

# Pervaporation Separation of Aqueous Organic Mixtures through Sulfated Zirconia-Poly(vinyl alcohol) Membrane

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**ABSTRACT:** Sulfated zirconia-poly(vinyl alcohol) membranes were prepared, and pervaporation performances for aqueous organic mixtures were investigated. These hydrophilic membranes were formed by crosslinking poly(vinyl alcohol) (PVA) with the solid acid of sulfated zirconia by an acid-catalyzed reaction. The pervaporation performances were measured as a function of the content ratio of sulfated zirconia to PVA, which affected the degree of swelling for water and the crosslinking density of the membrane. The membrane selectivity in pervaporation of aqueous organic mixtures increased in order of acetic acid < ethanol < 2-ethoxyethanol without sacrificing the permeation rate, depending on their feed compositions. The effects of feed temperature and concentration on the membrane performance were also significant. It was found that sulfated zirconia in the membrane preparation played an important role as a filler material as well as an effective crosslinking or insolubilization agent in improving and controlling the membrane performance, i.e., permeation rate and selectivity. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1450–1455, 2001

**Key words:** pervaporation; aqueous organic mixtures; acetic acid; sulfated zirconia; PVA membrane

## INTRODUCTION

A number of pervaporation membranes for dehydration of organic–water mixtures have been studied since the membrane process for manufacturing absolute ethanol was commercially developed in the early 1980s.<sup>1–3</sup> Hydrophilic poly(vinyl alcohol) (PVA) membranes, modified or crosslinked with other chemicals, can be used in the pervaporation of aqueous organic mixtures. However, it is inevitable for PVA to be insolubilized or crosslinked to improve the membrane stability to water. Now it is known that the crosslinking or insolubilization of PVA

has been performed with the following method. First, the PVA membranes were crosslinked with an organic chemical such as aldehyde and organic acid.<sup>2,3</sup> For example, glutaraldehyde or polyacrylic acid as a crosslinking agent was combined with PVA to become a polymer segment in the preparation of the membranes. In addition, maleic acid, formaldehyde, fumaric acid, etc., were also used for this purpose. Second, the PVA membranes were prepared with insolubilization by an acid-catalyzed dehydration in the presence of a mineral acid such as sulfuric acid or by gelation using peroxodisulphate such as potassium persulphate.<sup>4,5</sup> Unlike the crosslinking agent of aldehyde and organic acid, the insolubilization of PVA using a catalyst or an oxidizing agent could be achieved without directly combining a chemical into the

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polymer segment of the PVA membrane. Finally, adding a filler material such as zeolite to the polymer membrane network has been reported to improve the PVA membrane performance. In the case of hydrophilic zeolite, it facilitated the permeating of smaller molecules but hindered that of larger molecules.<sup>6</sup>

Sulfated zirconia has been used as a solid acid catalyst in many chemical reactions such as polymerization, isomerization, alkylation, carbonylation, and oxidation, because its highly porous solid surface exhibits strong Lewis and Brønsted acidities.<sup>7</sup> This catalyst can also be utilized for the preparation of PVA pervaporation membranes as a filler as well as an acid catalyst for a membrane insolubilization.

There are only a few studies on PVA membranes prepared using a solid acid of sulfated zirconia. This article is aimed at the preparation of sulfated zirconia–PVA membranes and investigation into their pervaporation membrane performance of organic–water mixtures including acetic acid, ethanol, and 2-ethoxyethanol.

## EXPERIMENTAL

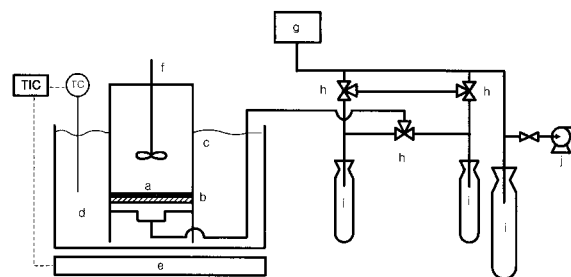
### Materials

Prior to the preparation of sulfated zirconia, hydrous zirconium oxide was obtained by hydrolyzing zirconyl chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) in aqueous ammonia solution (pH 10) at room temperature. Vigorous stirring was performed for 3 h. The product was filtered and washed with deionized water until free of chlorine, and then dried at 130°C overnight. Sulfated zirconia was then prepared by impregnation of the corresponding hydrous zirconium oxides with a 1 N  $\text{H}_2\text{SO}_4$  solution for 0.5 h, followed by filtration and drying at 130°C overnight. Finally, the solid was calcined at 600°C for 3 h.<sup>8</sup> This powder was milled to submicrometer size prior to membrane preparation using ultrasonic homogenizer (Model ULCD-200S).

PVA, with an average molecular weight of 89,000–98,000 (98% hydrolyzed), and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  were obtained from Aldrich Chem. Co. Ammonia solution, sulfuric acid, acetic acid, ethanol, and 2-ethoxyethanol were also obtained from Junsei Chem. Co. and used without further purification.

### Membrane Preparation

The mixtures of PVA and sulfated zirconia (abbreviated hereafter as SZ), which had the weight



a. Membrane, b. Sintered metal, c. Cell, d. Constant temperature bath, e. Heater, f. Mechanical stirrer, g. Pirani gauge, h. 3-Way valve, i. Cold trap, j. Vacuum pump  
TIC : Temperature indicating controller, TC : Thermocouple

**Figure 1** Pervaporation apparatus for aqueous organic mixtures.

ratio of SZ to PVA ( $\gamma = \text{SZ/PVA}$ ) in the range of 0.28 to 0.57, were prepared by vigorous mixing for 6 h in hot water of 90°C. The resulting solution was cast onto a glass plate using a casting knife and dried for over 24 h at 40°C. A PVA content in the casting solution ranged from 13.8 to 14.3 wt %. A typical casting formulation was: PVA, 3.5 g; sulfated zirconia, 1.5 g; water, 20 g. The average thickness of the membranes was about 27  $\mu\text{m}$ .

### Determination of Degree of Swelling

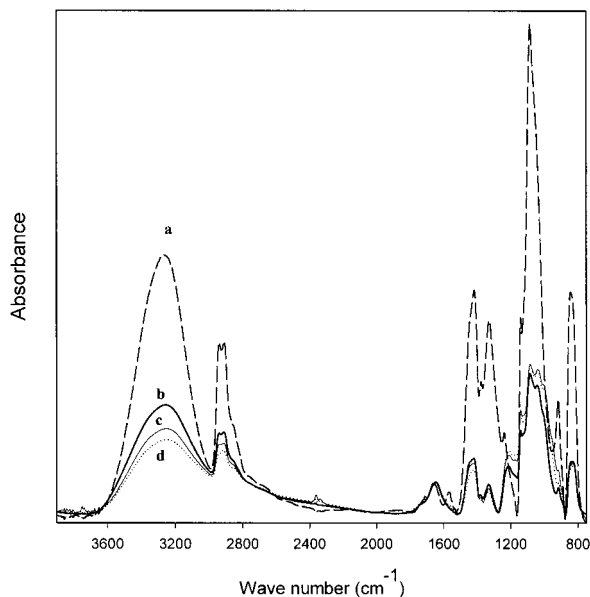
The degree of swelling is defined as follows: degree of swelling = (weight of swollen membrane – weight of dry membrane)/weight of dry membrane. Swelling characteristics were determined after measuring the weight variance between a swollen membrane and dry membrane. The swollen membrane was well equilibrated in water for several hours.

### FTIR Spectra Analysis

FTIR spectra were obtained by using a spectrometer (Perkin-Elmer, Spectrum GX-FT-IR) to verify the SZ-PVA membrane prepared. An ATR method was applied to FTIR measurement.

### Pervaporation

The pervaporation apparatus used is illustrated in Figure 1. The effective membrane area in the pervaporation cell was 14.5  $\text{cm}^2$ . The pressure at the downstream side was kept below 5 mmHg by a vacuum pump. Pervaporation experiments were performed at 30, 40, 50, and 60°C with the same membrane used for a given binary feed composition.



**Figure 2** FT/IR spectra of SZ-PVA membranes.  $\gamma$ (=SZ/PVA): a = 0 (PVA film), b = 0.28, c = 0.42, d = 0.57.

The feed concentration of aqueous organic mixtures for acetic acid, ethanol, and 2-ethoxyethanol, respectively, varied in the range of 70 to 95 wt %. The organic chemicals in the feed and the permeate were analyzed by a gas chromatograph (Model HP 6890) equipped with a capillary column (HP-5, 5% Phenyl Methyl Siloxane). The selectivity factor is defined as follows:

$$\alpha_{ij} = (y_i/y_j)/(x_i/x_j)$$

where  $x$  is the feed composition,  $y$  is the permeate composition, and  $i$  denotes the preferentially permeated component, i.e., water.

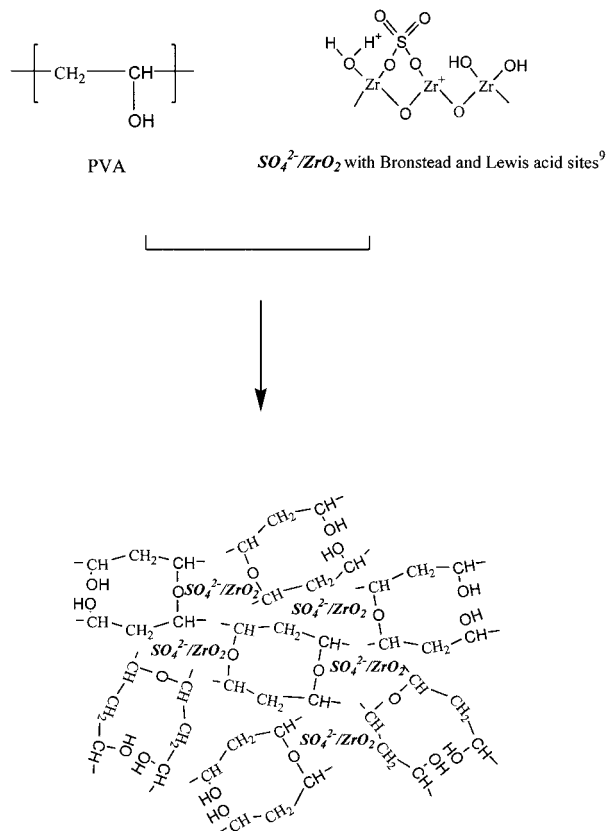
## RESULTS AND DISCUSSION

### Formation of SZ-PVA Membranes

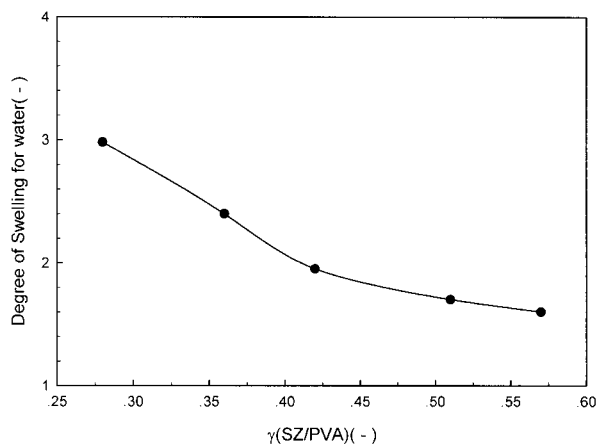
Figure 2 shows FTIR spectra of SZ-PVA membranes and a PVA film. In the figure, PVA film (a) means the chemically unmodified PVA film, obtained by drying it for over 24 h at 40°C after the aqueous PVA solution of 15 wt % was cast onto a glass plate. The absorbance peak for  $-\text{CH}_2-$  group in SZ-PVA membranes and the PVA film is located at 2800–3000 and 1400–1470  $\text{cm}^{-1}$ . The peak at 3200–3400  $\text{cm}^{-1}$  arises from hydroxyl group in PVA. In comparison with PVA film, SZ-

PVA membranes have a weak absorbency at 3200–3400 and 2800–3000  $\text{cm}^{-1}$ , even considering the inclusion of sulfated zirconia. This fact might be attributed to the nature of the insolubilized PVA membrane. Bidentate  $\text{SO}_4^{2-}$  ion peaks of SZ (b, c, d) at 1230–1240, 1160–1195, 1105–1110, and 1030–1035  $\text{cm}^{-1}$ , which are known to bring about the surface acidity due to a strong electron inductive effect,<sup>7</sup> are apparent in FTIR spectra of SZ-PVA membranes. This indicates that sulfated zirconia in the preparation of SZ-PVA membranes is entrapped into a PVA network structure as proposed in Figure 3. Also, it is notable that the peak at 1630–1650  $\text{cm}^{-1}$  due to the bending vibration of molecularly adsorbed water is detected in a considerable quantity in the membrane.

SZ as a solid acid seems to catalyze PVA polymers to form a crosslinked PVA membrane that is stable to water. Immelman et al.<sup>4</sup> obtained PVA membranes insolubilized by an acid-catalyzed dehydration in the presence of  $\text{H}_2\text{SO}_4$ . They explained the mechanism of insolubilization of PVA



**Figure 3** Schematic representation of entrapment of sulfated zirconia in the SZ-PVA membrane.



**Figure 4** Effect of sulfated zirconia content on degree of swelling for water.

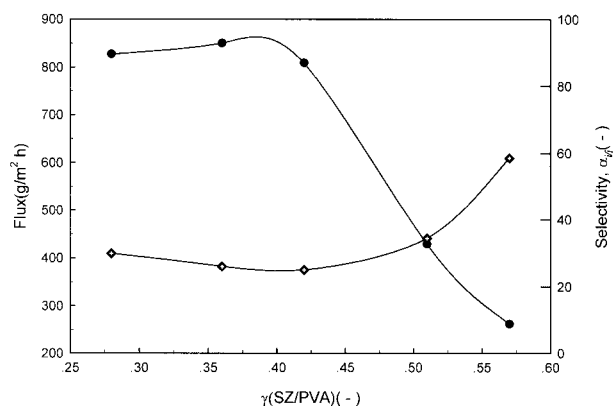
in terms of formation of ether crosslinks by nucleophilic substitution because  $\text{H}_2\text{SO}_4$  could produce proton acids. SZ keeps Brønsted acid sites in contact with water, although it is known in general that it retains strong Lewis acid sites in a dry solid state.<sup>9,10</sup> Such Brønsted acid sites in SZ are thought to combine PVA polymers together to a crosslinked PVA membrane by an acid-catalyzed dehydration as in the case of  $\text{H}_2\text{SO}_4$ . Accordingly, SZ-PVA membranes prepared can be interpreted to be in the form of ether crosslinks made by a catalytic reaction of SZ.

#### Effect of SZ Content

The swelling behavior of a preferential component affects the pervaporation membrane performance, i.e., permeation rate and separation factor. This property can be determined by the characteristic of raw membrane materials and their membrane preparation condition. A SZ content in the preparation of SZ-PVA membranes can play a key role in determining the crosslinking density of the membrane affecting the degree of swelling for water. Figure 4 illustrates the effect of a SZ content on the swelling of the membrane to water. The degree of swelling decreases with an increase in a SZ content in SZ-PVA membranes. It is thus related to the increase of the crosslinking density of the membranes to form a rigid PVA network structure.

Figure 5 shows the pervaporation membrane performance of SZ-PVA membranes for acetic–water mixtures as a function of SZ content in the membranes. With an increase in the  $\gamma(\text{SZ/PVA})$  the permeation rate and selectivity remain al-

most constant up to a certain level below  $\gamma = 0.42$ , and then beyond that level the permeation rate decreases while the selectivity increases. In general, as the crosslinking density increases, the degree of swelling and permeation rate decrease. In previous studies,<sup>11,12</sup> it was shown that the behavior of swelling for water, which was affected by crosslinking density, followed that of total flux in acetic–water mixtures or ethanol–water mixtures: the tendency of increase and decrease in the degree of swelling was similar to that in a permeation rate. This reflects the prevailing solution-diffusion mechanism for a preferential absorption in pervaporation. In comparing Figures 4 and 5, the low SZ content region below  $\gamma = 0.42$ , however, exhibits a different trend between the swelling degree and the permeation rate, while the high SZ content region above  $\gamma = 0.42$  shows a normal trend between the swelling degree and the permeation rate. In the former region, there are no significant changes in the permeation rate of acetic acid–water mixtures despite the decrease of the swelling degree. This trend might be due to the characteristics of SZ and the network structures of SZ-PVA membrane. The reduction of permeation rate with the increase of the crosslinking density in the low SZ content region may be compensated by the high hydrophilicity of the membrane and a resultant higher flux, because SZ is very hygroscopic and has higher adsorption capacity of polar molecules. Actually, the SZ-PVA membranes used absorbed water very quickly in a swelling test compared with other PVA membranes prepared using glutaraldehyde



**Figure 5** Pervaporation performance of SZ-PVA membranes as a function of sulfated zirconia content in the membranes. ●, for Flux; ◇, for Selectivity. Feed concentration: 80 wt % acetic acid; feed temperature: 50°C.

**Table I Pervaporation Performance of SZ-PVA Membrane for Organic–Water Mixtures**

Feed Concentration (wt %)	Flux (g/m <sup>2</sup> h)	Selectivity, $\alpha_{ij}$ (-)
Acetic acid	70	1449
	80	809
	90	125
	95	20
Ethanol	70	1036
	80	183
	90	105
	95	10
2-ethoxyethanol	70	1107
	80	300
	90	136
	95	16

$\gamma = 0.42$ ; feed temperature: 50°C.

or sulfuric acid. As a result, the permeation rate in the low SZ content region below  $\gamma = 0.42$  remains almost constant. On the other hand, in the high SZ content region beyond a certain level the permeation rate decreases with an increase of  $\gamma$  because the crosslinked membrane network structure can be dense enough to reduce a membrane flux.

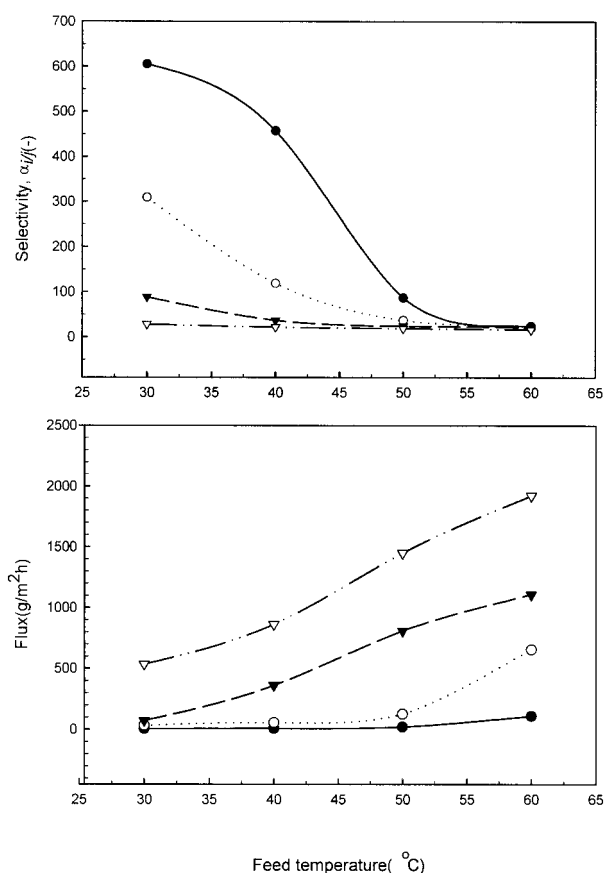
#### Pervaporation Performance for Organic–Water Mixtures

Pervaporation performances of SZ-PVA membranes for organic–water mixtures are presented as a function of feed concentration in Table I. As the feed concentration of organic–water mixtures increases, the permeation rate decreases and the selectivity increases. At the same feed composition for aqueous organic mixtures the membrane selectivity increases in the order of acetic acid < ethanol < 2-ethoxyethanol, and the permeation rate in the order of ethanol < 2-ethoxyethanol < acetic acid. Among aqueous organic mixtures the selectivity is drastically changed, compared to the permeation rate. In the case of 2-ethoxyethanol–water mixture, only water was collected in the permeate side without the organic component. This shows the dependence of membrane selectivity on the size of permeating molecules. It has been reported that as the molecular weight of permeated molecules in a given homologous series increases, the permeation flux decreases, and the separation increases.<sup>13,14</sup> In this study the

membrane selectivity in pervaporation of aqueous organic mixtures increases in the order of acetic < ethanol < 2-ethoxyethanol without sacrificing the permeation rate, depending on the feed composition.

#### Effect of Feed Temperature and Concentration

Figure 6 shows the effect of temperature and feed concentration on pervaporation membrane performance for acetic acid–water mixtures. The permeation rate increases as the feed temperature increases and the feed concentration decreases. The membrane selectivity shows a reverse trend. These results mean that the membrane performances depend simultaneously on the feed temperature and concentration. The permeation behavior is associated with swelling toward a preferential component, water. The smaller swelling in the high concentration region retards the pas-



**Figure 6** Effect of feed temperature and concentration on membrane performance of SZ-PVA membranes.  $\gamma = 0.42$ .  $\nabla$  70 wt % acetic acid in feed,  $\blacktriangledown$  80 wt % acetic acid in feed,  $\circ$  90 wt % acetic acid in feed,  $\bullet$  95 wt % acetic acid in feed.

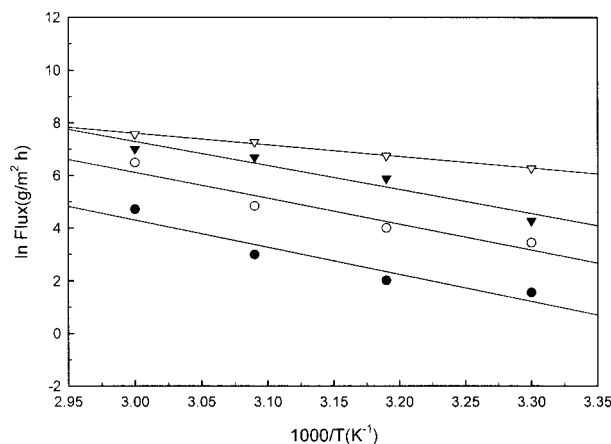
sage of permeated components. The feed including relatively a considerable amount of water in a lower concentration region can swell the membrane structure to allow permeated components to diffuse easily into the membrane. So the decrease in a feed concentration increases the permeation rate. The increase in a feed temperature makes the permeated components easy to pass through the membrane due to the flexibility of polymer segments. Meanwhile, the highest value of the membrane selectivity is shown at the lowest feed temperature and the highest feed concentration. The mobility of permeated molecules inside the membrane seems to be more limited in this condition.

#### Arrhenius Plot of Permeation Rate

Figure 7 shows Arrhenius plots to calculate the permeation activation energies of acetic acid–water mixtures with the variation of feed concentrations. The calculated value is listed in Table II. It shows that the higher activation energy is required for higher feed concentration, being consistent with the result of Figure 6.

#### CONCLUSIONS

PVA membranes crosslinked with SZ, which acts as a catalyst and filler, were prepared through a novel method. The SZ content in the membrane



**Figure 7** Arrhenius plots for permeation rates of acetic acid–water mixtures.  $\nabla$ : 70 wt % in feed;  $\blacktriangledown$ : 80 wt % in feed;  $\circ$ : 90 wt % in feed;  $\bullet$ : 95 wt % in feed.

**Table II** Permeation Activation Energy of Acetic Acid–Water Mixtures

Feed Concentration (wt %)	Activation Energy (kcal/mol)
95	20.4
90	19.5
80	18.1
70	8.7

preparation affected the swelling degree and the crosslinking density of the SZ-PVA membrane. In pervaporation of organic–water mixtures the membrane selectivity increased in order of acetic acid < ethanol < 2-ethoxyethanol without sacrificing the permeation rate, depending on their feed compositions. Sulfated zirconia, in the preparation of SZ-PVA membrane with a strong hydrophilicity, played an important role in improving and controlling the pervaporation performance.

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