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Selectivity performance for polyamide-6 membranes using pervaporation of water/methanol mixtures

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ABSTRACT

Polyamide-6 (PA-6) flat sheet membranes have been prepared via casting 20 wt.% solution of polymer in 80 wt.% formic acid onto a glass plate using a doctor blade and coagulation in water bath at ambient temperature. The obtained membranes have been characterized using scanning electron microscope. The pervaporation separation properties of PA-6 membranes were studied with alcohol binary mixtures of water/methanol. The membranes specified water perm-selectivity over a wide range of the feed composition. Thereby, the water perm-selectivity reached to a maximum at low water content (WC) in the feed mixture. In addition, the permeate flux increased with increasing WC in the feed and with increasing operating temperature. The results indicated that the increase of water in the feed and operating temperature led to decrease in the separation factor. Also, it was found with some PA-6 membranes that high permeation fluxes together with good separation selectivity could be obtained leading to interesting performances. Therefore, the PA-6 membrane was able to achieve molecular mixture separation with selectivity close to one which can be obtained with dense membranes. Moreover, the PA-6 membranes selectivity was strongly influenced by operating conditions as temperature, feed content, and molecular size.

Keywords: Polyamide-6 (PA-6) membrane; Casting; Phase inversion; Asymmetric membrane; Pervaporation

1. Introduction

Recently, the evaluation of asymmetric membranes with a good separation capability is still a major research goal in the membrane science and technology field [1,2]. Hence, a combining of a good separation properties and high flux is based on the use of membranes consisting of an asymmetric porous membrane with a tight thin dense layer [2,3].

Pervaporation (PV) technology has become an important separation technology over the past decades [4–6]. PV is a rate-governed membrane process for the separation of liquid mixtures. Currently, dehydration of alcohols is the best developed application of PV in the chemical processing industries [7–9].

PV separation, one of the interesting processes, offers potentially more economical alternatives for the industrial separation of aqueous mixtures, especially azeotropic zones, isomers, close-boiling point mixtures, and heat-sensitive mixtures which cannot be separated

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or concentrated by a distillation method. Furthermore, PV membrane technique has been an interest and more application for the selective separation of aqueous alcohol systems [10–12]. In recent years, significant progress has been achieved in the field of PV by several investigators. Thus, a large number of polymers have been tested for PV separation [13–29].

As the other membrane separation techniques, the suitable membrane raw material and its membrane-forming technique should be firstly found out to study separation of several mixtures systems with PV process [22]. Really, selection of the polymer membrane materials for separation with PV process is based mainly on three important features: good chemical resistance, sorption capacity, and high mechanical strength of the polymer film in the mixture solution. Therefore, it should have good interaction preferably with one of the components of the mixture for separation. Hence, the solubility parameter and membrane polarity [23,24] are the indices of interest in the development of polymer membrane materials.

The separation of the mixtures using PV process can be divided into three fields [2,25]:

- Dehydration of aqueous–organic mixtures;
- Removal of trace volatile organic compounds from aqueous solution;
- Separation of organic–organic solvent mixtures.

Separation mechanism with PV is carried out by permeation through non-porous (dense) polymeric films, which is usually described by the solution-diffusion model [25,26] that considers three successive steps for mass transfer (Fig. 1):

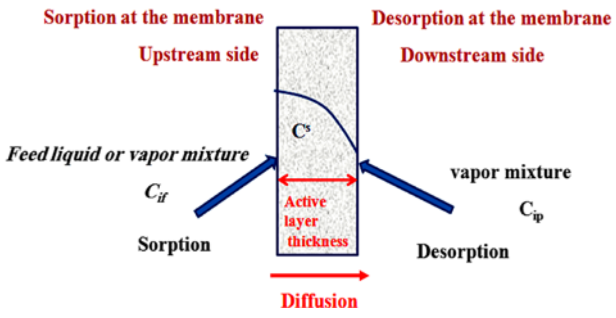


Fig. 1. Schematic of solution-diffusion model through non-porous polymeric materials. C_i, C^S and C_{ip} are the compositions of the feed, sorbed and permeated mixture, respectively, conventionally expressed as the mass fractions of the preferentially permeated species [25].

(1) The dissolution (or sorption) of molecules at the membrane upstream side in contact with the vapor or liquid.
(2) The diffusion step driven by the chemical potential across the membrane.
(3) The desorption of the permeated species at the membrane downstream side, that is usually considered as a non-limiting step.

Polyamides are usually referred to as “nylons,” a generic term 1 [17–21]. Polyamide (nylon) is one of the most important fibers. Nylon generally are strong, tough, rather resilient polymers with good barrier properties, high fatigue, and abrasion resistance, however they have high water absorption [5–21]. Polyamide-6 (PA-6) is one of the most widely used materials owing their balance [10–14].

In our previous work, PA-6 membranes were developed for the separation of para-nitro phenol from aqueous water mixture [1,28]. The scope of the present work is a continuation of a previous endeavor for development of a polyamide membrane fabricated by casting techniques. The goal is to explore the functional aspects of a developed PA-6 membrane for the separation of aqueous alcohol systems.

2. Experimental

2.1. Materials

PA-6 is used as a polymer with bulk density 0.25 gm/ml, particle size 50–160 μm was purchased from Leuna Werke AG (Germany). Formic acid (FA) is used as a solvent (FA) 85% by weight, its density at 20˚C is 1.198 gm/cm3, boiling point 100.7˚C. FA and methanol—both of analytical grade—were purchased from Sigma-Aldrich chemical company and used without further purification.

2.2. Preparation of asymmetric PA-6 membranes

The PA-6 asymmetric membrane was prepared using phase-inversion method. The polymer dope solution (20 wt.% in FA) was casted onto a glass plate using a doctor blade at 20˚C with the evaporation time 1 min. The glass plate was subsequently immersed in a gelation bath consisting of pure water at 28˚C. It was then rinsed in pure water to remove residual solvent. The effect of water as additive (5–10%) to polymer casting solution will be studied. The schematic flow diagram for the preparation of polyamide-6 membranes by casting technique was depicted in Fig. 2.

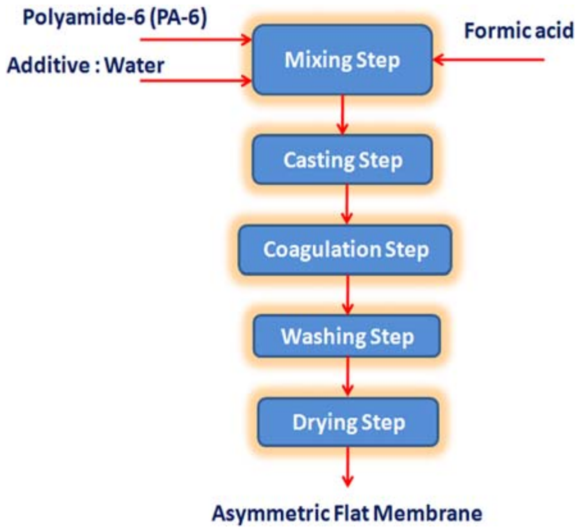


Fig. 2. Process block flow diagram for preparing polyamide-6 membranes by casting.

2.3. Membrane characterizations

2.3.1. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to observe the morphology of PA-6 membranes; however, samples of membranes were coated with gold to provide electrical conductivity. The top and bottom Snapshots of membranes were taken on a JEOL 5410 SEM was operating at 10 kV, where, significant views of surfaces were recorded.

2.3.2. Degree of water uptake

Water content (WC) of PA-6 membranes was obtained after soaking membranes in water for 48 h and the swollen membranes were blotted quickly and carefully with tissue paper to remove any surface solution. Then, the swelled membranes were weighted by a digital analytical balance. After that, the wet membranes were placed in an air-circulating oven at 80˚C for 48 h to be completely dried and finally, the dry membranes were determined. The percent of WC was calculated using the following equation:

$$WC\% = (W_{\mathrm{wet}} - W_{\mathrm{dry}})/W_{\mathrm{wet}} \times 100 \tag{1}$$

where WC is the membrane water content; W_{wet} and W_{dry} are the wet and dry weight of the membranes (g), respectively. In order to minimize the experimental errors, the membrane water uptake of each sample was measured several times (at least for three times) and the results were reported in average (the error of ± 2%).

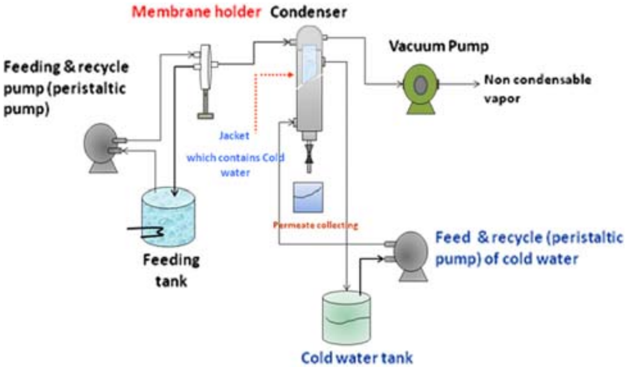


Fig. 3. Schematic diagram of the pervaporation experimental set-up.

2.4. PV experiments

2.4.1. Experimental setup

The experiments were carried out on PV system technique, (Fig. 3), which contained flat sheet membrane module that had three openings for feeding, recycling, and vacuum pressure. The feed was continuously fed to the membrane module from an open feeding tank (glass flask) using peristaltic feeding pump. Vacuum pressure was obtained using a vacuum pump. The feed mixture was heated using hot plate and the temperature was controlled by thermostat of hot plate and recorded by thermometer.

PV experiments with mixtures of alcohols/water mixtures were carried out to characterize the separation properties of the asymmetric polyamide (PA) membrane. All experiments were carried out in a state of continuous balance with a vacuum downstream and a constant temperature for feed mixtures. The composition of permeate which was collected from condenser downstream was determined for each mixture, the permeate enrichment and flux of permeation (J) were measured for several membrane samples (specific membrane area of $3.14\,10^{-4}\,\mathrm{m}^2$). The feed tank of the capacity of 100 gm was filled with different percentage of methanol water mixtures (from 0 to 100 wt.%), therefore pure methanol and water were tested respectively. The effect of the temperature on the membrane performances was studied in the range 30–60˚C. The weight of permeate was determined using a precise balance and the permeate composition was measured using gas chromatography (GC, TCD column). The PV performances were evaluated by the separation factor (α) and total flux (J). The separation factor is defined by:

$$\alpha = \frac{(Y_i \times X_j)}{(X_i \times Y_j)} \tag{2}$$

where Y_i: represents the weight fractions of the fastest compound in the permeate, Y_j: represents the weight fractions of the slowest compound in the permeate, and X_i and X_j represent the weight fractions of the component in the feed.

The permeation flux (*J*) was calculated using the expression:

$$J = \frac{Q}{(A \times T_t)} \tag{3}$$

where Q (kg) is the total mass of the permeate collected through the effective area of membrane A (m^2) and during the time T_t(h), once the state has been reached. The PV experiments set-up is shown in Fig. 3.

3. Results and discussion

3.1. Membrane morphology (SEM)

The preparation of asymmetric membranes was carried out according to the wet method using a non-solvent bath to induce phase inversion. The effect of water as additive (5–10%) to polymer solution on the morphology of PA-6 membranes was studied; however, the using SEM as a tool to optimize the phase inversion conditions can be guided to prepare PA-6 membranes having a thin tight top layer self supported on a highly porous sub-layer. The results were outlined and shown below. Table 1 illustrated the operating parameters for preparation of PA-6 membranes.

The aim of the addition of non-solvent to the polymer solution was to change the rate of demixing process and to study its effect on membrane morphology. The effects of non-solvent (water) addition to PA-6 solution on membranes morphology were presented in Figs. 4–6.

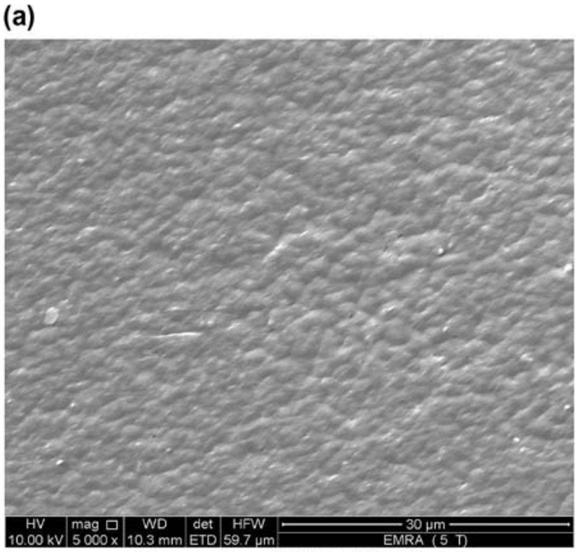
Table 1
Composition of the prepared PA-6 membranes

Membrane[a]	Casting solution		
	PA-6%	FA%	Water%
*M*1	20	80	0
*M*2	19	76	5
*M*3	18	72	10

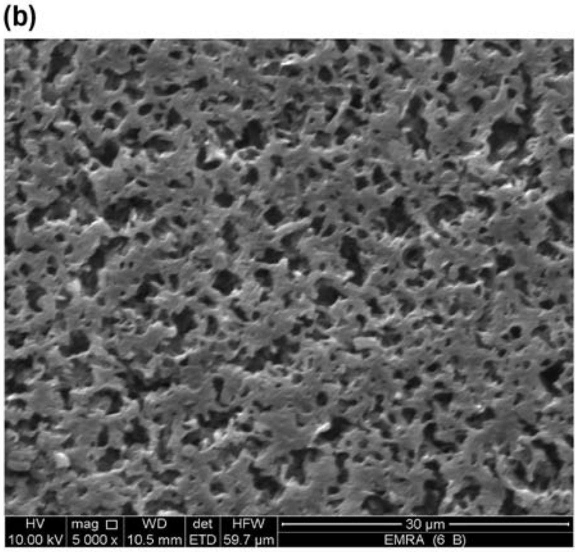
[a] Starting dope solution, before water addition was prepared by 20 wt.% PA6; 80 wt.% FA, pre-concentration time (1 min), immersion in water bath 1 h at 28 ± 2˚C. Where, P: polymer, W: water, FA: formic acid, after water addition the compositions of membranes are *M*1; $M_{20\text{wt }\%\text{P}}$,*M*2; $M_{19\text{wt }\%\text{P,5W}}$, *M*3; $M_{18\text{wt }\%\text{P,10W}}$.

SEM photography of the surface of asymmetric membranes $M_{20\text{wt.}\%\text{P,10w}}$ was presented in the Fig. 4. The SEM views of membranes which were prepared by the phase inversion (wet method) revealed that the corresponding structures gave the impression to be pore-free on the top (air side) but highly porous on the bottom (glass side) surfaces. These samples appeared to be asymmetric membranes.

Otherwise, SEM photography of the surface of asymmetric membranes $M_{18\text{wt.}\%\text{P,10W}}$ and $M_{19\text{wt.}\%\text{P,5W}}$ was presented in the Figs. 5 and 6. The SEM Snapshots of membranes $M_{18\text{wt.}\%\text{P,10W}}$ and $M_{19\text{wt.}\%\text{P,5W}}$ indicated that the corresponding structures have some pores on the top side (air side) but highly porous on

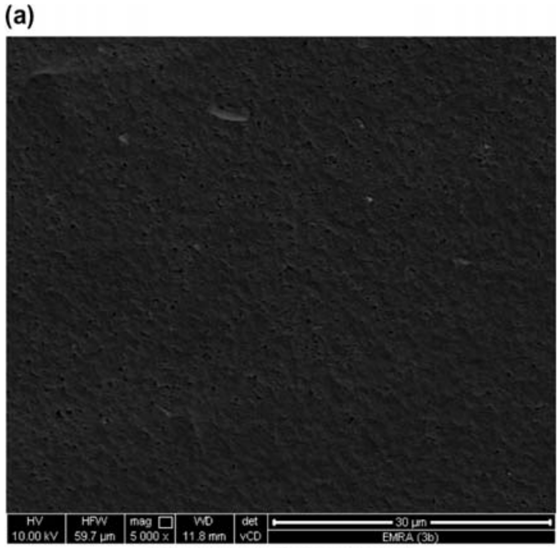


Top surface (20PA6/80FA)

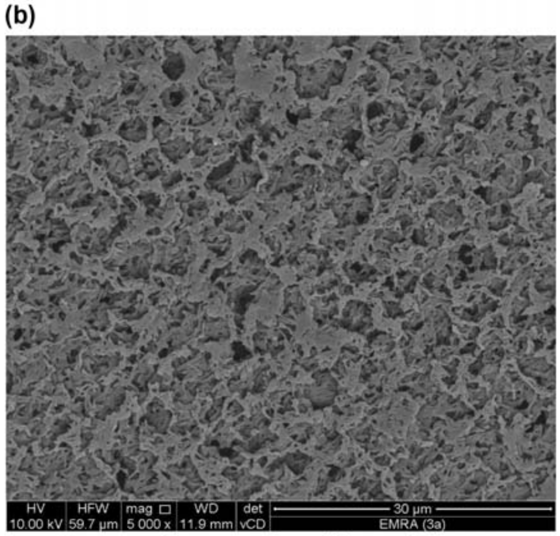


Bottom surface(20PA6/80FA) (big pores)

Fig. 4. SEM photograph surface of asymmetric PA-6 membranes with 20 wt % PA-6 (M1).

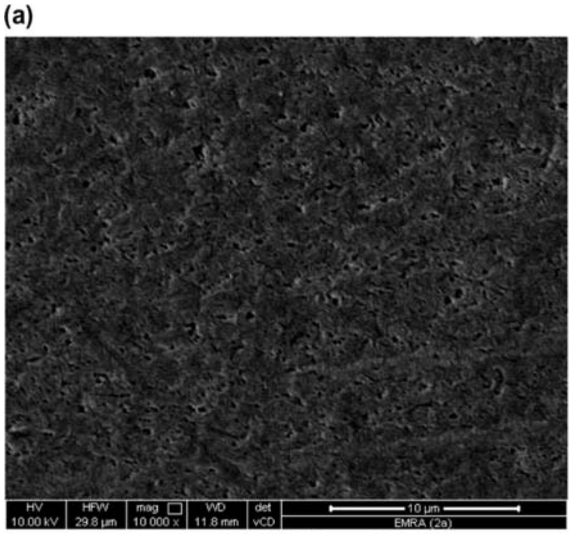


Top surface (small pores)

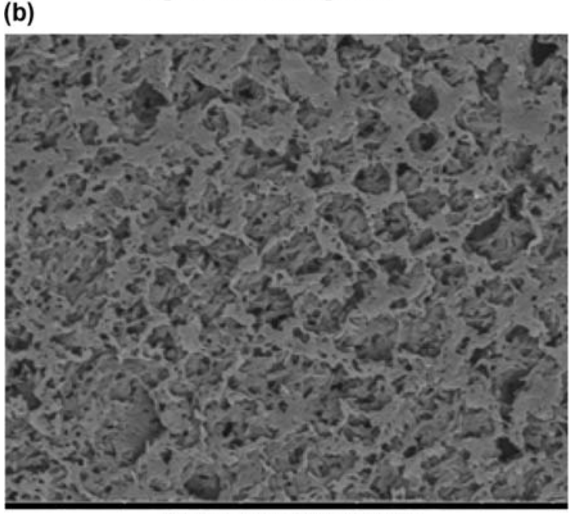


Bottom surface (big pores)

Fig. 5. SEM photograph surface of asymmetric PA-6 membranes with (*M*2; 19 wt.%, PA6, and 5 wt.% water).



Top surface (small pores)



Bottom surface (big pores)

Fig. 6. SEM photograph surface of asymmetric PA-6 membranes with (*M*3; 18 wt.%, PA6, and 10 wt.% water).

the bottom (glass side) surfaces. These flat sheets seemed to be ultrafiltration or microfiltration membranes, thus the membranes morphology will be checked on PV system. It was clear from this test that the addition of non-solvent (water 5–10 wt.%, Figs. 4–6) led to more porous structures.

3.2. PV performance

PV separation of the desired component takes place through a dense membrane by a solution–diffusion mechanism. Thus, the PV experiments were carried out on three different PA6 membranes to ensure which of the phase inversion procedures were able to lead to asymmetric defect-free membranes. However, the PV of water/methanol was tested to determine the appropriate asymmetric structure according to dense layer tightness of asymmetric membrane, also the effect of operating conditions on PV process were studied. Finally, binary mixtures (methanol/water) were used to study the molecular separation and determine the optimum structure of asymmetric membrane with flux and selectivity.

3.2.1. Effect of membrane morphology on PV performances

The permeation experiments of aqueous solution of 10 wt.% water and 90 wt.% methanol at 30°C were

Table 2
Effect of membrane morphology on selectivity

Membrane	Water in permeate (wt.%)	Thickness (μm)	WC (%)
$M_{20\text{wt.\%PA6}}$	99.9	160	5
$M_{19\text{wt.\%PA6,5wt.\%water}}$	11	180	8
$M_{18\text{wt.\%PA6,10wt.\%water}}$	10	210	17

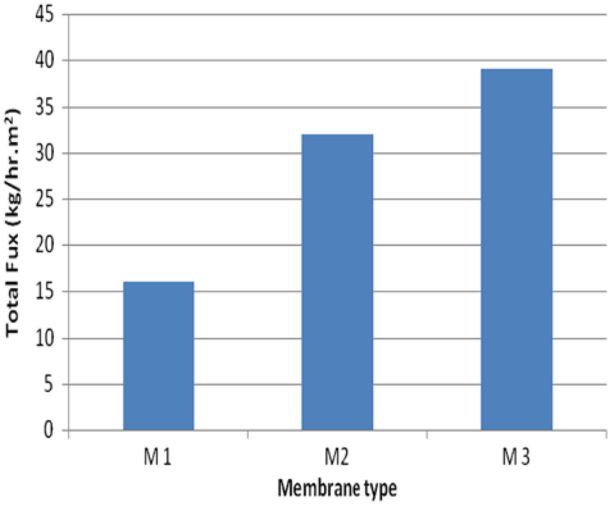
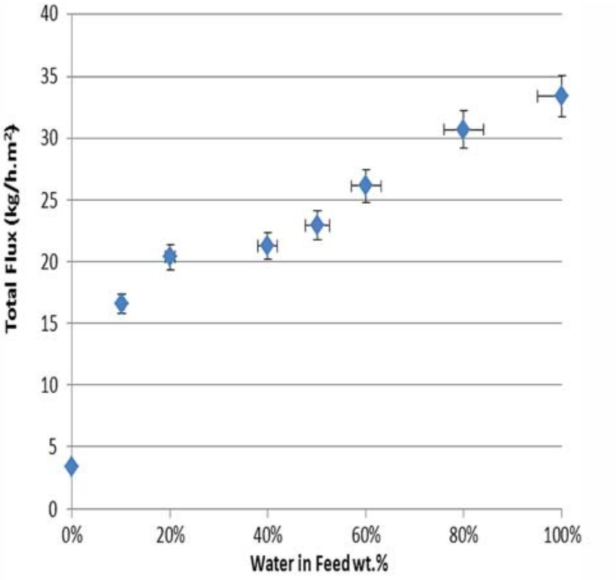


Fig. 7. Effect of membrane type on total flux (feed 10 wt.% water and 90 wt. % methanol, at 30℃). Where: $M1$; $M_{20\text{wt \%P}}$,$M2$; $M_{19\text{wt \%P,5W}}$, $M3$; $M_{18\text{wt \%P,10W}}$.

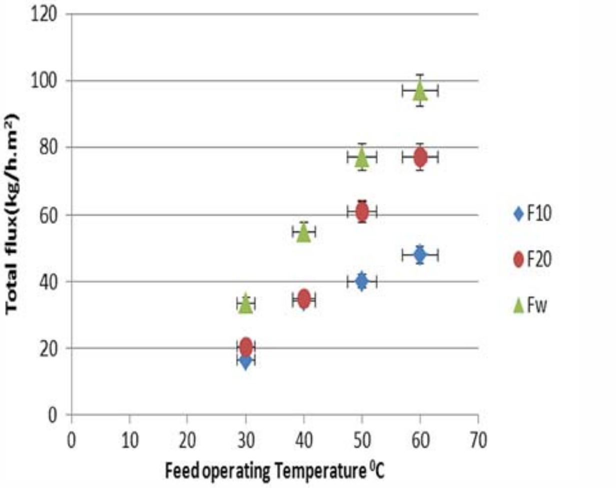
carried out to investigate the effect of membrane morphology on PV performances (selectivity, flux), and the results were represented in Table 2 and Fig. 7.

It was indicated from Table 2 that the asymmetric membrane ($M_{20\text{wt.\%PA6}}$) gave the highest selectivity than the other two membranes, while the other membranes ($M_{19\text{wt.\%PA6,5wt.\%water}}$ and $M_{18\text{wt.\%PA6,10wt.\%water}}$) did not give any selectivity at all. These results indicated that the asymmetric membranes were selective to water permeation when the asymmetric defect-free membranes have a good dense layer. Thus, the asymmetric membrane ($M_{20\text{wt.\%PA6}}$) was able to achieve molecular mixture separation with selectivity close to one which was obtained by dense membrane layer.

It was observed from Fig. 7 and Table 2 that the total flux and the water uptake increased with increasing water wt.% in polymer solution; these results were in agreement with membrane morphology as shown in previous SEM Figs. 4–6 according to the pores in the top layer, where denser layer can lead to low flux and high selectivity.



a. Effect of feed concentration on the total real flux of pervaporation at 30 °C.



b. Effect of feed operating temperature on the total real flux (F10: feed with 10 wt % of water, F20: feed with 20 wt % of water, Fw: feed pure water).

Fig. 8. Effect of operating condition on the total real flux (feed: water methanol mixture).

3.2.2. *Effect of operating condition (temperature and feed composition) on PV performance*

The permeation experiments of aqueous solution of water methanol mixtures, pure water, and pure methanol at different temperatures (30, 40, 50, and 60℃) were carried out to investigate the temperature dependence of PV performances. The results were presented in Tables 3–5 and Fig. 8 for the asymmetric membrane ($M_{20\text{wt\%PA6}}$).

Firstly, it should be underlined that all membranes were well stable during the PV experiments even at 60℃; also, long term PV experiments could be carried

Table 3
Effect of operating temperature on performance of the asymmetric membrane ($M_{20\text{wt }\%\text{PA6}}$)

Feed water/methanol	Separation factor				Permeate water content			
	30℃	40℃	50℃	60℃	30℃ (%)	40℃ (%)	50℃ (%)	60℃ (%)
10 wt.% w	891	81	9	4.5	99	90	50	33
20 wt.% w	23	11.5	8	5	85	74	67	55
40 wt.%. w	2.5	[a]			60			
50 wt.% w	3				75			
60 wt.% w	1.8	1.2	0.9	0.8	73	65	57	54
80 wt.% w	1				82			

[a] The effect of temperature on separation factor with feed content higher than 20 wt.% of water was not measured because the separation factor was very low at 30℃.

Table 4
Effect of operating temperature on the partial flux of the asymmetric membrane ($M_{\ 20\text{wt }\%\text{PA6}}$)

Feed water/ethanol	Water flux (F_W) kg/h m^2				Methanol flux (F_m) kg/h m^2			
	30℃	40℃	50℃	60℃	30℃	40℃	50℃	60℃
10 wt.% w	16.5	30.4	20	16	0	3.4	20	32
20 wt.% w	17	26	41	42.6	3	9	20	35
40 wt.% w	12.8				8.5			
50 wt.% w	17.25				5.8			
60 wt.% w	19	24	27	35	7	13	20	30
80 wt.% w	25.2				5.5			
Pure water	33.5	55	76.6	96.7				
Pure methanol					3.3	9.3	16	21

Table 5
Activation energy for the asymmetric membrane ($M_{20\text{wt }\%\text{ PA6}}$)

Feed	E_t (J K^{-1} mol^{-1})	E_w (J K^{-1} mol^{-1})	E_m (J K^{-1} mol^{-1})
0 wt.% w	64,500	–	64,500
10 wt.% w	54,500	9,178	12,0095
20 wt.% w	43,000	35,000	77,140
100 wt% w	34,000	34,000	–

E_t: the total activation energy for mixture, E_w: the activation energy for water, E_m: the activation energy for methanol.

out to ensure the temperature dependence (up to 7 days). As expected, the total flux of pure solvents and mixtures through all the PA6 membranes increased by increasing the feed operating temperature according to an Arrhenius law, where the temperature is dependent on diffusion coefficient of binary mixture (Fig. 8) [30,31].

$$D = D_0 e^{-Ea/\mathrm{RT}} \tag{4}$$

where:

D is the diffusion coefficient;

D_0 is the maximum diffusion coefficient (at infinite temperature);

E_a is the activation energy for diffusion in dimensions of (energy [amount of substance]$^{-1}$);

T is the temperature in unit of absolute temperature;

R is the gas constant.

In accordance with the absorption–diffusion model, a higher flux is a consequence of increasing driving force due to increase in vapor pressure of the components in the feed, also due to increase in mobility of the absorbed species [32–34]. Furthermore, from Table 3, it was observed that the separation factor decreased with increasing in feed operating temperature and WC in feed. These results indicated that the asymmetric membranes were selective to water permeation.

It was found from Table 3 that the water selectivity (water permeate) of asymmetric membranes had a drop with increasing in operating temperature due to the effect of the coupling molecules with

Table 6
Comparisons between pervaporation results for feed contain methanol/water mixtures with previous researches and present work

Membrane type	Feed concentration	Temperature (℃)	Separation factor	Flux (kg/h m^2)	Refs.
Agarose membranes	90 wt.% methanol/water	30	2	0.4	[37]
Polyvinyl alcohol (PVA) acetal membrane	85 wt.% methanol/water	40	35	0.18	[38]
Polyphenylmethylsiloxane (PPMS)-CA	5 wt.% methanol/water	30	50	0.7	[39]
Aromatic polyamide	90 wt.% methanol/water	25	4.8	0.474	[40]
Aromatic polyamide	90wt.% methanol/water	25	6.1	0.586	[41]
Polyamide-6	90 wt.% methanol/water	30	891	17	Present work

methanol ones. However, the selectivity of water decreased by increasing of feed temperature and with increasing of water concentration in feed. In the other words, the increasing in the flux as a function of temperature was accompanied by decreasing in selectivity. Moreover, selectivity was higher at lower temperature because there is less coupling between water and MeOH.

Furthermore, the effects of operating conditions (temperature and feed composition) on separation factor were presented in Table 3. It was observed that the separation factor decreased with increasing feed operating temperature and also with increasing WC in the feed. The separation factor reached to a maximum at lowest WCs in the feed mixture. The highest separation factor was found at 10 wt.% water in the feed at the lowest feed operating temperature (30℃) while the lowest separation factor was found at 80 wt.% water in feed at the highest operating temperature (60℃) for asymmetric PA6 membrane as illustrated in Table 3.

Verkerk et al. [35] and Elshof et al. [36] reported that the separation factor decreased with increasing WC in feed, this was often attributed to the so-called "drag" effect. However, the overall separation factor was governed by the contribution of the resistances of both the dense skin-layer and the porous substrate, the separation factor reached to the maximum at lowest WCs in the feed mixture such as dehydration of alcohols.

3.2.3. *Effect of temperature and feed composition on membrane flux*

The operating parameters (temperature and feed) data were plotted against the corresponding flux data for the asymmetric membranes, as shown in Fig. 8, which obviously illustrated that the membrane flux was strongly affected by the operating conditions. It was observed that the real flux through all the asymmetric membranes increased with increasing WC in the feed and also with increasing feed operating temperature, according to an Arrhenius law.

The activation energy for water/methanol mixtures in Table 5 was determined using Eq. (4). From Table 5 for PA-6 asymmetric membrane, the total activation energy for water/ methanol mixtures decreased with increasing WC. Otherwise, the partial activation energy of water in PA-6 membranes was lower than the total activation energy of mixture, while the partial activation energy of methanol was higher than the activation energy for mixture. It implied that the partial methanol flux increased more quickly than the partial water flux with the increasing of operating temperature, and it led to decrease in the separation factor of mixture using PA-6 membranes with temperature, the same result was reported by Yexin Xu et al. [34] in case of polyimide membrane.

The results of some of previous works for methanol–water pervaporative separation are summarized in Table 6. From the comparison in Table 6, it can be seen that the performance (permeate flux and separation factor) of PA-6 membrane was better than the performance obtained from the other membranes in previous researches.

4. Conclusion

Asymmetric PA-6 membranes were successfully prepared by the phase-inversion process. Theses membranes were suitable for the dehydration of aqueous alcohol solution by PV. Actually, the obtained PA-6 membranes were considered to be selective to water permeation when the asymmetric membranes have a good dense layer. Thus, the asymmetric membrane is able to achieve molecular mixture separation with selectivity close to one which can be obtained with dense membranes. However, the membrane performances were strongly influenced by operating conditions as temperature, feed content, and molecular size. Therefore, the permeate flux increased with increasing temperature. However, the increased in flux was accompanied by decreased in selectivity. This can be explained by the fact that increasing in the water flux induced to a higher methanol flux. Also, selectivity was higher at lower temperature, according to less coupling between water and methanol.

List of symblos

D — is the diffusion coefficient
D_0 — is the maximum diffusion coefficient (at infinite temperature)
E_a — is the activation energy for diffusion in dimensions of [energy (amount of substance)$^{-1}$]
E_t — the total activation energy of mixture
E_w — the activation energy for water
E_m — the activation energy for methanol
T — is the temperature in unit of absolute temperature
R — is the gas constant
A — the separation factor
J — total flux

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