

# Concentration of Bio-Ethanol through Cellulose Ester Membranes during Temperature-Difference Controlled Evapomeation

Tadashi Uragami

Department of Chemistry and Materials Engineering, Kansai University, Osaka, Japan; Development of Innovative Science and Technology, Kansai University, Osaka, Japan.  
Email: uragami@kansai-u.ac.jp

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## ABSTRACT

To evaluate the high-performance of membrane materials in the concentration of an aqueous solution of dilute bio-ethanol under temperature-difference controlled evapomeation (TDEV), asymmetric porous cellulose nitrate (CN) and cellulose acetate (CA) membranes were prepared by a phase inversion method. In the concentration of dilute ethanol under TDEV, these membranes showed a high permeation rate and high ethanol/water selectivity. In membranes with almost the similar pore size, the ethanol/water selectivity was considerably higher for the CN membrane than the corresponding CA membrane. This result suggested that the affinity between the membrane material and the permeant is an important factor in the separation selectivity.

**Keywords:** Bio-Ethanol, Concentration, Membrane, Cellulose Ester, Temperature-Difference Controlled Evapomeation

## 1. Introduction

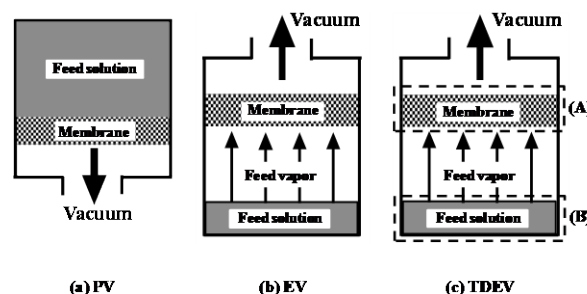
Ethanol that can be produced by biomass fermentation is a clean energy source, but typically its concentration is about 10 wt% in aqueous solution. To use such an aqueous ethanol solution as an energy source, we need to concentrate the dilute solution by distillation. However, distillation requires a high energy input. If the dilute ethanol solution could be concentrated by ethanol/water selective membranes with high permeation rate and high ethanol selectivity, this would offer a significant energy saving.

We have been studying the permeation and separation characteristics of aqueous ethanol solutions passed through various hydrophilic and hydrophobic polymer membranes. Hydrophilic membranes can selectively remove water from aqueous solutions of high ethanol concentration [1-6], whereas hydrophobic membranes allow ethanol permeation from aqueous solutions of dilute ethanol [7-9].

We have developed evapomeation (EV) [10,11], as shown in **Figure 1(b)**, as a new membrane separation technique which utilizes the advantages of pervaporation (PV) (see **Figure 1(a)**) while limiting its disadvantages.

We have also proposed temperature-difference controlled evapomeation (TDEV) [12-20] in which a temperature difference is established between the feed solution and the membrane surroundings as shown in **Figure 1(c)**. Poly(dimethylsiloxane) [7,8] and modified poly(dimethylsiloxane) [9] membranes in TDEV showed high ethanol/water selectivity for aqueous solutions of dilute ethanol.

In this study, to evaluate membrane materials in the concentration of bio-ethanol in TDEV, we selected cellulose nitrate (CN) and cellulose acetate (CA) as membrane materials, which have different affinities for etha-



**Figure 1.** Schematics showing fundamental principles of PV, EV and TDEV.

nol. Specifically, we describe in detail the permeation and separation characteristics of asymmetric porous CN and CA membranes during TDEV of an aqueous solution of dilute ethanol, and discuss the results in terms of the physical and chemical structures of the cellulose ester membranes.

## 2. Experimental Section

### 2.1. Materials

As membrane materials, cellulose nitrate (CN) having a nitro content of 11.5% was obtained from Daicel Chemical Industry and recrystallized from methanol/water, and cellulose acetate (CA) having an acetyl content of 40.1% was obtained from Wako Chemical Industries and recrystallized from acetone/water. Commercial methanol, 1,4-dioxane, and formamide from Wako Chemical Industries were used as solvents for casting solutions. Poly(ethylene glycol) (PEG) samples of 1000, 4000, and 6000 in average  $M_w$  were obtained by Sanyo Chemical Industries for use as feed solutes in ultrafiltration experiments.

### 2.2. Preparation of Asymmetric Porous CN and CA Membranes

The asymmetric porous membranes were prepared by a phase-inversion method [21,22]. The casting solutions of the CN and CA membranes were consisted of CN (13 wt%) and a mixture of methanol and 1,4-dioxane (as a non-solvent additive), and CA (13 wt%) and a mixture of 1,4-dioxane and formamide (as a non-solvent additive), respectively. The non-solvent additives in the casting solutions are selected as poor solvents for the membrane materials. Asymmetric porous CN and CA membranes were made by pouring the casting solutions onto a glass plate, drawing a blade across the plate, allowing the solvent to evaporate for 10 sec at 25°C, and immersing the glass plate together with the membrane into cold water (6°C - 7°C) as a gelation medium.

### 2.3. Permeation Measurements

The apparatus for the TDEV experiments is described in a previous paper [7,8]. **Figure 2** shows the permeation cell for the TDEV experiments. The TDEV experiments were performed by maintaining the temperature of the feed solution at 40°C and changing the temperature of the membrane surroundings while maintaining a pressure of 665 Pa at the downstream side. The ethanol concentrations in the feed solution and permeate were measured using gas chromatography (Shimadzu GC-9A).

### 2.4. Scanning Electron Microscopy (SEM)

Asymmetric porous CN and CA membranes were coated

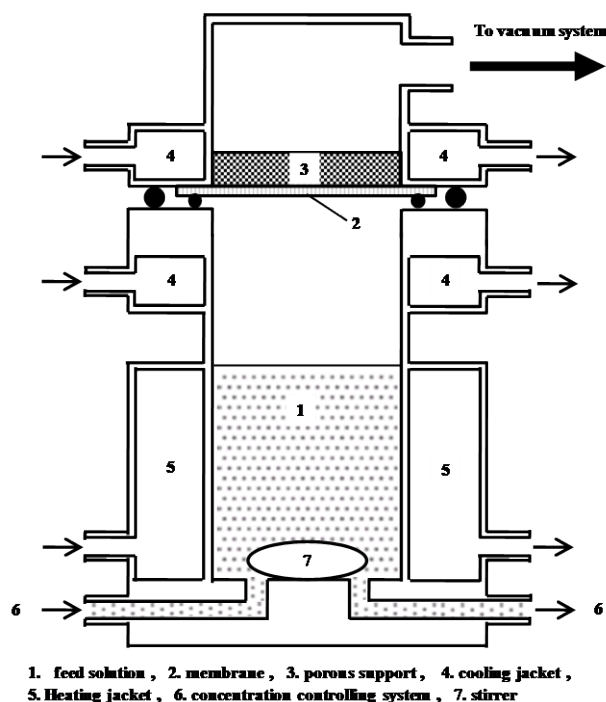


Figure 2. Permeation cell for TDEV.

with a layer of evaporated gold and the lyophilized membranes were observed through a scanning electron microscope (Japan Electron Optics, JEOL 100CX).

### 2.5. Determination of Average Pore Size of Asymmetric Porous Membranes

Porous membranes are known [23-25] to be subject to complex hydro-dynamic flow through pores of various sizes, and often a general mathematical analysis is used. In general, when a viscous liquid flows through a narrow pore, the flux of liquid,  $\bar{u}$ , is represented by the Hagen-Poiseuille equation [23]:

$$\bar{u} = Q/\rho = \Delta p g_c r^2 / 32l\eta \quad (1)$$

where  $r$  is the pore diameter,  $l$  is the length of the pore (skin layer thickness),  $\eta$  is the viscosity of the liquid,  $\Delta p$  is the pressure difference between the upstream solution and the downstream side of the membrane,  $\rho$  is the liquid density,  $g_c$  is the gravitational conversion factor, and  $Q$  is the flux.

The permeation of liquid through the skin layer of asymmetric porous CN and CA membranes may be due to both diffusive and viscous flows. Therefore, in this case, the permeation rate ( $PR$ ) of the liquid does not correspond exactly to the flux ( $Q$ ) given in Equation (1). However, if we assume that the flow through the skin layer of asymmetric porous CA and CN membranes follows viscous flow, Equation (3) can be obtained from

Equations (1) and (2), as

$$PR \propto 1/\eta^2 \quad (2)$$

$$PR = Q^2 \quad (3)$$

By substituting Equation (3) into Equation (1), the average apparent pore diameter in CA and CN membranes is given by

$$r = (32lrQ'/\Delta p g_c)^{1/2} \quad (4)$$

where  $Q'$  is  $PR^{1/2}$ , and  $\gamma$  is  $\eta/\rho$  (the kinetic viscosity).

The average apparent pore diameter in the skin layer of asymmetric porous CA and CN membranes can be estimated using Equation (4) and the permeation flux for water at various temperatures.

### 2.6. Measurement of Contact Angle

The contact angles of water and methylene iodide on the surface of asymmetric porous CA and CN membranes were measured by a contact angle meter (Erma, model G-1) at 25°C. The contact angles,  $\theta$ , were determined from the advancing contact angle ( $\theta_a$ ) and receding contact angle ( $\theta_r$ ) by Equation (5) [26].

$$\theta = \cos^{-1} \{(\cos \theta_a + \cos \theta_r)/2\} \quad (5)$$

In this study, the surface free energy was obtained from the contact angles of water and methylene iodide using Equation (6), which was proposed by Owens *et al.*, [27] as follows:

$$\{(1 + \cos \theta) \gamma_l / 2\} = (\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^p \gamma_l^p)^{1/2} \quad (6)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p$$

where  $\gamma_s^d$  and  $\gamma_l^p$  are the surface free energies of the solid and liquid, respectively, and  $\gamma_s^d$ ,  $\gamma_s^p$ ,  $\gamma_l^d$  and  $\gamma_l^p$  are the dispersion force components and polar force components of the surface free energies of the solid and liquid, respectively. The values for these components have been reported by Forkes [28,29].

### 2.7. Determination of Amount of Bound Water in Membranes

The amount of bound water in the asymmetric CA and CN membranes was measured using the water content of the membrane and the heat of fusion obtained from frozen water in the membrane,  $\Delta H$ , which was determined by differential scanning calorimetry (DSC) (Rigaku, TAS-200) based on reports by Frommer [30].

### 2.8. Ultrafiltration

Ultrafiltration experiments were performed by the method reported in a previous paper [31]. The effective

membrane area active in the cell was 12.7 cm<sup>2</sup>. All experiments were for the short-run type. The rejection percentage ( $R$ ) is defined as

$$R = (1 - C_t/C_f) \times 100 \quad (7)$$

where  $C_f$  is the starting feed concentration and  $C_t$  is the concentration in the permeate after  $t$  hours.

## 3. Results and Discussion

### 3.1. Structure of CN and CA Membranes

Figure 3 shows SEM images of cross sections of the CN and CA membranes formed by different amounts of the non-solvent additive in the casting solution. As can be seen from these images, the membrane structures are significantly influenced by the amount of non-solvent and the resulting membranes obtained from the wet method consist of a skin layer on the air side and a sponge layer on the glass-plate side. The examples shown are typical of asymmetric membranes.

### 3.2. Average Pore Diameter in Skin Layer of Asymmetric Porous CN and CA Membranes

Figure 4 shows the effects of the non-solvent additive in the casting solution on the average pore diameter of asymmetric cellulose ether membranes. As can be seen, as the amount of non-solvent is increased, the average pore diameter of the asymmetric CA membrane increases remarkably, whereas that of the asymmetric CN membrane hardly changes. These results suggest that the formamide added to the casting solution in preparation of the CA membrane is effective as a non-solvent in relation to CA. Consequently, more sponge like asymmetric CA membranes could be formed. In contrast, the 1,4-dioxane used in the preparation of the CN membrane does not

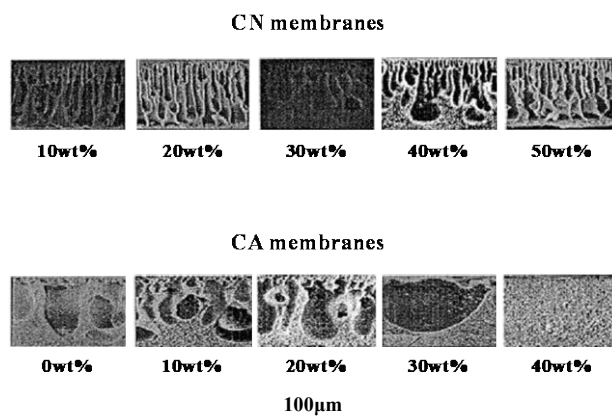


Figure 3. Effect of the amount of non-solvent additive in the casting solution on the cross-section structure of asymmetric CN and CA membranes as observed by SEM.

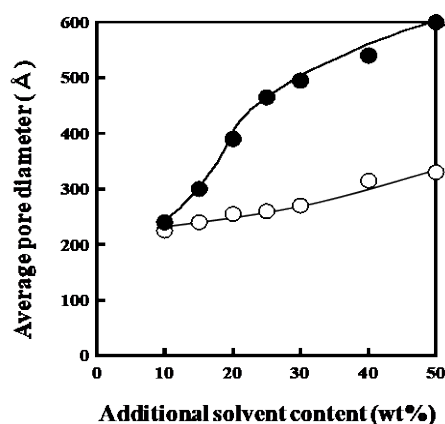


Figure 4. Effect of the amount of non-solvent additive in the casting solution on the average pore diameter in the skin layer of asymmetric CN (○) and CA (●) membranes.

appear to be effective as a non-solvent in relation to CN.

### 3.3. Surface Free Energy and Bound Water of CA and CN Membranes

Table 1 shows the contact angles for water and methylene iodide on the surface skin layer of the asymmetric porous CN and CA membranes, along with the surface free energies calculated from these contact angles. The surface free energy for the CN membrane was lower than that for the CA membrane. This indicates that the CN membrane is more hydrophobic and consequently has a higher affinity for ethanol over water in an aqueous ethanol solution. Table 2 summarizes the amounts of bound water in the asymmetric porous CN and CA membranes as determined by DSC measurements. The amount of bound water in the CN membrane is found to be considerably lower than that in the CA membrane. The results of the surface free energy and amount of bound water suggest that the CN membrane is more hydrophobic than the CA membrane.

### 3.4. Effect of Temperature of Membrane Surroundings in TDEV

Figure 5 shows the permeation and separation characteristics for an aqueous solution of 10 wt% ethanol passed through asymmetric CN and CA membranes during TDEV, in which the temperature of the feed was kept at 40°C and the temperature of the membrane surroundings was varied. As can be seen in the figure, when the temperature of the membrane surroundings is decreased, the ethanol concentration in the permeate increases but the permeation rate decreases in both the CN and CA membranes. Also both the ethanol concentration in the permeate and the permeation rate were higher in the CN membrane than in the CA membrane. The decrease in

Table 1. Contact angles and surface free energies of asymmetric CN and CA membranes.

membrane	Contact angle (deg)		Surface free energy (erg/cm <sup>2</sup> )		
	H <sub>2</sub> O	CH <sub>3</sub> I	$\gamma^d$	$\gamma^p$	$\gamma^h$
CA	56.2	29.8	35.2	16.4	51.6
CN	63.4	36.3	33.7	12.8	46.5

Table 2. Amount of bound water in CN and CA membranes.

Membrane	Amount of bound water (mol water/mol repeated unit in polymer)
CA	2.58
CN	0.67

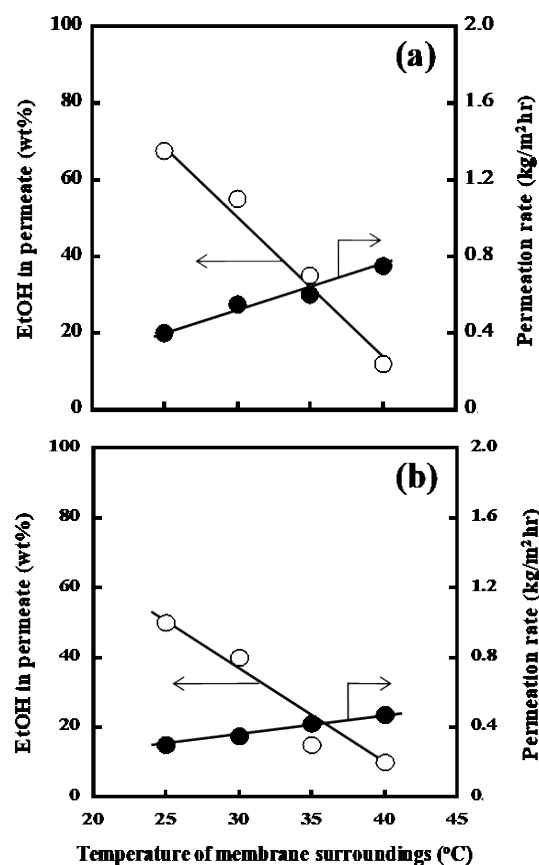
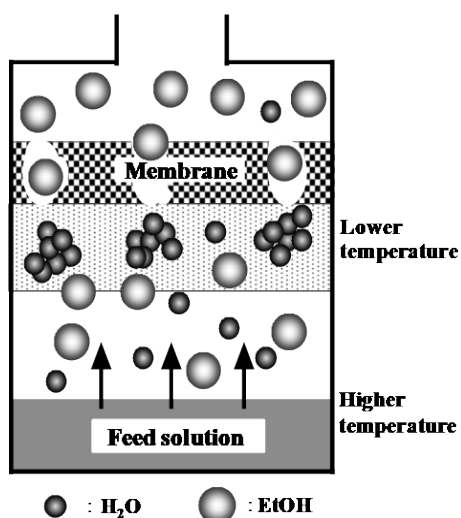


Figure 5. Effects of the temperature of the membrane surroundings on the permeation rate and ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol passed through asymmetric porous CN (a) and CA (b) membranes during TDEV. The temperature of the feed was kept at 40°C and that of the membrane surroundings was varied. The reduced pressure on the downstream side was 650 Pa. The average pore diameters of asymmetric CN and CA membranes were 280 and 284 Å, respectively.

permeation rate that occurs with a decrease in temperature of the membrane surroundings could be due to the fact that the increase in temperature difference between the feed and the feed vapor would lead to a decrease in the pressure difference between the feed side and the permeate side.

The increase in ethanol/water selectivity that occurs with decreasing temperature of the membrane surroundings in TDEV can be attributed to the tentative mechanism shown in **Figure 6**. That is, when water and ethanol molecules, vaporized from the feed solution, approach the lower-temperature membrane surroundings, the water vapor aggregates more readily than the ethanol vapor because the freezing point of water is much higher than that of ethanol. As such, the aggregated water molecules tend to liquefy as the temperature of the membrane surroundings becomes lower. On the other hand, because the membrane has a relatively high affinity to the ethanol molecules, they are absorbed within the pores of the membrane, and an adsorbed layer of ethanol is formed in the initial stage of permeation. Consequently, the vaporized ethanol molecules may be able to permeate across the membrane by surface diffusion on the adsorbed layer of the ethanol molecules within the pores.

Both mechanisms, aggregation of the water molecules and surface diffusion of the ethanol molecules in the pores, are considered to be responsible for the increase in the ethanol/water selectivity in TDEV. The level of increase in ethanol/water selectivity would then be related to the degree of water aggregation on the membrane surroundings and the thickness of the adsorbed layer of ethanol within the pores, which are significantly gov-

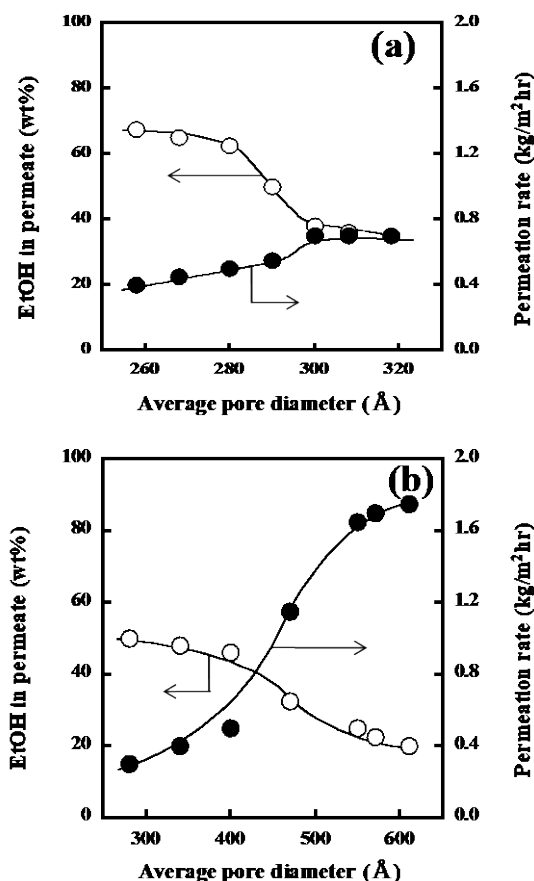


**Figure 6.** Tentative mechanism for the concentration of aqueous ethanol solutions through asymmetric porous CN and CA membranes in TDEV.

erned by the temperature of the membrane surroundings. When the temperature of the membrane surroundings becomes lower, the degree of water aggregation and the thickness of the adsorbed layer of ethanol are increased, corresponding to an increase in the ethanol/water selectivity for aqueous ethanol solutions. The observation that both the ethanol concentration in the permeate and the permeation rate were higher in the CN membrane than in the CA membrane can be easily understood based on the results of the surface free energy and amount of bound water obtained in the CN and CA membranes as shown in **Tables 1** and **2**.

### 3.5. Effect of Average Pore Diameter on Permeation and Concentration Characteristics in TDEV

**Figure 7** shows the permeation and concentration char-



**Figure 7.** Effects of the average pore diameter in the skin layer of asymmetric CN (a) and CA (b) membranes on the permeation rate and ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol during TDEV, in which the temperatures of the feed and the membrane surroundings were 40°C and 25°C, respectively. The reduced pressure on the downstream side was 650 Pa.

acteristics for an aqueous solution of 10 wt% ethanol passed through asymmetric CN and CA membranes during TDEV as a function of the average pore diameter in the skin layer of asymmetric cellulose ester membranes. In the experiments, the temperature of the feed was 40°C and that of the membrane surroundings was 20°C. As can be seen in both the CN and CA membranes, when the average pore diameter decreases, the ethanol concentration in the permeate increases and the permeation rate decreases. The decrease in permeation rate with decreasing average pore diameter is likely due to a decrease in the pore flow through these membranes.

### 3.6. Chemical and Physical Structure of Asymmetric Porous Membranes

**Table 3** shows the effects of the chemical and physical structure on the permeation rate and ethanol concentration in the permeate through asymmetric porous CN and CA membranes by TDEV for membranes with almost similar pore size and similar rejection values for some PEGs in ultrafiltration. These results suggest the physical structures of the CN and CA membranes are the same. As can be seen from the ethanol concentrations in the permeate in **Table 3**, it is found that the CN membrane has a higher ethanol/water selectivity than the CA membrane. This result can be attributed to the fact that the CN membrane is more hydrophilic than the CA membrane as mentioned above.

### 4. Conclusions

When asymmetric porous CN and CA membranes were applied to TDEV in the concentration of an aqueous ethanol solution, a high permeation rate and high ethanol/water selectivity were obtained. The characteristics of permeation and separation through the CN and CA membranes were significantly influenced by the temperature of the membrane surroundings. In the CN and

**Table 3. Characteristics of asymmetric porous CN and CA membranes.**

	Membrane	
	CN	CA
Average pore diameter (Å)	280	284
Rejection		
PEG 1000	13	11
PEG 4000	24	23
PEG 6000	46	46
EtOH in permeate	61	48

CA membranes, the ethanol/water selectivity was attributed to both aggregation of water molecules on the lower-temperature membrane surroundings and surface diffusion of the ethanol molecule via an absorbed layer of ethanol formed within the pores. The permeation rate and ethanol/water selectivity of the asymmetric porous membranes were significantly influenced by the degree of water aggregation, the thickness of the absorbed layer of ethanol and the pore size of the membrane. In this study, we have demonstrated that a high permeation rate and high ethanol/water selectivity can be achieved by applying porous membranes to TDEV. CN membranes, in particular, offer potential for selective separation of ethanol/water.

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