

# Removal of methyl *tert*-butyl ether from water by pervaporation using ceramic-supported polymer membranes

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## Abstract

Pervaporation removal of methyl *tert*-butyl ether (MTBE) from dilute aqueous solutions was demonstrated using ceramic-supported polymer (CSP) membranes. These membranes were created by the free radical graft polymerization of vinyl acetate onto a vinyl trimethoxysilane-activated porous silica substrate having a native average pore size of 500 Å. The resulting membranes consisted of poly(vinyl acetate) chains terminally and covalently anchored to the membrane surface. These pervaporation membranes performed with separation factors ranging from about 68 to 577 at total permeate fluxes of 0.31–0.70 kg/m<sup>2</sup> h over feed concentrations of 74–7400 ppm (0.01–1%, v/v). MTBE flux was controlled by the feed-side concentration boundary layer, while water permeation was controlled by the membrane resistance. The primary effect of the grafted PVAc in these CSP membranes was to increase separation by rejecting water, as opposed to increasing the flux of MTBE. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Pervaporation; Membrane preparation and structure; Graft polymerization; Ceramic membranes; Methyl *tert*-butyl ether

## 1. Introduction

In recent years there has been a growing concern regarding groundwater contamination by methyl *tert*-butyl ether (MTBE). MTBE has high aqueous solubility (42,000 mg/l solution at 19.8 °C) [1] and moderately low vapor–liquid partition (e.g., Henry's law constant =  $5.28 \times 10^{-4}$  atm m<sup>3</sup>/mol at 25 °C) [2]. Therefore, its removal by traditional treatment technologies, such as air stripping and activated carbon adsorption, is expected to be less effective relative to volatile organic compounds (VOCs) that are sparingly soluble in water and have a higher Henry's law constant. It is also noted that bioremediation of MTBE has been generally characterized by relatively slow removal rates, in part due to MTBE inhibition of microbial cell growth [3,4]. In recent years, membrane pervaporation technology, which has been previously demonstrated for the removal of other VOCs from water [5–18], has been explored as a possible alternative remediation method for removal of MTBE from dilute aqueous solutions [19,20].

The feasibility of MTBE pervaporation using hydrophobic polymeric hollow fiber membranes (300 Å pore size) was investigated by Keller and Bierwagen [20]. Separation factors were not reported but removal efficiencies were found to range from about 20% to over 95% (with decreasing feed flow rate) over a temperature range of 23–40 °C for a 100 ppm aqueous MTBE feed solution. In another recent study, Vane et al. [4] obtained MTBE separation factors up to 930 for pervaporation of 9–900 ppm aqueous MTBE solutions, at a temperature range of 40–80 °C, using silicon rubber sheet membranes. The maximum MTBE flux reported in the above study was about 0.03 kg/m<sup>2</sup> h. A previous study by Kujawski [19] compared pervaporation of up to 4% (w/w) aqueous MTBE solutions through polydimethylsiloxane (PDMS), zeolite-filled PDMS, and poly(ether-*block*-amide) membranes. For feed concentrations of 1% (w/w) MTBE, the PDMS membranes provided separation factors of up to 255 with respect to MTBE over a total permeation rate range of 0.025–0.2 kg/m<sup>2</sup> h; the zeolite content did not significantly impact the separation factor. Lower separation factors but higher fluxes were obtained by using poly(ether-*block*-amide) membranes. This membrane demonstrated a separation factor of 38 with respect to MTBE at a total permeation rate of about 0.7 kg/m<sup>2</sup> h.

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Previous MBTE/water pervaporation studies have focused on polymeric membranes, ranging from porous membranes with pore sizes as large as 300 Å to dense skin membranes. Studies on MTBE/water pervaporation with ceramic-based membranes have not been previously reported in the literature. In this paper we report on the extension of earlier work on ceramic-supported polymer (CSP) membranes [21,22]. The main objectives are to demonstrate that silica membranes, with relatively large pores (about 500 Å), can be made selective and with low membrane resistance for MTBE removal from aqueous solutions over a wide concentration range (74–7400 ppm). The present CSP membrane consists of a molecular separating layer of poly(vinyl acetate) (PVAc) chains that are terminally and covalently grafted onto a silica support membrane.

## 2. Experimental

### 2.1. Materials

The silica membrane supports were porous silica tubes 19 cm in length, 0.5 cm outer diameter, and 0.37 mm wall thickness, obtained from the Industrial Research Institute of Miyazaki (Tsunehisa, Japan). The unmodified substrate was homogeneous with an average pore size of 500 Å and a total pore surface area of 45.5 m<sup>2</sup>/g. Selective MTBE separation could not be accomplished with these unmodified membranes due to the large membrane pore size. In order to impart selectivity to the silica membranes, their surface was modified by PVAc following a series of steps. These steps included pretreatment, surface activation, and graft polymerization previously published in the literature [21,22]. Surface activation of the native silica support membrane was achieved by silylation using a solution of vinyltrimethoxysilane (VTMS) (Aldrich Chemical Co., Milwaukee, WI) in certified ACS grade isomeric xylenes (Fisher Scientific, Pittsburgh, PA). Following silylation the membranes were polymer-grafted for 360 min using a 10% (v/v) solution of vinyl acetate in ethyl acetate solvent at 60 °C. Vinyl acetate graft polymerization was performed using reagent grade vinyl acetate monomer (Fisher Scientific, Tustin, CA), ACS-grade ethyl acetate solvent (Fisher Scientific, Tustin,

CA), and  $\alpha,\alpha'$ -azobis(2,4-dimethylvaleronitrile) initiator (Dupont Co., Wilmington, DE). The polymer-modified ceramic membranes were washed with ethyl acetate solvent and vacuum dried overnight at 110 °C. Based on the recent study of Nguyen et al. [23], the number-average molecular weight of the surface PVAc chains, expected for the present reaction conditions, was estimated to be about 12,600.

Two polymer-grafted membranes were produced (Table 1) by first silylating the silica support membranes to obtain different surface concentration of vinyl groups (i.e. active sites for PVAc graft polymerization). Silylation yield was controlled by adjusting the surface water concentration prior to silylation [24]. Polymer grafting of the two membranes, CSP1 and CSP2, resulted in membranes with PVAc graft yields of 0.17 mg/m<sup>2</sup> (CSP1) and 0.23 mg/m<sup>2</sup> (CSP2). These polymer graft yields are lower than those reported for surface modification of impermeable particles (~0.8 mg/m<sup>2</sup>) under the same reaction conditions. However, previous SEM and micro-FTIR analyses of modified porous ceramic membranes [9,25] have suggested that these porous membranes are modified asymmetrically, with considerably higher polymer graft yield occurring near the separating (inner) surface where the membrane contacts the graft polymerization reaction mixture. Therefore, the presently reported membrane polymer graft yields, which are based on the overall membrane pore surfaces (45.5 cm<sup>2</sup>), can be treated as lower limit estimates. In all likelihood, the actual polymer graft yield (for the modified region) at the separating surface is considerably higher.

### 2.2. Pervaporation

Pervaporation of dilute aqueous MTBE solutions through the PVAc/silica membranes was carried out experimentally using a bench-scale apparatus (Fig. 1) previously described by Jou et al. [21]. A tedlar bag (Chromatography Research Supplies, Addison, IL) containing 1000 ml of feed solution was used as a feed reservoir. All tubing was made of stainless steel or Teflon in order to prevent permeation loss of MTBE from the feed. The feed solution (at 20 °C) was continuously circulated, from the feed reservoir through the tube side of the stainless steel membrane module (Fig. 2),

Table 1  
Properties and separation performance for MTBE/water pervaporation for PVAc-modified silica membranes<sup>a</sup>

PVAc grafted membrane	Silylation yield/PVAc yield (mg/m <sup>2</sup> )	Feed MTBE (% v/v)	Feed Reynolds number	Permeate flux <sup>b</sup> (kg/m <sup>2</sup> h)	$\beta$	$\alpha$
CSP1	0.69/0.17	0.01	2250	0.66	68	68
CSP1	0.69/0.17	0.10	2250	0.72	76	83
CSP1	0.69/0.17	1.00	2250	0.60	74	240
CSP2	0.87/0.23	0.10	2250	0.32	150	182
CSP2	0.87/0.23	0.10	5310	0.31	282	419
CSP2	0.87/0.23	0.10	6390	0.35	347	577

<sup>a</sup> Silica native pore size was 500 Å and all pervaporation experiments were conducted at 20 °C.

<sup>b</sup> Flux is based on the inner membrane geometric surface area (based on the inside tube radius).

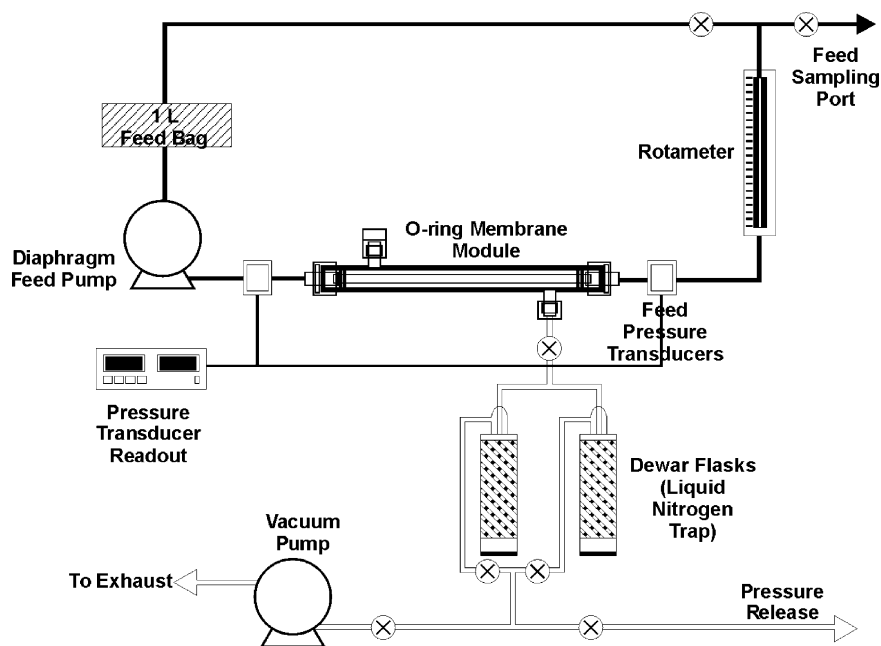


Fig. 1. Schematic diagram of pervaporation system.

using a variable speed diaphragm pump (Model 7553-57, Cole-Parmer, Vernon Hills, IL), with the feed flow rate measured by an online rotameter (Model 150 mm, Gilmont Instruments, Racine, WI). Feed-side pressure was measured by pressure transducers (DP15-52, Validyne, Northridge, CA), using a transducer controller (Model CD 223, Validyne, Northridge, CA). Permeate side pressures were measured with a vacuum gauge (PRM10, Pirani Vacuum Gauges, Edwards, Wilmington, MA) connected to a vacuum gauge controller (Controller 1101, Edwards, Wilmington, MA). A vacuum pump (Model M8C, Fisher Scientific, Pittsburgh, PA) served to maintain permeate-side pressure of approximately 266 Pa. The gaseous permeate was condensed and collected in sealed Dewar flasks immersed in liquid nitrogen. The feed and permeate compositions were determined

by GC analysis using a SRI 8610C gas chromatograph (SRI, Torrance, CA) with an FID detector. The GC column was a Supelco 0.317 cm  $\times$  3.05 m stainless steel column packed with 80/120 Carboxen B. The column was calibrated by injection of aqueous MTBE solutions in the 0.0074–3% (w/w) (74–30,000 ppm) range. Total and component permeate fluxes were determined based on the inner-tube geometric surface area (i.e., based on the inside tube radius).

Prior to each run, the system was equilibrated by running both the feed circulation pump and the vacuum pump for at least 1 h. A blank test was performed by running the system, with the permeate side of the module sealed, to ensure that there was no loss of MTBE from the feed side due to leaks or volatilization. Pervaporation studies were performed with

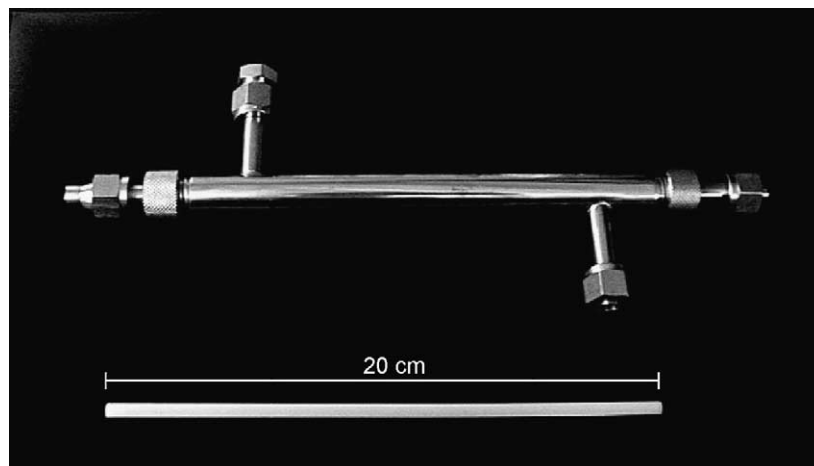


Fig. 2. Stainless steel membrane module (top) and 500 Å mean pore size silica membrane (bottom).

both membranes (Table 1) using aqueous feed solutions containing 1, 0.1, and 0.01% MTBE by volume (equivalent to concentrations of 7400, 740, and 74 ppm).

### 3. Analysis

The separation capability of the pervaporation membranes was quantified in terms of the MTBE separation factor,  $\alpha$

$$\alpha = \frac{x_{p,M}/x_{p,W}}{x_{f,M}/x_{f,W}} \quad (1)$$

where  $x_{p,M}$  and  $x_{p,W}$  are the mole fractions of MTBE and water, respectively, in the permeate, and  $x_{f,M}$  and  $x_{f,W}$  are their corresponding mole fractions in the feed. The MTBE separation quality was also evaluated in terms of the enrichment factor,  $\beta$

$$\beta = \frac{C_{p,M}}{C_{f,M}} = \alpha \frac{C_{p,W}}{C_{f,W}} \quad (2)$$

in which  $C_{p,M}$  and  $C_{p,W}$  are the MTBE and water concentrations in the condensed permeate, respectively, and  $C_{f,M}$  and  $C_{f,W}$  are the MTBE and water feed concentrations of respectively. The enrichment factor represents the concentration of the target species in the permeate relative to the feed. Since MTBE is the preferential permeant,  $C_{f,W} > C_{p,W}$  and thus  $\beta \leq \alpha$ .

The effect of the grafted polymer and feed-side hydrodynamics on membrane performance can be assessed by considering the component flux as per the simple resistance-in-series transport model [8,26–28]:

$$J_{p,k} = \frac{C_{f,k} - H_k C_{p,k}}{R_{ov,k}} \quad (3)$$

in which  $J_{p,k}$  is the permeate molar flux for component  $k$  ( $k = M$  or  $W$  for MTBE or water, respectively),  $C_{f,k}$  and  $C_{p,k}$  are the component feed and permeate concentrations, and  $H_k$  is a dimensionless equilibrium partition coefficient (i.e.,  $H_k = C_k^{liq}/C_k^{vap}$ ). The overall component mass transfer resistance,  $R_{ov,k}$ , consists of the sum of the feed-side ( $R_{f,k}$ ), membrane ( $R_{m,k}$ ), and permeate-side ( $R_{p,k}$ ) mass transfer resistances. When the permeate total pressure is sufficiently low, as was the case in the present work, the permeate-side resistance can be neglected and it is reasonable to assume that  $C_{f,k} \gg H_k C_{p,k}$ . Therefore, the separation factor can be approximated by combining Eqs. (1) and (3) as

$$\alpha = \frac{R_{ov,W}}{R_{ov,M}} = \frac{R_{f,W} + R_{m,W}}{R_{f,M} + R_{m,M}} \quad (4)$$

where use was made of the identity  $x_{p,k} = J_{p,k}/J_T$ , in which  $J_T$  is the total permeate flux and  $R_{m,W}$  and  $R_{m,M}$  are the intrinsic membrane mass transfer resistances for water and MTBE, respectively.

### 4. Results and discussion

The MTBE enrichment factors for the prototype CSP membranes ranged from 68 to 347 (separation factors of 68–577) with a total permeate flux range of 0.31–0.72 kg/m<sup>2</sup> h (Table 1). The total MTBE concentration in the permeate exceeded the aqueous solubility of MTBE (about 6% by volume or 42,000 ppm) for the 0.1 and 1% (by volume) feed solutions. At these enrichment levels the permeate separated into pure MTBE- and water-rich phases. Finally, we note that the PVAc–silica membranes were robust with reproducible performance over the year long course of the study.

Pervaporation results with the CSP1 membrane demonstrated that, as the MTBE feed concentration increased from 0.01 to 0.10% (v/v), changes in the enrichment and separation factors were marginal, while there was only 10% increase in the total permeate flux. The above result is not surprising since at these dilute concentrations,  $\alpha \approx \beta$  (since  $C_{p,W} \approx C_{f,W}$ ; see Eq. (2)). However, upon raising the feed concentration from 0.1 to 1.0% (v/v) MTBE, the separation factor nearly tripled while the change in the enrichment factor was negligible (i.e., within experimental error). It is noted that at the more concentrated feed of 1% (v/v) MTBE,  $C_{p,W}$  is significantly lower than  $C_{f,W}$ , and thus  $\alpha > \beta$  (see Eq. (2)). The above variations in  $\alpha$  and  $\beta$  suggest that the enrichment factor may be a more informative direct measure of the degree of product (i.e., permeate) concentration for the range of conditions in the present study.

Upon a modest increase of the polymer graft yield (about 26%), the separation factor for membrane CSP2 nearly doubled relative to membrane CSP1 (Table 1), at the same MTBE feed composition (0.1%, v/v) and tube-side Reynolds number ( $Re = dvp/\mu$ , where  $d$ ,  $v$ ,  $\rho$ , and  $\mu$  are the membrane inside tube diameter, average feed velocity, solution density and viscosity, respectively). The above separation factor rise was largely attributed to a decrease in the water flux (by a factor of about 2.4) while MTBE flux was only marginally affected (Fig. 3), as a consequence of the increased polymer graft yield.

The effect of feed-side hydrodynamics on the separation factor, as illustrated for membrane CSP2 (Table 1), was reflected by a factor of 3.2 increase in the separation factor (reaching a value of 577) over the Reynolds number range of 2250–6390. For the same conditions, the total flux varied by less than 15% (Table 1). Over the above Reynolds number range, MTBE flux increased by a factor of 1.7 while the water flux decreased by only about 14–17% (Fig. 4). As suggested by the component fluxes of MTBE and water (Fig. 4), the observed increase in the separation factor (Table 1) with Reynolds number is a direct result of the increase in MTBE flux rather than a decrease in water flux. The above behavior suggests that transport of MTBE in this pervaporation system is controlled by the feed-side concentration boundary layer. This assertion can be checked by comparing the observed concentration decline in the feed reservoir against

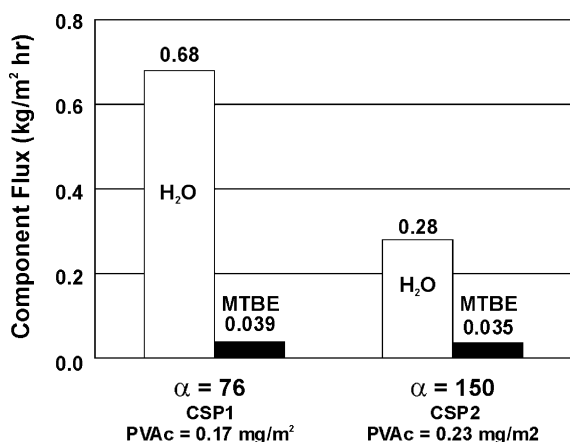


Fig. 3. Effect of polymer graft yield on the component pervaporation fluxes for initial MTBE feed composition of 0.1% (v/v) at  $Re = 2250$ .

model predictions. The simple pervaporation model used for this analysis considers only the tube feed-side concentration boundary layer resistance to MTBE transport. For the present study, given that the permeate flow rate is much less than the feed flow rate, one can show that the concentration decline in the feed reservoir can be approximated by the following simple model [29]:

$$\ln\left(\frac{C}{C_0}\right) = -\frac{k_{ov}A}{V_0}t \quad (5)$$

in which  $C$  and  $C_0$  are the MTBE concentrations at time  $t$  and initially in the reservoir, respectively,  $V_0$  the reservoir volume,  $A$  the membrane area, and  $k_{ov}$  the tube feed-side mass transfer coefficient which was estimated from a mass transfer correlation [7]. As illustrated in Fig. 5, for the 0.1% (by volume) initial MTBE feed composition, the feed reservoir concentration declined exponentially with time. Deviations of the predictions of Eq. (5) from the experimental data were in the range of 1.4–8%, suggesting that membrane resistance to MTBE transport was negligible, compared to the feed-side concentration boundary layer resistance (i.e.,  $R_{f,M} \gg R_{m,M}$ ), for the present range of initial MTBE concentrations. Also, we note that since the feed consists pri-

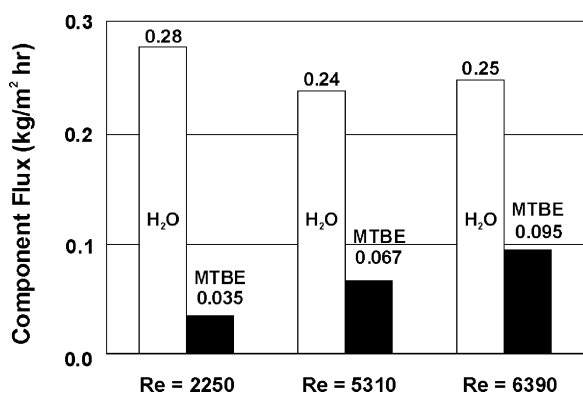


Fig. 4. Component fluxes (kg/m<sup>2</sup> h) of water and MTBE for PVAc grafted membrane CSP2 at initial MTBE feed composition of 0.1% (v/v).

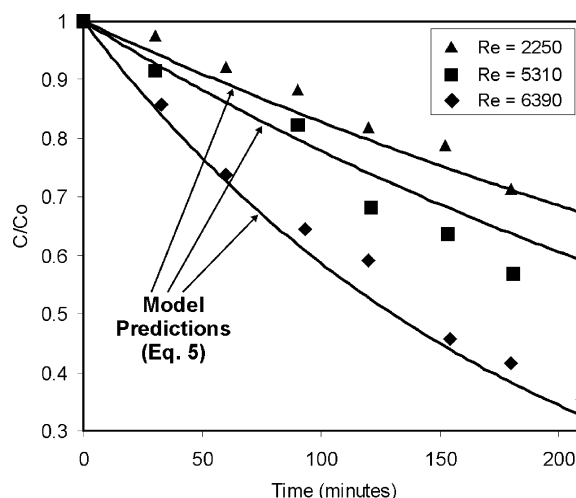


Fig. 5. Experimental and predicted (solid lines) decline of MTBE concentration in the feed reservoir (0.1% (v/v) initial MTBE concentration) at different Reynolds numbers using membrane CSP2.

marily of water (99–99.99%), the impact of concentration polarization on water permeation flux can be considered negligible and thus  $R_{m,W} \gg R_{f,W}$ . Accordingly, the MTBE separation factor as given by Eq. (4) simplifies to

$$\alpha \approx \frac{R_{m,W}}{R_{f,M}} \quad (6)$$

suggesting that the MTBE separation factor for the CSP membrane can be increased by decreasing the feed-side concentration boundary layer resistance for MTBE (i.e., by increasing the feed-side Reynolds number) or by increasing the membrane resistance to water by increasing the polymer graft yield (see Fig. 2). A further decrease in water transport through the membrane could be achieved by using a ceramic support membrane with a pore size smaller than the length and spacing of the grafted polymer chains. For example, for the present grafted chains (MW = 12,600), one could modify a native support membrane with pores of diameter of 60 Å or less, which should result in chain size (in a good solvent) and surface chain spacing smaller than the pore size. Larger chains could also be grafted by varying carrying the polymerization reaction at a higher initial monomer concentration [23].

## 5. Conclusions

Porous silica membranes of 500 Å native pore size modified by grafted PVAc chains were shown to be selective for MTBE over water for the separation of aqueous MTBE solutions. Separation factors varied from 68 to 577 at corresponding total flux range of 0.31–0.72 kg/m<sup>2</sup> h, depending on the feed-side Reynolds number and the extent of membrane modification. The PVAc–silica membrane offered negligible resistance to MTBE permeation, while the feed-side concentration boundary layer provided the ma-

por resistance to MTBE transport. The present study suggests that the separation performance of the PVAc–silica membrane can be increased by reducing water flux via a denser surface chain coverage and by increasing the grafted polymer chain size relative to the native membrane pore size.

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