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Vapor permeation of aqueous 2-propanol solutions through gelatin/Torlon® poly(amide imide) blended membranes[☆]

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Abstract

The vapor permeation of aqueous 2-PrOH mixtures was investigated by using the natural polymer, gelatin, as one of the membrane components in a polymer blend. The gelatin/Torlon® poly(amide imide) blended membranes preferentially permeated H₂O from aqueous 2-PrOH by vapor permeation. Membranes containing gelatin can be used as one of promising membranes for the dehydration of aqueous 2-PrOH. © 2004 Elsevier B.V. All rights reserved.

Keywords: Diffusion coefficients; Diffusivity selectivity; Gelatin; Green polymer; Permselectivity; Solubility selectivity; Torlon®; Vapor permeation

1. Introduction

It is an interesting and important subject to fabricate polymeric separation membranes from naturally occurring or 'green' polymers. From this viewpoint, agarose was adopted as a membrane material and pervaporation separation of methanol/methyl *tert*-butyl ether (MeOH/MTBE) through agarose membranes [1] or hydrophilic polymer/agarose blended membranes [2,3] and that of aqueous organic mixtures through agarose membranes [4,5] were investigated in previous studies.

Gelatin is one of a number of abundant renewable resources and is a biodegradable, environmentally-friendly 'green' polymer. Gelatin, which has been intensively studied in biomedical areas [6–11], is thought to be a candidate green polymer for membrane materials. From this viewpoint, the present study is concerned with gelatin as a useful material for membrane fabrication and separation.

It has been reported that the state of permeant, which is preferentially permeated through a given polymeric membrane, is different from that of bulk permeant; in other words, melting point depression of such a permeant in the membrane is observed in reverse osmosis [12–18] and pervaporation [19–22]. The existence of bound water in gelatin was confirmed by ¹H NMR [23] and by thermal analyses [24]. This implies that gelatin has the potential to permeate water preferentially from aqueous organic mixtures. This encouraged the authors to study dehydration of organics with gelatin membranes.

Pervaporation is perceived as one of the promising techniques to separate liquid mixtures, such as the dehydration of organics, removal of organics from water, and the separation of organic mixtures [25]. It should be noted that in pervaporation, the liquid feed mixtures are in direct contact with the polymeric membranes and the physical and chemical properties of the membranes are often influenced by the liquid feed mixtures. Vapor permeation, which is regarded as the youngest technique applied in membrane separation, is an alternative to pervaporation. In vapor permeation, the feed is a vapor, in contrast to pervaporation, where the feed is the liquid phase. Consequently, the swelling of polymeric

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membranes caused by direct contact with the feed solution is expected to be reduced by applying vapor permeation. To this end, vapor permeation of water/2-propanol mixtures through gelatin/Torlon blended membranes was investigated in the present study.

2. Experimental

2.1. Materials

Gelatin was purchased from Nacalai Tesque, Inc., Kyoto, Japan and used without further purification. It originated from ox skin. The amino acid composition of gelatin studied in the present study was not investigated. But it was thought to be that given in the literature [26]. Torlon grade[®] 4000T poly(amide imide) was kindly provided by BP Amoco Polymers Inc. (now Solvay Advanced Polymers). Dimethyl sulfoxide (DMSO) and 2-propanol (2-PrOH) were purified by the usual method [27]. Deionized water was employed throughout the experiments.

2.2. Membrane preparation

A 0.50 g of polymer mixtures of gelatin and Torlon was dissolved in 5.0 cm³ of DMSO. The solution was poured onto a glass plate with an applicator (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at 50 °C for 24 h. The thicknesses of the membranes thus prepared were in the range of 14–18 μm. The membranes were transparent and flexible even in their dried state, suggesting that they were essentially homogeneous blends. No further characterization of homogeneity was pursued. They showed high durability so that they can be bent under dry conditions.

2.3. Vapor permeation (VP) and pervaporation (PV)

VP experiments were carried out at a temperature of around 82 °C, at which the liquid mixture was refluxed under atmospheric pressure (ca. 0.101 MPa (ca. 1.0 atm)). The schematic diagram of the VP apparatus is shown in Fig. 1. The apparatus shown in Fig. 1 was connected to a vacuum line. Permeate was condensed and trapped by liquid nitrogen, in the same manner as in PV experiments [28]. The effective membrane area was 17.3 cm² and the downstream pressure was maintained at around 133.3 Pa (1.0 mmHg) in both VP and PV.

PV was performed by an ordinary pervaporation technique [28].

Separation analysis was carried out on Shimadzu GC-7APT with 3.0 m long column packed with polyethyleneglycol 6000 (Shimalite TPA).

The separation factor, α , is defined as

$$\alpha = \frac{Y_{\text{H}_2\text{O}}/Y_{2\text{-PrOH}}}{X_{\text{H}_2\text{O}}/X_{2\text{-PrOH}}}$$

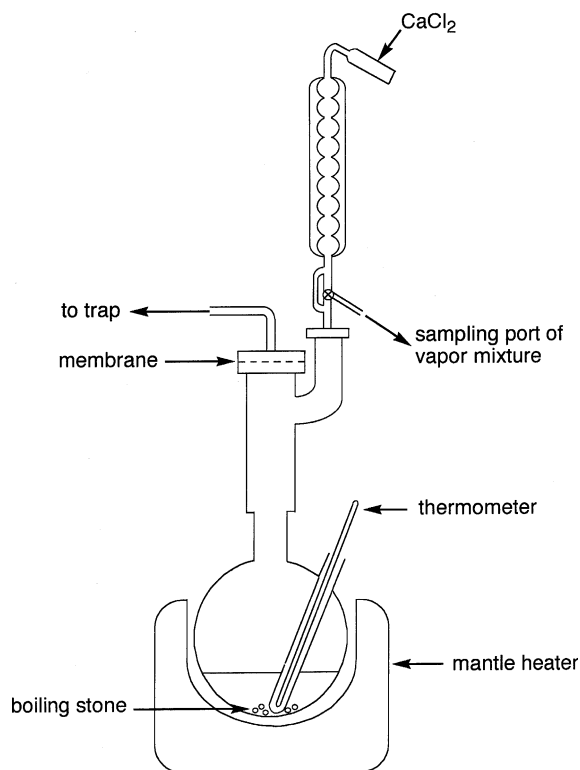


Fig. 1. Schematic diagram of apparatus for vapor permeation.

In vapor permeation, Y_i s are the weight fractions in permeate and X_i s are those in vapors in feed, respectively. In pervaporation, Y_i s are the weight fractions in permeate and X_i s are those in feed, respectively.

2.4. Sorption

The gelatin/Torlon blended membranes were equilibrated with water/2-PrOH vapor for sorption in vapor-phase or equilibrated with water/2-PrOH solution for that in liquid-phase at around 82 °C, at which the liquid mixture was refluxed. Sorption analysis was carried out as described previously [29].

The solubility selectivity, S_S , is defined as

$$S_S = \frac{Z_{\text{H}_2\text{O}}/Z_{2\text{-PrOH}}}{X_{\text{H}_2\text{O}}/X_{2\text{-PrOH}}}$$

In vapor-phase sorption, Z_i s are the weight fractions in the membrane and X_i s are those in vapor, respectively. In liquid-phase sorption, Z_i s are the weight fractions in the membrane and X_i s are those in the solution, respectively.

2.5. Measurement of diffusion coefficient

The permeation of vapors studied in the present study, such as H₂O and 2-PrOH, through the gelatin/Torlon blended membrane was measured at 82 °C. From the time-transport curve for each vapor, the diffusion coefficient was determined by applying the time-lag method [30].

3. Results and discussions

3.1. Vapor permeation

During the initial stages of the present study, the authors attempted to study membrane performance using pure gelatin membranes. However, gelatin membranes were found to be mechanically weak so that vapor permeation could not be studied. Even crosslinked gelatin membranes, which were crosslinked with hexamethylene diisocyanate according to the method described in the literature [31], did not show enough durability for vapor permeation and pervaporation. As a result, Torlon 4000T polyamide imide was adopted as a membrane matrix to impart mechanical strength. Blended membranes were prepared from gelatin and Torlon with gelatin contents in the range of 0–17%, and their membrane performance was studied.

First the weight fraction of vapor in the feed was fixed at around 3.0×10^{-3} and the effect of gelatin content on membrane performance was studied. The results are shown in Fig. 2. As expected from the previous reports that part of the water content in gelatin was observed as bound water [23,24], the blended membranes permeated H₂O in strong preference to 2-PrOH (α of 10^2 – 10^4 for most blend formulations). Torlon membrane itself selectively permeated H₂O from aqueous 2-PrOH solution as well, showing a selectiv-

ity of over 10^2 . Permselectivity toward water increased with the increase in gelatin content until the gelatin content was around 14.0 wt.%, while permselectivity toward water of the blended membrane at the gelatin content of 5.0 wt.% was almost the same as that of Torlon membrane. Above a gelatin content of ca. 14.0 wt.%, permselectivity toward water was drastically decreased. This profile may be explained as follows: the permselectivity toward water was increased through a certain content of gelatin in the membrane. Over this certain content, the effect of membrane swelling surpasses that of permselectivity caused by the incorporation of gelatin into Torlon. As a result, permselectivity toward water decreased with the increase in gelatin content, as shown in Fig. 2.

Following the initial study, blended membranes with a gelatin content of 14.0 wt.% were adopted thereafter and the dependence of vapor permeation performance on weight fraction of water in feed vapor was investigated. Fig. 3 shows the results of vapor permeation of aqueous 2-PrOH solutions through the gelatin/Torlon blended membrane with gelatin content of 14.0 wt.%. For all weight fractions of water in the feed solutions, water was permeated in preference to 2-PrOH. Permselectivity toward water showed a tendency to decrease by approximately one order of magnitude with the increase in H₂O content in feed from 10 to 90%. This profile can be explained by the swelling of the membrane with H₂O.

It is interesting to compare vapor permeation and pervaporation at the same feed composition, i.e., vapor mixture equi-

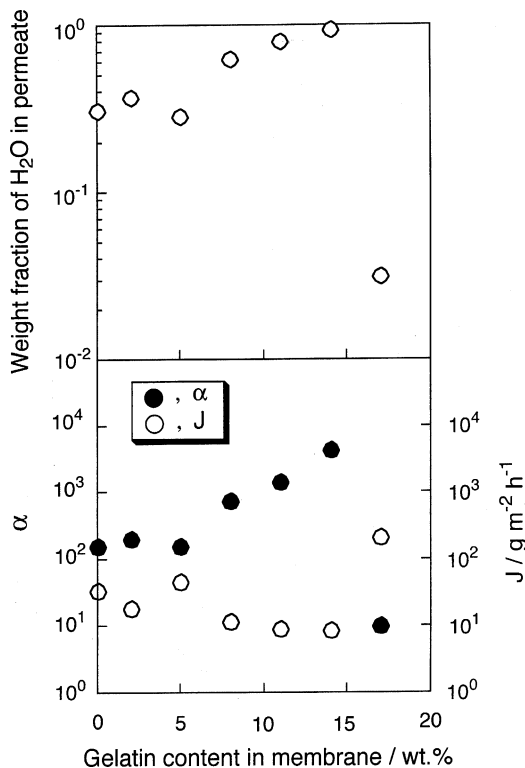


Fig. 2. Effect of gelatin content on the vapor permeation of H₂O/2-PrOH mixtures through gelatin/Torlon blended membranes. Weight fraction of vapor in feed, ca. 3.0×10^{-3} ; downstream pressure, 133.3 Pa (1.0 mmHg); operating temperature, ca. 82 °C.

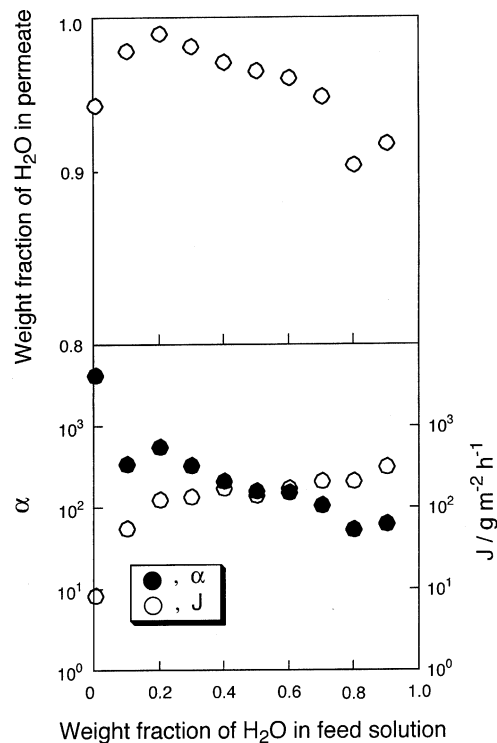


Fig. 3. Effect of feed composition on the vapor permeation of H₂O/2-PrOH mixtures through the gelatin/Torlon blended membrane. Gelatin content, 14 wt.%; downstream pressure, 133.3 Pa (1.0 mmHg) operating temperature, ca. 82 °C.

librated with liquid feed mixture for VP or the same liquid feed mixture for PV. The results are summarized in Table 1. It was expected that the separation factor would be higher for VP than for PV and that the flux would be much higher for PV as reported [32,33]. Against expectations, the membrane performance for PV is better or comparable to that for VP in the present study. At present, there is no explanation for the observed results.

3.2. Sorption

Sorption experiments were investigated so that we can elucidate factors, governing the permselectivity toward water. The blended membrane with a gelatin content of 14 wt.% was equilibrated with water/2-PrOH vapor or with water/2-PrOH solution at around 82 °C, the temperature at which this liquid mixture refluxes. The results are summarized in Table 2. As expected from the VP and PV results, H₂O was sorbed in the gelatin/Torlon blended membranes in preference to 2-PrOH.

Solubility selectivity S_S for each sorption experiment was calculated by using sorption data. Obeying the solution-diffusion theory, diffusivity selectivity ($S_D = D_{H_2O}/D_{2-PrOH}$; D_{H_2O} and D_{2-PrOH} are the diffusion coefficients of H₂O and 2-PrOH, respectively) for each case, VP or PV, can be estimated from separation factor α and solubility selectivity ($S_S = S_{H_2O}/S_{2-PrOH}$; S_{H_2O} and S_{2-PrOH} are the solubility coefficients of H₂O and 2-PrOH, respectively) [34]. The solubility selectivity and diffusivity selectivity for each case thus calculated are also summarized in Table 2. As often suggested in PV [35], the distribution of permeants in a given membrane for VP or PV and that for a sorption experiment

might be considerably different. In the distribution for VP or PV, one surface of the membrane, the one in contact with the feed mixture, is swollen. The degree of swelling in PV is thought to be higher than that in VP. The state of the membrane in contact with the feed solution might resemble that of the membrane for the sorption experiment. The other surface of the membrane, which is in contact with vacuum in VP or PV, maintains its dry state and contributes to giving permselectivity. The state of the membrane for the downstream side is considerably different from that of the upstream side. In other words, the state of the membrane surface in contact with vacuum, which plays an important role for permselectivity, is different from that of the sorption experiment even though the sorption experiment is carried out in a vapor phase. From this, the actual solubility selectivity should be higher than the estimated value using sorption data for both VP and PV. That is, the values of solubility selectivity given in Table 2 can be considered to be minimum values. In contrast, the diffusivity selectivities in Table 2 can be considered as maximum values; in other words, the actual diffusivity selectivities should be lower than that estimated using both separation factor and solubility selectivity. The degree of deviation of both solubility selectivities and diffusivity selectivities from true values in PV is thought to be greater than that in VP. To this end, we tried to obtain the diffusivity selectivities of the present membrane in the following section.

3.3. Diffusivity of permeant in the blended membrane

A typical time-transport curve of H₂O vapor through the gelatin/Torlon blended membrane at 82 °C is shown in Fig. 4. Diffusion coefficients of H₂O and 2-PrOH were determined by the time-lag method [30] from the permeation data of pure vapor at a prescribed vapor pressure. In the present study, each vapor, of which activity was below 0.06, was in contact with the membrane. This enabled the diffusion coefficient to be estimated for a given vapor in the active layer of the membrane in VP. The resulting determined diffusion coefficients for H₂O and 2-PrOH are summarized in Tables 3 and 4, respectively. The diffusion coefficients for H₂O and 2-PrOH are plotted as a function of activity of vapor in Figs. 5 and 6, respectively. For permeation, the diffusion coefficient D often depends on the local concentration of permeant itself [5,36–44]. In some cases, the concentration dependence of

Table 1
Pervaporation (PV) and vapor permeation (VP) of H₂O/2-PrOH mixture through gelatin/Torlon blended membrane^a

	$X_{H_2O}^b$	$Y_{H_2O}^c$	α^d	J (g m ⁻² h ⁻¹)
VP	0.00343	0.942	4700	8.7
PV	0.00491	0.988	16700	2.4

^a Downstream pressure, ca. 133.3 Pa (1.0 mmHg); operating temperature, ca. 82 °C.

^b Weight fraction of H₂O in vapor for VP and that in liquid feed mixture for PV.

^c Weight fraction of H₂O in permeate.

^d $\alpha = (Y_{H_2O}/Y_{2-PrOH})/(X_{H_2O}/X_{2-PrOH})$.

Table 2
Sorption of water/2-PrOH mixtures in the gelatin/Torlon blended membrane^a at 82 °C

Sorption experiment	Weight fraction of H ₂ O in solution (X_{H_2O})	Weight fraction of H ₂ O in membrane (Z_{H_2O})	Separation factor (α)	Solubility selectivity (S_S) ^b	Diffusivity selectivity (S_D) ^c	Amount sorbed in membrane (g/g-membrane)
Vapor ^d	0.00318	0.258	4700	110	43	0.339
Solution ^e	0.00348	0.140	16700	47	360	0.456

^a Gelatin content, 14.0 wt.%.

^b $S_S = (Z_{H_2O}/Z_{2-PrOH})/(X_{H_2O}/X_{2-PrOH})$.

^c $S_D = \alpha/S_S$.

^d The membrane was equilibrated with water/2-PrOH vapor.

^e The membrane was equilibrated with water/2-PrOH solution.

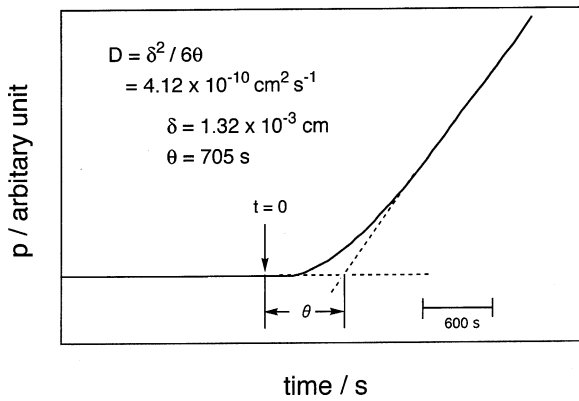


Fig. 4. Time-transport curve of H₂O vapor through the gelatin/Torlon blended membrane at 82 °C. Gelatin content, 14 wt.%; H₂O vapor pressure in upstream, 1333 Pa (10.0 mmHg).

the diffusion coefficient has been reported to be linear [40]:

$$D = D_0(1 + \gamma C)$$

and in other cases, an exponential form was observed [40]:

$$D = D_0(\exp \beta C)$$

In these two equations, D_0 is the D value as the permeant concentration approaches 0; γ and β are the coefficients characteristic of the membrane/permeant interaction and C denotes the permeant concentration in the membrane. The latter equation is used to simulate the concentration dependence of both H₂O and 2-PrOH diffusion in the present study. D_0 and β were determined to be $3.88 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and 2.23, respectively for H₂O and $3.55 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and 25.8, respectively for 2-PrOH. Adopting D_0 values for H₂O and 2-PrOH, the diffusivity selectivity $S_D (=D_{\text{H}_2\text{O}}/D_{2\text{-PrOH}})$ was determined to be 1.09.

Table 3
Diffusion coefficients of H₂O through gelatin/Torlon blended membrane^a

p (Pa)	p (mmHg)	$a(=p/p_0^b)$	θ (s)	D (cm ² s ⁻¹) ^c
866.5	6.50	0.016	720	4.03×10^{-10}
1333	10.0	0.025	705	4.12×10^{-10}
2066	15.5	0.040	690	4.21×10^{-10}
2799	21.0	0.054	660	4.40×10^{-10}

^a Measurements were carried out at the constant temperature of 82 °C; gelatin content, 14.0 wt.%.
^b $p_0 = 51320 \text{ Pa}$ (385.0 mmHg).
^c The thickness of the membrane was 13.2 μm .

Table 4
Diffusion coefficients of 2-PrOH through gelatin/Torlon blended membrane^a

p (Pa)	p (mmHg)	$a(=p/p_0^b)$	θ (s)	D (cm ² s ⁻¹) ^c
1066	8.00	0.011	930	3.12×10^{-10}
2066	15.5	0.021	540	5.38×10^{-10}
3266	24.5	0.035	354	8.20×10^{-10}
4399	33.0	0.043	243	11.95×10^{-10}

^a Measurements were carried out at the constant temperature of 82 °C; gelatin content, 14.0 wt.%.
^b $p_0 = 1.006 \times 10^5 \text{ Pa}$ (754.7 mmHg).
^c The thickness of the membrane was 13.2 μm .

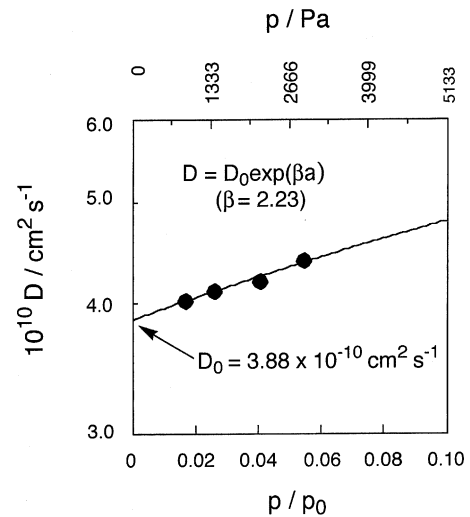


Fig. 5. Concentration dependence of diffusion coefficient of water vapor through the gelatin/Torlon blended membrane at 82 °C. The saturation vapor pressure, p_0 , of water at 82 °C is 51.3 kPa (385 mmHg).

Assuming that the effective diameter of the diffusing entity is roughly inversely proportional to the diffusion coefficient, one sees

$$\frac{r_{2\text{-PrOH}}}{r_{\text{H}_2\text{O}}} = \frac{D_{\text{H}_2\text{O}}}{D_{2\text{-PrOH}}} = 1.09$$

Therefore the ratio of volume of 2-PrOH to that of H₂O was calculated to be

$$\frac{V_{2\text{-PrOH}}}{V_{\text{H}_2\text{O}}} = (1.09)^3 = 1.3$$

Assuming that 2-PrOH diffused in and through the membrane unimolecularly, the apparent volume of H₂O ($V_{\text{H}_2\text{O}}$) diffusing in the membrane was estimated by us-

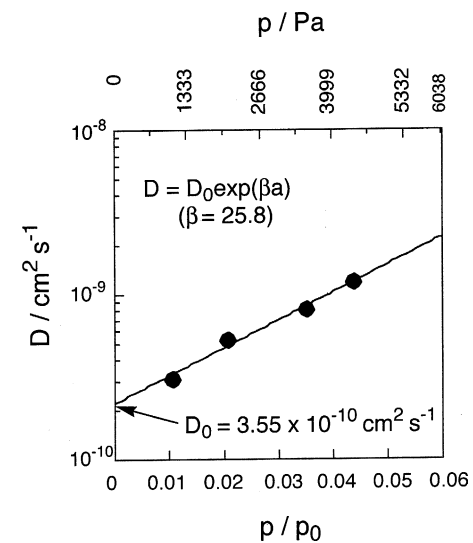


Fig. 6. Concentration dependence of diffusion coefficient of 2-PrOH vapor through the gelatin/Torlon blended membrane at 82 °C. The saturation vapor pressure, p_0 , of water at 82 °C is 101 kPa (755 mmHg).

ing $18.0 \text{ cm}^3 \text{ mol}^{-1}$ for the molar volume of H_2O and $76.9 \text{ cm}^3 \text{ mol}^{-1}$ for that of 2-PrOH [27]:

$$V_{\text{H}_2\text{O}} = \frac{V_{2\text{-PrOH}}}{1.3} = 59.2 \text{ cm}^3$$

The 59.2 cm^3 volume of H_2O diffusing in the membrane corresponds to around 3.3 water molecules ($V_{\text{H}_2\text{O}}/\bar{V}_{\text{H}_2\text{O}} = 59.2/18.0 = 3.3$). That is, in the case of diffusion of water in the membrane, a water cluster consisting of around 3.3 water molecules diffused in the present study.

Based on the diffusivity selectivity of 1.09 the present study, the solubility selectivities in VP and PV are estimated to be 4300 and 15,300, respectively. This led to the conclusion that the permselectivity toward water for the present membrane was mostly dependent on solubility selectivity.

4. Conclusions

In the present study, vapor permeation of aqueous 2-propanol mixtures was investigated using the natural polymer, gelatin, as a membrane material. Membranes were prepared from blends of gelatin with Torlon in order to improve the mechanical properties and durability. Following the initial study in which various ratios of gelatin were blended with Torlon, a 14% gelatin/Torlon was adopted. The 14% gelatin/Torlon blended membranes preferentially permeated H_2O from aqueous 2-PrOH mixtures. Sorption and diffusion experiments led to the conclusion that both solubility selectivity and diffusivity selectivity showed a preference for H_2O . Among them, the solubility selectivity is by far the dominant factor governing permselectivity, and the present membrane, as a result, showed permselectivity toward water in vapor permeation. The present study showed that gelatin is a promising membrane material for the dehydration of water miscible organics.

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