & Wang, X. F. (2013). *Chitosan/sulfonated polyethersulfone–polyethersulfone (CS/SPES–PES) composite membranes for pervaporative dehydration of ethanol*, *52*, 5772–5780.