Vapor Permeation of Aqueous Ethanol through Agarose-Sericin Membrane

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Abstract: A self-standing membrane was obtained from renewable polymers, such as agarose and sericin. Differential scanning calorimetric study revealed that there were two states of water in the membrane, such as bound water and free water. The membrane preferentially transported water from aqueous ethanol mixture by vapor permeation. Preliminary study revealed that the present membrane was applicable to forward osmosis.

Keywords: Agarose, Melting Point Depression, Membranes, Vapor Permeation, Sericin.

1. INTRODUCTION

Membrane separation is regarded and expected to solve the critical global issues we have faced. As for the critical global issues, the following three types of problem are enumerated; (1) environmental problems, including water pollution, air pollution, etc., (2) energy/resource problems, such as water resources, biomass production, fuel cell, concentration difference power generation and so forth, and (3) health problems, such as artificial organs, hemofiltration, etc. From above, membranes are expected to contribute to support safe, secure and sustainable society.

Among three of critical globe issues, possibility of application of agarose membrane to pervaporation of methanol/methyl *tert*-butyl ether (MTBE) [1-3], that of aqueous organic mixtures [4,5] and vapor permeation of aqueous ethanol solution [6] was investigated in a link of energy/resource problems. Considering the application of agarose membrane to dehydration of fermentation broth, vapor permeation is thought to be more suitable than pervaporation. In pervaporation, a given membrane is in contact with fermentation broth and this leads to fouling, which causes a reduction of flux. Contrary to this, in vapor permeation, vapor of the permeant is in contact with the membrane, which eliminates the effect of fouling and concentration polarization, which is often observed in liquid phase separation. In the previous study [6], it was revealed that agarose was a promising membrane material for vapor permeation of aqueous ethanol mixture.

Sericin is the second main component in silk cocoons. Sericin is removed in the silk reeling processes of the raw silk industry and most of them are abandoned. Sericin is composed of 65 % amino acids that contain hydrophilic amino acid residues, such as serine and aspartic acid, and glycine [7-9]. From this, sericin shows a hydrophilic property. Therefore sericin is used in skin and hair products in cosmetics. The authors' research group also studied the possibility of sericin as a membrane material for ultrafiltration and chiral separation performances [10]. It is an indispensable subject to develop potential utilization of sericin as a raw material in connection with preservation and efficient utilization of natural resources. As one of promising utilization of sericin, a blended membrane was prepared from agarose and sericin and its vapor permeation of aqueous ethanol and forward osmosis ability were studied.

2. EXPERIMENTAL

2.1. Materials

Agarose (Standard Low-M_r) was purchased from Bio-Rad Laboratories and used without further purification. Sericin was kindly provided by SEIREN Co., Ltd. (Tokyo, Japan). Sodium azide and ethanol were used without further purification. Deionized water was employed throughout the experiments.

2.2. Membrane Preparation

The membrane was prepared following the procedure previously reported [1]. A 0.40 g of agarose was dissolved in a 39.60 g of deionized water. After a 8.0 mg (0.02 wt.%) of sodium azide was added as a fungicide, 0.40 g of sericin was added to the solution and dissolved at 70 °C. The aqueous solution thus prepared was poured onto a tray (14 cm long x 15 cm wide), and was allowed to stand at ambient

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E-ISSN: 1929-6037/15

temperature. The obtained agarose-sericin gel was sandwiched between two porous Teflon sheets and both outsides were covered with a few sheets of filter papers. The agarose-sericin gel thus covered was allowed to evaporate water at ambient temperature under compression of the constant pressure of 104 g cm^{-2}. The thickness of the membrane thus obtained was ca.35 μm.

2.3. Differential Scanning Calorimetry (DSC)

The differential scanning calorimeter used was a Shimadzu DSC-60. A membrane sample was hermetically sealed to prevent evaporation. The sample was cooled down to -120 °C at a cooling rate of 5 °C min^{-1} by using liquid nitrogen and then heated at a scanning rate of 10 °C min^{-1} up to 60 °C. Nitrogen at the flow rate of 300 cm^3 min^{-1} was used throughout all DSC measurements.

2.4. Vapor Permeation

Vapor permeation was carried out at a reflux temperature of each aqueous ethanol mixture, under atmospheric pressure [ca. 0.101 MPa (ca. 1.0 atm)]. The apparatus was connected to avacuum line and permeate was condensed and trapped by liquid nitrogen in the same manner in the pervaporation experiments [11, 12]. The effective membrane area was 17.3 cm^2 and the downstream pressure was maintained at around 66.7 Pa (ca. 0.5 mmHg).

Separation analysis was carried out on a Shimadzu GC-7APT gas chromatography instrument with a 3.0-m-long column packed with polyethylene glycol 6000 (Shimalite TPA).

The separation factor, $\alpha_{H2O/EtOH}$, is defined as

$$\alpha_{H2O/EtOH} = (Y_{H2O} / Y_{EtOH}) / (X_{H2O} / X_{EtOH}) \quad (1)$$

where Y_is are the weight fractions in permeate and X_is are those in vapor in feed.

2.5. Estimation of Diffusion Coefficient

The permeation of H_2O or ethanol vapor through the membrane in the present study was measured at 78.4 °C, which corresponds to the reflux temperature for a weight fraction of H_2O in liquid feed of ca. 0.10 [13]. From the time-transport curves for each vapor, the apparent diffusion coefficient was determined by applying the time-lag method [14-17].

3. RESULTS AND DISCUSSION

3.1. State of Water in the Agarose-Sericin Membrane

Before studying vapor permeation performance, the state of water, such as bound (non-freezing) water and bulk (free) water, in the agarose-sericin membrane was investigated. Melting endotherms of water in membrane, of dry membrane and bulk water are shown in Figure **1**. The area of endothermic curve at 0 °C decreased with decrease in water content in the membrane (Figure **3f–b**). In Figure **3c** and **b**, the endotherms of water were hardly observed around its melting point of 0 °C, even though water was still in the membrane. No other new endotherm was observed in the temperature range of -120 °C to 60 °C.

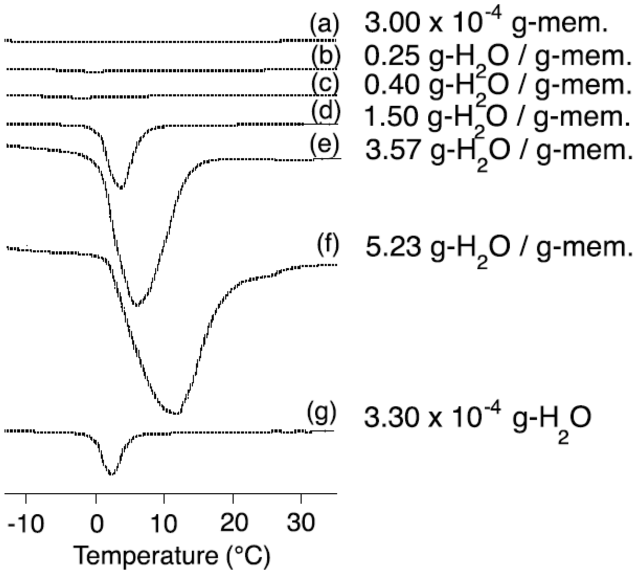

Figure 1: DSC heating curves of agarose-sericin dry membrane (a), membrane water (b-f) and pure water (g).

Figure **2** shows the relationship between enthalpic heat and water content for the membrane. The experimental data showed a straight-line relationship with a slope that was approximately equal to 333.4 J g^{-1} [18-20]. Extrapolation to $\Delta H = 0$ should intercept at the water content axis at a point that the total bound water in the membrane. The total bound water content was determined to be 0.45 g-H_2O/g-membrane. From the fact that bound water was found in the membrane and the results previously reported [6], it is expected that the agarose-sericin membrane showed permselectivity toward water in vapor permeation of aqueous ethanol mixture. To this end, vapor permeation of water-ethanol mixture was investigated, of which results will be given in the next section.

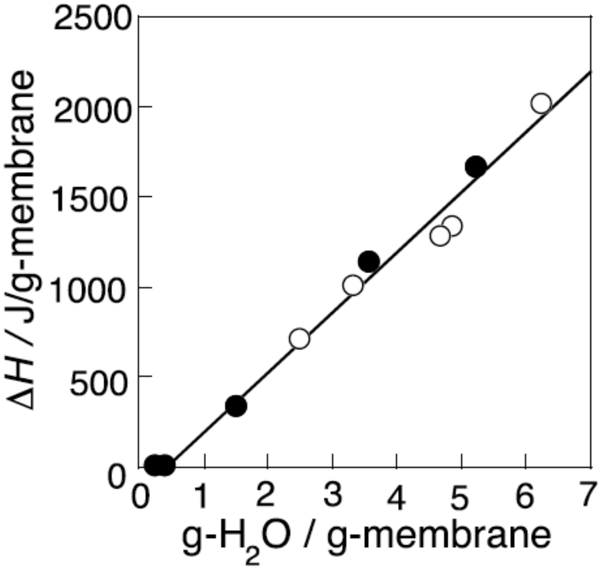

Figure 2: Water content dependence of the heat of melting for freezing water, Δ*H*, in the agarose-sericin membrane. (The closed circles in the relationship were the data shown in Figure **1**).

3.2. Vapor Permeation of Aqueous Ethanol Mixture

Vapor permeation results for the present membrane are given in Figure **3**. As expected, the membrane transported water in preference to ethanol. As often observed, permselectivity toward water decreased with the increase in weight fraction of water in feed liquid, while a flux increased with the increase in water content in feed liquid. The vapor permeation performance of the present membrane was inferior to those of the pristine agarose membrane [6]. This might be due to the poor compatibility between agarose and sericin, though, at the moment, authors had no data to support the poor compatibility of those membrane materials. However, the experimental data, supporting the above speculation, will be provided in the next section.

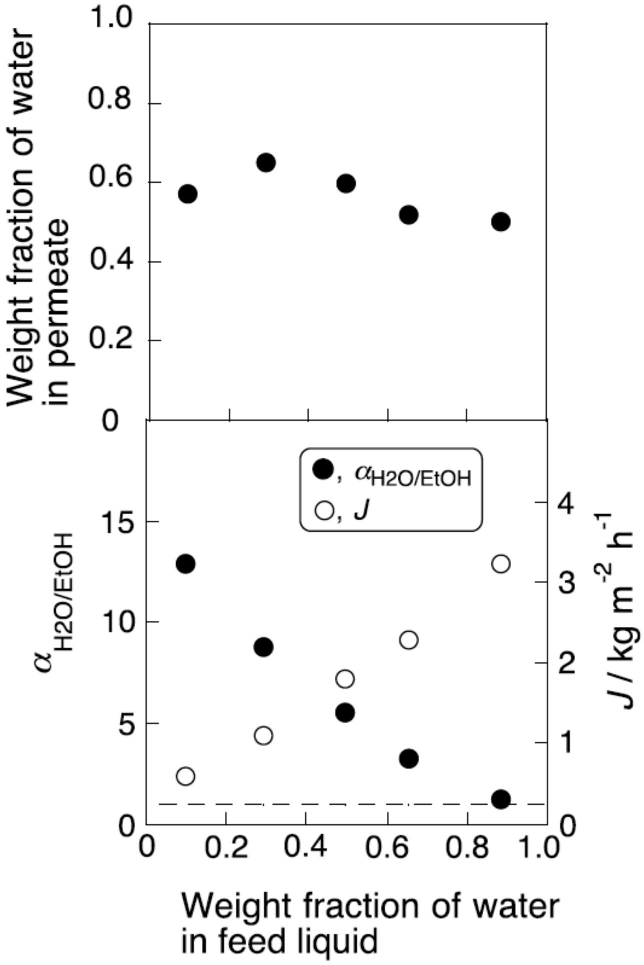

Figure 3: Effect of feed composition on the vapor permeation of H_2O/EtOH mixtures through the agarose-sericin membrane. (Downstream pressure, ca. 66.7 Pa (ca. 0.50 mmHg); operating temperature, each reflux temperature).

3.3. Mechanism for the Expression of Permselectivity toward Water Vapor

It is interesting and indispensable to study the mechanism for the expression of permselecivity for the molecular engineering of vapor permeation membranes. There are two methods to study the factors governing permselectivity. One is that diffusivity selectivity is determined from separation factor and solubility selectivity. The other is a reverse way, solubility selectivity is determined from separation factor and diffusivity selectivity. Though both methods obey solution-diffusion theory [17,21], the governing factors elucidated by the latter method might show a great accuracy than that by the former method, considering the distribution of permeant in a membrane [6,22]. From this, diffusivity selectivity was tried to be determined so that the governing factors for permselectivity could be elucidated.

Time-transport curves of H_2O vapor at 78.4 °C are shown in Figure **4**. In the present study, vapor permeation experiments were carried out at each reflux temperature of the aqueous ethanol solution as described in 2.4, which was not equal to 78.4 °C, which was the reflux temperature of the aqueous ethanol mixture with the weight fraction of water of 0.10 [13]. Diffusion coefficients were determined by the time-lag method [14-17,21] from the permeation data of pure vapor with low activity region. Strictly speaking, the obtained diffusion coefficients determined in the present study are apparent diffusion coefficients since neither sorption isotherm nor state of membrane, such as glassy state or rubbery state, were known [23,24].

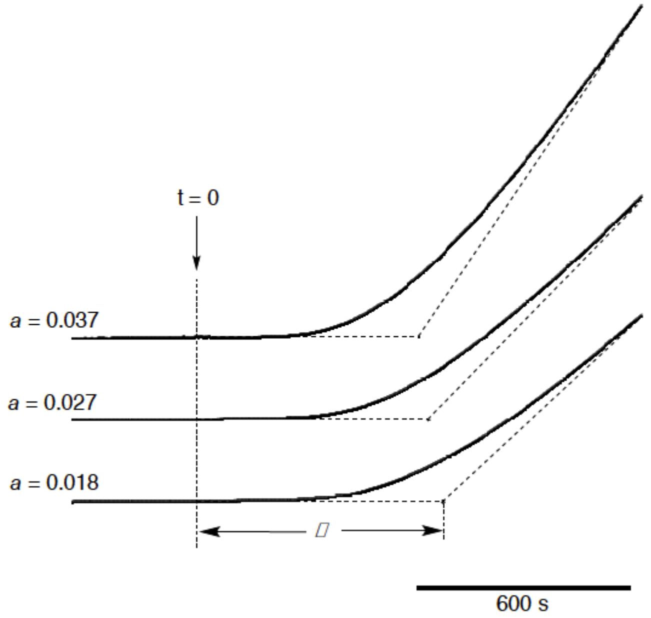

Figure 4: Time-transport curves of H_2O vapor through the agarose-sericin membrane at 78.4 °C.

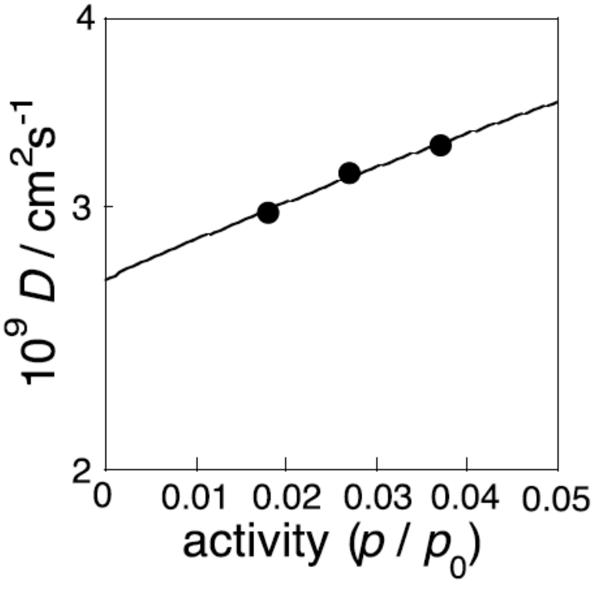

Figure 5: Concentration dependence of diffusion coefficient of water at 78.4 °C. (The saturation vapor pressure p_0 of water at 78.4 °C is 44.4 kPa (333 mmHg).

The diffusion coefficients of H_2O are plotted as a function of activity of vapor in Figure **5**. The diffusion coefficient is often dependent on the local concentration of permeant [25-29]. In the present study, the following equation, eq. (2), is used to simulate the concentration dependence of diffusion coefficient for H_2O.

$$D = D_0 \exp(\beta C) \tag{2}$$

where D_0 is the D value at the permeant concentration approaches 0, β is the coefficient characteristic of the membrane/permeant interaction and C denotes the permeant concentration in the membrane. From Figure **5**, D_0 was determined to be 2.69 x 10^{-9} cm^2 s^{-1} and β to be 5.58.

Contrary to the determination of diffusion coefficient of water, that for ethanol was too high to be determined; at the activity of ethanol vapor of 0.028, of which vapor pressure of ethanol being 2850 Pa (21.4 mmHg) at 78.4 °C, the time lag was less than 1 s. If the time lag was assumed to be 1 s, the diffusion coefficient of ethanol at the activity of 0.028 was elucidated to be 2.04 x 10^{-6} cm^2 s^{-1}. Comparing the diffusion coefficient of H_2O for the present membrane, it is unlikely that the diffusion coefficient of ethanol was three orders of magnitude higher than that of H_2O. This might be due to the poor compatibility between agarose and sericin, as suggested in the previous section. The above speculation will be explained by using Figure **6**. In the diffusion of H_2O through the agarose-sericin membrane, H_2O molecule interacted with membrane material, agarose and sericin, by hydrogen bonding and migrated from the upstream side to the downstream side as schematically shown in Figure **6a**. In the figure, sericin was depicted as membrane material. Contrary to the diffusion of H_2O, ethanol molecule would not interact firmly with the membrane as shown in Figure **6b** and passed through the defect between agarose and sericin without resistance. If agarose and sericin showed good compatibility, such a fast migration of ethanol could not be occurred. During the vapor permeation of H_2O-ethanol mixtures, even though ethanol would not interact firmly with membrane, the presence of H_2O prevented a fast migration of ethanol. As a result, as observed in the vapor permeation experiments, water was preferentially transported, though the permselectivity was not so high.

In order to enhance permselectivity toward water, addition of low molecular weight compounds with low vapor pressure to the membrane might be one way so that such compounds lead to good compatibility between agarose and sericin. Introduction of cross-linking might be the other way to narrow gaps between agarose and sericin.

3.4. Preliminary Study on Forward Osmosis

The present membrane showed permselectivity toward water by vapor permeation. This stimulated us to study the possibility of forward osmosis [30-32],

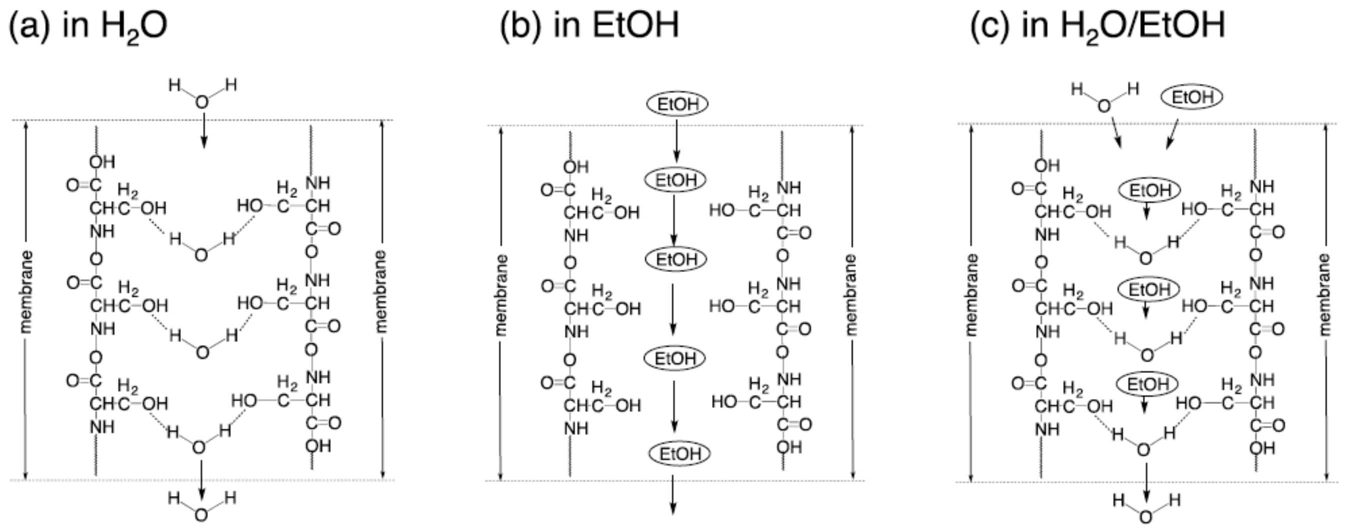

Figure 6: Tentative scheme of diffusion of water (**a**), ethanol (**b**) and mixture of water and ethanol (**c**).

since osmotic converter by mixing fresh water and seawater is expected to be one of renewable and clean energies in the future world [33]. To this end, 25.0 wt.% aqueous NaCl solution was adopted as draw solution and deionized water as feed, the forward osmosis with the present membrane was preliminarily studied. Water flow of 34.8 L m^{-2} h^{-1} was observed.

4. CONCLUSIONS

A self-standing membrane was obtained from natural polymers, such as agarose and sericin. Differential scanning calorimetric melting endotherms of the water-swollen membrane were studied to clarify the state of water in the membrane. The results revealed that there were two states of water in the membrane, such as bound water and free water. The membrane transported water in preference to ethanol from aqueous ethanol mixture by vapor permeation. In addition, preliminary study revealed that the present membrane was applicable to forward osmosis.

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Received on 16-07-2015 Accepted on 24-08-2015 Published on 14-09-2015

DOI: http://dx.doi.org/10.6000/1929-6037.2015.04.03.3