



Pervaporation of methanol from methylacetate mixture using polyamide-6 membrane

H. Abdallah^a, A. El-Gendi^{a,*}, E. El-Zanati^a, T. Matsuura^b

^aChemical Engineering & Pilot Plant Department, National Research Center, El Buhouth St., Dokki, Cairo 12311, Egypt

Tel. +202 33335494; Fax: +202 33370931; email: aymantaha2010@yahoo.com

^bDepartment of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur, Ottawa, K1V 1Z5, Canada

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ABSTRACT

This article presents the results concerning the preparation of asymmetric polyamide-6 (PA-6) membrane using the wet phase inversion technique. The membrane was prepared from a casting dope containing 20 wt.% of PA-6 in formic acid at 18°C. The membrane was then characterized by scanning electron microscopy and further tested for the separation of methanol/methyl acetate solutions by pervaporation. The effects of feed methanol concentration, operating temperature and the feed liquid flow rate on the membrane performance were investigated. The permeation flux increased with increasing feed methanol concentration, feed temperature, and feed flow rate. Some typical data of separation factor were: at the operating temperature of 40°C, feed 80% methanol/20% methyl acetate and the feed liquid flow rate of 16.5, 20.6 mL/s, the separation factor was 50 and 83 respectively.

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

1. Introduction

Pervaporation (PV) process is considered an economic alternative in terms of energy consumption [1,2], and has a high separation efficiency of azeotropic mixtures, close-boiling point compounds, and isomeric or heat-sensitive liquid mixtures [3–7]. A feed mixture contacts one side of a non-porous permselective membrane; the permeate is removed as a vapor from the other side.

The driving force induced by the difference in partial pressure between the liquid feed solution and

vapor permeate is considered as the main factor in transportation through the membrane, where the permeate liquid undergoes a phase change, from liquid to vapor state, during its transport through the membrane barrier [4].

Although the pervaporation mechanism can be explained in different ways [5,6], most researchers are in agreement with the transport of the vapor through a non-porous (dense) film involving three successive steps (solution–diffusion mechanism) as follows [7,8]:

- (a) The feed components in the upstream will be fractionated between the flowing liquid mixture

*Corresponding author.

and the swollen upstream layer of the membrane (sorption step).

- (b) Diffusion of the penetrants can occur through the unevenly swollen permselective barriers (diffusion step).
- (c) The desorption of permeate can take place at the downstream surface of the film (desorption step).

Generally, the pervaporation membranes comprise of symmetrical membranes, asymmetric membranes, and composite membranes [9,10]. Symmetrical membranes can be porous or dense, and the morphology remains the same across the cross-section. Asymmetric membranes have a reasonably dense thin surface layer supported on a porous membrane [11,12]. The surface layer is the layer in which the pervaporation separation is performed, and also the surface layer is the principal barriers for the flow through the membrane [13,14].

The separation of the azeotropic mixtures has become a topic of great practical importance for the chemical industry. On one hand, the azeotropic mixtures are formed in chemical industry, resulting in extended separation demand. On the other hand, most liquid mixtures of organic components form non-ideal systems. The formations of azeotropes are often due to the presence of some specific groups such as polar groups (oxygen, nitrogen, chlorine, and fluorine).

Methyl acetate is produced by esterification of acetic acid with methanol. The thermodynamic equilibrium and formation of two azeotropic mixtures (methyl acetate/methanol and methyl acetate/water) can cause difficulties in the production of methyl acetate with high purity [3].

A series of vacuum and atmospheric distillation columns can be used to separate the methylacetate–water azeotrope mixture [15,16]. The produced methyl acetate from esterification reaction is separated from the reaction mixture, and the methyl acetate–methanol azeotrope is then recycled to the reactors. To separate methyl acetate from methanol, several atmospheric or extractive distillation columns and a column with an extracting agent have been used, where ethylene glycol mono-ethyl ether is used to act as an entrainer [17,18].

The first attempts to produce high purity methyl acetate using distillation failed due to the formation of azeotropes. The recent researches revealed that the separation of methyl acetate–methanol azeotrope can occur in a reactive distillation column, but the refined methyl acetate cannot be obtained in the primary reactive distillation column, and a secondary column is required to break up methyl acetate from methyl

acetate–methanol azeotrope [3–6]. Further problems are created in commercial processes by the presence of impurities in the methanol and acetic acid feedstocks. These impurities can contaminate the product, accumulate in the process recycle streams. Hence, it may require additional distillation columns for their separations [19].

Previously, Sain et al. [20] studied the separation of methanol–methyl acetate mixtures by pervaporation at 30 and 45°C using cuprophane membranes, where the separation factor was reached 7.9. Recently, some researchers [21,22] have reported the pervaporation separation at 40–60°C using PVA-based membranes with different thicknesses and PVA contents in the skin layer. It was concluded that increasing in thickness of membrane could lead to an increase in separation factor and a decrease in permeate flux. On the other hand, polyamide-6 (PA-6) membranes were developed to separate para-nitro phenol (PNP) from its aqueous solution [23]. To the best knowledge of the authors, however, no attempts have been made to use PA-6 membrane for the purpose of methanol–methyl acetate separation by PV. Therefore, it is the objective of the present work to separate methanol from methanol–methyl acetate mixtures by pervaporation using a home-made PA-6 membrane prepared by the dry–wet phase inversion technique. The results of some of the previous work for methanol–methyl acetate pervaporative are summarized in Table 1 together with the result obtained in this work. From table, it is obvious that the performance (permeate flux and separation factor) of our home-made PA-6 membrane is better than the performance which was obtained from the membranes of other researchers.

2. Experimental

2.1. Materials

PA-6 (bulk density 0.25 gm/ml) of particle size 50–160 µm was purchased from Leuna Werke AG (Germany). Formic acid (FA) 85% by weight with MW 46.026 g/mol was used as the solvent; its density at 20°C is 1.198 gm/cm³ and the boiling point 100.7°C. Formic acid, methanol and methyl acetate of analytical grade were purchased from Sigma-Aldrich Chemical Company and used without further purification.

2.2. Membrane preparation

The PA-6 membranes were prepared via the wet-phase inversion technique. The polymer dope (20 wt. % in formic acid) was casted onto a glass plate to a

Table 1
Comparison of the results obtained for PV separation of methanol/methyl acetate mixtures

Membrane	Feed concentration (wt.% MeOH)	Temperature (°C)	Total flux (kg m ⁻² h ⁻¹)	Permeate concentration (wt.% MeOH)	Separation factor	References
Cuprophane	19.9	45	0.453	66.3	7.9	[20]
Pervap 2,255–40	21	45	4.1	45.5	3.1	[21]
Pervap 2,255–50	24	45	1.5	60.5	4.9	[21]
Pervap 2,255–60	23.5	45	0.55	63.6	5.7	[21]
Pervap 2,255–30	20	40	2.44	54.4	4.8	[22]
Polyamide-6 membrane	20	40	7.5	99	344	Present work

thickness of 400 μm using a film applicator. Then, the cast film together with the glass plate was immersed in a coagulation bath consisting of pure water at 18°C for one hour. It was then rinsed in pure water for one hour to remove residual solvent. The schematic flow diagram for preparation of PA-6 membrane by the wet-phase inversion method is depicted in Fig. 1.

2.3. Membrane characterizations

2.3.1. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to observe the morphology of PA-6 membrane. The membrane sample was coated with gold to provide electrical conductivity. The top-and-bottom snapshots of membrane were taken on a JEOL 5410 SEM conducted at 10 kV.

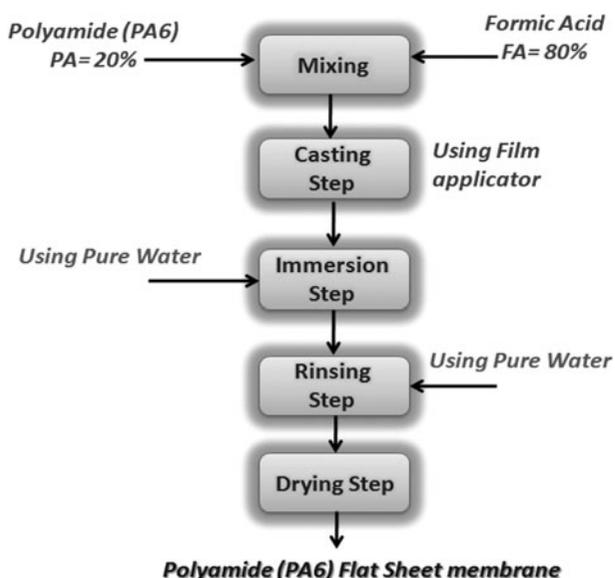


Fig. 1. Process block flow diagram for preparing PA-6 membrane by casting.

2.4. Pervaporation experiments

2.4.1. Experimental setup

The experiments were carried out by a PV system illustrated in Fig. 2 [24,25]. The system includes a flat-sheet membrane module (specific area $4.15 \times 10^{-4} \text{ m}^2$), which has three openings for feed, recycle and permeate. The feed was continuously fed to the membrane module from the feeding tank (glass flask, 100 ml) using a peristaltic feeding pump. The methanol concentration in the feed was changed from 0 to 100 wt.%. Vacuum (200 mbar) was applied on the permeate side using a vacuum pump. The feed mixture was heated in a water bath that was placed on top of a hot plate. The temperature (40–60°C) was controlled by a thermostat and recorded by a thermometer. Product was collected from the bottom of the condenser for a predetermined period and weighed by a double precision balance. Methanol concentration in the permeate was determined by gas chromatography.

The weight of permeate was determined using a double precision balance. The pervaporation performances were evaluated by the separation factor (α) and total flux (J). The separation factor is defined by

$$\alpha = \frac{(Y_i \times X_j)}{(X_i \times Y_j)} \quad (1)$$

where

Y_i and Y_j are the weight fractions of methanol and methyl acetate in the permeate, respectively and X_i and X_j are the weight fractions of methanol and methyl acetate in the feed, respectively.

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

$$J = \frac{Q}{(A \times T_i)} \quad (2)$$

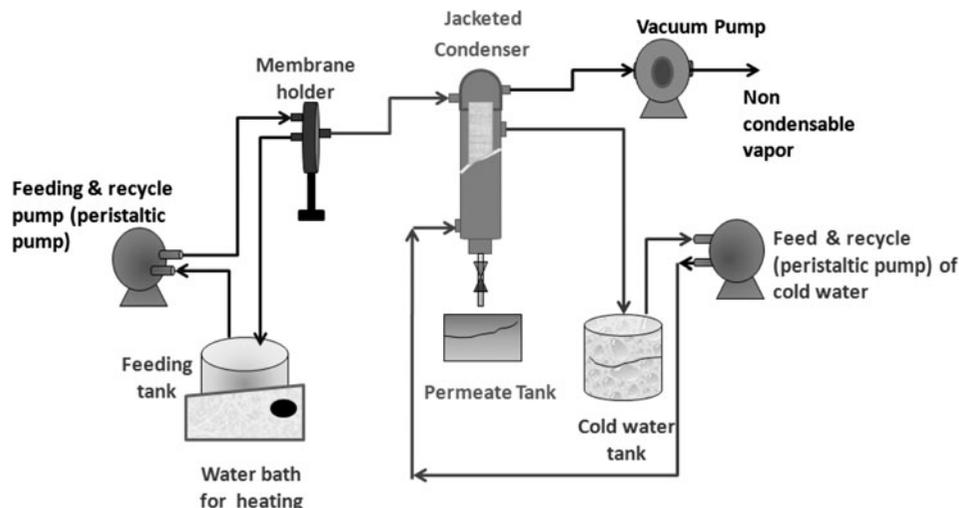


Fig. 2. Schematic diagram of the pervaporation experimental set-up.

where Q (kg) is the total mass of the permeate collected through the effective area of membrane A (m^2) during the time T_t (h), once the steady state has been reached.

3. Results and discussion

3.1. Membrane morphology (SEM)

SEM photography of the surface of the asymmetric membrane is presented in Fig. 3. The SEM views of the (PA-6) membrane revealed that the top surface was pore-free while the bottom (glass side) surface was highly porous.

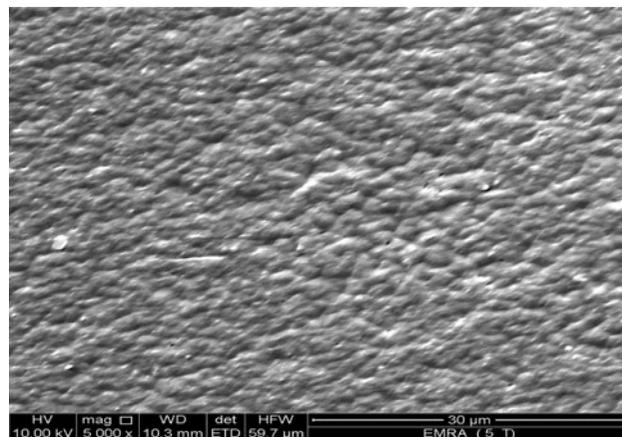
3.2. Pervaporation performance

3.2.1. Effect of operating condition on pervaporation performance

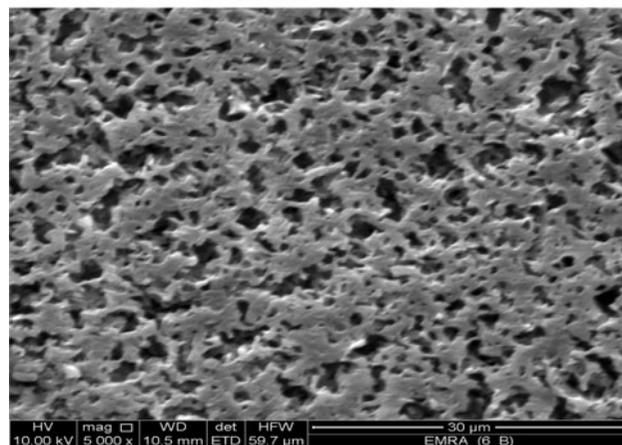
3.2.1.1. Selectivity. The permeation experiments of methanol/methyl acetate mixtures at different temperatures (40, 50, and 60°C) were carried out to investigate the temperature dependence of pervaporation performances. The results were presented in Tables 2 and 3 and Fig. 4 for the asymmetric membrane ($M_{20\text{wt}\%}$).

Firstly, it should be underlined that the asymmetric membrane was stable during the PV experiments even at 60°C; also long-term PV experiments could be carried out to ensure the temperature dependence. As expected, the total flux of pure solvents and mixtures through the PA-6 membrane increased by increasing the feed and operating temperature as a result of change both in partition and diffusion coefficients with the change in temperature [26,27].

Tables 2 and 3 summarize the data for the separation factor. From the tables, it is obvious that the



b. Top surface



a. Bottom surface

Fig. 3. SEM picture of the surface of the PA-6 membrane.

Table 2

Effect of feed composition and operating temperature on separation factor of the asymmetric membrane at flow rate 12.2 mL/s

Feed methanol/methyl acetate	Separation factor		
	40°C	50°C	60°C
80 wt.% methanol	36	15	15
60 wt.% methanol	166	56	45
50 wt.% methanol	167	58	45
20 wt.% methanol	344	99	65

Table 3

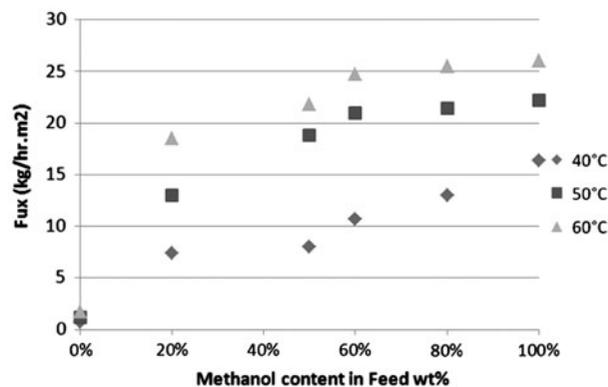
Effect of feed flow rate on membrane performance (feed 80% methanol/20% methyl acetate)

Feed flow rate (mL/s)	Separation factor		
	40°C	50°C	60°C
12.2	36	15	15
16.5	50	31	23
20.6	83	356	50
25.5	~∞	125	125
30.5	~∞	~∞	~∞

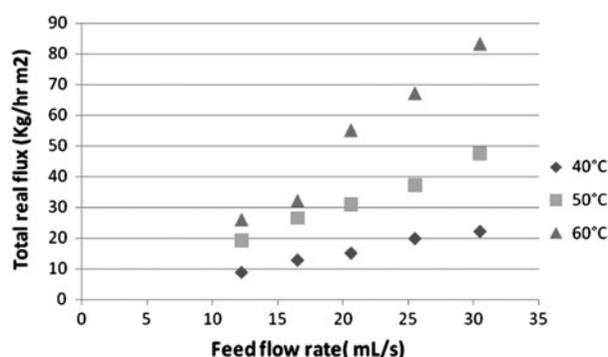
membrane is selective to methanol. No definite trend can be observed in the change of separation factor with feed methanol concentration, but considering the data for separation factor is less reliable when the feed methanol concentration is high (a small change in the permeate methanol concentration makes a large change in separation factor), it seems that the separation factor decreases with an increase in feed methanol concentration (Table 2). The separation factor also decreases with an increase in temperature (Tables 2 and 3), due most likely to the enhanced coupling effect. On the other hand, the separation factor increases with an increase in flow rate (Table 3).

3.2.1.2. Membrane flux. The data on the total flux are summarized in Fig. 4. The figures show that the total flux increases with an increase in the feed methanol concentration, the feed temperature and the feed flow rate. The higher flux at the higher feed temperature is due to the increase in the vapor pressures of both components as well as the mobility of the sorbed species [28,29].

Increase in separation factor as well as the flux with an increase in flow rate, shown in Table 3 and Fig. 4b, respectively, indicates the effect of concentration polarization. According to Fig. 4, these results were considered due to concentration polarization phenomena which reduced the concentration difference of



a. Effect of feed content and operating temperature on permeate flux at feed flow rate 12.2 mL/s.



b. Effect of Feed flow rate on membrane flux (feed 80% methanol/ 20% methyl acetate)

Fig. 4. Effect of operating condition on permeate flux.

permeating components across the membrane, thereby lowering the flux and the membrane selectivity; however, when the feed concentration is considerably high, the concentration polarization is unlikely to pose a severe problem to the separation performance. Concentration polarization occurs because the feed mixture components permeate from the membrane at different rates, which can provide a gradual build-up in the concentration of non-permeating or slowly permeating components in the feed as the more permeable components pass through the membrane, whereby the solution immediately adjacent to the membrane surface becomes depleted in the permeating solute on the feed side of the membrane [30,31]. As a result, the separation factor as well as the permeation rate decrease. The concentration polarization effect can be reduced by increasing the feed liquid flow rate that results in enhanced turbulent mixing [32,33].

The prepared PA-6 membranes showed such a good performance in both of the selectivity and permeate flux. These two performance indices are kinds of trade-off in nature, except a new architecture design of the membranes is made. So, the composite architecture

of the prepared PA-6 membranes has to reveal with the simple Bondi method, for analyzing fractional-free volume.

3.2.1.3. Fractional free volume. The correlation between apparent fractional-free volume and membrane performance was established to probe the structure–property relationship of the pervaporation membranes. There are two main methods to obtain the fractional-free volume (FFV): either polymer density and group contribution theory, or positron annihilation lifetime spectroscopy (PALS) [34]. Only PALS actually measures FFV while the other method is in fact an estimation based on:

$$\text{FFV} = (V - V_0)/V \quad (3)$$

Hamad et al. [35] calculated the free volume fraction (FVF) according to the following equation [36]:

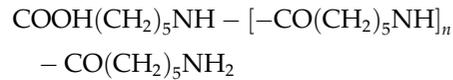
$$\text{FVF} = 1 - V_W \rho / M \quad (4)$$

where V_W is the Van der Waals molar volume of the polymer which was estimated by the group contribution method by Bondi [37,38], M is the molecular weight of the polymer, and ρ is the corresponding membrane density. A well-dried membrane sample was first weighed in air and then the volume of the membrane was measured. From the weight in air and the volume, the density of the polymer membrane was calculated. Table 4 summarizes the results of the free-volume fraction calculations estimated by the group contribution method by Bondi. In our present work, membrane permeation test was carried out at room temperature, so we analyzed experiment data according the fractional-free volume measured at room temperature.

Table 4
Van derWaals molar volume [39,40] and chemical groups forming the repeat units of PA-6

No.	Chemical group	V_W (cm ³ /mol)
1	CH ₂	10.23
2	NH	4
3	CO	11.7
4	NH ₂	7.44
5	OH	8
6	COOH	19.7
7	–CO(CH ₂) ₅ NH–	66.85
8	–CO(CH ₂) ₅ NH ₂	70.29
9	COOH (CH ₂) ₅ NH	74.85

The chemical formula of PA-6:



Calculation is made below based on the entire macromolecule.

Formula weight of COOH(CH₂)₅NH = 130, Formula weight of CO(CH₂)₅NH = 113

Formula weight of CO(CH₂)₅NH₂ = 114

Molecular weight of the macromolecule = $M = 130 + (113) \times n + 114 = 24,000$

Therefore, the number of the repeat unit $n = 210$.

V_W of the macromolecule is $70.29 + 66.85 \times 210 + 74.85 = 14,183.64$ (cm³/mol)

$\rho = 0.68$ g/cm³, $M = 24,000$ g/mol

$\text{FVF} = 1 - V_W \rho / M = 1 - (14,183.64 \times 0.68 / 24,000) = 0.6$

Some of researchers [40,41] have reported the fractional-free volume (FFV) calculation using Eqs. (5), (5a) and (5b) as follows:

$$\text{FFV} = V - V_0 / V \quad (5)$$

$$V = M / \rho \quad (5a)$$

$$V_0 = 1.3 V_W \quad (5b)$$

where V is the total molar volume of Membrane monomer (cm³/mol), M is the molar mass of monomer which is g/mol, ρ is the density of the membrane, V_0 is the volume occupied by the polymer chains (cm³/mol) and V_W is the van der Waals volume which can be estimated by the group contribution method.

$V = M / \rho = 35,294$ cm³/mol

$V_0 = 1.3 V_W = 1.3 \times 14183.64 = 18,438$ cm³/mol

$\text{FFV} = V - V_0 / V = 0.478$

Notice that the calculated V_W can be given on the basis of either the repeat unit or the entire macromolecule. The results are not different when the molecular weight is as large as 24,000.

The calculated FFV of the prepared PA-6 in this work is much higher than the values previously reported in the literature for the other membranes [35–42] such as glassy polymer membrane materials [41]. Also, in literature, one can find two values of FFV for PA-6 at T_g : 0.034 [42] and 0.061 [43].

4. Conclusion

A polyamide-6 membrane was successfully prepared by the phase inversion technique using formic

acid as solvent. The resulting membrane was effective in the separation of methanol/methyl acetate mixtures by pervaporation. The effects of the operating conditions were as follows:

- (1) The separation factor decreased with an increase in methanol concentration in feed.
- (2) The separation factor decreased with an increase in operating temperature.
- (3) The separation factor increased with an increase in feed liquid flow rate.
- (4) The membrane flux increased with an increase in methanol concentration.
- (5) The membrane flux increased with an increase in operating temperature.
- (6) The membrane flux increased with an increase in feed liquid flow rate.
- (7) Some typical examples of membrane performance were:

At the feed methanol concentration of 80 wt.% and the operating temperature of 50 °C, the separation factors were 31 and 356 respectively, for the feed liquid flow rate of 16.5 and 20.6 mL/s.

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