

# Pervaporation Performance of Ag-PVA Nanocomposite Membranes: Effect of Operating Temperature

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## Abstract

The features of pervaporation are continuously improved with the production of more and more efficient membranes. In our present study, silver nanoparticles are in-situ generated in a poly (vinyl alcohol) using solution-casting in order to enhance its capability for pervaporation. The membrane is tested on the case study of ethanol dehydration by pervaporation. Effect of silver content on the pervaporation separation index and the enrichment factor of the membrane at 15 % mass water at 40 °C are reported. Pervaporation data for nanocomposite membranes show around 100 % increase in the water permeance values while the intrinsic selectivity decreases that is typical for pervaporation membranes. The water permeances of original crosslinked PVA membrane and the 2.5 % silver loaded PVA membrane are 26.65 and 70.45 (g/m<sup>2</sup>.kPa.h), respectively. The values of total flux are closely related to water flux, showing that membranes could be successfully assigned to separate water from ethanol even at the azeotropic point. The influence of temperature on the efficiency of the pervaporation process, permeation parameter and diffusion coefficient of the feed component is also discussed. The negative heat of sorption ( $\Delta H_s$ ) values calculated on the basis of the estimated Arrhenius activation energy values indicates that the sorption process is controlled by Langmuir's mode. Our results show that the 0.5 mass% silver loaded poly (vinyl alcohol) membrane exhibits excellent PV performance.

## Keywords

poly (vinyl alcohol), silver nanoparticles, pervaporation, ethanol-water system

## 1 Introduction

It is well known that bio-fuels including bio-ethanol have several environmental benefits. Among them, absolute ethanol containing 99.5 % (by mass) or more ethanol is in the greatest demand [1]. Ethanol was used to be dehydrated by the distillation separation process. However, high costs, low productivity are recognized as challenging problems leading to a crucial disadvantage and result in increasing the costs of the process essentially the industrial production of highly concentrated bioethanol [2, 3]. Pervaporation technology (PV) has received much attention due to its potential in energy efficiency, simplicity, economically friendly and high efficiency of separation [4-6].

Pervaporation has been demonstrated as an efficient membrane process for ethanol dehydration and as a promising alternative for conventional energy-intensive technologies

such as distillation [7]. Poly(vinyl alcohol) (PVA) has been widely used for pervaporation process owing to its high hydrophilicity, film-forming ability, resistance to organic pollution, non-toxicity, biodegradable and chemical/thermal stability. PVA is a water-soluble synthesis polymer with -OH groups on its backbone, which crucially provides distinguishing sorption and diffusion of water in it and facilitates its modification [8, 9]. On the other hand, Silver nanoparticles represent an auspicious functional filler because of their unique and tunable properties [10].

The aim of this paper is to investigate the effect of feed temperature on dehydration performance of the prepared Ag-PVA nanocomposite membrane for 85 wt% ethanol at 40, 50, and 60 °C. Effect of silver content on diffusion and several pervaporation properties was reported.

Activation energies of permeation, diffusion, and heat of sorption  $\Delta H_s$  are evaluated and the results are discussed.

## 2 Material and methods

Nanocomposite membranes are prepared in one step polyol process reaction [11-14]. In brief, different amount of silver nitrate (99 %, MW 196.88, Molar chemicals, Hungary) based solutions are dropped wisely to equal amounts of PVA solution. The PVA solution is 5 wt% and prepared by dissolving PVA (85000-124000 g/mol and 99 % + hydrolyzed, Sigma-Aldrich, Germany) powder in distilled water at 90 °C under stirring condition until a homogeneous solution was formed. The mixture solution is heated for 1 h at 70-80 °C under continuous stirring, then subjected to an ultrasonic bath for 45 min. Then the final solutions are left over the night so that it cools down and gets rid of air bubbles. The solutions are then poured onto clean Petri dishes and dried in air for 48 h before annealing at 60 °C in an oven for 24 h. The membranes are entitled M0, M0.5, M1, M1.5, M2, M2.5 according to the silver nitrate concentration with respect to PVA.

### 2.1 Swelling degree measurements

Swelling measurements were done by immersing the dry weighted membranes in a different water-ethanol mixture at 30 °C for 24 h to achieve equilibrium. Therefore, the membranes were taken out and dried carefully with tissue paper to remove the surface solution and weighted as fast as possible and immersed in the mixture solutions again. Each membrane was measured three times and the average was taken as the final result. The degree of swelling percentage is calculated by Eq. (1):

$$DS\% = ((M_s - M_d) / M_d) \times 100. \quad (1)$$

### 2.2 Pervaporation Experiments

Pervaporation dehydration experiments are carried out using a P-28 membrane unit (CM-Celfa AG Company, Switzerland) with the effective membrane area 28.0 cm<sup>2</sup>. The pressure in the permeate side is maintained 5.4 mbar using a vacuum pump. All the membranes are swelled in the feed for 2 h before the PV test, and the permeate is collected in cold traps immersed in liquid nitrogen. The concentration of the feed and permeate is measured by the RA-620 (accuracy  $\pm 0.00002$ , KEM Kyoto Electronics, Japan) refractometer. Separation performances of the membranes can be calculated on the basis of total flux ( $J$ ) and separation factor ( $\alpha_{PV}$ ):

$$J = W / (A * t) \quad (2)$$

$$\alpha_{PV} = (P_w / P_{eth}) / (F_w / F_{eth}) \quad (3)$$

where  $J$  is the flux;  $W$  is the collected permeate mass (kg);  $A$  is the effective area of the membrane (m<sup>2</sup>), and  $t$  is the permeation time (h),  $P_w$ ,  $P_{eth}$  is the weight fraction of water and ethanol in the permeate mixture and,  $F_w$ ,  $F_{eth}$  are the mass fraction of water and ethanol in the feed mixture, respectively. The permeance ( $Q_i$ ) and selectivity ( $\beta$ ) can be calculated as follows:

$$Q_i = P_i / L = J_i / (x_i \gamma_i P_{i,feed}^\circ - y_i P_{permeate}) \quad (4)$$

$$\beta = Q_{water} / Q_{ethanol} \quad (5)$$

where  $P_i$  is the permeability of component  $i$  through the membrane,  $L$  is the membrane thickness (m),  $J_i$  is the mass flux of component  $i$  (g/m<sup>2</sup>h),  $x_i$  is the mole fraction of component  $i$  in the feed liquid,  $\gamma_i$  is the liquid activity coefficient of component  $i$  in the feed,  $P_{i,feed}^\circ$  is the pure component  $i$  feed vapor pressure under feed temperature (kPa) and  $y_i$  is the mole fraction of component  $i$  in the permeate,  $P_{permeate}$  is the pressure in the permeate side of the membrane (kPa).

## 3 Results and discussion

### 3.1 Effect of silver content on pervaporation properties

Generation of silver nanoparticles with different content into PVA strongly affects membrane properties. Fig. 1 summarizes the flux and separation factor data for the pervaporation separation of the ethanol/water (85/15, w/w) feed mixture at 40 °C as a function of silver nanoparticle contents in the membranes. The plot shows a dramatic permeation flux increase for the M2.5 membrane (0.15 kg/m<sup>2</sup>.h), however, the virgin membrane's one is (0.052 kg/m<sup>2</sup>.h). It implies that the three-fold increase of

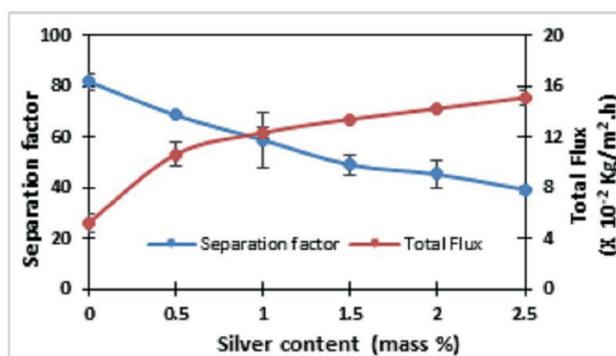


Fig. 1 Effect of silver nanoparticle content on pervaporation flux and separation factor, 15 wt% water in feed at 40 °C

flux sets the trend that continues with the increase of the silver nanoparticle content in the membrane. The separation factor, on the other hand, decreases from 81.7 to 39.1.

The swelling study is carried out under the same conditions as the pervaporation study. Fig. 2 shows a plot of the swelling degree as a function of silver nanoparticle content. It can be seen that the swelling degree increases together with increasing the silver nanoparticles content. This indicates that the in-situ generation of the silver nanoparticles in the PVA matrix increases the affinity of the membrane toward the water due to the interaction of –OH groups with the AgNPs and the formation of hydrogen bonds [15]. Additionally, it demonstrates that the PVA crystallinity declines due to the sufficient receding in the PVA matrix crystalline region [16]. This manifests the increase the hydrophilicity upon the incorporation of AgNPs [17]. Subsequently, this promotes the permeation flux of the AgNPs nanocomposite membranes of both water and ethanol through the membrane while the separation factor decreases due to the decrease in the selectivity of water [15, 18].

To estimate the effect of nanoparticle generation on the pervaporation performance, the component fluxes of the feed component as functions of the silver nanoparticle content are investigated and the results are shown in Fig. 3(A).

It reveals that the values of total flux and water flux are close to each other, indicating that membranes can be effectively used to break the azeotropic point of ethanol-water. Additionally, according to Baker et al. [19], permeance and selectivity are more suitable to understand the real membrane intrinsic properties as shown in Fig. 3(B) and obtained from Eq. (4) and (5), respectively.

### 3.2 Determination of diffusion coefficient

The diffusion coefficient is an important factor to estimate the diffusion of individual components through the

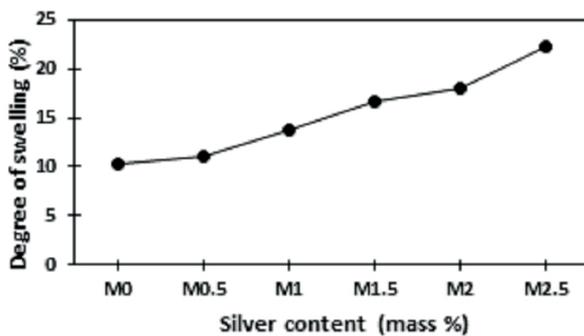


Fig. 2 Nanocomposite membranes swelling behavior at 15 wt% water in feed at 30 °C

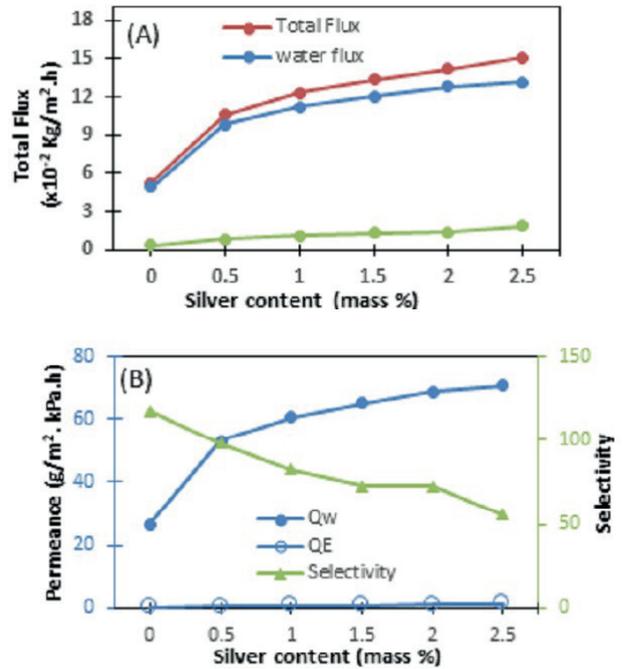


Fig. 3 Effect of silver content on total flux and individual fluxes (A), pervaporation permeance (B) of water and ethanol nanoparticles content at 15 % mass of water in the feed at 40 °C

membranes. The individual flux of component *i* through the membrane can be expressed by Fick's law Eq. (6) as:

$$J_i = -D_i(dC_i/dx) \tag{6}$$

where,  $J_i$ ,  $D_i$ , and  $C_i$  are the permeation flux (kg/m<sup>2</sup>s), the diffusion coefficient (m<sup>2</sup>/s) and the concentration (kg/m<sup>3</sup>) of component *i* in the membranes. For the sake of simplicity, it is assumed that the concentration profile along the diffusion length is linear and therefore, concentration-averaged diffusion coefficient  $D_i$  can be calculated with the following modified equation (Eq. (7)) where  $\delta$  is membrane thickness [20, 21].

$$D_i = (J_i\delta)/C_i. \tag{7}$$

From Fig. 4, it is observed that the diffusion coefficients of both water and ethanol are increasing with increasing the silver content in the nanocomposite membrane. However, compared to water, the magnitude of diffusion coefficients of ethanol is negligible but it slightly increases with the silver content. This suggests that the elaborated membranes are highly selective towards water. These results are presented in Fig. 3(A) and (B). Moreover, the effect of temperature on the diffusion coefficient of both water and ethanol of 15 wt% H<sub>2</sub>O in ethanol are evaluated and presented in Table 1.

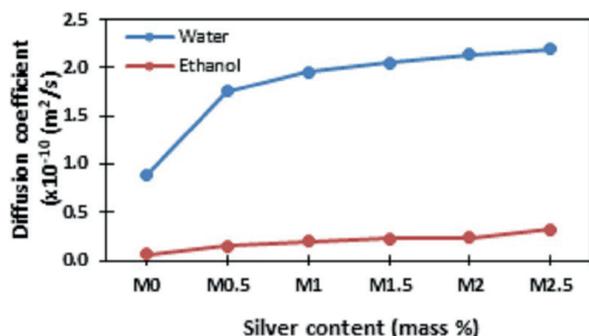


Fig. 4 Silver content dependence of concentration-averaged diffusion coefficient for 15 wt% feed water at 40 °C

### 3.3 Effect of temperature on pervaporation properties

Despite the membrane properties and characteristic, permeates are the main parameters on a PV membrane representation. The process operating conditions such as operating temperature can show high influence on the separation performances. The temperature is a dominant factor for the pervaporation process since changing the temperature can influence solubility and diffusivity of compounds within the membrane [1]. The effect of operating temperature on pervaporation properties for ethanol/water mixtures at 15 mass% of water in the feed is shown in Fig. 5(A) and (B). It is noticed that with increasing temperature the permeation rate increases while the selectivity decreases for every membrane.

These results can be attributed to the enhancement of permeation for both feed components due to the plasticizing effect of water on the membrane. On the other hand, by rising the temperature results in a considerable increase of the vapor pressure difference between the membrane sides which leads to improve the driving force and thus the permeation of water across the membrane. Both reasons result in increasing the total permeation flux while decreasing the selectivity. The temperature dependence of

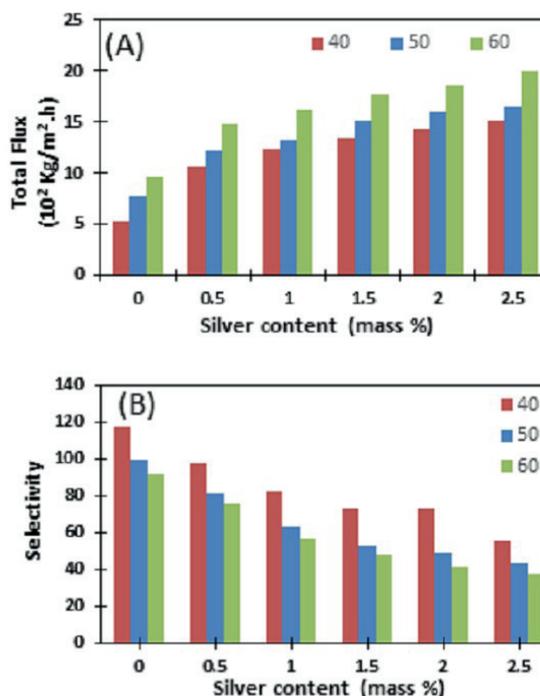


Fig. 5 Influence of feed temperature on Pervaporation performance

permeation and diffusion can be properly expressed by an Arrhenius type equation (Eq. (8)):

$$X = X_0 * \exp((-E_x)/RT) \quad (8)$$

where  $E_x$  represents apparent activation energy for permeation or diffusion depending on the transport process under consideration and  $RT$  is the usual energy term. Arrhenius plots for temperature dependence on permeation flux and diffusion are shown in Fig. 6(A) and (B), respectively. It can be seen that there is a linear trend for both the permeation flux and diffusion. From the least-squares fits of these linear plots, we can estimate the activation energies for total permeation ( $E_p$ ) and total diffusion ( $E_D$ ). Similarly, the activation energies for permeation of water ( $E_{p,w}$ ) and ethanol ( $E_{p,E}$ ), and diffusion of water ( $E_{D,w}$ ) are estimated. The results are

Table 1 Effects of temperature on diffusion coefficient in pervaporation of 15 wt% H<sub>2</sub>O in ethanol

		D Water (x10 <sup>-10</sup> m <sup>2</sup> /s)					
T [°C]		M0	M0.5	M1	M1.5	M2	M2.5
40		0.893	1.755	1.960	2.056	2.135	2.192
50		1.290	2.009	2.093	2.290	2.380	2.386
60		1.613	2.433	2.563	2.718	2.779	2.894
		D Ethanol (x10 <sup>-10</sup> m <sup>2</sup> /s)					
T [°C]		M0	M0.5	M1	M1.5	M2	M2.5
40		0.062	0.145	0.192	0.228	0.237	0.317
50		0.094	0.179	0.237	0.310	0.346	0.392
60		0.119	0.217	0.305	0.380	0.454	0.520

presented in Table 2. Using these activation energy values in Table 2, the heat of sorption can be calculated by Eq. (9) [22]:

$$\Delta H_s = E_p - E_D \tag{9}$$

From Table 2, it is observed that the activation energy values of water ( $E_{p,w}$ ) are apparently lower than those of ethanol ( $E_{p,E}$ ), suggesting that membranes developed here have higher separation efficiency towards water. Additionally, the activation energy values for water permeation and total permeation ( $E_p$ ) are closed to each other. It is also noticed that as the silver content is increased in membrane M0.5 to M2.5, the difference between the water and total permeation values also increase, indicating that the selectivity of the membranes decreases with

increasing silver content. However, the activation energy of both permeation ( $E_p$ ) and diffusion ( $E_D$ ) are decreasing with increasing the silver content but they are close to each other, indicating that both permeation and diffusion contribute almost equally to the pervaporation process.

The negative heat of sorption  $\Delta H_s$  values indicates that the sorption process is controlled by Langmuir's mode. Finally, to evaluate the overall performance of the pervaporation dehydration process of nanocomposite membranes, the pervaporation separation index (PSI) and Enrichment factor are used. For large-scale design as a guideline the membrane performance is calculated applying Eq. (10) and (11) [23]. The results are shown in Fig. 7.

$$PSI = J * (\alpha_{PV} - 1) \tag{10}$$

$$\text{Enrichment factor} = Y_w / X_w \tag{11}$$

For the sake of comparison, Table 3 displays results of the separation performance for ethanol dehydration of Ag-PVA membranes produced in this work and PVA-based hybrid membranes found in the literature. It is apparent that the Ag-PVA nanocomposite membranes exhibit in most cases higher permeation flux as well as a more satisfactory separation factor values than those of

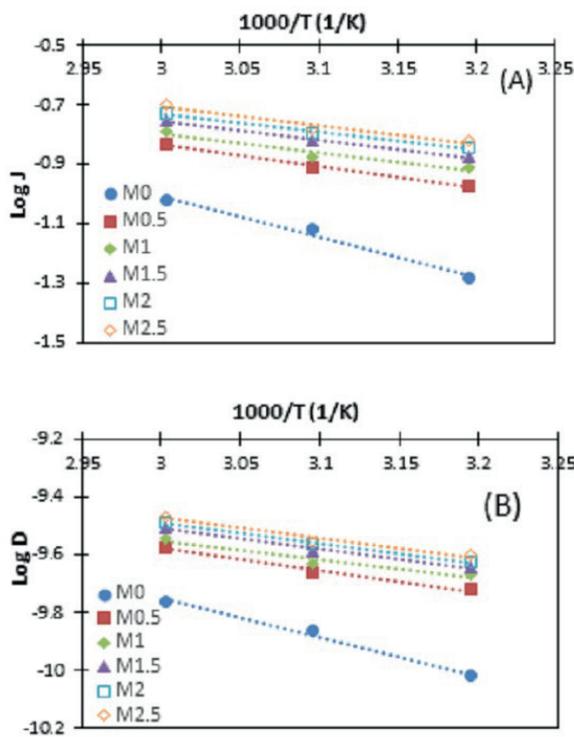


Fig. 6 Variation of log J (A), log D (B) with temperature for PVA and Ag-PVA nanocomposites composite membranes at 15 mass% of water in the feed

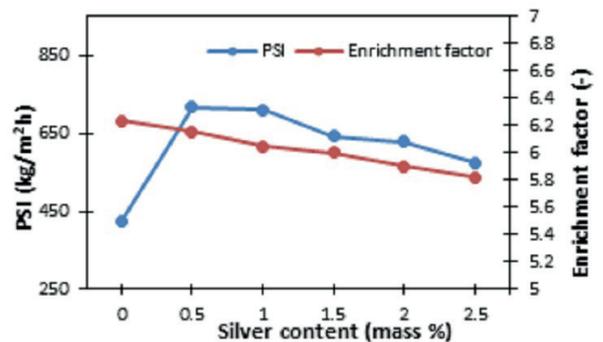


Fig. 7 Variation of pervaporation separation index PSI and Enrichment factor with silver content at feed concentration 85 % ethanol at 40 °C

Table 2 Arrhenius Activation Parameters for Permeation and Diffusion and heat of sorption

Parameters (kJ/mol)	M0	M0.5	M1	M1.5	M2	M2.5
$E_p$	11.33	6.14	5.08	5.28	5.10	5.28
$E_{p,w}$	11.25	6.02	4.72	4.79	4.23	4.72
$E_{p,E}$	12.49	7.48	8.40	9.17	11.54	8.44
$E_D$	11.41	6.25	5.37	5.72	5.82	5.77
$E_{D,w}$	11.16	6.08	5.01	5.24	4.95	5.20
$\Delta H_s$	-0.08	-0.11	-0.29	-0.44	-0.73	-0.49

**Table 3** Comparison of PV performance using different membranes

Membrane	Temperature (°C)	Feed water content (wt%)	Flux (g/m <sup>2</sup> h)	Separation factor	Ref.
PVA/fumed silica	30	10	40	180	[24]
0.3rGO/PVA	50	20	56	51.2	[25]
PVA/APTEOS	50	15	90	88	[26]
Modified Chitosan	70	10	80	52	[27]
Cellulose acetate	60	4	200	5.9	[8]
Ag-PVA (M0.5)	40	15	106.2	86.5	This study
Ag-PVA (M2.5)			150	39.5	

the PVA based hybrid membranes found in the literature. In contrast with other preparation methods, the blending of nanoparticles in the PVA matrix, that is, where AgNPs nanoparticles with cross-linking and filling functions are in-situ generated and homogeneously dispersed within the PVA matrix, creates a comparable separation performance for the dehydration of ethanol.

#### 4 Conclusions

Pervaporation data of water-ethanol mixtures of 15 % mass water in the feed at three different temperatures are applied to study and evaluate the Ag-PVA nanocomposite membranes. Increasing the silver content leads to a simultaneous increase in the total permeation flux, individual fluxes and permeance of water and ethanol through the membrane but the separation factor and selectivity decrease as usual in the case of pervaporation membranes. The experimental data show that the total flux and water flux are close to each other for all the membranes concluding that the prepared membranes are highly selective towards water. Operating temperature show a significant effect on the permeation flux and membrane selectivity, hence it directly proportional with the flux and inversely proportional with the selectivity.

This is discussed on the basis of the plasticizing effect of water and the increase of vapor pressure difference between the feed and permeate sides which improves the transport of driving force. The significantly lower activation energy values obtained for water permeation as compared to ethanol prove that the membranes developed in this work demonstrate excellent separation efficiency towards water. The close magnitudes of  $\alpha_{PV}$  and  $\Delta H_s$  indicate that both permeation and diffusion contribute almost equally to the pervaporation process. The negative sorption heat values ( $\Delta H_s$ ) for the membranes suggest that the sorption process can be controlled by the Langmuir's theory. Finally, the separation index indicates that the overall pervaporation performance of M0.5 membrane is enhanced approximately 70 % compared to that of common PVA membranes.

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#### Nomenclature

DS	Degree of swelling
Ms	Mass of swollen membrane
Md	Mass of swollen membrane
$J, J_i$	Total and individual fluxes (kg/m <sup>2</sup> .h)
$W$	Mass of collected permeate
$A$	Effective membrane area (m <sup>2</sup> )
$t$	Pervaporation operation time (h)
$\alpha_{PV}$	Separation Factor
$P_w, P_{eth}$	Weight fractions of water and ethanol in permeate
$F_w, F_{eth}$	Weight fractions of water and ethanol in feed
$Q_i$	Permeance of component $i$ (g/m <sup>2</sup> .kPa.h)
$P_i$	Permeability of component $i$
$L, \delta$	Thickness of membrane (m)
$x_i, y_i$	Mole fraction of $i$ in the feed and permeate
$\gamma_i$	Liquid activity coefficient of component $i$
$P_i^0$	Pure component $i$ vapor pressure
$D_i$	Diffusion coefficient of $i$ (m <sup>2</sup> /s)
$C_i$	Concentration (kg/ m <sup>3</sup> )
$E_x$	Apparent activation Energy for Permeation or diffusion
$\Delta H_s$	Heat of sorption
PSI	Pervaporation Separation Index

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