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Pervaporation Characteristics of Silica-Zirconia Membranes for Separation of Aqueous Organic Solutions

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Abstract: Application of pervaporation membranes to practical separation and purification processes would be much more attractive if the separation performance (flux and selectivity) can be further improved. In addition to higher flux and selectivity, membrane stability at higher temperatures is quite important for efficient and economic separation in practical processes, considering that pervaporation at higher temperature preferably gives higher fluxes, resulting in smaller required membrane areas. In this respect, inorganic porous membranes could find a wider application in practical separation and purification processes.

In this work, porous silica-zirconia membranes of pore size less than 1 nm were fabricated by improved sol-gel techniques to study the pervaporation characteristics of various aqueous organic solutions (isopropanol, 1-propanol, acetone, tetrahydrofuran, and ethanol) at temperatures from 50°C to their normal boiling points. The water fluxes for these aqueous mixtures, with the exception of aqueous ethanol solution at the normal boiling point, exceeded $7\,\mathrm{kg \cdot m^{-2} \cdot h^{-1}}$ with separation factors larger than several hundreds at 10 wt% water in the feed. The water-flux dependency on the feed concentration can be determined roughly by the vapor-liquid equilibrium; however, it is not always proportional to the partial vapor pressure of the feed at the separation temperature. The detailed separation characteristics are discussed based on a simple model of porous membranes proposed previously.

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INTRODUCTION

Membrane separation has been regarded as one of the most efficient and energy-conservative methods for separation of azeotropic or close-boiling-point mixtures when the process is combined with conventional separation methods such as hybrid separation processes (1). Higher pervaporation or vapor-permeation performance of membranes would naturally make membrane separation much more attractive and promising as a practical separation process for liquid mixtures such as aqueous organic solutions. There are, however, some problems: for example, small permeation fluxes, especially for organic polymer separation membranes [e.g., water flux: $0.01-0.8\,\mathrm{kg \cdot m^{-2} \cdot h^{-1}}$ for isopropanol (IPA)/water (10 wt %) mixtures at 30–80°C (2–4)]. Due to their swelling or dissolving, some of these membranes are not stable against organic solvents nor are they stable at temperatures higher than around 80°C. The relatively low separation temperature limit for organic polymer membranes is clearly one of the reasons for the rather small pervaporation fluxes. At present, inorganic membranes are quite attractive in these respects, despite their relatively high cost. Such membranes are essentially stable at high temperatures since they are usually fired at a high temperature in their fabrication processes (e.g., the sol-gel techniques for sol-gel-derived membranes and hydrothermal synthesis for zeolite membranes). The literature contains many reports describing zeolite membranes (5–10), which are quite attractive for their uniform pore size and high selectivity. On the other hand, sol-gel techniques are very flexible for membrane fabrication of various single or composite inorganic materials such as silica, alumina, titania, silica-zirconia, and silica-alumina. While zeolite membranes of moderate alumina content are hydrophilic and show high water selectivity (separation factor $>$ 10,000) with relatively large permeation flux [$1.76\,\mathrm{kg \cdot m^{-2} \cdot h^{-1}}$ for IPA/water (10 wt %) mixtures at 75°C (7)], sol-gel-derived silica membranes are generally highly porous and give large permeation fluxes. The stability of these silica membranes against water is poor even at low water concentrations (i.e., around 10 wt %) in aqueous alcohol solutions (11), although such membranes are rather stable in aqueous organic acids (12–14) and in nonaqueous organic solutions (15, 16). Zirconia and titania are often added to silica to produce composite membranes that can achieve higher stability against water and also provide novel separation characteristics. The pore-size control of such composite membranes is rather difficult, but some silica-zirconia membranes have been developed for nanofiltration (17–19) and for gas separation (20–22). A few works (11, 23–25) have reported on pervaporation of aqueous organic solutions. Sekulič et al. (24) developed SiO_2/ZrO_2 and TiO_2/TiO_2 membranes for pervaporation of IPA/water mixtures. The separation performance of these membranes is not sufficiently high (water flux: $0.67-0.86\,\mathrm{kg \cdot m^{-2} \cdot h^{-1}}$ at 10 wt% water at 80°C, separation factor

<400); however, their performance is quite close to those of organic polymer membranes. Considering that a high flux cannot be expected if membranes comprise amorphous porous structures with dispersed ZrO_2 crystals through which none of the components can permeate, Asaeda et al. (25) developed modified sol-gel methods for fabrication of silica-zirconia membranes for pervaporation of aqueous IPA solutions. The homogeneity of the composite silica-zirconia structures was found to be quite important for the stability of the membranes against water at high temperatures (11), since silica or silica-rich phases are soluble in water to some extent (several 10s of ppm at room temperature). When applied to pervaporation of aqueous IPA solution, the separation performance of the porous silica-zirconia membranes was somewhat like molecular sieving. The membranes showed high water selectivity or separation factors larger than a few thousand with large water fluxes of about $8\,kg \cdot m^{-2} \cdot h^{-1}$ at 10 wt % water and at the normal boiling point of the IPA/water mixture. The interaction between the participating molecules and the pore wall was assumed to play an important role in preventing IPA molecules from permeating through relatively large pores (pinholes) left in the sol-gel-derived porous membranes. This suggests that the separation performance (flux and selectivity) may be dependent on the kind of organic chemicals present in feed solutions.

In this work, porous silica-zirconia membranes of pore sizes less than 1 nm were fabricated by the improved sol-gel procedures. The pore sizes were controlled by the average particle size (or concentration) of silica-zirconia colloidal sols to study the pervaporation characteristics of various kinds of aqueous solutions of organic solvents such as IPA, 1-propanol, acetone, tetrahydrofuran (THF), and ethanol at temperatures from 50°C to their normal boiling points. The separation characteristics are discussed based on a simple model (23) of porous membranes proposed previously.

EXPERIMENTAL

Membrane Fabrication and Characteristics

Sol-gel procedures were applied to fabricate porous silica-zirconia membranes of pore sizes less than 1 nm. First, silica-zirconia colloidal sols were carefully prepared by hydrolysis and condensation reactions of alkoxides with HNO_3 as the catalyst. As was suggested in the previous work (11), 50% zirconia was added to silica to produce high membrane stability against water. The sols were coated on cylindrical porous alumina tubes by hot coating methods and fired at high temperatures.

Preparation of Colloidal Sols

Silica-zirconia colloidal sols were prepared by the hydrolysis and condensation reactions of tetraethoxysilane (TEOS) and zirconium tetra-*n*-butoxide (ZrTB). First, silica-zirconia polymer sols were prepared by careful hydrolysis and condensation reactions in ethanol. Second, the solutions were boiled for about 10 h to obtain colloidal sols. The preparation methods for silica-zirconia polymer sols are somewhat different from those in our previous work (11, 25). TEOS (e.g., 3.52 g) was dissolved in ethanol (50 g) containing 50% water for complete hydrolysis of the TEOS and nitric acid (61 wt %, 0.05 g). Then, ZrTB (6.48 g) dissolved in ethanol (50 g) was added and mixed well before adding another half of equivalent water dissolved in ethanol (25 g). The solution was left about 12 h at room temperature. The amount of water equivalent for the complete hydrolysis of ZrTB and TEOS was then added. Thereafter, a specified amount of nitric acid (61 wt %, 3 g) and a large amount of water (500 g) were added before the solution was boiled for about 10 h to remove the organic chemicals and to obtain a silica-zirconia colloidal sol in water (2 wt % sol/equivalent alkoxides weight percent in the final solution). Four kinds of sols were prepared—2, 1.5, 0.8, and 0.5 wt % sol—to control the pore size of porous silica-zirconia membranes.

Membrane Coating

The procedures of membrane coating are mostly the same as those reported previously (11, 25). A piece of porous α-alumina cylindrical tube (outer diameter: 10 mm, length: 100 mm, average pore size: 1 μm, porosity: around 45%) was connected to a glass tube on each end and was used as the support for a thin porous silica-zirconia membrane. One end of the connected glass tube was closed, and the other end was open to permit collection of permeates in pervaporation tests. In order to make the surface smooth, two kinds of fine alumina powder (average diameters: 1.9 and 0.2 μm) were deposited on the outer surface of the substrates (supports) with a colloidal sol, 2 wt % sol, as the binder. They were then fired at 550°C for about 15 min after drying at room temperature. These procedures were repeated four times. Thereafter, the substrates were heated to around 160–180°C before coating with the colloidal sols by the hot coating methods (11, 15, 25), in which coating was done by quickly contacting the hot substrate with a wet cloth with colloidal sol for quick and simultaneous coating and drying. The membrane was then directly inserted in a furnace at a temperature at 450°C and kept there for 10–15 min. These procedures were repeated several times with each colloidal sol diluted to 1/5–1/10 of the original concentration.

XRD Observation and Pore-size Measurements

Powder samples of gels obtained from the colloidal sols were fired at 500°C for 2 h for observation of X-ray diffraction (XRD) patterns. The pore sizes of the intermediate and the final membranes were observed by the "dynamical permeation methods of humid gas permeation" (15), applying Kelvin's capillary condensation theory.

Pervaporation Measurements

Simple schematic diagrams of the apparatus for pervaporation measurements at normal boiling points and at constant feed temperatures are shown in Figs. 1(a) and 1(b), respectively. A membrane fabricated in this work was dipped in a boiling mixture under atmospheric pressure or in a circulating liquid mixture at constant temperature (50–85°C) as shown in the figure. The inside of the cylindrical membrane was evacuated by a vacuum pump after collecting permeates by a cold trap cooled by liquid nitrogen. The feed and permeate concentrations were determined by gas chromatography (GC-9A, Shimazu). The permeation flux was obtained from the weight of the condensates in the cold trap in a specified time interval [mostly 3 min, except in the high feed concentration (<30 min)]. The pressure on the permeate side, as measured by a simple diaphragm-type vacuum gauge, was

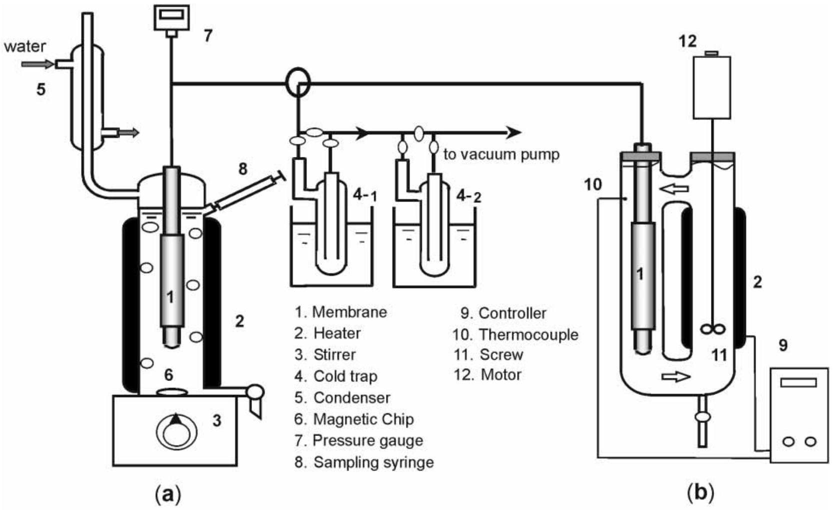


Figure 1. Simple schematic diagrams of pervaporation apparatus for (a) measurements at normal boiling points and (b) at constant temperatures.

less than several torr at the highest reading. The measurements were performed for a wide range of feed concentrations (about 10–100 mol % of organic components). Each measurement was performed after >20 min to achieve a new quasi–steady state.

RESULTS AND DISCUSSION

Observed XRD Patterns

As was indicated in the previous work (11), the homogeneity of the membranes and the ZrO_2 content are quite important for membrane stability against water. Gel homogeneity depends not only on the composite characteristics of the sol itself but also on the drying and firing conditions. When the original sols are not completely homogeneous, the slow drying sometimes produces segregated heterogeneous gel structures. Sharp peaks in XRD patterns for the SiO_2-ZrO_2 gels indicate the presence of crystalline structures (or the heterogeneity of composite SiO_2-ZrO_2). This finding implicitly suggests that there are phases of low ZrO_2 content, or silica-rich phases, which are soluble in water. Since relatively high durability of porous SiO_2-ZrO_2 composite membranes in water appears for homogeneous amorphous structures of ZiO_2 content higher than about 40% (11), structural heterogeneity should be one of the primary factors in membrane instability against water.

For this paper, the preparation methods for colloidal sols were improved so that the sols would give relatively homogeneous gel structures even when dried slowly. Figure 2 compares some XRD patterns for quick- and slow-dried gel samples obtained from sols prepared with HCl and HNO_3 as the catalyst and for pH control. In addition to the drying conditions, the kind of acids added had pronounced effects on the XRD patterns. Gel obtained from colloidal sols prepared with HCl showed different patterns for gels quickly dried [pattern (b)] and for those slowly dried [pattern (c)] in Fig. 2. Judging from these two patterns, segregation of zirconia seems to occur for colloidal sols prepared with HCl when the gel samples were dried slowly. On the other hand, gel samples obtained from the sols prepared with HNO_3 did not show any sharp peaks of crystalline ZrO_2 structures, as shown by patterns (d) and (e), even if they were dried slowly over a few days. The larger swell around $2\theta = 31$degees in pattern (e) for a higher ZrO_2 content of 80% suggests that tiny crystallites must be dispersed among amorphous silica-zirconia structures.

The fact that no sharp peak appears in the XRD patterns for gels from sols with HNO_3 allows simplified membrane coating. In the previous work (11) with colloidal sols prepared with HCl, intermediate membranes (i.e., just after the particle deposition) had to be washed in boiling water to remove soluble

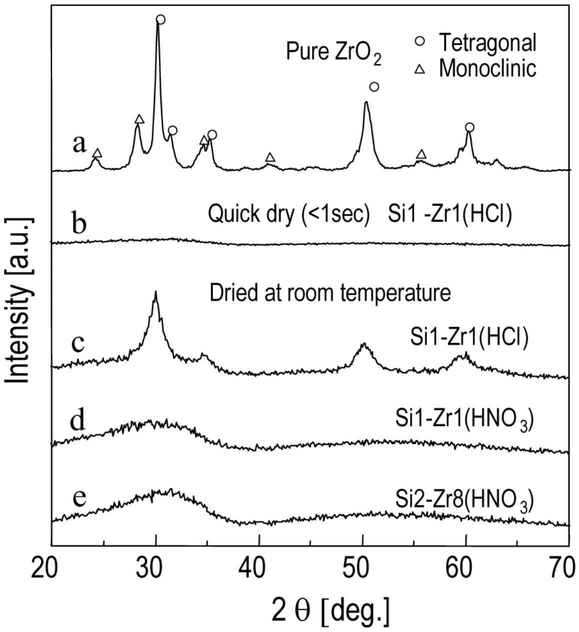
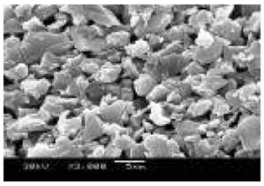


Figure 2. Observed XRD patterns for SiO_2-ZrO_2 gels obtained from sols prepared with HCl and HNO_3.

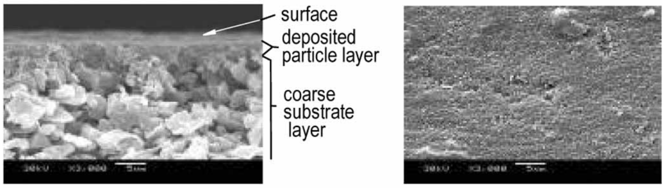
silica, or the silica-rich phase, to ensure stability of the final membranes against water. Because no appreciable phase segregation occurred in the HNO_3-prepared sols in this work, this washing was not required.

Membrane Structures and Pore-Size Distributions

The structure of the membranes has a large effect on the permeation flux. Figure 3 shows SEM photographs (cross-section and surface) of the intermediate and final membranes. The dents and large pores on the coarse surface of the substrate [Fig. 3(a)] are filled with the deposited particles, as shown in Fig. 3(b). The active layer of the membrane is clearly the thin layer at the top, as seen in Fig. 3(c). The thickness of the thin layer is observed to be around 0.3 μm. Some bumps on the surface due to large particles of the substrate beneath can be covered completely with a thin film by hot coating methods. Figure 4 shows the pore-size distributions (Kelvin's condensation diameter) observed for intermediate and final membranes after coating with 2.0, 1.5, 0.8, and 0.5 wt % sols (several times with each sol) in this order. The pore-size distribution shown with open

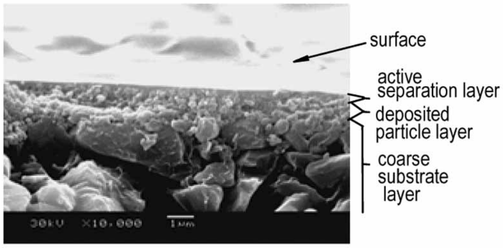


(a) Surface of porous α-alumina substrate



cross section **surface**

(b) Cross section and surface after particle deposition



(c) Cross section of final porous membrane

Figure 3. SEM photographs of membrane surfaces and cross sections.

diamond symbols was obtained after coating 15 times total: 5 times with 2.0 wt %, then 5 times with 1.5 wt % and 5 more times with 0.8 wt % sols. Repetition of coating preferably reduces the tailing (pinholes) in the pore-size distribution, as can be seen from the rightmost two curves after 2.0 wt % sol coatings, though the permeance becomes somewhat smaller. The pore-size distribution with a smaller tailing (shown with triangle symbols) naturally gave a final membrane (Membrane B) of a sharper pore-size distribution. The dynamic permeation methods of humid gas permeation may not be appropriate to accurately determine a pore size of less than ~1 nm. Judging from the pervaporation results in the following section, however, the methods seem to give some effective and useful information on pore-size distribution. The selectivity of membranes was largely dependent on pinholes (tailing) in the final membranes, which mainly originate in unfortunate stochastic results at the particle deposition step.

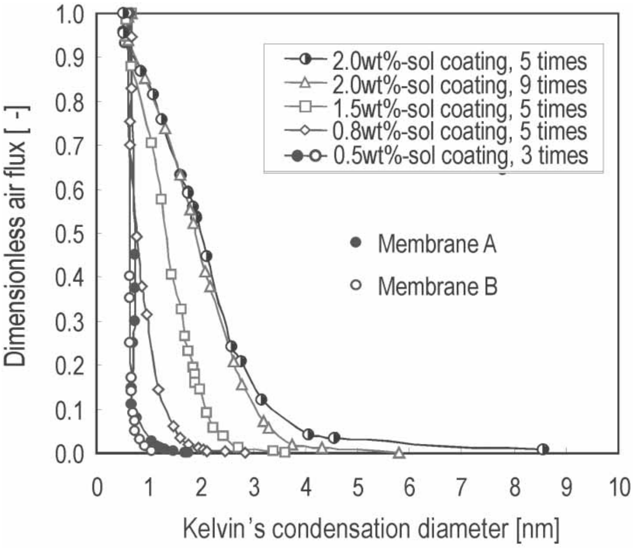


Figure 4. Pore-size distributions of intermediate and final membranes.

Pervaporation Results and Discussion

After 0.5 wt % sol coating, porous silica-zirconia membranes (Membranes A and B) were tested for their pervaporation performance. Membrane A, which has a pore size of ~0.6 nm with a slight tailing in pore-size distribution up to 1.3 nm (Fig. 4), was used for pervaporation of aqueous solutions of IPA, 1-propanol, THF, and acetone at their normal boiling points. Figure 5 shows the pervaporation results for IPA/water mixtures at normal boiling points. The water flux is quite large, around 500 $\text{mol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ at 73 mol % IPA or 10 wt % water (nearly at the azeotropic point) in the feed. The separation factor at this concentration is not very large (about 500), probably due to some large pores (tailing) in the pore-size distribution shown in Fig. 4. The flux or leakage rate of IPA shows a peak at ~15 mol % IPA and then decreases to nearly zero as the IPA concentration approaches 100%. This phenomenon can be understood, as suggested in previous studies (11, 25), by considering the adsorption/reaction of IPA on the surface of the relatively large pores through which IPA molecules can permeate. Such adsorption/reaction can reduce the effective pore size to the extent that IPA molecules cannot permeate. Because of these characteristics of IPA permeation, the separation factor at high feed concentration becomes quite large, as shown in Fig. 5. This result suggests that the membrane contains few very large pinholes through which the leakage rate of IPA can increase.

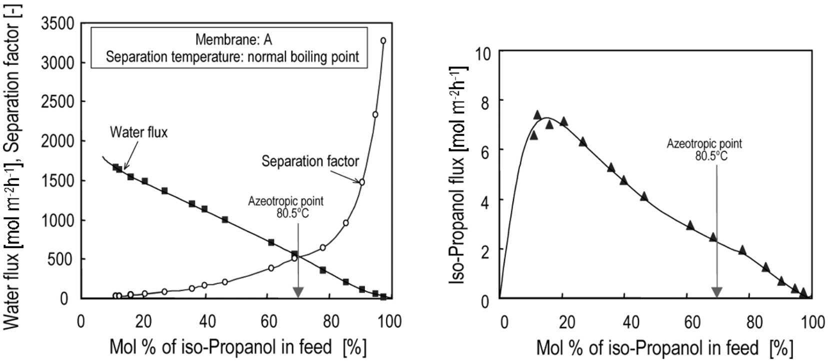


Figure 5. Pervaporation results for IPA/water mixture at the normal boiling point.

Despite of their largely different vapor-liquid characteristics (26), the pervaporation results for 1-propanol/water mixtures at the normal boiling points are quite similar to those for IPA/water mixtures, as shown in Fig. 6. Pervaporation of aqueous acetone solutions shows somewhat different results, as shown in Fig. 7, indicating a smaller separation factor due to a smaller water flux and a comparatively large leakage rate of acetone, which is less adsorptive on pore surfaces covered with hydroxyl groups.

Pervaporation of aqueous THF solution showed high separation performance, as shown in Fig. 8. The flux of THF was comparatively small, given the large separation factors. This is probably due to the molecular structure of THF. Alcohol molecules can be considered to be highly adsorptive on the hydrophilic surface, giving smaller fluxes of alcohol due to the reduction in effective pore size. Acetone and THF seem less adsorptive because of their molecular structures. However, the leakage rates of these

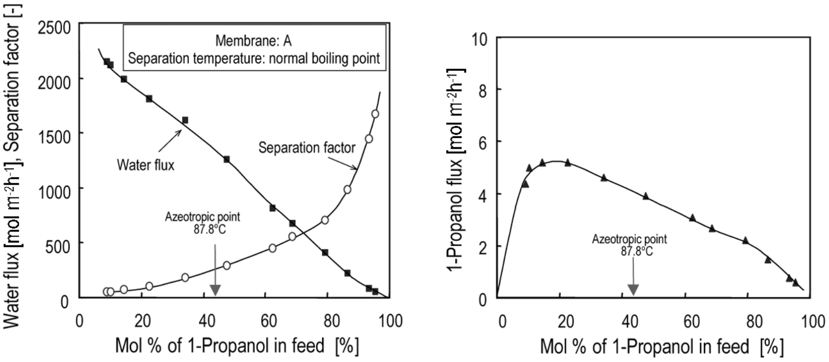


Figure 6. Pervaporation results for 1-propanol/water mixture at the normal boiling point.

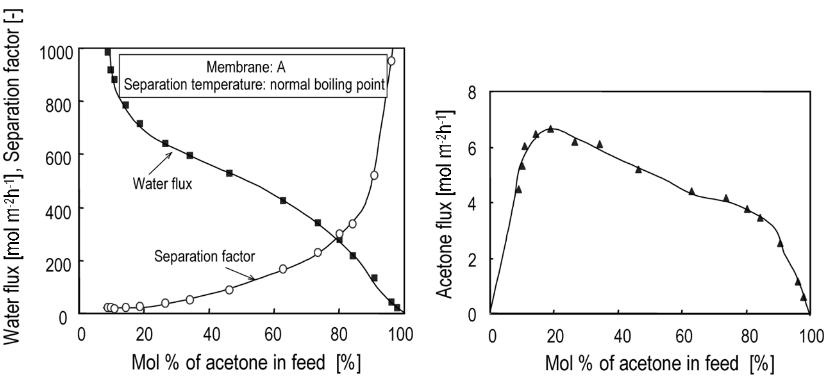


Figure 7. Pervaporation results for acetone/water mixture at the normal boiling point.

solvents also decreased unexpectedly in the higher concentration region as can be seen in Figs. 7 and 8.

Figure 9 shows a temperature dependency of pervaporation performance for 1-propanol/water mixture at 73 mol % with Membrane B, the pore-size distribution of which is shown in Fig. 4. The selectivity depends on the separation temperature and decreases as the temperature becomes higher. At the normal boiling point, however, the separation factor increased, presumably due to the reaction between 1-propanol molecules and −OH groups on the pore surface. The large separation factor for this membrane is primarily the result of the pinholes left in the membrane, as shown in Fig. 4. Pervaporation of the ethanol/water mixture with Membrane B gave fairly good results: water flux of $140\,\mathrm{mol \cdot m^{-2} \cdot h^{-1}}$ with a separation factor of 210, at 91 mol % ethanol in the feed at the normal boiling point. The pore size of this membrane seems a little too large to permit higher selectivity in ethanol/water

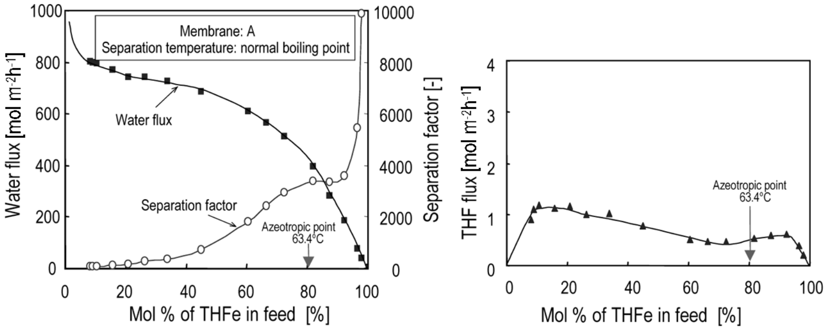


Figure 8. Pervaporation results for THF/water mixture at the normal boiling point.

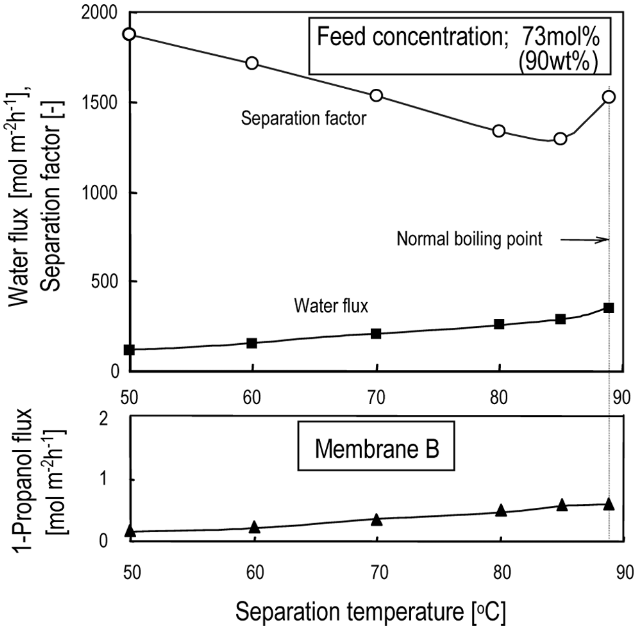


Figure 9. Example of temperature dependency of pervaporation performance for 1-propanol/water mixture at 73 mol %.

separation. Pervaporation of 1-propanol/water mixtures with Membrane B showed a high water flux of 920 mol · m^{-2} · h^{-1} with a separation factor of 610 at a feed concentration of 41 mol % 1-propanol and at the normal boiling point. (That with Membrane A was 1300 mol · m^{-2} · h^{-1} with a separation factor of 220.)

The stability of pervaporation membranes against water is essentially important, especially when applied to pervaporation of aqueous solutions. Since almost every inorganic material dissolves in hot water to some extent, no perfectly stable inorganic porous membrane can be expected. However, the silica-zirconia membranes prepared in this paper seem to be relatively stable. This assessment is based on the finding that after pervaporation measurements of high water flux for about 1.5 h with Membrane A at 92 mol % water and at the normal boiling point (water flux: 2220 mol · m^{-2} · h^{-1}, or 40 kg · m^{-2} · h^{-1}, at 93.5°C) for 1-propanol/water mixture, no appreciable degradation in the pervaporation performance was observed in the higher-concentration region of 1-propanol or in the following observations for acetone/water and THF/water mixtures.

Figure 10 shows a simple pervaporation model (23) [Fig.10(a)] and some simulated results [Fig. 10(b)] based on the model. Four resistances are assumed for the model: (a) mass transfer resistance in the concentration

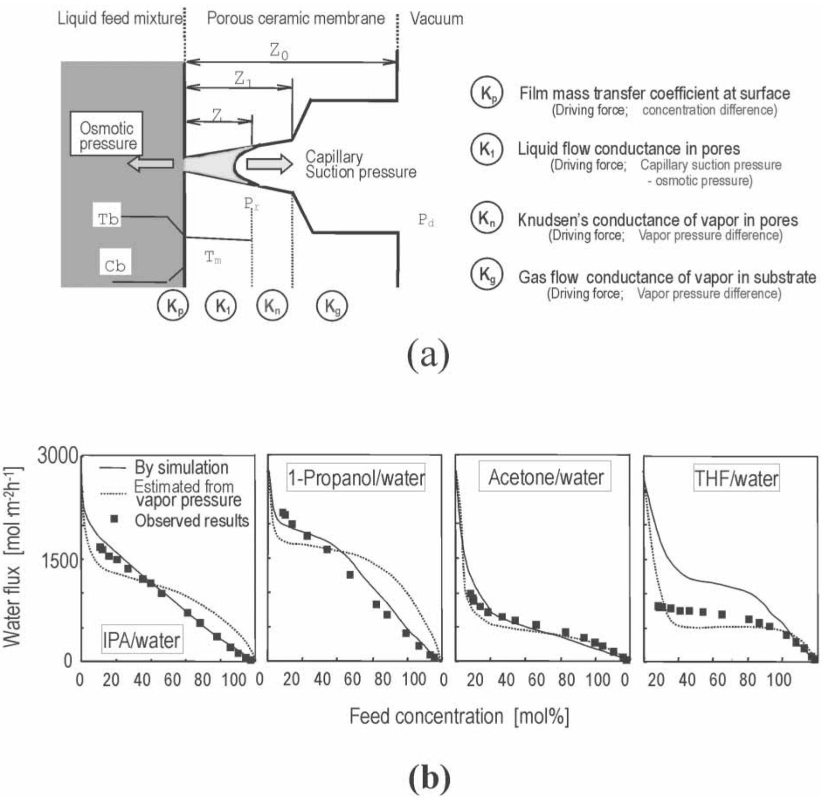


Figure 10. Schematic diagram of (a) simple pervaporation model and (b) simulation results.

polarization on the membrane surface, (b) flow resistance of liquid water in the micropores, (c) vapor permeation resistance in the micropores, and (d) gas flow resistance through pores of the substrate and the evacuation tubing. The pressure difference between osmotic and capillary suction pressures can be considered as the driving force for the liquid water flow in the micropores. The simulation results with the same membrane properties (parameters) required for the calculation are compared with those observed in Fig. 10(b), indicating relatively good coincidence with the observed results for aqueous solutions of IPA, 1-propanol, and acetone. The estimated results for THF/water mixtures, however, are largely different from the observed ones. The reasons for this are not known; however, one possible explanation is the assumed Darcy-type liquid flow in the micropores. The temperature dependency of liquid flow in such fine pores (~1 nm) may be larger than that of viscous flow. The dotted curves in Fig. 10(b) show the concentration dependency of partial vapor pressure of water for these aqueous solutions at their normal boiling points. It can be seen from these results that the equilibrium partial vapor pressure of water as the driving force does not always give adequate water flux dependency on the feed concentration.

CONCLUSIONS

Porous silica-zirconia membranes of pore size less than ~1 nm were fabricated by improved sol-gel techniques to study the pervaporation characteristics of aqueous solutions of organic solvents such as IPA, 1-propanol, acetone, THF, and ethanol at temperatures from 50°C to their normal boiling points.

Composite SiO_2-ZrO_2 colloidal sols could be prepared by the careful hydrolysis and condensation reactions of TEOS and ZrTB with HNO_3 as the catalyst and for pH control. The sol-gel-derived SiO_2-ZrO_2 membranes, fabricated with the sols prepared here, were relatively stable in the aqueous organic solutions. No appreciable degradation in the pervaporation performance was observed, even after about 1.5 h of pervaporation measurements of high water flux at 92 mol % water and at the normal boiling point (water flux: $40\,\mathrm{kg \cdot m^{-2} \cdot h^{-1}}$ at 93.5°C) for 1-propanol/water mixture.

The fluxes for these aqueous mixtures, except for aqueous ethanol solution at the normal boiling points, exceeded $\sim 7\,\mathrm{kg \cdot m^{-2} \cdot h^{-1}}$, with separation factors larger than several hundreds at around 10 wt % water in the feed.

The water flux dependency on the feed concentration was not precisely dependent on the vapor-liquid equilibrium. The flux was not always proportional to the partial water vapor pressure of the feed at the separation temperature and concentration. A simple pervaporation model previously proposed gave a relatively good accordance with the observed results for aqueous solutions of IPA, 1-propanol, and acetone.

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