Vulcanized Paper for Separation of Alcohol Aqueous Solutions by Pervaporation

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ABSTRACT: Paper membranes made from vulcanized cellulose were used for the pervaporation (PV) of aqueous solutions containing methanol, ethanol, and isopropanol. It was noted that the vulcanized cellulose paper membranes (VCPM) could effectively separate alcohol and water from the mixture solutions. To observe the effect of the separation of alcohol aqueous mixtures, the permeation behavior of water and alcohol was examined by means of the separation factor and the permeation flux. The values of the permeation flux in the ethanol/water mixtures were found to vary from 6.2 kg/m^{2}h to 2.1 kg/m^{2}h, as the concentration of ethanol increased from 8 to 87 wt %, and the separation factor (α) changed from $\alpha = 2.6$ to 6.6, respectively. This showed that the VCPM enhanced the separation of water and alcohol. The highest value observed for the permeation flux was 11 kg/m^{2}h at 87 wt % of methanol concentration and the separation factor at this condition was 4.1. It was shown also that an efficient separation was obtained in the isopropanol/water mixture with a separation factor of 16.6. The contact angles of alcohol/water droplets on the VCPM were measured as well as the wettability of the membrane. There was a tendency of decrease for the contact angle, as the alcohol concentration decreased. This suggested that the solvent wettability decreased in high alcohol concentrations. It was concluded that a high permeabilitty of water through the VCPM resulted in the separation of alcohols and water in the PV process. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 639–647, 2011

Key words: pervaporation; alcohol-water separation; vulcanized paper; contact angle; swelling degree

INTRODUCTION

Pervaporation (PV) is a separation process which involves partial vaporization of a liquid feed mixture through a nonporous polymeric membrane and has gained much importance in several areas related with separation purposes.[1,2] Because PV is a highly efficient membrane separation process for the dehydration of organic solvents, the PV process becomes suitable for the separation to water and alcohol. In the case of wide variety of azeotropes mixtures having components with very close boiling points which cannot be easily separated by distillation, the PV process can be effectively broken up without heat energy. Therefore, the dehydration of alcohols using the PV process has received great attention because of its potential in industrial applications.[3]

So far, many researchers have studied and developed membrane materials for this purpose. In recent years, numerous investigations have been carried out regarding to the PV process of water/alcohol mixtures through polymeric membranes.[4–8] As it is known, several polymeric[9–11] and composite membranes[12–16] containing synthetic cellulose units were developed for the dehydration of alcohol mixtures by the PV processes. As a result, it was recognized that hydrophilic polymer was better for the dehydration of various solvents in the PV process. It was known that the PV process depended on the mass transfer of solute generally by solution-diffusion.[17] Thus, the mechanism of liquid transportation through the polymeric membrane was considered to include: (i) sorption of feed composition to the upstream side of the membrane, (ii) diffusion of the permeant through membrane, and (iii) desorption at the downstream side of the membrane under a low-pressure.

Therefore, in this article, we have focused on paper, which is a very common natural material based on cellulose, since cellulose is paper component polymer and is known for its excellent biocompatibility as well as thermal and mechanical properties.[18] Besides, paper materials are widely available to use as sheets because of the abundance of cellulose at low costs. However, for suitable PV purposes, due to its difficulty in curing and vulcanizing the cellulose fibers, is needed to treat alcohol/water solutions. In addition, such biopolymers are of great

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interest as renewable natural resources and promising as a solution to the environmental problem of plastic waste disposal.[19–21] In these purposes, it was found that, alginic acid membranes[22] and regenerated cellulose membranes[23] were reported to show good selectivity in the dehydration process of water-alcohol mixtures. In addition, chitosan membranes having cationic polysachcaride segments,[24] chitosan-silica complex membranes[25] and cellulose acetate membranes modified with ultra-thin polyion complex layers[26] presented high selectivity in the water/alcohol separation. PV membranes made from a blend of chitosan and polyvinyl alcohol[27] were also investigated for dehydration of water-alcohol system. However, vulcanized cellulose paper membranes (VCPM) used in the present work became of interest in the PV process, because of the paper materials having plastic- like properties.[28] The vulcanized process of cotton can make the paper membranes flexible, tough, and durable without the need of resin or bonding materials.[29] It has also the advantage that the VCPM has common cellulose segments without modification of OH side groups. Because of the hydrophilic nature of the VCPM, therefore, we have noted that the VCPM has capability for water permeability in the azeotropes as well as other polysaccharide membranes. In addition, until now, no studies have been performed using such the VCPM for the PV processes. Thus, as a first report, we have studied PV processes for methanol, ethanol and isopropanol solutions using the VCPM for separation of alcohol/water mixtures at different concentrations. The aim of the present article is to report separation of alcohol-water binary mixture by using vulcanized cellulose paper membranes.

EXPERMENTAL

Materials

Methanol and ethanol were purchased from Nacalai Tesque Inc. (Tokyo, Japan) and isopropanol was purchased from Hampton Research (USA). VCPM, having 250 μm of thickness, was received from Hokuetsu Paper Mills (Tokyo, Japan). Water was deionized and distilled before use. The feed solutions for the experiments were binary aqueous solutions containing methanol, ethanol, and isopropanol, respectively, with different ratios of water/alcohol in the mixtures.

Characteristics of VCPM

Scanning electron microscopy was used to study the morphology of the surface and the cross section of the vulcanized cellulose paper membrane. In the measurement, the VCPM was fractured in liquid nitrogen and then the fractured part was coated with a conductive layer of sputtered gold. The surface and the cross section of the VCPM were investigated using a JSM-5300LV (JEOL, Japan).

Contact angles of different alcohol/water mixtures were measured using a Drop Master100 contact angle meter (Kiowa Interface Science Co.LTD) at room temperature. The droplet volume of the aqueous alcohol solutions was approximately 2 μL. The values of contact angle were measured at five different sites of the VCPM and the average value was referred as the contact angle of the membrane. In addition with the water contact angle, we measured air contact angle on the VCPM surface. In this case, the VCPM was in water and 2 mL air was attached on the surface to measure the contact angle.

To evaluate the swelling behavior of the VCPM in alcohol/water mixture solution, the solvent content (SC) in the VCPM was determined as followed: Weighed dry VCPMs were immersed in each alcohol/water solution in a sealed vessel at room temperature for 24 h. The membranes were then rapidly taken out from the solution, wiped it with filter paper, and then weighed. The SC was determined from the difference of weight of the VCPM before and after immersion in the solutions. The SC was expressed as (1):

$$SC = [(W_s - W_d)/W_d] \times 100\% \quad (1)$$

where W_d and W_s denoted the weight of the VCPM before and after immersion in the solution, respectively.

The degree of swelling (DS) of the VCPM was evaluated by comparing the diameter of the used membrane according to eq. (2),

$$DS = V_a/V_b \quad (2)$$

where, V_b and V_a are the volumes of the VCPM before and after immersion in the solution, respectively.

Pervaporation experiments of alcohol/water solutions

A schematic diagram of the PV apparatus and a detailed description of the procedure for performing the PV experiment are shown in Figure 1. In this work, the PV process was carried out in a batch system. The permeation experiments were carried out using a PV apparatus with a common membrane cell, which was connected using a magnetic holder to fit the VCPM ($\Phi = 46$ mm) having effective membrane area of 17×10^{-4} m^2. The membrane cell

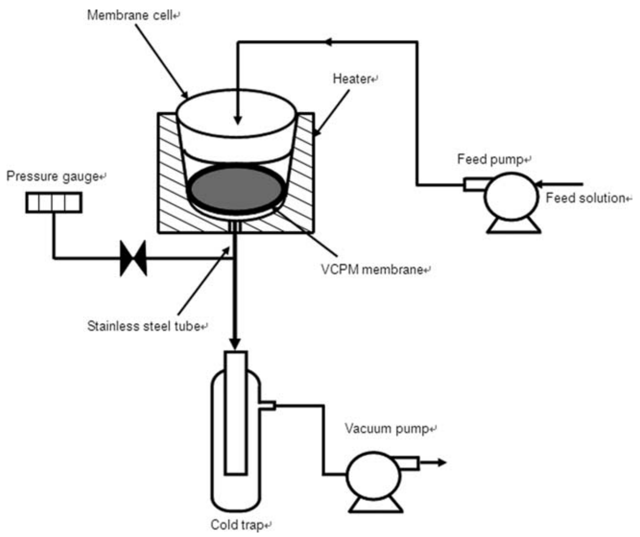

Figure 1 Schematic diagram of the pervaporation apparatus.

inside was filled with alcohol/water solution up to 150 mL. Here, the solution was exposed to atmospheric pressure on the upper side and the solution amount was fed by of addition alcohol-water solution from the upper side by means of a feed pump. In the bottom of the membrane cell, a stainless tube having an inner diameter of 58 mm was connected to a cold trap and a vacuum pump (ULVAC, DA-20D, Tokyo, Japan). Then, the inside pressure was kept at 124 (±0.5) Pa by using the vacuum pump through the cold trap. The inside pressure was measured with a pressure gauge (MKS Baratron, 122A). We confirmed that the cold trap was collected the whole permeated liquid vapors by setting an additional trap on the downstream. For the PV process, the experimental conditions were chosen in the following two series. One series of the experiments was performed at room temperature and variable feed alcohol at concentrations in the range of 0 to 100 wt % to investigate effect of the alcohol in the PV process of the VCPM. Another series was conducted under variable feed temperature in the range of 25–45°C and a fixed feed alcohol concentration of 25 wt %, to evaluate the effect of the temperature on the permeability of solute through the VCPM. The permeate stream was condensed and collected in a cold trap by freezing with liquid nitrogen after the pumping was started. At this process, the inside pressure was 124 Pa and the permeation was collected with the inside trap. The condensed sample was collected at a given period of time and then weighed. To evaluate alcohol and water concentrations in the permeated sample solution, a gas chromatography equipment (Shimadzu TC 14B) was used with Helium as the carrier gas in a pack column (Poly A-135) at 140°C.

The permeability of the VCPM for alcohol/water was calculated via the separation factor (α) defined as

$$\alpha_{w/a} = (y_w/y_a)/(x_w/x_a) \quad (3)$$

where x and y were the weight fractions of the species in the feed and the permeate, respectively. For the description of alcohol and water, the subscripts a and w were used, respectively.

Permeate flux, J was calculated by using the following eq. (4)

$$J = Q/At \quad (4)$$

where Q (g) was the total mass of permeate for t hours and A (m^2) denoted the effective area (17×10^{-4} m^2) of the VCPM.

It was confirmed that no weight loss in the VCPM was observed after the experiments were done in SC, DS, and PV process.

RESULTS AND DICSUSSION

Characteristics of VCPM for different alcoholic water solutions

The SEM morphologies of the VCPM used are shown in Figure 2 for (a) the cross section and (b) the surface of the VCPM. From (a), the VCPM used had a cross section thickness of 250 μm and a dense paper layer through the membrane thickness. From the surface image (b) of the VCPM, it could be seen that the minute ravines distributed on the surface of the vulcanized membrane. Also, the surface image showed that the VCPM had dense structure on the surface.

To consider the PV process of alcohol/water solutions by using the VCPM, knowing the interaction of solute with VCPM is very important. For the estimation of the liquid-solid interface, the contact angle method is a technique used to determine the affinity between alcohol/water mixture and the membrane substrate. Therefore, we examined contact angle of different alcohol/water mixtures on the VCPM. Figure 3 shows changes in contact angle of the droplets with time. In all cases, there was a tendency for the value of contact angle on to decrease with the increase in observation time. Also, when the alcohol concentration in the aqueous solutions was high, the value of contact angle on the VCPM decreased, that is, a higher affinity was obtained between VCPM and the high aqueous alcohol solution concentration. For example, at 120 s, at the alcohol contents of 8 wt % and 65 wt %, the values of contact angle of, 25°(±1°) and 7°(±1°) for the methanol/water system, 24°(±1°) and 10°(±1°) for the ethanol/water

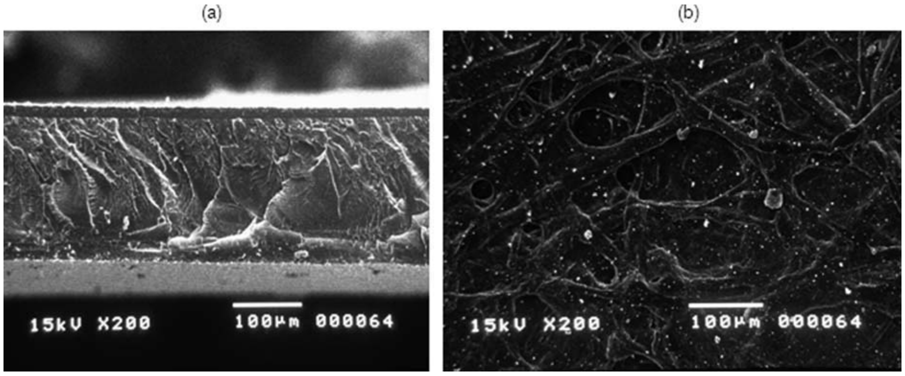

Figure 2 SEM pictures of the VCPM for (a) cross section and (b) surface of the VCPM.

system, 40°(±1°) and 12°(±1°) for the isopropanol/water system, respectively. This meant that all of alcohol mixtures wet the membrane and their liquids would penetrate spontaneously into the inside membrane. To confirm these phenomena, surface free energy of VCPM was also evaluated. It was measured in water that the value of the air contact angle was 52°(±1°). According to Andrade method,[30] surface free energy γ_{SL} was evaluated as 37.4 m*N*/m by using water contact angle and the air contact angle. This result indicated that the surface of the VCPM had somewhat high surface tension of 22.75 m*N*/m for methanol, 25.5 m*N*/m for paraffin.[31] and similar surface tension of 44 m*N*/m of polystyrene[32] This meant that the hydrophobic segment of cellulose in the VCPM arranged on the membrane surface, indicating that alcohol spread easily on the surface.

Figures 4 present the values SC of the VCPM observed at different alcohol concentrations in the aqueous mixtures. In all cases, the values of the SC decreased with the increase of alcohol concentration in the aqueous solutions. This confirmed that the VCPM made of cellulose preferentially adsorbed water as compared with alcohols. It could be seen that, as the alcohol concentration increased from 0 to 100 wt %, the value of the SC decreased from 58.9% to 7.8% for the methanol/water, 56.5% to 4.9% for the ethanol/water, and 55.2% to 3.6% for the isopropanol/water, respectively. It was shown that the values of SC in the VCPM for the methanol/water mixtures were larger than those for the ethanol/water and the isopropanol/water mixtures.

Permeation and separation of alcohol and water mixtures using VCPM

To determine the PV characteristics of the VCPM, experiments were carried out with binary alcohol-water mixtures at alcohol concentration ranging from 0–100% (wt) at 25°C. The effects of alcohol composition in the feed solution for methanol/water, ethanol/water, and isopropanol/water mixture on total permeation flux are shown in Figure 5. The value of the total permeation flux of VCPM for water was 6.8 kg/m^{2}h, and there was tendency to increase with increasing methanol concentration in the feed. It was observed that the total permeation flux for methanol mixture was 11.0 kg/m^{2}h at 87 wt % concentration, and 12.1 kg/m^{2}h for methanol meaning that these values were greater than water (6.8 kg/m^{2}h), ethanol (3.9 kg/m^{2}h), and isopropanol (2.1 kg/m^{2}h). On the other hand, the total permeation flux of the binary mixtures of ethanol/water and isopropanol/water gradually decreased with increase in alcohol concentration in the feed up to 87 wt %, but increased thereafter. The total flux decreased from 6.6 to 2.0 kg/m^{2}h with ethanol concentration in the feed increasing from 5 to 87 wt %. With regards to isopropanol, the total permeation flux decreased from 6.4 to 1.2 kg/m^{2}h with isopropanol concentration increasing from 5 to 87 wt %. While methanol showed increase in the total permeation flux over the entire concentration range 0–100 wt % in the feed, ethanol and isopropanol showed a minimum in the total permeation flux at 87 wt %. This is attributable to the occurrence of azeotropic mixture in ethanol/water and isopropanol/water binary mixtures; whereas methanol does form and nonazeatropic mixture with water.

Figures 6 shows the separation factor (α) calculated at each alcohol concentration in (a) and water flux in (b). When the isopropanol concentration increased from 25 to 87 wt %, the value of α increased from 4.9 to 16.6, respectively. In the case of ethanol, it was seen that the values of separation factor increase from 2.9 to 6.6 in the range of ethanol concentrations of 25 to 87 wt %, respectively. For the methanol/water mixture, the values of separation factor were 2.7 and 4.1 for the methanol concentration of 25 to 87 wt %, respectively. While the separation factor increased with alcohol concentration in the feed solution for all alcohol/water mixtures, it increased geometrically with alcohol concentration

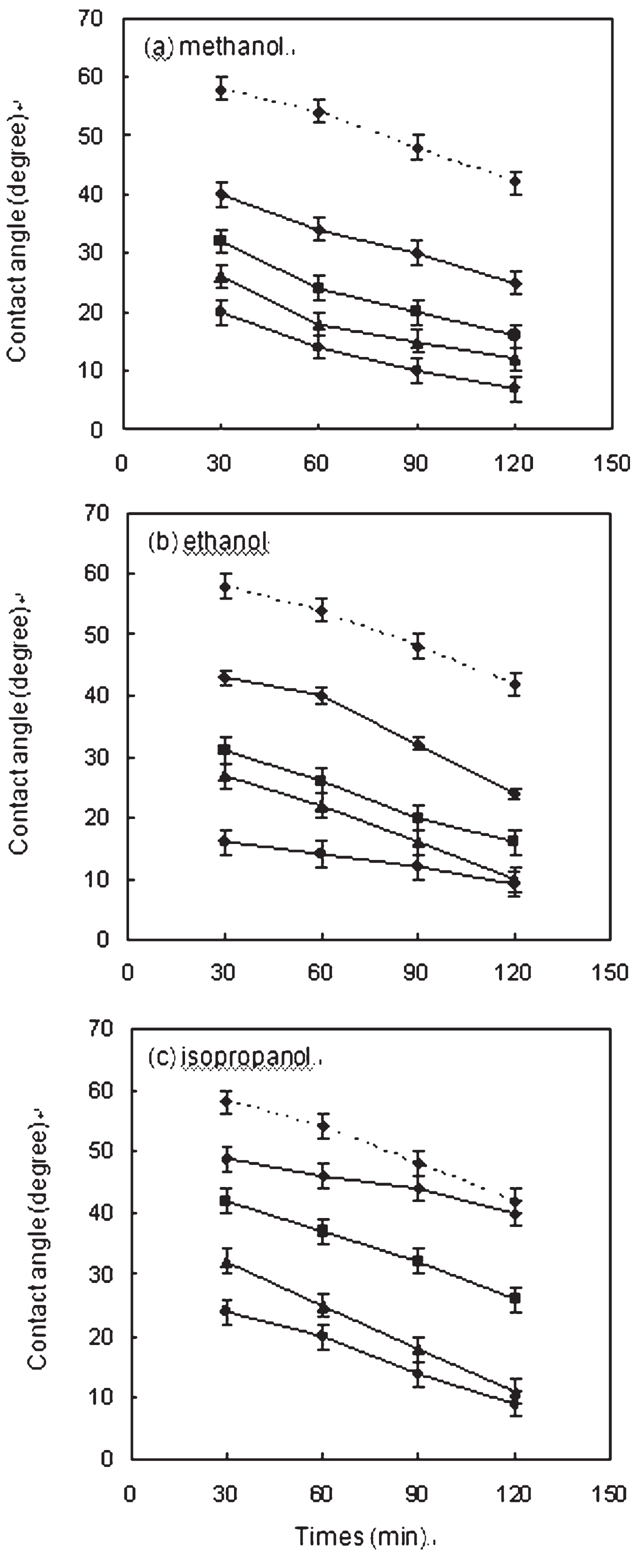

Figure 3 Changes in contact angle of the droplets alcohol/water mixtures with time --◆-- 0 wt —◆—: 8 wt %, —■—: 25 wt %, —▲—: 45 wt %, —●—: 65 wt %.

for isopropanol/water mixture at Figure 6(a). It was apparent that the separation factor increased with the alkyl chain length of the alcohol used in the mixture, whereas the total permeation flux decreased

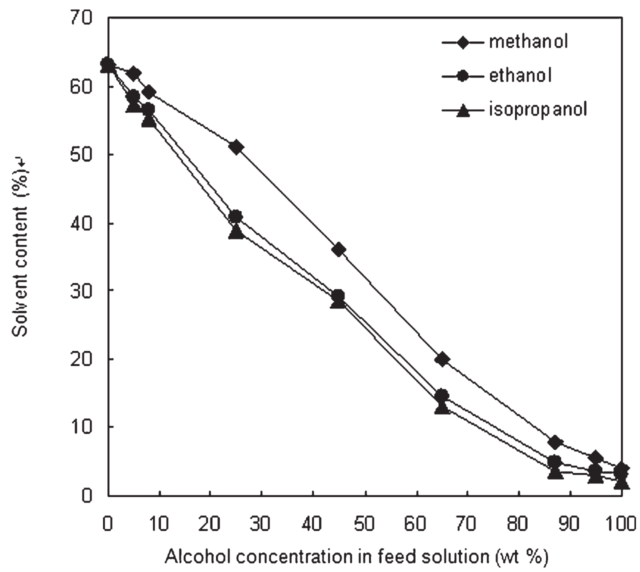

Figure 4 Solvent content of the VCPM observed at different alcohol concentration.

with the alkyl chain length. Water fluxes were calculated from the permeate compositions, and the value of water flux as a function of alcohol concentration in the feed is shown in Figure 6(b). The pattern of water flux from alcohol/water mixtures with increasing alcohol concentration was similar to total permeation flux for alcohol/water mixtures as seen in Figure 5. However, water flux from methanol/water mixture steadily increased with increasing methanol concentration, and it was higher than from water containing no alcohol. This is presumably due to flow coupling that water permeability is affected by the gradient of methanol.

Figure 7(a) depicts the water permeation results as a function of water content in the feed mixture. It

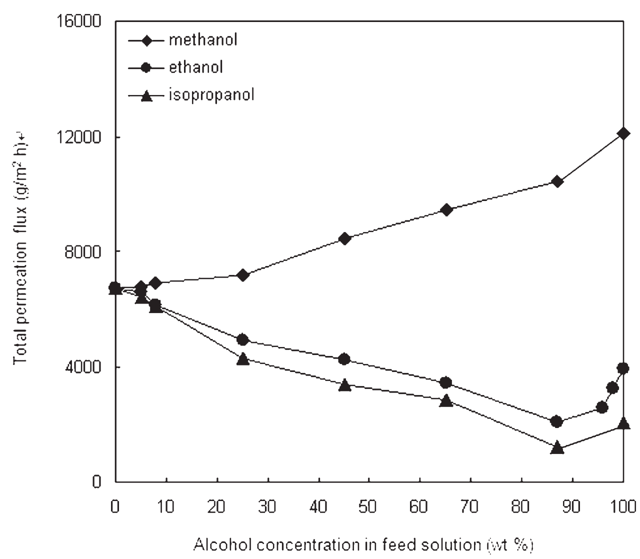

Figure 5 Effect of alcohol feed concentration on total permeation flux.

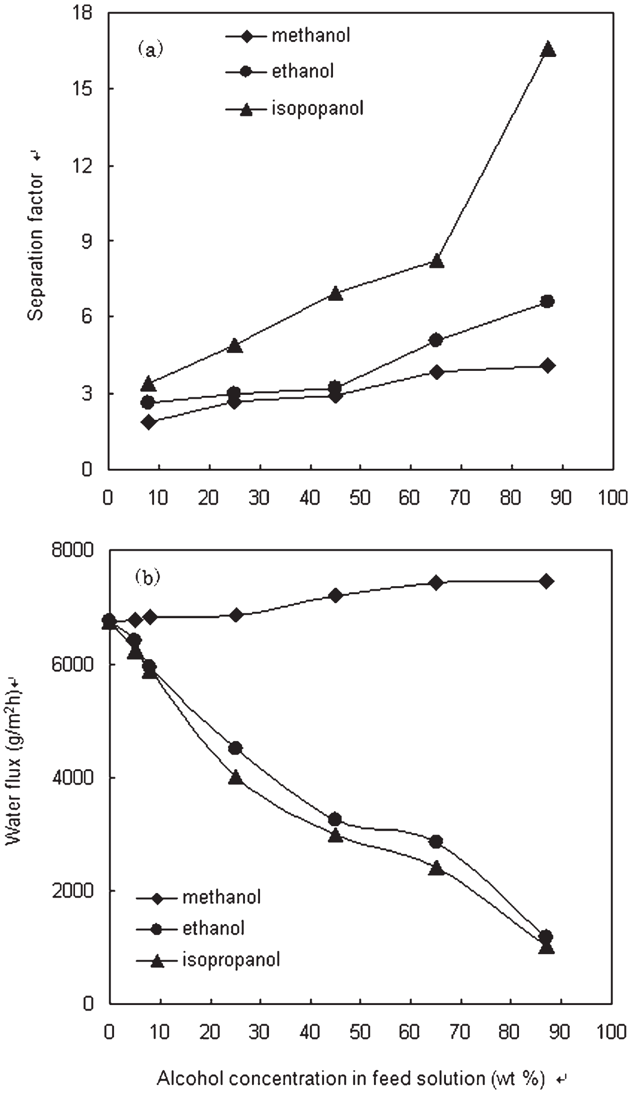

Figure 6 Effect of alcohol feed concentration on (a) separation factor, (b) water flux.

tor with total permeation flux in the methanol/water mixture. Thus, permeation behavior of methanol/water mixture through VCPM was different from that of ethanol/water and isopropanol/water mixtures. The high total permeation flux for methanol/water mixture, which increased with methanol concentration in the feed might be accounted for by the fact that methanol, being a more polar liquid compared with ethanol and isopropanol, could be sorbed by the hydrophilic VCPM along with water leading to greater swelling of the membrane and diffusion through the membrane. However, with increasing methanol concentration in the feed, preferential sorption and permeability of water appeared to increase to a smaller extent, compared with ethanol/water and isopropanol/water mixtures. Thus, this resulted in small increases in separation factor. As considered the separation of aqueous alcohol

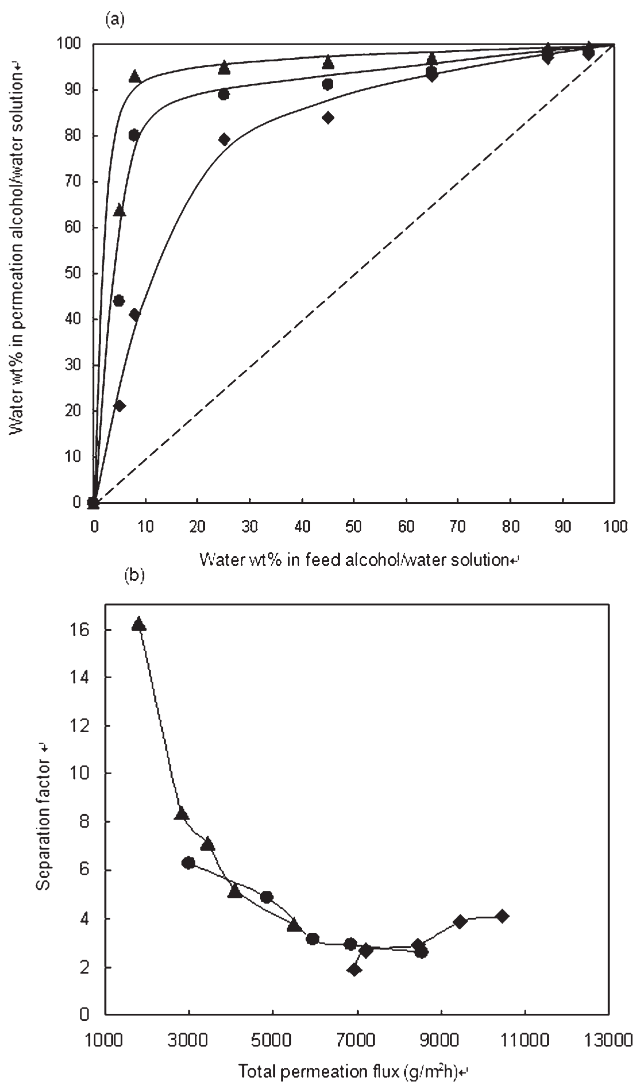

Figure 7 Relationship between (a) water feed concentration and water permeate concentration before and after the PV, respectively, (b) separation factor and total permeation flux; ◆, methanol; ●, ethanol; ▲, isopropanol.

was shown that water content in the permeate increases rapidly with water content in the feed concentration for ethanol/water and isopropanol/water mixtures, but more slowly for methanol/water mixture. This indicated that the VCPM preferentially sorbed water supporting that water could permeate more selectively through VCPM in the alcohol/water mixtures. Similar observations were made with alginic membrane[22] and regenerated cellulose membranes.[23] The relationship between separation factor and total permeation flux for alcohol/water mixtures is shown in Figure 7(b). As a general trend, separation factor decreases with increase in total permeation flux from 16.6 to 1.5 with total flux increasing from 1.7 to 10.0 kg/m^2·h. A careful examination of the plot indicated that the inverse relationship was true for ethanol/water and isopropanol/water mixtures, but little for methanol/water mixture. There was a small change in the separation fac-

TABLE I
Effect of Temperature on Total Permeation Flux and Separation Factor for 25 wt % Alcohol/Water System by the VCPM

	Total permeation flux kg/(m^{2}h)			Separation factor (a)		
T(°C)	Methanol	Ethanol	Isopropanol	Methanolol	Ethanol	Isopropanol
25	7.2	4.9	4.3	2.7	2.9	4.9
35	7.4	5.0	4.5	2.3	2.6	4.3
45	7.5	5.3	4.7	1.9	2.2	3.9

mixtures where the water molecules are smaller than alcohol molecules and the size of alcohol molecules as following methanol < ethanol < isopropanol, the hydrophilic VCPM could favor both solubility and diffusivity for selective permeation of water than alcohol molecules. This was because that the smaller permeating molecules normally exhibited larger diffusivity, while the solubility was often influenced by the chemical affinity of the permeating species to the membrane material. It could also be observed in Figure 5 that the total permeation flux of their pure alcohols was an order of magnitude of methanol, ethanol and isopropanol when their solvents were permeated through the VCPM. Namely, the resultant total permeation fluxes were in the order of methanol (12 kg/m^{2}h), ethanol (3.9 kg/m^{2}h), and isopropanol (2.1 kg/m^{2}h). It was noted that the value of water flux was 6.8 kg/m^{2}h and also larger than that of ethanol and isopropanol, but smaller than methanol. This was mainly caused by hydrophilic nature of the VCPM and less accessibility of ethanol and isopropanol was of influence in the permeation as shown in Figure 7(a). This meant that the hydrophilic VCPM included water molecules in the matrix side. From these effects, the permeability of water might be retarded relative to that of methanol. It was quite reasonable that the VCPM presented highly hydrophilic properties in the both data of contact angle and SC. Therefore, these results indicated that the high permeation flux and selectivity of water by the membranes was due to hydrophilic nature of the VCPM.

Effect of PV process on PV characteristics

It is very interested to investigate the PV characteristics of the VCPM for different operation conditions. Thus, we operated the PV process on different temperatures and times. Table I presents the effect of feed temperature on the PV performance of the VCPM for 25 wt % methanol/water, ethanol/water, and isopropanol/water mixtures. As seen, the total permeation fluxes for all mixture systems showed slightly increased values with the increase of temperature. The values of separation factor were slightly decreased when the temperature increased. This could be explained based on the fact that the permeating molecules diffused through free volumes of the membrane easily at higher temperatures because of thermal expansion of the membrane and consequent increase in space of free volumes. Thus, thermal motions of the polymer chains of the VCPM randomly might produce free volumes at higher temperature.[33,34] At 25, 35, and 45°C, the resultant water flux also increased as the temperature became higher. It was also seen that, as feed temperature increased, the separation factors showed lower values, meaning that the polymer motion lowered selectivity of the water permeability at high temperature. In each system, the values of SC and DS were furthermore obtained in the VCPM maintained at 25, 35, and 45°C. Figure 8 present the value of both SC and DS on the VCPM were slightly increased as the temperature of feed solution increased.

Generally, some polymer membranes have the disadvantage of chemical, mechanical, and heat structural instability at either higher temperature or with longer operating times. In the present work, we examined the effect of PV operating time and the resultant values of the total permeation flux and the separation factor of the VCPM. The VCPM showed stability and beneficial membrane process as the PV performance when the permeation flux and selectivity showed no change in the operation time within a period of 8 h as shown in Figure 9, with the total permeation fluxes reached within a short time, the resultant values of the permeation flux were 7.2, 4.9, and 4.3 kg/m^{2}h and separation factor of 2.7, 2.9, and 4.9 for methanol, ethanol, and isopropanol, respectively.

To know the PV performance of the VCPM, several polymeric membranes of (1) chitosan- silica complex,[26] (2) chitosan- HPC,[35] and (3) chitosan- cellulose acetate[36] were compared for dehydration of ethanol by the PV process. These processes of (1), (2), and (3) showed excellent separation performance of $\alpha = 234$, 919, and 1124 with 0.234, 0.41, and 0.132 kg/m^{2}h, respectively, when the ethanol concentration was 90 wt %. In contrast, the VCPM showed high permeability but moderate separation performance with 2.1 kg/m^{2}h and $\alpha = 6.6$ for the ethanol/water mixture. In the chitosan systems, positively charge groups in the membranes might be of influence on the accessibility of water to the hydrophilic

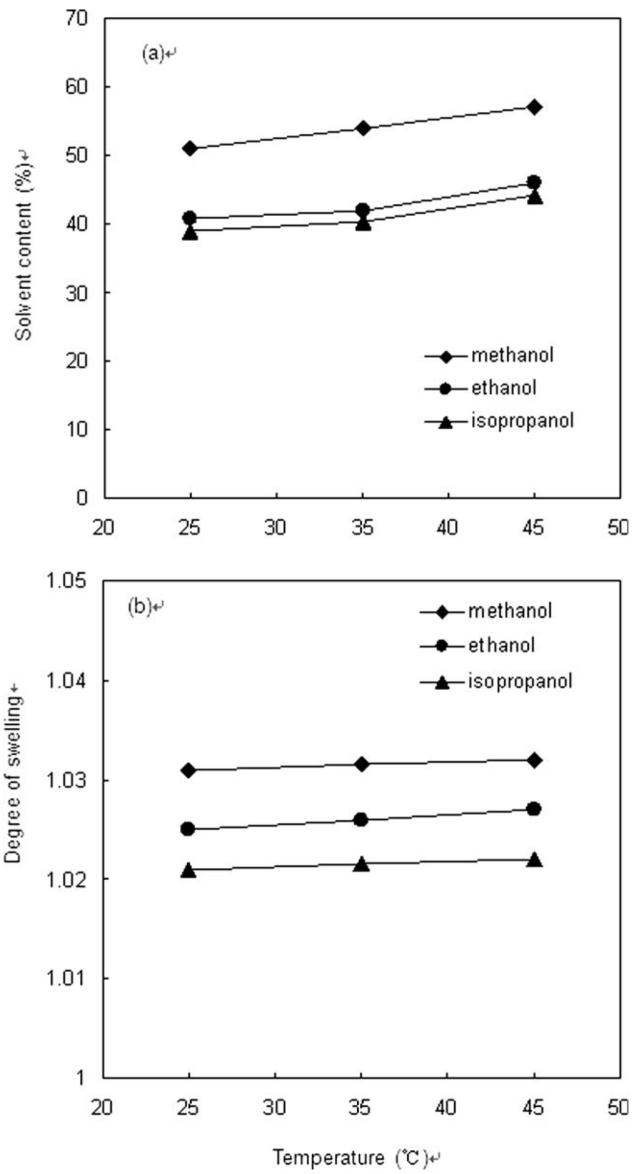

Figure 8 Effect of temperature on (a) solvent content, (b) degree of swelling for 25 wt % alcohol/water system by the VCPM.

membranes. But, the present VCPM has no charge groups in the chemical structure of cellulose paper. While this could not be directly compared in these systems with the VCPM system, we could conclude that the VCPM would become promising as novel paper sheet for the PV system with high permeation flux and stable operation for separation of alcohol/water mixtures.

CONCLUSIONS

This study mentioned as first report of the PV process using vulcanized paper membranes for alcohol/water separation. The VCPM made of pure cellulose showed a very good stability with beneficial separation mixtures of methanol, ethanol, and isopropanol in aqueous solutions by the PV process. The separation process of alcohol/water mixtures was studied for the cases to specify alcohol concentrations in feed solution. It was found that the VCPM were effective in the separation of alcohol/water mixtures with separation factor of 16.6 for isopropanol/water mixtures. The VCPM also separated similarly ethanol/water and methanol/water mixtures in the following order: isopropanol/water > ethanol/water > methanol/water. The permeation flux increased with increase of operation temperature but the separation factor decreased. In conclusion, the separation behaviors of the VCPM for the alcohol/water separation were mainly characterized by high water permeability though the VCPM.

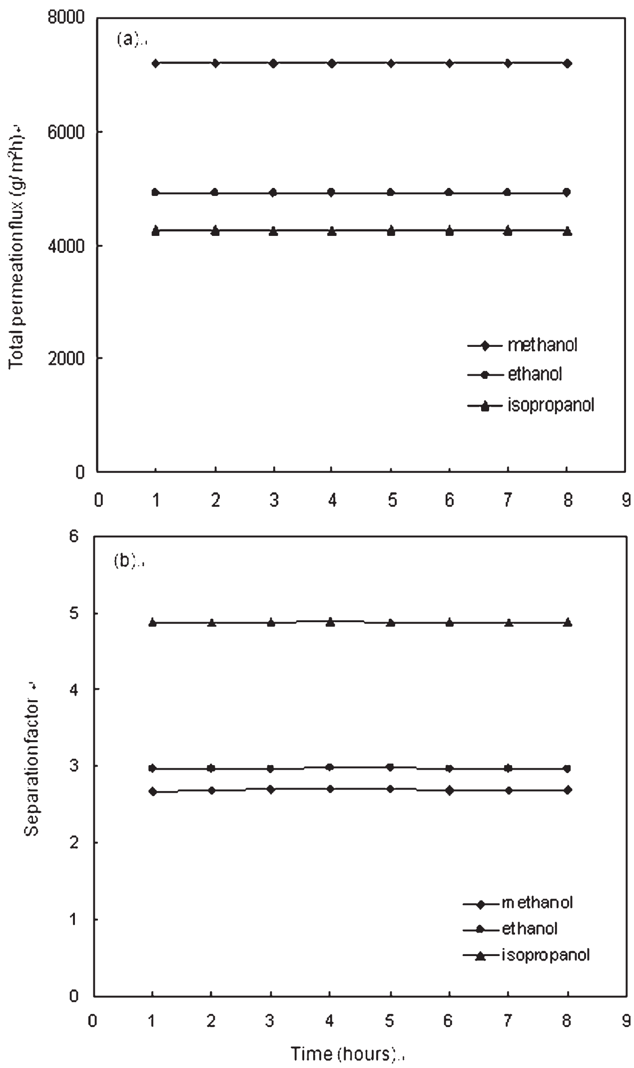

Figure 9 Effect of operating time on (a) total permeation flux, (b) separation factor for 25 wt % alcohol/water system by the VCPM.

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