

Ceramic-supported polymer membranes for pervaporation of binary organic/organic mixtures

Wayne Yoshida, Yoram Cohen*

Department of Chemical Engineering, University of California, 5531 Boelter Hall 405 Hilgard Avenue, Los Angeles, CA 90095-1590, USA

Received 29 May 2002; received in revised form 13 September 2002; accepted 16 September 2002

Abstract

Asymmetric tubular alumina-supported poly(vinyl acetate) (PVAc) and poly(vinyl pyrrolidone) (PVP) membranes were created and characterized by pervaporation separation of binary mixtures of methanol and methyl *tert*-butyl ether (MTBE). The active separation layer was created by free-radical graft polymerization of PVAc and PVP onto a vinylsilane-modified alumina substrate with an average native pore diameter of 50 Å. The separation layer consisted of a surface phase of terminally anchored polymer chains with estimated radius of gyration about a factor of 4.5–6.8 larger than the membrane pore radius. The methanol separation factors for the PVP and PVAc-grafted pervaporation membranes reached values of 26 and 100, respectively, at the lower range of methanol concentrations (1–5% v/v) tested in the study. The separation impact of the grafted polymer chains was apparent given that the native (unmodified) and vinylsilylated alumina membranes lacked selectivity for the MTBE/methanol system. Total permeate flux attained with the PVAc and PVP-based membranes ranged from 0.055 to 1.26 and 0.55 to 6.19 kg/m² h, respectively, over the respective feed methanol concentration ranges of 1–90 and 5–90% (v/v). A tradeoff between separation and permeate flux was apparent from the decrease in permeation flux with increasing separation factor. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pervaporation; Organic separations; Composite membranes; Graft polymerization; Inorganic membranes

1. Introduction

Membrane pervaporation for the separation of liquid chemical mixtures is a research area of growing interest and importance [1]. Currently, most commercial pervaporation processes involve dehydration of alcohols and other organic solvents, or recovery of organic solvents from dilute aqueous streams. In recent years, the potential use of pervaporation technology for the separation of organic/organic mixtures

(especially azeotropic or close boiling mixtures) has attracted significant attention in the research community. To date, the use of commercially available polymeric membranes in the above application has not attained widespread industrial acceptance owing, in part, to degradation of membrane performance in organic mixtures which cause swelling and loss of membrane integrity [2,3]. In order to improve membrane stability, the common approach proposed in the literature has been to utilize cross-linked [4–6] and/or blended polymeric membrane materials [5–9] that are optimized for specific chemical mixtures and operating conditions. An alternate approach is the adaptation of ceramic materials as a stable support structure for the polymeric membrane, thereby providing sufficient

* Corresponding author. Tel.: +1-310-825-8766; fax: +1-310-206-4107.
E-mail address: yoram@ucla.edu (Y. Cohen).
URL: <http://www.polysep.ucla.edu>

chemical and thermal stability to withstand anhydrous solvents and higher temperatures.

The emergence of robust inorganic membranes of controlled pore size [10] has resulted in the creation of ceramic-supported polymer (CSP) membranes [11] in which a polymer layer governs the separation performance of the membrane, while the inorganic support provides the desired mechanical integrity. The majority of the proposed inorganic-polymer composite membranes for pervaporation have relied on physical attachment of the polymer to the inorganic substrate via solution casting [12], coating [13,14], dip-coating a porous ceramic substrate followed by subsequent cross-linking [15], asymmetric incorporation of inorganic materials as a powder in a polymer matrix [16], or pore-filling of a porous ceramic substrate with acrylamide, followed by cross-linking [17]. In contrast, ceramic-supported polymer membranes are created by terminally and covalently bonding a layer of polymer chains onto the surface of a porous ceramic support. The polymer surface chains are expected to have greater mobility than cross-linked chains, yet the polymer phase is stable even when contacted by liquid mixtures in which the native polymer is completely soluble. In principle, temperature stability of the CSP membrane is limited only by the temperature at which thermal degradation of the polymer backbone or side groups may occur. This membrane type is particularly attractive because a wide variety of monomers can be used in the graft polymerization reaction, thereby allowing one to tailor design such membranes for an array of different pervaporation applications. For example, Leger et al. [18] grafted preformed polydimethylsiloxane (PDMS) onto the surface of an alumina support membrane by contacting the support surfaces with a heated silicone oil. The resulting pervaporation membrane was tested for the separation of aqueous solutions of 5 wt.% 1-butanol and 10 wt.% tetrahydrofuran (THF), resulting in a THF separation factor of 20 and 1-butanol separation factor of 20 for these respective solutions. Total permeation fluxes for the THF and 1-butanol aqueous solutions were 0.1 and 0.31 kg/m² h, respectively. A different approach was taken by Jou et al. [11] who reported on a class of organic-selective pervaporation membranes prepared by a two-step surface free-radical graft polymerization process. The pervaporation membranes consisted of an active layer of PVAc chains terminally and

covalently anchored onto the surface of a 500 Å pore size silica support membrane. These membranes performed with separation factors of up to 106 and 118 for aqueous solutions of trichloroethylene (TCE) and chloroform (500–700 ppm), respectively, with permeation fluxes of up to 0.37 kg/m² h and negligible membrane mass transfer resistance for the organic species. More recently, a pervaporation membrane created by pore-filling plasma polymerization of a methyl acrylate monomer onto a porous silica support was reported by Kai et al. [3]. The resulting pervaporation membranes were shown to separate 28% (w/w) solutions of *n*-hexane in chloroform with chloroform separation factors as high as 16.3 at a permeation rate of 0.5 kg/m² h.

In the present work, the method of Jou et al. [11] was adapted to produce selective pervaporation membranes by grafting a molecular layer of terminally anchored poly(vinyl pyrrolidone) (PVP) or poly(vinyl acetate) (PVAc) polymer chains to an otherwise non-selective porous alumina membrane with 50 Å average pore size. The performance of the resulting membranes was examined in the pervaporation separation of methanol/methyl *tert*-butyl ether (MeOH/MTBE) mixtures over the complete composition range from pure MTBE to pure methanol, and the role of the separation layer structure was elucidated based on a scaling analysis of the relative size of the grafted polymer chains, surface chain density, and substrate pore size.

2. Experimental

2.1. Materials

The native alumina substrate used for the CSP membrane was a tubular asymmetric composite membrane 25 cm in length, with 0.65 cm i.d. and 1.0 cm o.d., obtained from US Filter (DeLand, FL). The membrane consisted of a 5 μm thick layer of γ-alumina with average pore size of 50 Å (as reported by the manufacturer) on a multilayer support of porous α-alumina. Silica particles (Novacite L207-A, Malvern Materials Co., Hot Springs, AR) of 5 μm size and γ-alumina particles (Alfa Aesar, Ward Hill, MA) of up to 250 μm (~60 mesh), with corresponding surface areas of 2.2 and 158 m²/g, were used as surrogate particles to

determine the polymer graft yield. Hydrochloric acid (HCl) used for cleaning was ACS certified quality (Fisher Scientific, Tustin, CA). Surface activation prior to graft polymerization was performed using vinyl trimethoxysilane (VTMS) (98% pure, Aldrich Chemical Co., Milwaukee, WI) and reagent-grade xylenes solvent (Fisher Scientific, Tustin, CA). Graft polymerization reactions were performed using reagent grade vinyl acetate monomer (Fisher Scientific, Tustin, CA), 1-vinyl-2-pyrrolidone monomer (99+%, Aldrich Chemical Co., Milwaukee, WI), ACS-grade ethyl acetate solvent (Fisher Scientific, Tustin, CA), hydrogen peroxide (30% w/w in H₂O, Fisher Scientific, Tustin, CA), ammonium hydroxide (58% v/v in H₂O, Aldrich Chemical Co., Milwaukee, WI), and α,α' -azobis(2,4-dimethylvaleronitrile) initiator obtained from Dupont Co. (Wilmington, DE). All water used was distilled and deionized using a Milli-Q filtration system (Millipore, Bedford, MA). Pervaporation experiments were performed using chromatographic-grade methanol and MTBE obtained from VWR Scientific (San Dimas, CA). A set of poly(styrene), poly(vinyl pyrrolidone), and poly(vinyl acetate) molecular calibration standards in the 17,000–189,000 MW range were obtained from American Polymer Standards (Mentor, OH) for use in molecular weight determination.

2.2. Surface modification

Surface modification of the porous support was performed in three steps: pretreatment, surface activation, and graft polymerization. Pretreatment consisted of cleaning and hydroxylating the native alumina membrane using a dilute (1%) aqueous solution of HCl. The membrane was dried, then equilibrated in a 50% relative humidity atmosphere for 15 h at 23 °C [19], after which the resulting membrane substrate was loaded into a stainless steel module for in situ surface activation with VTMS. Anhydrous surface silylation was performed by pumping a solution of 10% VTMS in xylenes solvent through the feed side of the membrane, such that the solution contacted the inner (separating) surface of the tubular membrane. The shell side of the module was filled with pure xylenes and sealed prior to the reaction to prevent convective infiltration of the feed-side reaction mixture into the porous support. The VTMS solution

was maintained at a temperature of 137 °C during the 5 h reaction. At the termination of the silylation reaction, the membrane was rinsed by pumping pure xylenes solvent through the tube side of the membrane for 1 h, replacing the solvent every 20 min. Subsequently, the membrane was removed from the module, rinsed again in fresh xylenes, and dried in a vacuum oven overnight at 140 °C. The resulting surface vinyl groups provided the necessary active anchoring sites for the subsequent graft polymerization step. For PVP grafting, the VTMS-modified membrane was immersed in a potassium hydroxide solution (pH = 9) for 72 h period prior to graft polymerization to hydrolyze any remaining alkoxy groups [20]. This surface treatment improves the wettability of the membrane, thereby enabling more efficient contacting of the membrane surface by the aqueous vinyl pyrrolidone reaction mixture. No such treatment was necessary for the PVAc grafting since the reaction was carried out in an organic medium.

Graft polymerization of the silylated membrane was performed using a 1.5 l jacketed reactor under a nitrogen atmosphere. The reaction mixture was stirred by impeller and was maintained at the desired reaction temperature using a temperature controlled water circulator (Neslab Instruments Inc., Portsmouth, NH). The reaction solution was pumped from the reactor and through the tube side of the membrane module using a diaphragm pump. The shell side of the module was filled with the reaction solvent (ethyl acetate or water) and sealed prior to the reaction in order to prevent reaction mixture infiltration into the membrane support. Poly(vinyl acetate) grafting was accomplished following the procedure described by Jou [21], with a 40% (v/v) solution of vinyl acetate monomer in ethyl acetate at 60 °C, initiated with 0.03 M 2,2'-azobis(2,4-dimethylpentanenitrile). PVP grafting was carried out at 80 °C using a 30% (v/v) aqueous solution of vinyl pyrrolidone containing 0.034 M ammonium hydroxide, using hydrogen peroxide (0.03 M) as the initiator [22]. Each graft polymerization reaction proceeded for a period of 6 h. At the termination of the reaction the membrane was rinsed by pumping fresh solvent through the membrane tube-side for a period of 1 h, changing the wash solvent every 20 min. Following the rinse the membrane was removed from the module, rinsed a final time with fresh solvent, and dried overnight under vacuum at 110 °C.

The resultant polymer surface layer consisted of a molecular layer and thus using a direct gravimetric or other non-destructive method to determine the polymer graft yield was not feasible. Therefore, the polymer graft yield was estimated based on graft polymerization studies with surrogate silica and γ -alumina particles, under the same surface silylation and polymerization reaction conditions, in a slurry reactor following the procedures described by Nguyen et al. [22] and Rovira-Bru et al. [23]. The polymer graft yield, determined by thermogravimetric analysis (TGA) using a TGS-2 system (Perkin-Elmer, Norwalk, CT), was 2.66 mg/m^2 for PVAc grafting and 1.97 mg/m^2 for PVP. The average molecular weight of the PVP and PVAc polymer chains, for the present reaction conditions, was estimated by size exclusion chromatography (SEC) to be 13,000 and 39,700, respectively.

2.3. Pervaporation

Pervaporation experiments were carried out in a typical bench-scale apparatus as shown in Fig. 1. A Tedlar bag (Chromatography Research Supplies, Addison,

IL) that served as the feed reservoir was filled with 1000 ml of MeOH/MTBE feed solution just prior to each pervaporation experiment. The feed solution (at 20°C) was pumped through the tube side of the membrane module using a variable speed diaphragm pump, with the feed flow rate measured by an online rotameter. Feed-side pressure was measured by pressure transducers (Model CD 223, Validyne, Northridge, CA), and a vacuum gauge (Pirani Vacuum Gauges, Edwards, Wilmington, MA) was used to monitor permeate side pressure. A vacuum pump (Model M8C, Fisher Scientific, Pittsburgh, PA) was used to maintain permeate-side pressures of approximately 2 Torr. The low-pressure vapor permeate was collected using two dewar flasks immersed in liquid nitrogen. Prior to each run, the system was equilibrated by running both the feed circulation pump and the vacuum pump for at least 1 h. The composition of the feed and permeate were determined using a SRI 8610C gas chromatograph (SRI, Torrance, CA) with a FID detector heated to 200°C and oven temperature maintained at 150°C . The column used was a Supelco $1/8'' \times 10'$ stainless steel column packed with 80/120 Carbowax B.

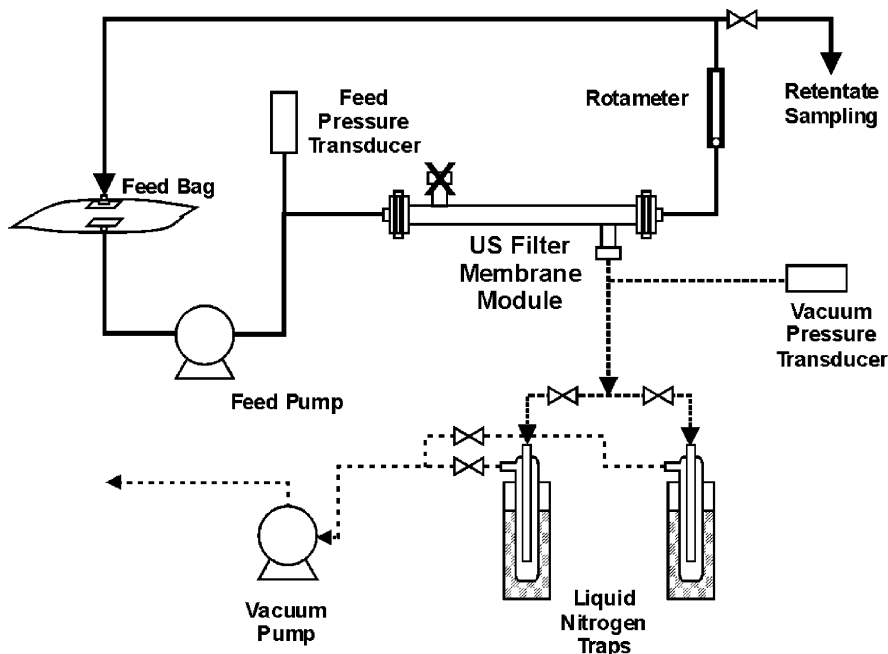


Fig. 1. Schematic of pervaporation apparatus.

3. Analysis

The generally accepted measure of the separation capability of a pervaporation membrane for a specific binary mixture is the separation factor, α , defined as:

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

where $x_{p,i}$ and $x_{p,j}$ are the mole fractions of the preferential and secondary permeants, respectively, in the permeate, and $x_{f,i}$ and $x_{f,j}$ are their corresponding mole fractions in the feed. The separation factor can vary from unity (indicating no separation) to infinity, where larger α -values indicate increased selectivity. The separation factor as measured experimentally is a composite indicator of a system's overall separation performance and can vary depending on feed hydrodynamic conditions, permeate resistance due to elevated partial pressures, changes to the diffusion rate caused by membrane swelling, or changes to membrane/component solubility. The separation factor can also be expressed in terms of the component permeate fluxes as

$$\alpha = \frac{J_i x_{f,j}}{J_j x_{f,i}} \quad (2)$$

in which J_i and J_j are the fluxes of the preferential and secondary components. Expressions for the component permeate fluxes are commonly obtained by using the mass transfer resistance-in-series model [2,24–26]. Accordingly, J_k , the overall permeate flux for a component k (where $k = i$ or $k = j$ for a binary feed), can be written as

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

in which $C_{f,k}$ and $C_{p,k}$ are the component feed and permeate concentrations, H_k is a dimensionless equilibrium partition coefficient (i.e. $H_k = C_k^{liq}/C_k^{vap}$) and $R_{ov,k}$ is the overall component mass transfer resistance. Under typical pervaporation conditions, the permeate total pressure is much lower than the component vapor pressures, and it is reasonable to assume that $C_{p,k} \sim 0$. We note that for most cases of interest $C_{f,k} \gg H_k C_{p,k}$, and therefore the separation factor can be reasonably approximated in terms of the component

resistances [27,28] by combining Eqs. (2) and (3),

$$\alpha = \frac{R_{ov,j}}{R_{ov,i}} \quad (4)$$

The overall component resistance, $R_{ov,k}$, is the sum of the feed-side ($R_{f,k}$), membrane ($R_{m,k}$), and permeate-side ($R_{p,k}$) mass transfer resistances:

$$R_{ov,k} = R_{f,k} + R_{m,k} + R_{p,k} \quad (5)$$

It is noted that when the permeate total pressure is sufficiently low, as was the case in the present work, the permeate-side resistance $R_{p,k}$ can be neglected compared to the other two resistances [29]. Moreover, to evaluate the pervaporative properties of the grafted polymer layer, feed-side hydrodynamic conditions were selected such that the membrane resistance was the dominant mass transfer resistance.

In order for pervaporation to occur, the effective pore size of the membrane (i.e. permeability) must be reduced to the point where pressure-driven liquid flux is small compared to pervaporation flux. The decrease in effective pore size due to silylation and grafting is manifested by a decrease in the Darcy's permeability for a pure component k , k_k (cm^2), calculated from [30]:

$$k_k = \frac{j_k \mu_k r_i \ln(r_o/r_i)}{\Delta P_m} \quad (6)$$

in which r_i and r_o are the inside and outside membrane tube radii (cm), respectively, μ_k is the pure component viscosity, ΔP_m is the transmembrane pressure, and j_k (cm/s) is the liquid permeation flux.

4. Results and discussion

4.1. Surface modification and membrane permeability

PVAc-alumina and PVP-alumina asymmetric composite membranes were produced and subsequently characterized via a series of pervaporation separation experiments for methanol/MTBE mixtures. The active polymer surface layer consisted of polymer chains that are terminally and covalently bonded onto the membrane surface. When chain spacing is sufficiently large such that the surface chains do not overlap, the polymer surface chains resemble a hemisphere with

Table 1
Reaction conditions and characteristics of PVAc and PVP-grafted polymers

Polymer	Graft reaction conditions ^a		M_n	Polymer graft yield (mg/m ²)	Radius of gyration, R_g^b , (Å)	Chain spacing, D^c (Å)	Brush height, L^d (Å)
	M (%)	T (°C)					
Poly(vinyl acetate)	40	60	3.97×10^4	2.66	171	49	388
Poly(vinyl pyrrolidone)	30	80	1.30×10^4	1.97	113	33	258

^a M is initial monomer concentration by volume percent and T the reaction temperature.

^b Polymer chain radius of gyration in a good solvent ($R_g \approx N^{3/5}a$).

^c Polymer surface density is defined as $\sigma = a^2/D^2$.

^d Height of polymer brush (in a good solvent) $L \approx Na\sigma^{1/3}$.

a radius that under good solvent conditions is essentially equivalent to the Flory radius [31], R_F , given as $R_F = N^{3/5}a$, where N is the number of monomer per chain and a is the monomer size. The monomer size, a , was estimated to be 4.3 and 6.4 Å for vinyl acetate (VAc) and vinyl pyrrolidone (VP), respectively, based on molecular modeling calculations (Hyperchem 6.0, Spartan 4.1). Since the average polymer molecular weights of PVAc and PVP are 3.9×10^4 and 1.3×10^4 , the corresponding numbers of monomers per chain N are 461 and 120, respectively. Accordingly, the estimated Flory radii of the PVAc and PVP-grafted polymers are 170 and 113 Å, clearly larger than the 50 Å native support membrane pore size. These results are summarized in Table 1.

Although, it is plausible that chain grafting inside the pores may have occurred to some degree, the pore size is only about 8–11 times larger than the monomer size and severe hindered pore diffusion would prevent grafting of a significant amount of even fairly short chains within the pore. Based on the classical hindered pore diffusion model [32], upon grafting a seven-mer chain within the 50 Å pore, monomer diffusivity within the pore would be reduced by two orders of magnitude; we also note that for polymers with $N > 10$, the Flory radius would exceed the pore radius. In addition, the development of the surface polymer layer would also serve to screen the pores and prevent reactants from reaching the pore interior. Since the average PVP or PVAc surface chain consists of 100–400 monomers, it is likely that the majority of the PVAc and PVP chains are grafted onto the surface of the membrane support rather than in the pore interiors. The average spacing between these surface chains can be estimated as $D = (GN_A/M_n)^{-1/2}$ where G (g/m²) is the polymer graft yield, M_n is

the number-average molecular weight of the grafted polymer and N_A is Avogadro's number. For the present PVAc and PVP-based membranes, the average chain-to-chain spacing expected for the present reaction conditions was estimated at 49 and 33 Å, which is less than the average native membrane pore diameter. Since the polymer Flory radii greatly exceed the chain spacing, under good solvent conditions these terminally anchored surface chains should extend away from the surface in a "brush" due to volume exclusion interactions. Grafted chains can be considered to be in this so-called dense "brush" regime when the chain spacing, D , is sufficiently small such that the brush criterion $\sigma = (a/D)^2 > N^{-6/5}$ is fulfilled. This condition was verified for the grafted PVAc and PVP using values from Table 1. The average chain extension (e.g. swollen brush height), L_c , for good solvent conditions can then be estimated based on a simple scaling analysis [31], $L_c \simeq Na(a/D)^{1/3}$, leading to brush heights of 388 and 258 Å for PVAc and PVP surface chains. These brush heights represent the approximate thickness of the separating layers.

On the average, the polymer chains are spaced less than a pore diameter distance apart, and both the chain extension and Flory radii are larger than the pore diameter by factors of 5–8 and 2–4, respectively. Therefore, it is probable that the terminally anchored polymer chains cover the pore openings, providing a continuous molecular coverage over the microporous surface and enabling pervaporation to occur. Previous work with silica-PVAc membranes has suggested that for pervaporative separation capability to exist, the Darcy (liquid) permeability (Eq. (6)) of the membrane has to be reduced by polymer grafting to approximately 10^{-15} cm² [11], a criterion that was demonstrated for the pure components (Table 2) of the binary mixture

Table 2
Hydraulic permeability for the native, silylated and polymer-grafted membranes

Membrane ^a	Hydraulic permeability (cm ²)	
	MeOH	MTBE
Native alumina	1.0×10^{-13}	1.6×10^{-13}
Silylated	6.6×10^{-15}	5.4×10^{-15}
PVP-grafted	1.1×10^{-15}	Impermeable ^c
PVAc-grafted	Impermeable ^b	Impermeable ^c

^a All modified membranes are based on the same alumina support membrane.

^b Measurable permeation not observed at transmembrane pressures up to 40 psi.

^c Measurable permeation not observed at transmembrane pressures up to 50 psi.

in the current study. The measured Darcy permeabilities were a preliminary indication of the pervaporative potential of the CSP membranes at various stages of modification.

4.2. Membrane separation capability

The PVP and PVAc-grafted membranes demonstrated preferential methanol permeation, while the silylated and native membrane supports displayed little or no separation capability. This behavior is illustrated in Fig. 2 for a 50/50 (v/v) methanol/MTBE mixture. The unmodified alumina support had a

separation factor of 0.76 with respect to methanol (i.e. slight preferential permeability for MTBE) and a significantly higher flux than those reported for methanol/MTBE pervaporation with polymeric membranes [5,33]. A methanol separation factor of 1.1 was observed for the VTMS-modified membrane, but the flux was reduced by nearly 50% relative to the native membrane support. These results are consistent with the open pore structure expected for the unmodified and silylated membranes, and suggest that the observed separation values result primarily from vacuum distillation [18]. In vacuum distillation [34], the selectivity is determined by the vapor–liquid equilibrium of the methanol/MTBE components while the permeation is only limited by the evaporation rate. Above the azeotropic point, selectivity via vacuum distillation should favor the more volatile MTBE, as can be verified from vapor–liquid equilibrium data for the MTBE/methanol system [35]. In contrast, the polymer-grafted membranes are selective for methanol, with a methanol separation factor of approximately 9 (Fig. 2). The pore size reduction of the grafted membranes (suggested by the reduction in Darcy permeabilities; Table 2) resulted in decreased total flux and increased methanol separation factor relative to the ungrafted membranes, similar to the flux/selectivity tradeoff commonly observed for pervaporation membranes.

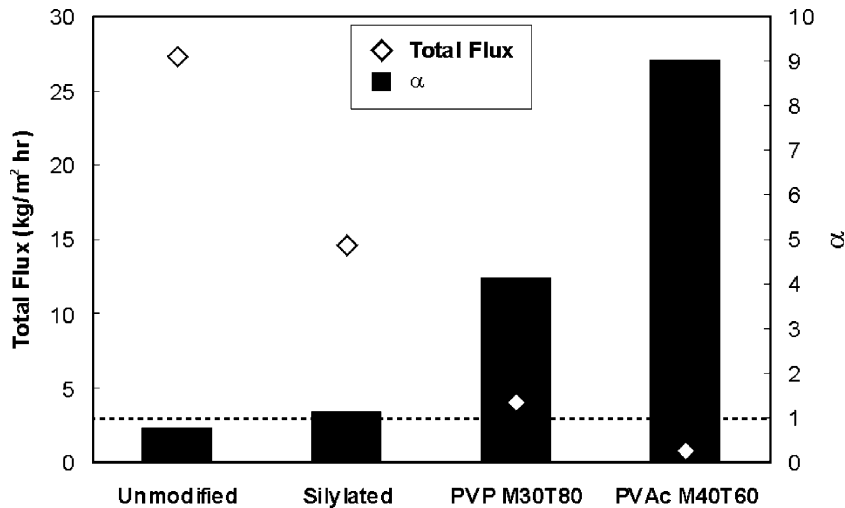


Fig. 2. Comparison of separation factor (for methanol) and fluxes for 50/50 (v/v) mixtures of methanol and MTBE for unmodified, VTMS silylated, and PVP and PVAc-grafted membranes (dotted line indicates separation factor of unity).

The separation factors and permeate fluxes for the PVP and PVAc-based membranes, measured over a Reynolds number range of about 400–3000, demonstrated an average variation of only 6.3 and 2.4%, respectively, which can be considered to be well within the range of the overall experimental error. In contrast, separation factor and permeate fluxes varied with feed concentration by one to two orders of magnitude over the range of concentrations tested. This behavior suggests that the mass transfer resistance associated with the feed concentration boundary layer is small relative to that which is associated with the membrane itself (Eq. (5)). Therefore, the mass transfer resistance and hence the separation factor observed can be considered intrinsic properties of the grafted polymer layer of the CSP membrane [2].

4.3. Effect of feed concentration on pervaporation

The pervaporation separation factor and total fluxes of the two types of grafted membranes were tested over the complete range of methanol/MTBE feed concentrations, and the resulting values are given in Figs. 3 and 4. Both types of grafted membrane displayed the commonly observed [2] tradeoff between decreased separation and increased flux as the volume fraction of methanol in the feed is increased. Both types of CSP membrane were selective toward methanol ($\alpha > 1$) and achieved separation factors as high as 26 for the PVP-grafted membrane and 100

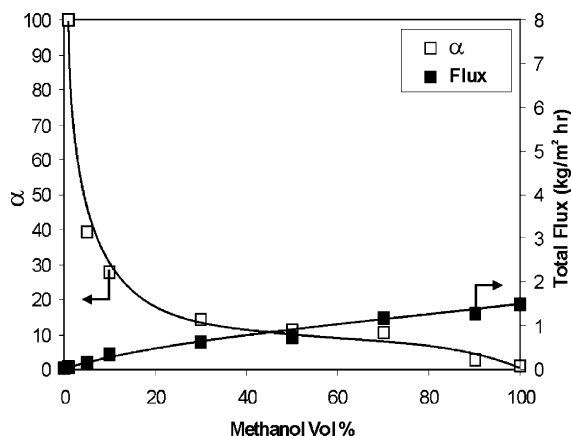


Fig. 3. Effect of feed composition on methanol separation factor and total flux for PVAc-grafted membrane.

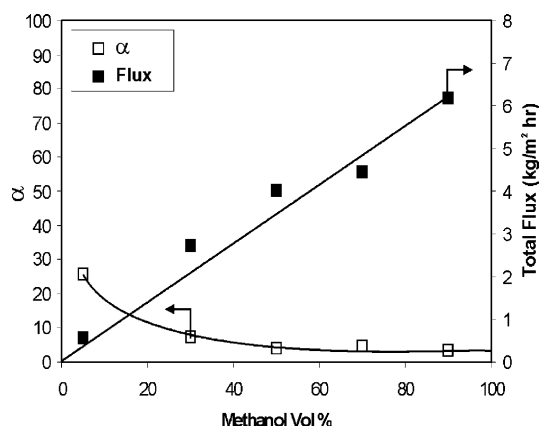


Fig. 4. Effect of feed composition on methanol separation factor and total flux for PVP-grafted membrane.

for the PVAc-grafted membrane at methanol volume fractions of 5 and 1%, respectively. The total permeate flux at these conditions was 0.55 kg/m² h for the PVP-grafted membrane and 0.055 kg/m² h for the PVAc-grafted membrane. Both membranes greatly outperformed the vapor–liquid equilibrium separation achievable by vacuum distillation and neither membrane was affected by the presence of the methanol/MTBE azeotrope, as shown in Fig. 5.

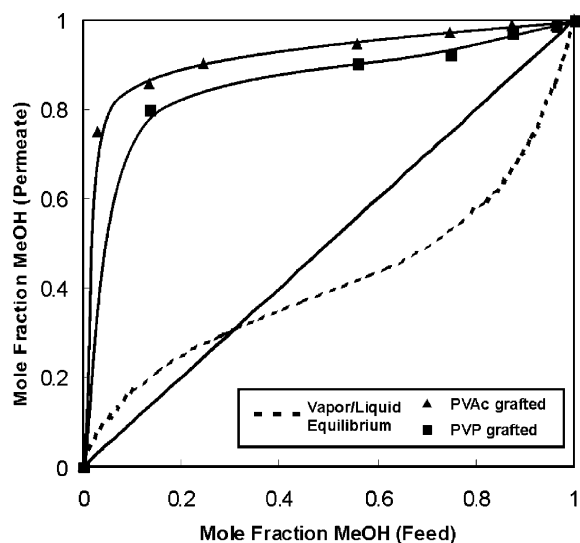


Fig. 5. Methanol/MTBE vapor–liquid equilibrium relative to separation achievable by grafted PVP and PVAc membranes (equilibrium data measured at 101.32 kPa by Arce et al. [35]).

However, the PVAc membrane had a higher separation factor and lower flux than the PVP-grafted membrane at all feed concentrations. Since both grafted membranes were created from identical support substrates, it is reasonable to attribute the differences in their separation characteristics to the differences in the partitioning and diffusivity of the feed components in the grafted layer. The diffusivity of methanol in the grafted polymer layer is expected to be higher than MTBE due to its smaller molecular size, favoring the selectivity of methanol over MTBE in both membranes. Polymer solubility tests at 23 °C demonstrated that while methanol is a good solvent for both polymers, PVAc was only moderately soluble in MTBE, while PVP was essentially insoluble in MTBE. Based on solubility considerations alone one would expect both membranes to be more selective towards methanol with the PVP membrane having a higher selectivity for methanol.

The experimentally observed separation characteristics of the two membranes can be attributed to differences in both the grafted layer structure and polymer–solvent compatibility. As shown by Castro et al. [36], the apparent pore size (or permeability) for PVP-grafted membranes increases as the solvent quality decreases. Since MTBE is a poor solvent for PVP, when the polymer chains are exposed to the MTBE/methanol feed, the chains are likely to be in a

less swollen state relative to the PVAc chains. Since the grafted PVP chains are also physically smaller than the grafted PVAc chains (Table 1), contraction of the chains toward the surface would lead to an increase in effective pore size and a decrease in the grafted polymer brush height, which is consistent with the observed higher permeation flux and lower selectivity of the PVP-based membrane relative to the PVAc membrane. The above argument suggests that when modification of membrane substrates is performed, careful consideration must be given to the relationship between the native pore diameter and the size of the grafted polymer chains.

4.4. Component fluxes

The permeate flux for species k in the feed, J_k , was determined from measurements of the total permeate flux (J_{tot}) and the permeate composition ($x_{p,k}$) as $J_k = J_{\text{tot}}x_{p,k}$. The methanol permeation flux (Figs. 6 and 7) increased essentially linearly over the range of compositions studied for both the PVP and PVAc membranes. In contrast, a maximum in MTBE permeation flux through the PVAc and PVP membranes was observed at methanol feed concentrations of 5 and 11 mol/l (20% v/v and 45% v/v methanol), respectively. Above these maxima, the MTBE component fluxes decreased with increasing methanol

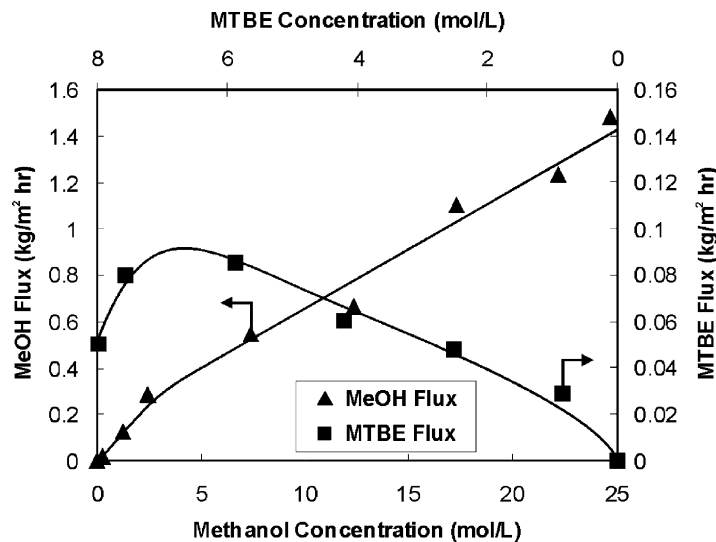


Fig. 6. Component fluxes for pervaporation of methanol/MTBE mixtures through PVAc-grafted membrane.

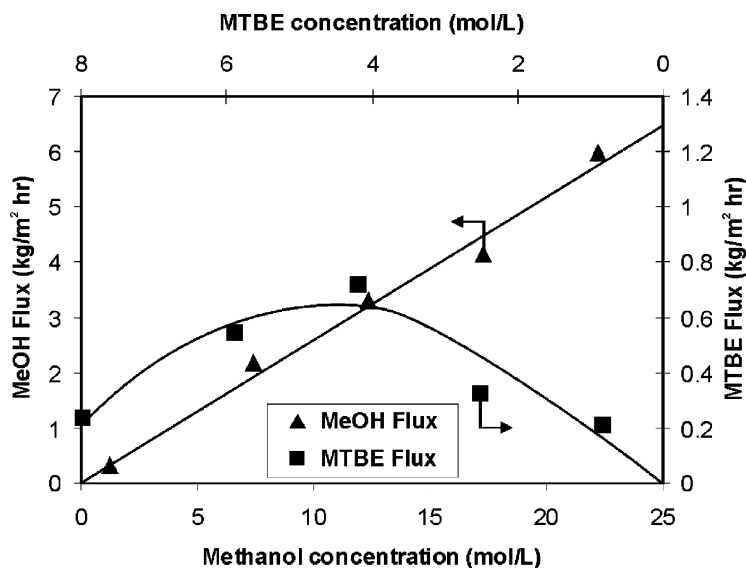


Fig. 7. Component fluxes for pervaporation of methanol/MTBE mixtures through PVP-grafted membrane.

concentration due to the decline in the MTBE concentration driving force, a result expected from pervaporation solution–diffusion theory (Eq. (3)). However, below these maxima, the MTBE flux increased with increasing methanol concentration despite the decreasing MTBE driving force.

The fact that a maximum in flux with respect to composition exists for MTBE but not for methanol

suggests that the maximum is not due to changes in diffusion behavior through the membrane (which would affect both components), but rather the non-ideal solubility behavior of MTBE in the presence of methanol. Indeed, a maximum in MTBE sorption capacity with respect to solution composition has been previously reported in the literature for sorption of methanol/MTBE mixtures by polyimide films [37], and similar

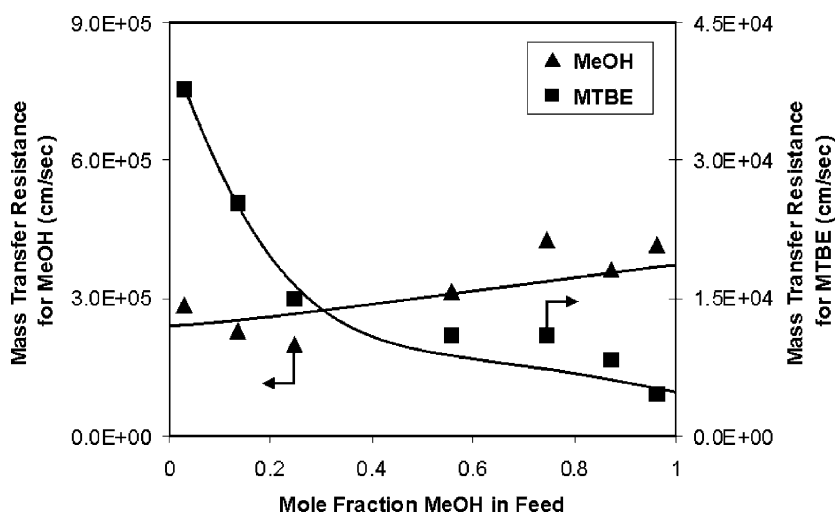


Fig. 8. Effect of feed composition on mass transfer resistances of methanol and MTBE for PVAc-grafted membrane.

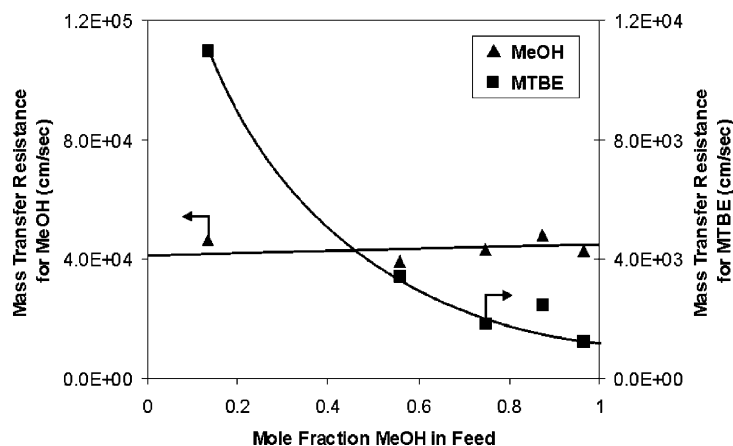


Fig. 9. Effect of feed composition on mass transfer resistances of methanol and MTBE for PVAc-grafted membrane.

solubility behavior has also been noted for polyvinyl alcohol films in alcohol/water solutions [38]. Since the magnitude of the MTBE pervaporation flux is directly proportional to its solubility in the membrane, the similarity between the pervaporation flux curve in this work and sorption isotherms reported in literature implies that the flux/separation trade-off observed in this work may be primarily due to changes in MTBE solubility in the polymer phase. Direct evaluation of the partitioning of methanol and MTBE into the grafted polymer phase is a challenging endeavor, but such studies will clearly be needed to better understand the intricate relationship between flux, partitioning and membrane resistance.

The component membrane resistances (Eq. (3)) for methanol and MTBE are shown in Figs. 8 and 9 for the PVAc and PVP membranes, respectively. Although there is some scatter in the calculated methanol resistance data, it is evident that resistance to methanol transport for the PVAc-grafted membrane (Fig. 8) increases by approximately 45% as the methanol mole fraction increases from zero to unity. In contrast, methanol resistance for the PVP membrane (Fig. 9) was essentially constant (with a deviation of about 6%) over the range of concentrations studied. For both the PVAc and PVP-grafted membranes, resistance to MTBE transport decreased with increasing methanol concentration in the feed. For the PVAc-grafted membrane, MTBE resistance decreased by a factor of about 2.5 as the methanol feed mole fraction increased from 0.03 to 0.3 (corresponding to 1–10% methanol by

volume). For the PVP-grafted membrane, resistance to MTBE transport decreased by a factor of 5.9 as the methanol feed composition increased from 0.13 to 0.75 mole fraction (corresponding to 5–50% methanol by volume). The strong dependence of MTBE membrane resistance on feed concentration coupled with the weak dependence of methanol membrane resistance on feed concentration suggests that the decline in methanol separation factor with rising methanol feed concentration (Fig. 3) is due to a significant increase in the membrane's permeability for MTBE rather than a decrease in methanol permeability.

5. Conclusion

Alumina support membranes of 50 Å native pore size were modified by a two-step free-radical graft polymerization of either vinyl acetate or vinyl pyrrolidone to create ceramic-supported polymer (CSP) pervaporation membranes for organic–organic separation. The active poly(vinyl acetate) and poly(vinyl pyrrolidone) separation layers consisted of molecular layers of terminally anchored polymer chains. The present CSP membranes were found to be methanol selective for the pervaporation of methanol/MTBE mixtures, achieving separation factors of up to 100 (PVAc) or 26 (PVP). As methanol feed concentration increased, the membranes displayed a tradeoff of increasing flux accompanied by decreasing methanol separation factor. The separation ability of these membranes was shown

to be due to the graft polymerized surface chains. In contrast, the unmodified and silylated membranes had negligible separation capabilities. The study suggests that pervaporation separation, rather than vacuum distillation, occurs with these modified membranes because the grafted polymer chain size is larger than the native pore size, while the chain spacing is smaller than the native pore size. The CSP membrane can be tailored for specific separations of organic mixtures with the proper choice of polymer chemistry; however, increase in selectivity would also require careful optimization of grafted polymer chain spacing and chain length relative to the support pore size.

References

- [1] N. Wynn, Pervaporation comes of age, *Chem. Eng. Progress* 97 (10) (2001) 66–72.
- [2] X. Feng, R.Y.M. Huang, Liquid separation by membrane pervaporation: a review, *Ind. Eng. Chem. Res.* 36 (1997) 1048–1066.
- [3] T. Kai, T. Yamaguchi, S. Nakao, Preparation of organic/inorganic composite membranes by plasma-graft filling polymerization technique for organic-liquid separation, *Ind. Eng. Chem. Res.* 39 (2000) 3284–3290.
- [4] Y.S. Kang, S.W. Lee, U.Y. Lee, J.S. Shim, Pervaporation of water-ethanol mixtures through crosslinked and surface-modified poly(vinyl alcohol) membrane, *J. Membr. Sci.* 51 (1990) 215–226.
- [5] J.W. Rhim, R.K. Kim, Pervaporation separation of MTBE-methanol mixtures using cross-linked PVA membranes, *J. Appl. Polym. Sci.* 75 (2000) 1699–1707.
- [6] S.C. George, K.N. Ninan, S. Thomas, Pervaporation separation of chlorinated hydrocarbon and acetone mixtures with crosslinked styrene-butadiene rubber and natural rubber blend membranes, *J. Membr. Sci.* 176 (1) (2000) 131–142.
- [7] M. Niang, G. Luo, P. Schaetzel, Pervaporation separation of methyl *tert*-butyl ether/methanol mixtures using a high-performance blended membrane, *J. Appl. Polym. Sci.* 64 (1997) 875–882.
- [8] R.Y.M. Huang, R. Pal, G.Y. Moon, Pervaporation dehydration of aqueous ethanol and isopropanol mixtures through alginate/chitosan two-ply composite membranes supported by poly(vinylidene fluoride) porous membrane, *J. Membr. Sci.* 167 (2) (2000) 275–289.
- [9] A.A. Bhat, V.G. Pangarkar, Methanol-selective membranes for the pervaporative separation of methanol-toluene mixtures, *J. Membr. Sci.* 167 (2) (2000) 187–201.
- [10] C.J. Brinker, R. Sehgal, S.L. Hietala, R. Deshpande, D.M. Smith, D. Loy, C.S. Ashley, Sol-gel strategies for controlled porosity inorganic materials, *J. Membr. Sci.* 94 (1994) 85–102.
- [11] J.D. Jou, W. Yoshida, Y. Cohen, A novel ceramic-supported polymer membrane for pervaporation of dilute volatile organic compounds, *J. Membr. Sci.* 162 (1999) 269–284.
- [12] M. Goldman, D. Fraenkel, G. Levin, A zeolite/polymer membrane for separation of ethanol-water azeotrope, *J. Appl. Polym. Sci.* 37 (1989) 1791.
- [13] K.M. Song, W.H. Hong, Dehydration of ethanol and isopropanol using tubular type cellulose acetate membrane with ceramic support in pervaporation process, *J. Membr. Sci.* 123 (1997) 27–33.
- [14] Y. Zhu, R.G. Minet, T.T. Tsotsis, A continuous pervaporation membrane reactor for the study of esterification reactions using a composite polymeric/ceramic membrane, *Chem. Eng. Sci.* 51 (N17) (1996) 4103.
- [15] Y. Zhu, H. Chen, Pervaporation separation and pervaporation-esterification coupling using crosslinked PVA composite catalytic membranes on porous ceramic plate, *J. Membr. Sci.* 138 (1998) 123.
- [16] S. Ulutan, T. Nakagawa, Separability of ethanol and water mixtures through PTMSP-silica membranes in pervaporation, *J. Membr. Sci.* 143 (1998) 275.
- [17] S. Sakohara, F. Muramoto, T. Sakata, M. Asaeda, Separation of acetone/water mixture by thin acrylamide gel membrane prepared in pores of thin ceramic membrane, *J. Chem. Eng. Jpn.* 23 (1990) 40.
- [18] C. Leger, H.DeL. Lira, R. Paterson, Preparation and properties of surface modified ceramic membranes. II. Gas and liquid permeabilities of 5 nm alumina membranes modified by a monolayer of bound polydimethylsiloxane (PDMS) silicone oil, *J. Membr. Sci.* 120 (1996) 135–146.
- [19] W. Yoshida, R. Castro, J.D. Jou, Y. Cohen, Multilayer alkoxysilane silylation of oxide surfaces, *Langmuir* 17 (2001) 5882–5888.
- [20] R.P. Castro, H.G. Monbouquette, Y. Cohen, Shear-induced permeability changes in a polymer grafted silica membrane, *J. Membr. Sci.* 179 (1–2) (2000) 207–220.
- [21] J.D. Jou, Graft Polymerization and Application to Membrane Pervaporation, Ph.D. Dissertation, University of California Los Angeles, Los Angeles, 1998.
- [22] V. Nguyen, W. Yoshida, J.D. Jou, Y. Cohen, Kinetics of free-radical graft polymerization of 1-vinyl-2-pyrrolidone onto silica, *J. Polym. Sci. A V40* (2002) 26–42.
- [23] M. Rovira-Bru, F. Giralt, Y. Cohen, Protein adsorption onto zirconia modified with terminally grafted polyvinylpyrrolidone, *J. Coll. Interf. Sci.* 235 (1) (2001) 70–79.
- [24] X. Feng, R. Huang, Concentration polarization in pervaporation separation processes, *J. Membr. Sci.* 92 (1994) 201–208.
- [25] J.G. Wijmans, A.L. Athayde, R. Daniels, J.H. Ly, H.D. Kamaruddin, I. Pinnau, The role of boundary layers in the removal of volatile organic compounds from water by pervaporation, *J. Membr. Sci.* 109 (1996) 135.
- [26] B. Raghunath, S.T. Hwang, General treatment of liquid-phase boundary layer resistance in the pervaporation of dilute aqueous organics through tubular membranes, *J. Membr. Sci.* 75 (1992) 29.
- [27] J. Néel, P. Aptel, R. Clément, Basic aspects of pervaporation, *Desalination* 53 (1985) 297–326.

- [28] M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht, 1991.
- [29] E. Bode, M. Busse, K. Ruthenberg, Consideration on interface resistances in the process of permeation of dense membranes, *J. Membr. Sci.* 77 (1993) 69.
- [30] R. Faibish, Y. Cohen, Fouling-resistant ceramic-supported polymer membranes for ultrafiltration of oil-in-water microemulsions, *J. Membr. Sci.* 185 (2001) 129–143.
- [31] P. de Gennes, Conformations of polymers attached to an interface, *Macromolecules* 13 (1980) 1069.
- [32] B. Robertson, A. Zydney, Hindered protein diffusion in asymmetric ultrafiltration membranes with highly constricted pores, *J. Membr. Sci.* 49 (1990) 287–303.
- [33] S. Ray, S. Sawant, V. Pangarkar, Development of methanol selective membranes for separation of methanol–methyl tertiary butyl ether mixtures for pervaporation, *J. Appl. Polym. Sci.* V74 (2000) 1699–1701.
- [34] C. Gostoli, G.C. Sarti, Separation of liquid mixtures by membrane distillation, *J. Membr. Sci.* 41 (1989) 211–224.
- [35] A. Arce, J. Martinez-Ageitos, A. Soto, VLE measurements of binary mixtures of methanol, ethanol, 2-methoxy-2-methylpropane, and 2-methoxy-2-methylbutane at 101.32 kPa, *J. Chem. Eng. Data* 41 (1996) 718–723.
- [36] R.P. Castro, Y. Cohen, H.G. Monbouquette, The permeability behavior of poly(vinylpyrrolidone)-modified porous silica membranes, *J. Membr. Sci.* 84 (1–2) (1993) 151–160.
- [37] H.D. Kamaruddin, W. Koros, Sorption of methanol/MTBE and diffusion of methanol in 6FDA-ODA polyimide, *J. Polym. Sci. B* V38 (2000) 2254–2267.
- [38] J. Hauser, G.A. Reinhardt, F. Stumm, A. Heintz, Non-ideal solubility of liquid mixtures in poly(vinyl alcohol) and its influence on pervaporation, *J. Membr. Sci.* 47 (3) (1989) 261–276.