Solution Diffusion Modeling of a Composite PVA/Fumed Silica Ceramic Supported Membrane

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Abstract

The permeation behavior of thin films of fumed silica loaded polyvinyl alcohol (PVA) coated over tubular porous ceramic supports were investigated. Mullite based support enhances mechanical strength of PVA membranes. Effects of temperature, fumed silica loading and active layer thickness on the permeation behavior of the prepared membranes were studied in terms of permeation flux and water selectivity. Experimental data were obtained by dehydration of 90 wt. % ethanol using pervaporation (PV). The privileges of the synthesized membrane to its rivals, superior permeation flux (0.05 to 2.92 kg/m²h), water selectivity (3 to 180) and pervaporation separation index (PSI) (5.84 to 82.81) along with its low manufacturing costs, let it have a potential to be used for dehydrated ethanol production in industrial scale. A solution diffusion based mathematical model, including surface exchange and bulk diffusion resistances, was developed to predict permeation flux of both components as functions of temperature, fumed silica loading, active layer thickness and feed composition. Results showed that permeation flux enhances with temperature, fumed silica loading and diminishes with membrane thickness. Besides, increasing temperature and fumed silica loading reduces selectivity while increasing membrane thickness increases selectivity.

Keywords: Solution diffusion, Mathematical modeling, Pervaporation, Composite membranes.

1. Introduction

Ordinary distillation cannot be used to purify Ethanol–Water solution beyond 95.6 vol%. Further ethanol purification could be performed by desiccation using absorbents or azeotropic and extractive distillation. Notwithstanding successes these ethanol purification techniques achieved, they all have their own disadvantages. Azeotropic distillation performance diminishes by presence of third component as an impurity and has high energy consumption [1-5]. Pervaporation (PV) separation of azeotropic solutions such as Ethanol–Water has attracted more attentions due to its lower energy consumption and higher performance in recent decades. Despite the benefits of PV, it is not the most widely used process due to the lack of suitable membrane which simultaneously possesses high permeation flux, selectivity and durability in tough operating conditions [6, 7]. Zeolitic and polymeric membranes are two major types used for pervaporation dehydration of ethanol. Zeolite membranes have high selectivity, permeation flux and physical stability, but they are expensive, hard to prepare and sensitive to thermal tensions. On the other side, polymeric membranes are not sensitive to thermal tensions but unfortunately they exhibit low permeabilities and poor physical stabilities. Composite membrane of a polymeric active layer on a porous ceramic support gathers desirable characteristics of these two major types in one membrane [8-11]. Some studies on pervaporation performance of composite membranes prepared from a polymeric active layer on a ceramic support is summarized in Table 1.

Table 1: Composite membranes prepared from a polymeric active layer on a ceramic support
applied in pervaporation

Polymeric Active Layer	Ceramic Support	Feed	Reference
PDMS	ZrO ₂ /Al ₂ O ₃	Ethanol–Water	[12]
PDMS, PVA and chitosan	Commercialized macroporous ceramic supports	bio-fuels	[13]
PDMS	ZrO ₂ /Al ₂ O ₃	Ethanol–Water	[14]
PDMS	ZrO ₂ /Al ₂ O ₃	Ethanol–Water	[15]
Silicone rubber	Silicalite membranes	Ethanol–Water	[16]
PDMS	ceramic supports	n-octane/thiophene	[17]
PDMS	ceramic supports	Isopropanol–Water	[18]
PVAc and PVP	vinylsilane-modified alumina substrate	Methanol–Methyl tert-butyl ether (MTBE)	[19]
PVA	ZrO ₂ /Al ₂ O ₃	Ethyl acetate–Water	[20]
PVAc	porous tubular silica substrate	Trichloroethylene and chloroform–Water	[21]

Selectivity and permeation flux through polymeric membranes are strong functions of the membrane composition, preparation method, membrane thickness and operating conditions such as temperature, components partial pressure gradient across the membrane [6, 22]. As experimental evaluation of the membrane permeation behavior is time and money consuming, the need for an accurate and simple model is rising. Furthermore, a precise model plays a crucial rule in pervaporation scale up. Many researchers [23-30] attempted to model permeation behavior of polymeric membranes. Transport model through dense membranes are based on irreversible processes thermodynamics [31], Maxwell–Stefan theory [32] and Fick’s law [33]. Applying these models to pervaporation process and considering possible transport mechanisms result in five main categories of models including, solution-diffusion

model, pore flow model, thermodynamic vapor liquid equilibrium model, pseudo phase change solution–diffusion models and dusty gas model.

Considering solution–diffusion model which is the most widely accepted one for pervaporation; this process could be described in four sequential steps, feed side bulk diffusion, membranes feed side superficial sorption, diffusion through the membrane and membranes permeate side superficial desorption [34]. The main governing steps are feed side sorption and diffusion through the membrane. In pore flow model, the membrane was assumed as a microporous layer [35]. The third model is thermodynamic vapor liquid equilibrium model in which pervaporation process was described as vapor sorption and diffusion through the membrane [36]. It is assumed that the vapor is in equilibrium with feed. In addition, it is assumed that the sorption step is governed by Henry's law and the diffusion coefficient is constant. Due to these assumptions this model could only be used over small range of feed concentrations where the mentioned suppositions are acceptable. Extending the solution–diffusion model for vapor and liquid flows through the membrane, and considering the fact that phase change occurs gradually inside the membrane body, beside taking into account the pressure variation across the membrane, pseudophase–exchange solution–diffusion model developed which is similar to pore flow model [37]. Since the governing transport mechanism through zeolite and polymeric membranes are different, which could be attributed to the strong superficial forces inside the zeolite pores, Karger et al. proposed dusty gas model based on diffusion of a phase formed from adsorbed molecules, called intra – crystalline diffusion [38].

Pervaporation models usually have insufficiencies in predicting the pervaporation behavior of non–ideal systems such as alcohol–water–PVA mixtures. This issue could be attributed to the strong hydrogen bonding and swelling effects [39]. It even became more challenging to model a pervaporation system with PVA based composite membranes. Researchers tried to

develop new models and test existing ones, but despite their efforts there are still some weaknesses.

The purposes of this paper are studying preparation of a new, high performance PVA composite membrane and developing a simple and accurate solution–diffusion based model to explain permeation behavior of the polymeric–ceramic composite membranes. To fulfill this, a thin high–permselective polymeric layer was coated over a tubular porous ceramic support and the synthesized membranes were used in ethanol dehydration. PVA membranes have number of weaknesses, including low permeability and insufficient mechanical strength. To increase membrane permeability, it should be prepared as thin as possible and thus as mentioned, it is necessary to be supported mechanically. A porous ceramic MF membrane was used as support to enhance mechanical strength of thin PVA membrane and thus the PVA active layer could be prepared as thin as possible. Consequently, higher permeabilities and PSI values were obtained. In addition, tubular membrane configuration provides higher surface per volume and thus membrane module size for specific separation reduces [40-42].

2. Experiments

2.1. Materials

PVA (MW: 145,000) with a degree of hydrolysis of more than 98%, ethanol 96%, glutaraldehyde (GA, 50%) and hydrochloric acid were all purchased from Merck. Aerosil 200 was purchased from Evonika Co. with particle size of 12 nm, surface area of 200 m²/g, density of 50 gr/lit, and purity of higher than 99.9%. Kaolin powder was supplied by IRAN China Clay Industries Co. Deionized water, with a conductivity of 20 µS/cm, was produced in the laboratory using Permionics pilot plant (Vadodara, India).

2.2. Membrane preparation

Firstly, the kaolin clay was suspended in deionized water and allowed to settle inside its container. After removal of the upper clear water, a homogeneous mud was obtained. Tubular membranes were then prepared by extrusion of the aged uniformed mud. After an overnight drying of extrudates at room temperature, sintering was performed at 1200 °C for 3 h, with a heating and cooling rate of 1 °C/min. The prepared ceramic support had average pore radius of 318.2 nm and porosity of 30.45%. Complete preparation procedure and characterizations of mullite tubular microfiltration supports were reported in our previous work [43]. Homogeneous coating solution was obtained by dissolving PVA in deionized water at 90 °C and stirred for a while. It must be noted that duration of stirring depends on the solution concentration. Various amount of fumed silica were introduced to the solution. In situ crosslinking was performed by adding GA and hydrochloric acid to the solution and continuous stirring for 1 h. After homogenization and degasification, the solution was ready to be coated on the ceramic support. While the ceramic support was slowly (60 rpm) spun, the outer surface was coated with the PVA solution and dried. Afterward, the coating process was repeated again. After drying for 24 h at room temperature, complete drying and cross-linking were performed in an electric oven at 110 °C for 1 h. Membrane preparation procedure was described in details elsewhere [42].

2.3. Pervaporation Experiments

The prepared membranes were evaluated in PV dehydration of ethanol–water (90/10) mixture at different temperatures using a setup shown in Figure 1. The effective membrane area was 132 cm². The downstream pressure was controlled to be 12 mm Hg, while the feed pressure was atmospheric. To establish the steady-state conditions, before performing the PV measurements the membrane was swelled in the feed for 2 h. The permeate sample collected

in a cold trap was weighed to determine the permeation flux. To eliminate the experimental errors, each test was repeated three times, and the average results were reported.

Fig. 1: Schematic diagram of the PV apparatus

Permeation properties of the membranes were characterized by PV selectivity (α_{PV}), total permeation flux (J_P) and PV separation index (PSI) defined as the following equations, respectively [44, 45]:

$$\alpha_{PV} = \frac{y_A / y_B}{x_A / x_B} \quad (1)$$

$$J_P = \frac{Q}{A \times \Delta t} \quad (2)$$

$$PSI = J_P \times (\alpha_{PV} - 1) \quad (3)$$

Where y_A and y_B are mass fractions of water and ethanol in the permeate, respectively and x_A and x_B are mass fractions of water and ethanol in the feed, respectively. The permeate flux, J_P ($\text{kg}/\text{m}^2\text{h}$), was calculated using Q ; the permeate mass (kg), A ; the effective membrane area (m^2) and Δt ; the permeation time (h).

3. Model development

Basis of pervaporation is preferential permeation of liquid mixture components and removal of species in the permeate side as vapor using partial vacuum. A schematic pervaporation membrane and profiles of pressure, chemical potentials and activities of a binary solution are illustrated in Figure 2. Obviously, three phases of feed, membrane and permeate can be indicated. As clearly observed, chemical potentials of both components varies along the membrane.

Fig. 2: Schematic PV membrane and profiles of pressure, chemical potentials and activities of a binary solution

For feed and membrane phases, chemical potentials were formulated using equation (4) while equation (5) was used for permeate phase [46].

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i c_i) + v_i(p - p_{i_{sat}}) \quad (4)$$

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i c_i) + RT \ln\left(\frac{P}{p_{i_{sat}}}\right) \quad (5)$$

In these two equations, chemical potential of pure species i at saturation pressure of $p_{i_{sat}}$ is indicated as μ_i^0 . c_i and γ_i are molar concentration and activity coefficient of species i ,

respectively. Considering much higher absorption and desorption rates at the membrane interfaces compared to diffusion rate through the membrane, equilibrium at the either membrane interfaces can be assumed. Besides, it is assumed that pressure remains equal to the feed side pressure within the membrane and chemical potential through the membrane is expressed as concentration. Chemical potential gradient is driving force of species transported through the membrane, thus permeation flux can be formulated as equation (6).

$$J_i = -L_i \frac{d\mu_i}{dx} \quad (6)$$

By introducing chemical potential into equations (4) and (5), and using equation (6), J_i can be written as:

$$J_i = \frac{D_i(c_{i_{o(m)}} - c_{i_{l(m)}})}{l} \quad (7)$$

Molar concentration of species i in the membrane at the feed side interface ($c_{i_{o(m)}}$) and the permeate side interface ($c_{i_{l(m)}}$) can be calculated using equations (8) and (9), respectively. In $c_{i_{o(m)}}$ and $c_{i_{l(m)}}$, o and l stand for feed and permeate sides, respectively. These equations are based on the equal chemical potential of each species in the feed and permeate solutions with the chemical potential of that species in the membrane body at the adjacent interface [46].

$$c_{i_{o(m)}} = \frac{\gamma_{i_o} c_{i_o}}{\gamma_{i_{o(m)}}} = K_i \times c_{i_o} \quad (8)$$

$$c_{i_{l(m)}} = \frac{\gamma_{i_l} c_{i_o}}{\gamma_{i_{o(m)}}} \times \frac{p_l}{p_{i_{sat}}} = \frac{\gamma_{i_l}}{\gamma_{i_{o(m)}}} \times \frac{p_{i_l}}{p_{i_{sat}}} = K_i^G \cdot p_{i_l} \quad (9)$$

In these equations, K_i and K_i^G are liquid and gas phase sorption coefficients of species i , respectively. Considering a hypothetical vapor in equilibrium with feed solution, equation (8) can be written as;

$$c_{i_{o(m)}} = \frac{\gamma_{i_o}^G}{\gamma_{i_{o(m)}}} \times \frac{p_{i_o}}{p_{i_{sat}}} = K_i^G \cdot p_{i_o} \quad (10)$$

Combining equation (7), (9) and (10) and considering $P_i^G = K_i^G \cdot D_i$ gives

$$J_i = \frac{P_i^G}{l} (p_{i_o} - p_{i_l}) = \frac{P_i^G}{l} \left(\frac{c_{i_o} \cdot \gamma_{i_o}^L \cdot P_{i_{sat}}}{\gamma_{i_o}^G} - p_{i_l} \right) = \frac{P_i^G}{l} (c_{i_o} \cdot H_i - p_{i_l}) \quad (11)$$

Equation (11) is the basic solution diffusion model which governs permeation behavior of a dense neat polymeric membrane. A membrane consists of a single neat polymer acts like a single phase which is in equilibrium with feed phase and permeate phase as assumed in solution diffusion basis assumptions [46]. However, for a membrane which is not a single phase, conditions are different. Presence of fumed silica in the polymeric membrane body and its hydrophilic nature result in higher water fraction in the polymer layer adjacent to these particles, and this leads to formation of much more swollen layer of polymer around the fumed silica particles during pervaporation tests due to tremendous water absorbed by these particles. Presence of these highly swollen regions throughout the membrane body affects its permeation behavior and cannot accurately model using solution diffusion theory [41, 47, 48]. Therefore, some modifications should be performed on the basic solution diffusion model. Since these two phases present both on the membrane surface and inside the membrane body, sorption and diffusion properties of the membrane are affected by their intrinsic properties. Clearly, sorption and diffusion properties of the whole composite membrane should be functions of amounts of these two phases and also the fumed silica loading. Two main parameters are affected by fumed silica loading, H_i ; Henry law coefficient and P_i^G ; permeability of species i . To introduce effects of fumed silica loading on these two, two contribution coefficients were defined. Contribution coefficient of the extremely swollen polymer interface in Henry law coefficient was introduced to the model as

$$CC \cdot H_{Swl};$$

$$cc_{H_{Swl}} = (X_{FS})^a \quad (12)$$

And contribution coefficient of the extremely swollen polymer body in permeability was introduced to the model as $cc_{P_{Swl}}$;

$$cc_{P_{Swl}} = (X_{FS})^b \quad (13)$$

In equations (12) and (13), X_{FS} is weight fraction of fumed silica in the membrane and a and b are constants.

Sum of the main polymer and extremely swollen polymer contribution coefficients in both Henry law coefficient and permeability should be one. Thus, contribution coefficients of the common polymer should be:

$$cc_{H_{com}} = 1 - (X_{FS})^a \quad (14)$$

$$cc_{P_{com}} = 1 - (X_{FS})^b \quad (15)$$

Where $cc_{H_{com}}$ and $cc_{P_{com}}$ are contribution coefficients of the common polymer phase in Henry law coefficient and permeability of the membrane respectively. Now, Henry law coefficient and permeability of the membrane could be formulated as equation (16) and (17) respectively.

$$H_i = cc_{H_{com}} \times H_{i_{com}} + cc_{H_{Swl}} \times H_{i_{Swl}} \quad (16)$$

$$P_i^G = cc_{P_{com}} \times P_{i_{com}}^G + cc_{P_{Swl}} \times P_{i_{Swl}}^G \quad (17)$$

Equations (18) and (19) show Henry law coefficient and permeability which were defined to have Arrhenius temperature functionality [46].

$$H_{i_X} = H_{0i_X} \times e^{\frac{-E_{H,iX}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)} \quad (18)$$

$$P_{i_X}^G = P_{0i_X}^G \times e^{\frac{-E_{P,iX}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)} \quad (19)$$

Where H_{0i_x} and $P_{0i_x}^G$ are Henry law coefficient and permeability of species i in the extremely swollen polymer ($X = Swl$) or common polymer phase ($X = com$). E_{H,i_x} and E_{P,i_x} are activation energies of sorption and permeation of component i in the extremely swelled polymer ($x = Swl$) or common polymer phase ($x = com$).

In addition to consider effects of fumed silica content on membrane permeation performance model as contribution coefficients in permeability and Henry law coefficient, its effects was also introduced using a modified thickness called membrane effective thickness as shown in equation (20).

$$l_{effective} = l \times (1 + c \times X_{FS}^d) \quad (20)$$

In this equation, c and d are constants which are determined using the model. Therefore the modified model now predicts the permeation flux for any species based on the following equation;

$$J_i = \frac{P_i^G}{l_{effective}} (c_{i_o} \cdot H_i - p_{i_i}) \quad (21)$$

4. Results and discussion

4.1. Characterization

Presence of specific chemical groups in the PVA active layer of the composite membrane was studied using Fourier Transform Infrared Spectroscopy (FTIR). The active layer FTIR spectra, as presented in Figure 3, were obtained in the range of wavenumber from 4000 to 600 cm^{-1} during 16 scans (Bruker Equinox 55, Bruker Optics Inc., Billerica, MA, USA).

Fig. 3: non-crosslinked (dashed Line) and crosslinked (full Line) PVA layer FTIR spectra

As clearly observed, O-H group of the intermolecular and intramolecular hydrogen bonds ($3550\text{--}3200\text{ cm}^{-1}$) and C-H group of the alkyl groups ($3000\text{--}2840\text{ cm}^{-1}$) are present in the synthetic PVA layer. Reaction of PVA in the presence of GA forms acetal bridges which lead to peak intensity reduction of the crosslinked PVA O-H group compared with that of the non-crosslinked PVA. SEM micrographs of the composite ceramic-supported PVA membranes are shown in Figure 4.

Fig. 4: SEM micrographs of membrane surface (a), cross section (b) and vast surface area (c)

From the SEM micrographs, it can be clearly observed that the PVA layers are defect free. More details of the membrane characterization is available elsewhere [42].

4.2. Model validation

Nonlinear regression method was used to find the developed model parameters. Error minimization was performed while root mean square deviation (RMSD) was the objective

function. Furthermore, square of the Pearson product moment correlation coefficient (R^2) was calculated. Parity plot between experimental and calculated data is presented in Figure 5.

Fig. 5: Parity plot between experimental and calculated permeation flux data

As illustrated, a rather good agreement was established between experimental and calculated data. Values of activation energies, pre-exponential coefficients and contribution coefficients constants are summarized in Table 2.

Table 2: Model parameters

parameters	Calculated values for	
	Water	Ethanol
$P_{0i_{com}}^G$	6.42E-09	3.85E-10
$E_{Pj_{com}}$	-9.63E+03	-5.64E+04
$H_{0i_{com}}$	8.58E-01	1.45E-02
$E_{Hj_{com}}$	3.67E+04	1.23E+05
$P_{0i_{Swl}}^G$	6.00E-07	9.08E-08
$E_{Pj_{Swl}}$	-8.91E+05	-1.88E+05
$H_{0i_{Swl}}$	2.94E+03	7.61E+02
$E_{Hj_{Swl}}$	1.70E+04	1.40E+05
a	1.87E+00	1.56E-01
b	1.87E+00	2.40E+00
c	3.01E+04	3.15E+01
d	3.60E+00	7.53E-01

4.3. Pervaporation

The modified model was based on the solution–diffusion model which describes permeation through membranes by means of a thermodynamically based sorption and kinetically based diffusion. In the following parts, effects of membrane thickness, fumed silica loading and temperature on solution and diffusion terms in the proposed model are investigated.

4.3.1. Effect of PVA layer thickness

As seen in Figure 6, higher selectivity is achievable in pervaporation process using thicker active layer however, Figure 7 clearly illustrates that increasing membrane thickness diminishes permeation flux. This phenomenon can be related to the diffusion portion of the separation mechanism. As clearly observed in Equation (21), permeation flux of species is

reversely proportional to membrane thickness and increasing membrane thickness results in lower permeation flux of both ethanol and water. The thicker active layer means the membrane is more defect free with less defects and this restricts ethanol permeation. This results in higher diffusion resistance establish for ethanol compared to water and in the other words selectivity increases which is in agreement with experimental results as revealed in Figure 6, however in the developed model, which is based on the solution diffusion, the membrane is assumed to be ideal and thus selectivity does not depend on membrane thickness and varies with other parameters as demonstrated in Figures 6 to 9.

Fig. 6: Effect of membrane active layer thickness on experimental and model predicted water selectivity of pure PVA membrane (a), and 2 wt.% silica fumed loaded PVA membrane (b)

Fig. 7: Effect of membrane active layer thickness on experimental and model predicted permeation flux of pure PVA membrane (a), and 2 wt.% silica fumed loaded PVA membrane (b)

4.3.2. Effect of temperature

Equations (18) and (19) formulate temperature dependencies of Henry law coefficient and permeability of species i in different phases. The model proposes an Arrhenius temperature functionality of these two. Using the predicted model constants, increasing temperature reduces both water and ethanol permeability in both common and swollen polymeric

portions. However, water permeability through common polymer and through swollen polymer are the least and the most temperature dependent permeabilities.

Water and ethanol Henry law coefficients also demonstrate an Arrhenius functionality of temperature. Henry law coefficients of water and ethanol related to the common polymer phase were calculated to be somehow equal at 30 °C ($H_{E_{com}} = 0.7 \times H_{W_{com}}$) [49] and both increase as temperature rises. However, due to higher temperature dependency of ethanol Henry law coefficient, at temperatures around 60 °C Henry law coefficient of ethanol is about 16 times greater than that of water. In the swollen polymer portion, Henry law coefficient of water is always smaller than that of ethanol and also its temperature dependency is weaker, thus by increasing temperature Henry law coefficient of ethanol in swollen polymer becomes much more bigger than that of water.

Considering equation (17) which predicts water and ethanol permeabilities through the whole body of the membrane which consists of common and swollen polymer portions, temperature dependencies of $P_{i_{com}}$ and $P_{i_{swl}}$, and model constants were evaluated. The model predicts that permeability of water through the whole body of the membrane decreases almost linearly by increasing temperature. However, the model predicted that permeability of ethanol decreases asymptotically and increasing temperature above 50 °C does not affect ethanol permeability significantly.

The model predicts that Henry law coefficients of both water and ethanol increase by rising temperature. It should be noted that water Henry law coefficient like water permeability is almost a linear function of temperature, while ethanol Henry law coefficient at temperature below 50 °C shows asymptotic behavior.

Figures 8 and 9 illustrate effects of temperature on experimental and model predicted permeation flux and selectivity of neat and fumed silica loaded PVA membranes.

Fig. 8: Effects of fumed silica loading and temperature on experimental and model predicted water selectivity of PVA membranes with 10 μm (a), 15 μm (b) and 20 μm (c)

Fig. 9: Effects of fumed silica loading and temperature on experimental and model predicted permeation flux of PVA membranes with 10 μm (a), 15 μm (b) and 20 μm (c)

Increasing temperature enhances permeation flux, while diminishes membrane selectivity. The developed model predicts total permeation flux from water and ethanol permeation fluxes. As predicted by the model, water and ethanol permeation fluxes in common polymeric portion increases with increasing temperature, while their fluxes through swollen polymeric portion of the membrane behave differently. By increasing temperature, ethanol permeation flux increases, while water permeation flux through the membrane increases within the temperature range for membranes containing 0, 2, 4 and 6 wt.% of fumed silica, however for membrane loaded with 8 wt.% of fumed silica, water permeation flux increases up to its maximum value at about 45 °C and afterward, decreases significantly.

4.3.3. Effect of fumed Silica loading

From the data presented in Figures 8 and 9, it is observed that permeation flux increases, and membrane selectivity decreases with increasing fumed silica loading throughout the studied temperature range. Permeability and Henry law coefficients of water and ethanol in common and swollen polymeric portions of the membrane are independent on fumed silica loading. However, permeability and Henry law coefficients of both species through the membrane are related to fumed silica loading via equations (16) and (17). Water permeability varies less than 1% when fumed silica loading increases from zero to 8 wt.%. However, ethanol permeability significantly depends in fumed silica loading and decreases on 70% by increasing fumed silica loading from zero to 8 wt.%. On the other hand, Henry law coefficients of both species increase with increasing fumed silica loading. Henry law coefficient of water increases about 10 times, while that of ethanol increases about 360 times by increasing fumed silica loading from zero to 8 wt.%. In addition, modified thickness increases about 5 times for both components and this can be related to membrane swelling increment by increasing fumed silica loading [50].

By increasing fumed silica loading, ethanol permeation flux increases in both common and swollen portions of the membrane. Water permeation fluxes in these two portions have maximum and decrease afterward unless for the swollen portion at low temperatures which increases and never decreases throughout the experimental temperature range studied.

5. Conclusion

A composite membrane consists of a thin hydrophilic fumed silica loaded PVA layer coated on a tubular porous ceramic support was prepared. Prepared membranes were evaluated using ethanol pervaporation dehydration. Hydrophilic and cross-linked structure of the synthesized membranes resulted in high permeation flux and selectivity. A solution diffusion based mathematical model was developed to predict water and ethanol permeation fluxes through the membrane. Using this model, permeation flux and selectivity of different composite membranes operated at different conditions were evaluated. The distinctive features of the developed model can be summarized as follows:

- the model can predict permeation flux and selectivity with good accuracy (RMSE= 0.24)
- the model is an explicit function of all operating parameters
- the model can predict effects of fumed silica loading

The results illustrate that by increasing temperature, water and ethanol permeabilities of the common and extremely swollen polymer and thus the entire permeability decrease while the Henry law coefficient of water and ethanol increase. Water and ethanol vapor pressures also increase with increasing temperature. Increasing water and ethanol fluxes can be related to the dominant effects of their Henry law coefficient and vapor pressures increment compared to their permeabilities. However, based on the model predictions, at high temperature, when the composite membrane is highly loaded with fumed silica, the dominant affective

parameter changes to be water permeability and this leads to a maximum water permeation flux.

Increasing fumed silica loading decreases permeabilities, while increases Henry law coefficients of water and ethanol and the effective thickness of the membrane. Increasing $l_{effective}$ and decreasing P_{Water}^G and $P_{Ethanol}^G$ reversely affect permeation fluxes of species while increasing H_{Water}^G and $H_{Ethanol}^G$ enhance permeation fluxes. As the dominant effects are increment of water and ethanol Henry law coefficients permeation fluxes of both components increase with increasing fumed silica loading. It should be noted that by increasing temperature, the superiority of H_{Water}^G and $H_{Ethanol}^G$ diminishes and undesirable effects of $l_{effective}$ increment and P_{Water}^G and $P_{Ethanol}^G$ reduction, which all lead to lower permeation performance, become dominant. Therefore, water permeation flux exhibits a maximum value at 6 wt.% fumed silica loading.

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