

# Selective Pervaporation of Water through a Nonselective Microporous Titania Membrane by a Dynamically Induced Molecular Sieving Mechanism

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Pervaporation experiments were performed on microporous titania membranes using several binary liquids containing 2–20 wt % water. The membrane was nonselective in the separation of water from alcohols and *p*-dioxane but showed a remarkably high selectivity in the separation of water from ethylene glycol/water mixtures with  $\leq 15$  mol % water. The absence of selectivity under most conditions is explained by the large pore size (0.9 nm) of microporous titania. The high selectivity for water in the separation from ethylene glycol can be explained by the formation of a hydrogen-bonded network of ethylene glycol in the micropores, which blocks transport of ethylene glycol, while water can still permeate through. These networks are disrupted by water at higher concentrations, leading to full loss of membrane selectivity.

## 1. Introduction

Pervaporation is an energy efficient process with which liquid mixtures can be separated by a combination of membrane permeation and evaporation.<sup>1</sup> Components of a liquid feed permeate through a membrane and evaporate into the downstream. The driving force behind pervaporation of a component is the difference in partial vapor pressure of that component at opposite sides of the membrane.

The most widely investigated ceramic membranes for pervaporation are microporous silica and silica-based composites.<sup>2–7</sup> The pore size of silica is  $\sim 0.3$  nm, and it is possible to separate small molecules such as water with a kinetic diameter of 0.24 nm from larger species based on a molecular size sieving mechanism.<sup>8</sup> The high selectivity of silica to water in the separation from oxygenated hydrocarbons such as butanol or *p*-dioxane is thought to be due to the large size ( $>0.5$  nm) of the organic molecules,<sup>2,7</sup> which prevents them from entering the microporous matrix. In the absence of size exclusion, it is still possible to achieve selective separation of one component, because different components may have different degrees of sorption and rates of diffusion inside the membrane.<sup>2,9</sup>

We recently developed a microporous ceramic membrane with a maximum pore size of  $\sim 0.9$  nm based on the amorphous phase of titania.<sup>10</sup> This membrane showed 40%

retention of diethylene glycol (molecular size,  $\sim 0.4$  nm) in water in nanofiltration experiments and 65% retention of triethylene glycol ( $\sim 0.55$  nm).<sup>10</sup> However, highly selective separation of water by pervaporation based on molecular size differences only is unlikely. In this paper, it is shown that the membrane is indeed nonselective in most common pervaporation processes involving water and small organic species. However it does show a remarkable selectivity to water in the separation from ethylene glycol under specific operating conditions. As will be discussed below, the high selectivity can be explained by an in situ modification of the internal pore structure during operation.

## 2. Experimental Section

**Membranes.** Stacked membrane systems  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-(ZrO<sub>2</sub>)-TiO<sub>2</sub> were used in the experiments. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports (disk-shaped; diameter, 39 mm; thickness, 2 mm) were prepared by colloidal filtration.<sup>11</sup> The supports had a mean pore radius of 100 nm and a porosity of  $\sim 30\%$ . The intermediate mesoporous layer (1  $\mu$ m thick; pore size, 5–8 nm) was either anatase titania calcined at 450 °C or zirconia-doped titania containing 5–20 mol % of zirconia and calcined at 450–700 °C.<sup>12</sup> The top layer, made of amorphous titania, had an average thickness of 50–100 nm and a maximum pore size of  $\sim 0.9$  nm.<sup>10</sup> The absence of mesopores and/or defects in the top layer was checked by permoporometry.<sup>2</sup>

**Pervaporation Experiments.** Pervaporation experiments were carried out using a laboratory scale pervaporation unit. The feed mixture, contained in a 2 L heated vessel under a pressure of 2–3 bar, was pumped continuously in the pulls mode through the feed compartment of the pervaporation unit, where it came into direct contact with the top layer of the membrane. The retentate was recycled to the feed vessel. The permeate side of the membranes was kept under near vacuum (6–8 mbar) with a vacuum pump. Steady-state fluxes were determined by collecting the vapors at the permeate side in an ethanol-based cold trap and measuring the weight increase with time. The compositions of feed and permeate were determined by Karl Fischer titration (784 KFP Titrimo, Metrohm, Switzerland). Pervaporation experiments were performed in the temperature range of 40–90 °C. The feed mixtures were binary liquids with 2–20 wt % water (on total weight) in 2-propanol, 2-butanol, *p*-dioxane, or ethylene glycol (all obtained from Merck). The

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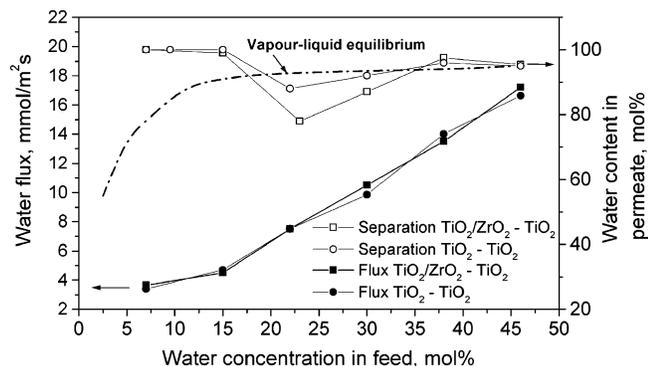
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**Figure 1.** Influence of water concentration in the feed on flux and selectivity of microporous titania membranes at 80 °C in pervaporation of ethylene glycol/water mixtures.

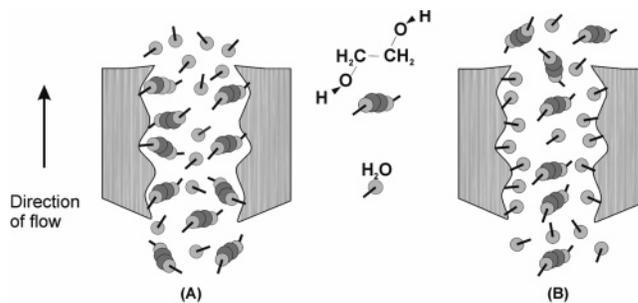
partial vapor pressures of the different components in the feed stream were calculated from thermodynamic data.<sup>13</sup>

### 3. Results and Discussion

Pervaporation experiments with binary liquids containing water and 2-propanol, 2-butanol, or *p*-dioxane showed no selective separation of water over the other component. This can be explained by the relatively large pore size of the microporous titania layer. Although it is difficult to identify reliable values for the kinetic diameters of the permeating species, approximate values adopted from both literature sources and ab initio modeling are 0.24, 0.45, 0.55, and 0.7 nm for water, 2-propanol, 2-butanol, and *p*-dioxane, respectively.<sup>2,9,14</sup> Since the maximum pore size of the microporous titania layer is ~0.9 nm,<sup>10</sup> the occurrence of a molecular sieving mechanism to selectively separate water is unlikely.

Contrary to these results, very high selectivities to water were measured for some ethylene glycol/water mixtures at 80 °C, as shown in Figure 1. The selectivity of the membrane is expressed in terms of water concentration in the permeate. Although ethylene glycol has a molecular size of only ~0.45 nm, no ethylene glycol flux was observed when the water concentration in the feed was smaller than ~20 mol %. The water flux and selectivity of both a mesoporous anatase-supported microporous titania membrane, and a mesoporous zirconia-doped titania-supported microporous titania membrane are compared in Figure 1. No significant differences can be observed between these two systems. This confirms the absence of an influence of the mesoporous intermediate layer on the transport properties of the top layer.

In view of the large pore size of titania, it is most likely that transport of water and ethylene glycol takes place by an adsorption–diffusion mechanism.<sup>2,9</sup> Since ethylene glycol has a relatively large dipole moment (2.28 D) and two –OH groups, relatively strong attractive interactions between ethylene glycol and titania will occur. This may result in substantial adsorption of ethylene glycol on the internal pore walls of the microporous titania layer. Interactions between ethylene glycol molecules and the pore surface, as well as hydrogen bonding between “free” and adsorbed ethylene glycol molecules, may lead to micropores that are (partially) filled by hydrogen-bonded networks of ethylene glycol, through which water molecules can still pass, but transport of ethylene glycol is inhibited completely. This would give a strongly increased selectivity for water transport. This molecular picture,



**Figure 2.** Schematic representation of a separation mechanism in pervaporation of an ethylene glycol/water mixture at (A) low and (B) high water concentrations.

schematically shown in Figure 2a, is in qualitative agreement with the findings of Kurihara et al.,<sup>15</sup> who reported that ethylene glycol can form hydrogen-bonded macroclusters on surfaces.

The selectivity decreased considerably when more than 15 mol % water was present in the feed. At concentrations higher than ~20 mol %, the composition of the permeate was similar to the equilibrium vapor composition of the liquid feed,<sup>13</sup> indicating “free” flow of vapor molecules through the membrane. This shows that in the range of feed compositions with 20–100 mol % water, the high water concentration in the permeate is entirely due to preferential evaporation of water from the feed, rather than being caused by the membrane. The loss of selectivity can be understood by considering that water may disrupt the physically bonded ethylene glycol network. A similar type of network disruption has also been observed upon addition of water to diethylene glycol.<sup>16</sup> Furthermore, stronger competition between water (dipole moment, 1.85 D) and ethylene glycol adsorption will occur since an increased number of water molecules are available for adsorption on the titania surface. Beyond a certain concentration, the water molecules will effectively replace the adsorbed ethylene glycol. Consequently, lower selectivities are expected at higher water concentrations, in agreement with the experimental findings. This situation is schematically depicted in Figure 2b.

Micropore blocking by strongly adsorbed species has also been observed on several other systems. Shah et al. reported very low water fluxes in the separation of water from *N,N*-dimethyl formamide (DMF)/water mixtures by hydrophilic zeolite NaA membranes,<sup>17</sup> which was attributed to pore blocking by strongly bound DMF molecules (dipole moment, 3.82 D) on the internal zeolite surface. In another study, we compared the pervaporation of methanol/water, 1,4-dioxane/water, and DMF/water through microporous silica membranes and observed the same phenomenon.<sup>2</sup> The behavior of ethylene glycol on amorphous titania is most likely qualitatively similar. However, to our knowledge the occurrence of high selectivity to water transport on a membrane with an intrinsically nonselective micropore structure, resulting from in situ modification of the membrane under controlled operating conditions, has not been reported to date.

The flux increased gradually with temperature as shown in Figure 3. The permeate contained 100 mol % water in the whole temperature range at a feed water concentration of 15 mol %. However, with 30 mol % water and

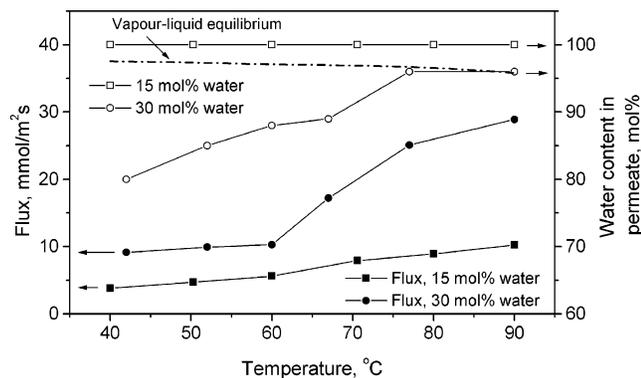
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**Figure 3.** Influence of temperature on flux and selectivity of microporous titania membranes in pervaporation of ethylene glycol/water mixtures using feed compositions with 15 and 30 mol % water in ethylene glycol, respectively. The vapor-liquid equilibrium line indicates the equilibrium vapor composition of a liquid feed containing 30 mol % water.

temperatures below 75 °C the water concentration in the permeate was lower than the vapor equilibrium composition. Hence, the water concentration is between that of the liquid feed and the equilibrium vapor concentration. This indicates a small contribution of (nonselective) Darcy type liquid flow to the total flux.<sup>18</sup> Unlike pervaporation flow, which is driven by temperature-dependent partial vapor pressure differences over the membrane, Darcy type flow is proportional to the absolute pressure difference over the membrane and is less temperature dependent. It increases only because of a decrease of viscosity with temperature. The contribution of Darcy flow is therefore relatively large at lower temperatures, while it becomes negligible above ~75 °C, where all transport is dominated by pervaporation.

The temperature dependency of permeance  $F_i = J_i/\Delta P_i$ , with  $J_i$  the flux of component  $i$ , and  $\Delta P_i$  the partial vapor pressure difference of component  $i$  over the membrane, provides a measure to compare the thermally activated nature of transport of different species through a membrane.<sup>19</sup> At feed concentrations of 15 and 30 mol % water, the activation energies of  $F_{H_2O}$  were the same within

experimental error, i.e.,  $-26 \pm 3$  and  $-21 \pm 15$  kJ/mol, respectively. Since water is the majority permeating species under all conditions, this activation energy can be regarded as the difference between the activation energy of diffusion,  $E_{D,water}$ , and the heat of adsorption of water inside the titania micropores,  $Q_{water}$ ,<sup>2</sup> i.e.,  $E_{act,water} = E_{D,water} - Q_{water}$ . The negative values obtained here for  $E_{act,water}$  suggest that  $E_{D,water} < Q_{water}$ , so that it can be concluded that the permeance of water decreases with temperature due to a decreasing level of water adsorption in the titania micropores, regardless of water concentration.

#### 4. Conclusions

The absence of selective separation of water from binary liquids involving alcohols or 1,4-dioxane showed that the pore size of microporous titania is too large for size-exclusion-based separation. The very high selectivity for water obtained with ethylene glycol/water mixtures under water-lean conditions therefore indicates a dynamically induced mode of selective separation, despite the fact that the pores were also insufficiently small to retain the glycol component. The selectivity can be explained by the presence of a hydrogen-bonded network of ethylene glycol in the micropores, which inhibits virtually all transport of ethylene glycol. The same principle may also be exploited to increase the membrane selectivity in other dewatering processes. By adding organic compounds to a feed mixture that adsorb strongly on the internal pore surface of a microporous ceramic membrane, it should be possible to modify the permeability of the microporous layer toward certain components. Such pore modifiers should be molecules with a reasonable molecular size, a large dipole moment, and/or the possibility to form more than one hydrogen bond.

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