

EFFECT OF METHANOL CONCENTRATION ON THE PERFORMANCE OF ASYMMETRIC CELLULOSE ACETATE REVERSE OSMOSIS MEMBRANES USING DRY/WET PHASE INVERSION TECHNIQUE

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Abstract. Asymmetric membranes were prepared from a multicomponent dope polymer solution consisting of cellulose acetate, acetone, formamide and methanol. In this work, the dry/wet phase inversion technique is used and the presence of methanol is studied. In addition, this work also presents the fundamental issues involved in altering flat sheet casting solutions to produce solutions, potentially useful for preparing hollow fibers within, defect free selective layers. Variations in the composition of multicomponent casting solution resulted in membranes with drastically different reverse osmosis performance. The membrane performance are determined experimentally by primary parameters such as the pure water permeation rate (*PWP*), salt permeation rate (*PR*) and rejection rates. From these data, the secondary parameters such as pure water permeability constant (*A*), solute transport parameter ($D_{AM}/K\delta$) and mass transfer coefficient (*k*) are determined. These parameters are important in the prediction of reverse osmosis performance and also in characterising membrane morphology. The results revealed that the presence of methanol in the dope formulation increases the percentage of salt rejection and flux flow. The relatively lower value of ($D_{AM}/K\delta$) for a reference solute indicates a relatively smaller average pore size on the membrane surface.

Key words: Asymmetric membrane, reverse osmosis, cellulose acetate, dry/wet phase inversion

Abstrak. Membran asimetrik telah dihasilkan daripada larutan polimer multikomponen yang terdiri daripada selulosa asetat, aseton, formamid dan metanol. Dalam kajian ini, teknik fasa balikan kering/basah telah digunakan dan kehadiran metanol dikaji. Selain daripada itu, kajian ini juga mengemukakan isu asas yang terlibat dalam pengubahsuaian larutan tuangan kepingan rata, bagi menghasilkan larutan yang berpotensi untuk digunakan bagi penyediaan membran gentian geronggang, yang mempunyai lapisan memilih yang bebas daripada kecacatan. Pengubahsuaian komposisi larutan multikomponen telah menghasilkan membran osmosis balikan yang berbeza prestasinya. Prestasi membran ditentukan secara uji kaji oleh pemboleh ubah asas seperti fluks air tulen (*PWP*), kadar kebolehtelapan air garam (*PR*) dan kadar buangan. Daripada data tersebut, parameter sekunder seperti pemalar kebolehtelapan air tulen (*A*), parameter pengangkutan bahan larut ($D_{AM}/K\delta$) dan pekali pemindahan jisim (*k*) dapat ditentukan. Parameter tersebut adalah penting dalam meramal prestasi membran osmosis balikan dan pencirian morfologi membran. Keputusan uji kaji menunjukkan bahawa kehadiran metanol dalam formulasi larutan polimer

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telah meningkatkan kadar buangan dan aliran fluks. Nilai ($D_{AM}/K\delta$) yang lebih rendah bagi larutan rujukan menunjukkan bahawa purata saiz liang pada permukaan membran secara bandingan adalah lebih kecil.

Kata kunci: Asimetrik membran, osmosis balikan, selulosa asetat, fasa balikan.

1.0 INTRODUCTION

Integrally skinned asymmetric membranes can be fabricated by a process called dry/wet phase inversion [1–4]. In this process, the outermost region is induced by solvent evaporation and the remaining membrane structure is subsequently formed by solvent-nonsolvent exchange during a quench step. This concept is known as *forced convective evaporation-induced phase separation*. The physical events occurring during the evaporation have been acknowledged as the most important aspect of dry/wet phase inversion for the production of asymmetric membranes for gas separation [5]. In the past, the wet phase separation process was successfully implemented in the 1960's by Loeb and Sourirajan for the casting of cellulose acetate along with other solvents and nonsolvents onto a glass plate [6–7]. Frommer and Lancet had also studied the mechanism of membrane formation [8] and believed that the morphology of membranes and their rates of precipitation were so significantly determined by the nature of the casting solvent. The dry/wet technique requires multi-component casting solutions consisting of polymer, at least one volatile solvent and one less volatile nonsolvent and also a swelling agent. The effect of adding the nonsolvent, methanol to the dope formulation on the morphology was characterized by changes in pure water permeability constant (A), the solute transport parameter ($D_{AM}/K\delta$) for sodium chloride and mass transfer coefficient on the high pressure side of membrane (k).

The use of formamide as a swelling agent in the film casting solution was first introduced by Manjikian *et al.*, [9–10], in the preparation of cellulose acetate (CA) reverse osmosis membranes by the dry/wet techniques [7,11]. Such membranes are referred to as the CA-F membranes. Even though CA-F membranes have been extensively studied by Pilon *et al.*, [11], very few studies have been reported on the effects of using nonsolvents such as methanol on the morphology and performance of CA-F membranes. The choice of nonsolvent additive for the casting solution is extensive. Numerous nonsolvents are available which span a wide range of volatility and water miscibility, amongst them are the aliphatic alcohols such as ethanol, 2-propanol and 1-propanol. The addition of a nonsolvent into the membrane casting solution is very important in order to obtain the optimal membrane structure with an improved performance of the resulting membranes. Recent development in the preparation of gas separation membranes is essentially based on the concept of introducing nonsolvent additive into the membrane casting solution. Pinnau and Koros [5] has emphasized necessity to make the composition of the casting solution close to the precipitation point as much as possible by adding a nonsolvent into the

solution. The incorporation of certain amounts of nonsolvents brings the dope composition close to the binodal boundary thus facilitating rapid coagulation in the dry gap for effective phase separation. As a result, membranes with thinner skin layer and a more uniform structure could be obtained. Besides enhancing permeation flux, macrovoids in the sublayer of the asymmetric membrane can be suppressed by the presence of suitable nonsolvent-additive in the membrane casting solution [12]. In high pressure processes such as reverse osmosis and gas separation, the presence of large macrovoids is detrimental.

This paper describes the study on the effect addition of methanol which is a nonsolvent into the casting solution on the performance of asymmetric cellulose acetate for reverse osmosis process. In this case, the other casting conditions are kept constant in order to investigate the influence of methanol on membrane performance. Membrane performance is measured in terms of rejection rate, pure water permeability and product rate which are obtained experimentally. Based on these experimental results, pure water permeability constant, (A) and solute transport parameter ($D_{AM}/K\delta$) for the suitable reference solute [7], product rate PR and solute separation f can then be evaluated. The pure water permeability constant (A) reflects the overall porosity of a membrane, and ($D_{AM}/K\delta$) depicts the role of a mass transfer coefficient with respect to solute transport through the membrane pores. Membrane morphology can also be expressed in terms of pure water permeation rate PWP , and a set of parameters specifying the pore size distribution on the membrane surface on the basis of the surface force-pore model or RO transport [7]. This technique of characterizing membranes using the above mentioned parameters has been extensively used by many researchers such as Wang *et al.*, [7], Sourirajan and Matsuura [13], Wang *et al.*, [12] and Liu *et al.*, [14].

2.0 EXPERIMENTAL

2.1 Materials

Cellulose acetate (CA-398-3) with an acetyl content of 39.8% used in this study was purchased from Aldrich. The solvent, acetone (> 99%), and the swelling agent, formamide were supplied by Merck. The nonsolvent, methanol used in the casting solution was also supplied by Merck. All solvent, swelling agent and nonsolvent used were reagent grade and used as received.

2.2 Membrane Casting

Asymmetric reverse osmosis membranes were produced by a simple dry/wet phase inversion technique. Membranes were prepared from five different dope compositions (Table 1). The membranes were manually casted onto a glass plate at room temperature using a spreading knife with a notch height of 200 μm . Once cast, the

nascent membranes were immediately flushed with nitrogen gas to induce dry phase separation prior to immersion in pure water coagulation bath at 4°C. After 24 hours immersion in water bath at room temperature, the cellulose acetate membranes were dipped in hot water bath for another 10 minutes at 80°C before ready for testing.

2.3 Membrane Evaluation

A reverse osmosis permeation cell was used in the evaluation of the membranes performance. All tests were conducted at three different pressures 1000, 2000 and 3000 kPa using a 1500 mg/l sodium chloride (NaCl) solution at room temperature in the high pressure reverse osmosis test cell. The cell has a feed capacity of 35 ml and pressurized with nitrogen gas. The test cell has an effective membrane area of 7.1 cm². All membranes were subjected to a 1000 kPa with pure water prior to testing at the same pressure. Since the product rate (*PR*) for the cell was so much smaller than the feed flow rate *Q*, the difference in the concentrations of the feed solution entering and leaving the cell on the high pressure side of the membrane was negligible. In each experiment, the following data were collected; pure water permeation rate (*PWP*) and the product rate (*PR*) in gm/hr and salt separation. The salt separation *f* is given as follows:

$$f = 1 - \frac{C_{A3}}{C_{A1}} \quad (1)$$

where C_{A3} is concentration of sodium chloride in the permeate and C_{A1} the sodium chloride concentration in the feed. Sodium chloride is the solute chosen in this work. Pure water permeability constant, *A* is given by

$$A = (PWP) / (M_W \times S \times P \times 3600) \quad (2)$$

Water flux N_B is given by

$$N_B = A [P - \pi(X_{A2}) + \pi(X_{A3})] \quad (3)$$

Solute flux N_A is given by

$$N_A = \left(\frac{D_{AM}}{k\delta} \right) (c_2 X_{A2} - c_3 X_{A3}) \quad (4)$$

$$\text{Since } X_{A3} = \frac{N_A}{N_A + N_B} \text{ and } N_B = N_A \left(\frac{1 - X_{A3}}{X_{A3}} \right)$$

$$N_B = \left(\frac{D_{AM}}{K\delta} \right) \left(\frac{1 - X_{A3}}{X_{A3}} \right) (c_2 X_{A2} - c_3 X_{A3}) \quad (5)$$

Using film theory $k = D_{AB}/l$ [13], the water flux can also be expressed as follows,

$$N_B = c_1 k (1 - X_{A3}) \ln \left[\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}} \right] \quad (6)$$

2.4 Analytical Techniques

A digital conductivity meter (Hanna Instruments Model HI8633) was used for measuring the conductivities of the feed solution and the permeate samples. From the conductivities of the feed and permeate measured at 25°C and calibration curves and the percent salt rejection was determined.

3.0 RESULTS AND DISCUSSION

The compositions of the various membranes produced are shown in Table 1. This table depicts some of the primary reverse osmosis data such as pure water perme-

Table 1 Experimental data, *PWP*, *PR* and percentage salt separation

Compositions	Pressure (kPa)	PWP (l/hr/m ²)	PR (l/hr/m ²)	% <i>f</i>
Membrane A1 CA: 25%, Ace: 37.5% and For:37.5%	1000	34.11	32.08	19.74
	2000	62.95	59.11	28.76
	3000	91.78	86.14	32.19
Membrane A2 CA: 25%, Ace: 31% For: 31% and MeOH: 13%	1000	34.79	30.15	47.83
	2000	55.25	41.69	56.52
	3000	14.34	14.32	65.22
Membrane A3 CA: 25%, Ace: 37% For:: 24% and MeOH: 13%	1000	8.43	7.67	51.07
	2000	27.22	25.96	68.67
	3000	9.62	8.95	75.54
Membrane A4 CA: 27%, Ace: 36.5% and For: 36.5%	1000	26.65	25.57	21.74
	2000	41.36	39.21	34.80
	3000	56.07	52.84	43.50
Membrane A5 CA: 27%, Ace: 31.5% For: 31.5% and MeOH: 10%	1000	10.04	1.26	46.70
	2000	14.22	11.88	65.90
	3000	27.10	16.72	73.50

ability (*PWP*), product rate (*PR*) and % solute separation. The set of reverse osmosis data when analyzed through the basic transport using Equations (2) – (5) yields a local data on pure water permeability constant, *A*, solute transport parameter, ($D_{AM}/K\delta$) and mass transfer coefficient, *k* which is applicable for the particular membrane and the solute under the local operating conditions. These values are shown in Table 2. It is interesting to note that the presence of methanol as could be seen in the membrane A2, A3 and A5 has increased the % solute separation of sodium chloride. If compared with membrane A1 and A4, these membranes showed a much improved separation performance. The results shown in Table 1 could be illustrated clearly in the form of Figures (1) – (3). Figure 1 clearly shows that the percentage of salt separation are higher with the presence of the nonsolvent in the casting solution. However, there is a reduction in the permeation rate of these membranes as expected. Higher separation factor is always followed by low permeation rates.

The quantity ($D_{AM}/K\delta$) is a function of the chemical nature of the solute, that of the membrane material and the average pore size on the membrane surface which reflects both the equilibrium and the kinetic effects governing reverse osmosis trans-

Table 2 Pure water permeability constant (*A*), solute transport parameters, ($D_{AM}/K\delta$) and mass transfer coefficient *k*.

Compositions	Pressure (kPa)	$A \times 10^6$ (g-mol/cm ² .s. atm)	$(D_{AM}/K\delta) \times 10^4$ (cm/s)	$K \times 10^{-4}$ (cm/s)
Membrane A1 CA: 25%, Ace: 37.5% and For: 37.5%	1000	5.320	14.280	9.410
	2000	4.919	11.400	12.780
	3000	4.778	10.520	15.250
Membrane A2 CA: 25%, Ace: 31% For: 31% and MeOH: 13%	1000	2.717	1.246	4.054
	2000	2.876	0.817	12.11
	3000	2.281	0.018	0.162
Membrane A3 CA: 25%, Ace: 37% For:: 24% and MeOH: 13%	1000	1.317	1.373	5.301
	2000	1.417	1.953	13.60
	3000	0.752	0.525	5.679
Membrane A4 CA: 27%, Ace: 36.5% and For: 36.5%	1000	4.163	16.22	14.750
	2000	3.231	8.034	11.740
	3000	2.919	5.759	12.170
Membrane A5 CA: 27%, Ace: 31.5% For: 31.5% and MeOH: 10%	1000	1.597	0.025	0.127
	2000	1.110	0.402	2.330
	3000	1.411	0.128	1.809

Note: The abbreviations for CA, Ace, For and MeOH refers to cellulose acetate, acetone, formamide and methanol respectively.

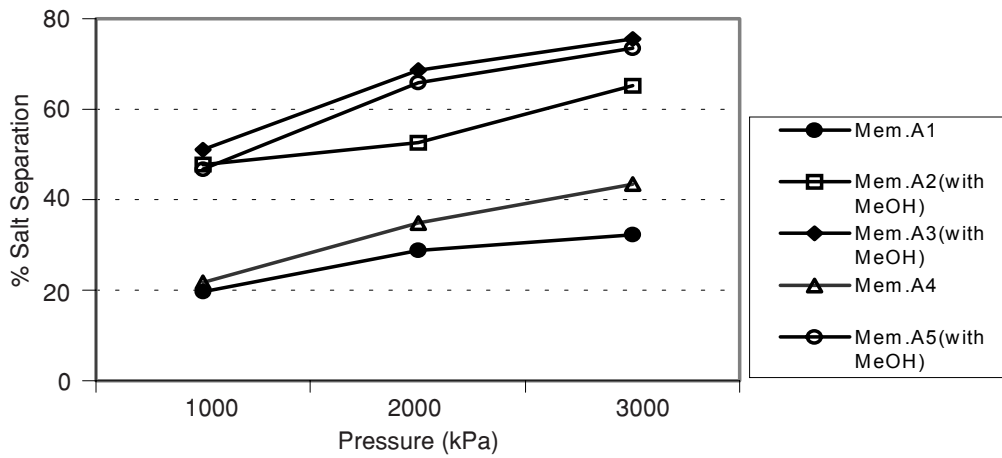


Figure 1 Percentage salt separation versus pressure

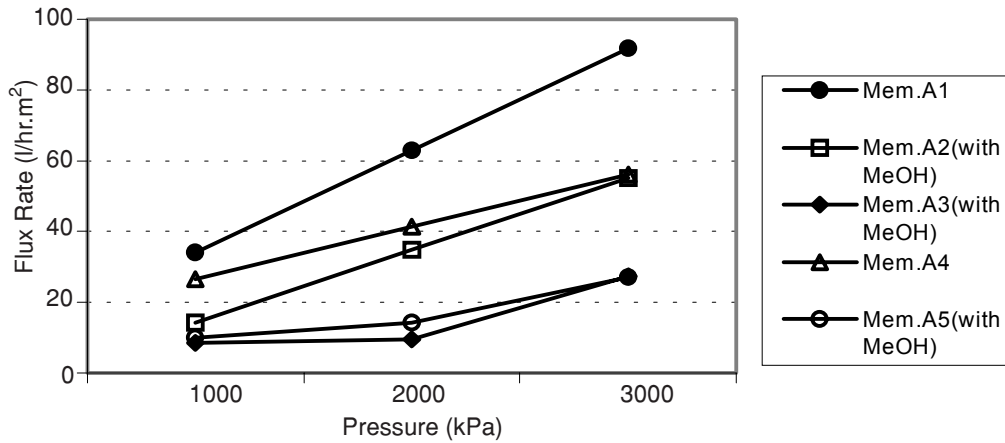


Figure 2 Pure water permeation flux rate (PWP) versus pressure

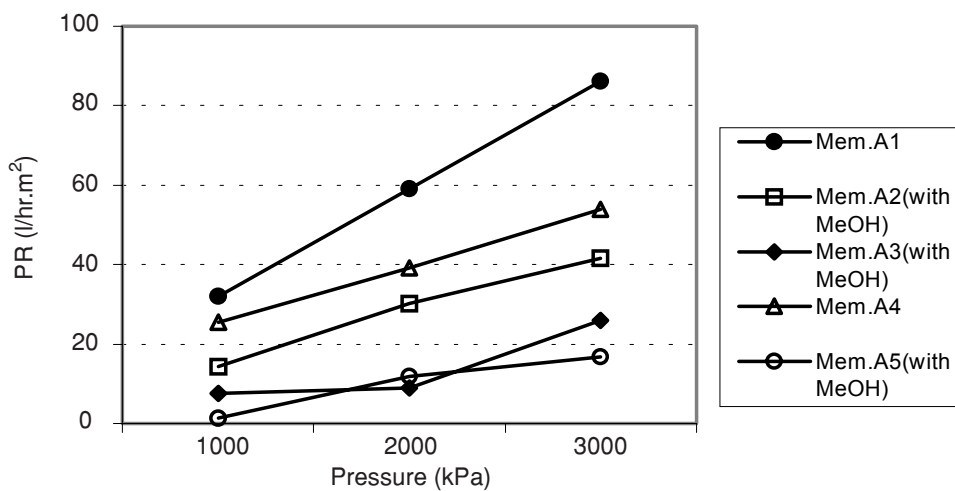


Figure 3 Salt permeation flux versus pressure

port. Under otherwise identical operating conditions, a relatively lower value of $(D_{AM}/K\delta)$ for a reference solute indicates a relatively smaller average pore size on the membrane surface; likewise, for a given membrane a relatively low value of $(D_{AM}/K\delta)$ for any solute indicates less solute transport through the membrane and hence a higher solute separation in reverse osmosis (13). It is also observed that $(D_{AM}/K\delta)$ tends to decrease with increase in operating pressure. The rapid decrease in the values of A and $(D_{AM}/K\delta)$ respectively as shown in Figures 4 and 5 indicate that a remarkable decrease in the average pore size on the membrane surface might have occurred with an abrupt change in surface morphology of the membrane. The remarkable decrease in the average pore size on the membrane surface of membrane A2, A3 and A4 is due to the addition of the methanol into the dope solution. This seems to be in agreement with the work done by Wang [12] and Pinnau and Koros [1–3] which explain, the addition of nonsolvent, methanol in this case, into the membrane casting solution will accelerate the coagulation process from solution to gel when the casting solution is immersed in the coagulation bath. As a result, a membrane with a thinner skin layer and a more uniform structure could be obtained. Although no SEM images are taken, the parameters A and $(D_{AM}/K\delta)$ indirectly indicates there is a change in the morphology of the membranes produced and this technique has been used by Wang and other researchers.

It is also believed that the presence of methanol provoked changes on the internal membrane structure, which were apparent as a result of variations in demixing rates [6]. Based on the membrane performance and the values of A and $(D_{AM}/K\delta)$ obtained from this study, it is suggested that methanol promotes better membrane structure, thus better separation performance could be achieved.

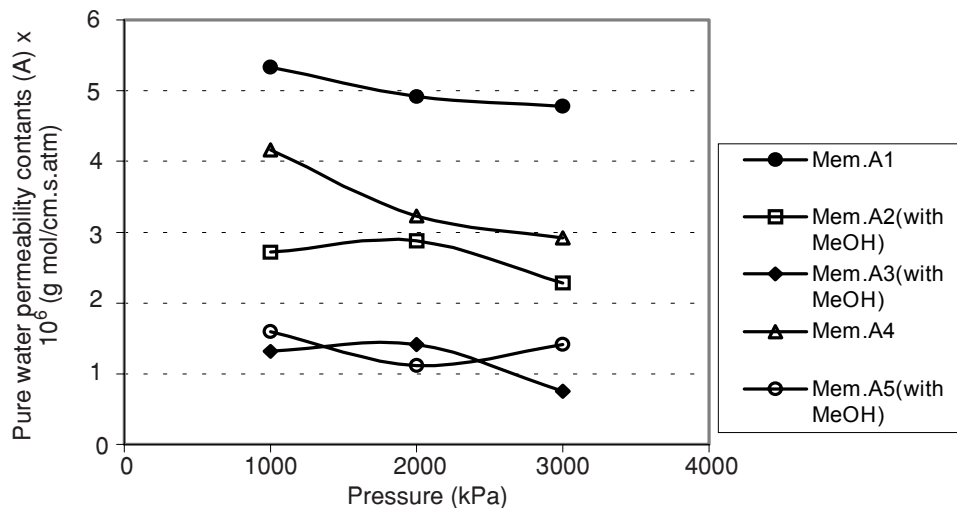


Figure 4 Pure water permeability constant versus pressure

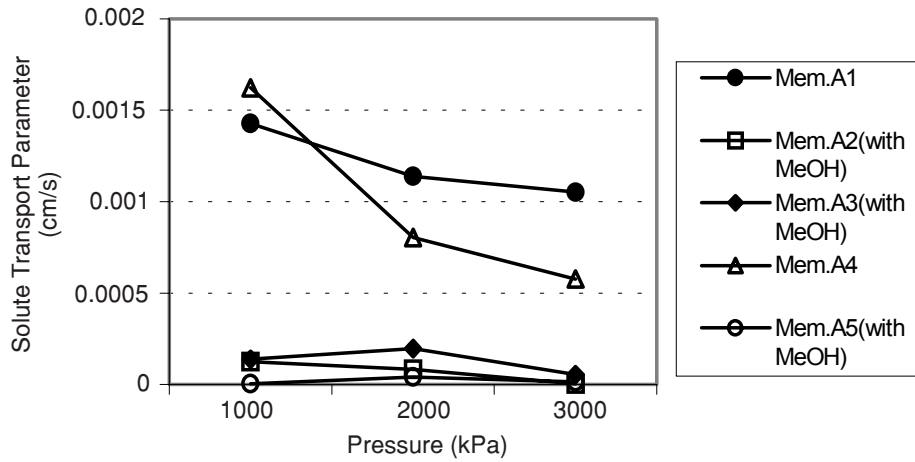


Figure 5 Solute transport parameter versus pressure

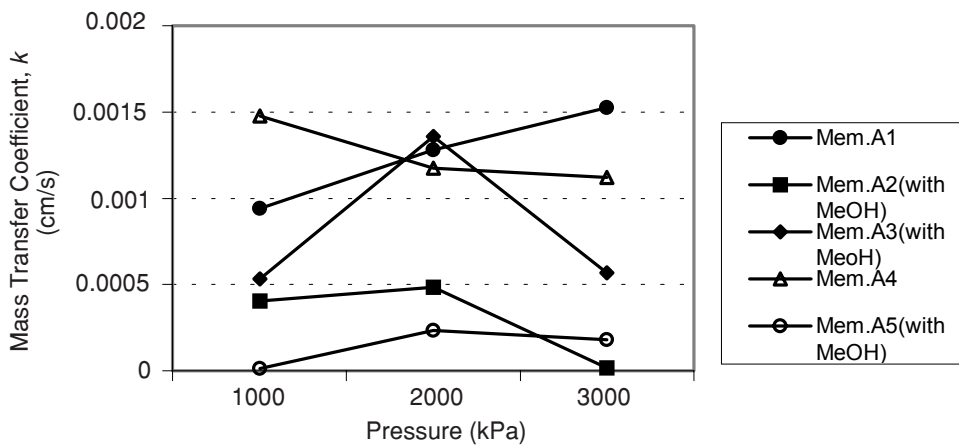


Figure 6 Mass transfer coefficient (k) versus pressure

4.0 CONCLUSION

The presence of methanol in the cellulose acetate-formamide type membrane has a large effect on the membrane performance and morphology. Formulations containing methanol seemed to exhibit better performance in terms of rejection rates. Changes in the water permeability constants A and solute transport parameter ($D_{AM}/K\delta$) for sodium chloride indicates that there is a marked change in the morphology. The remarkable decrease in both of these mentioned values indicate that there is a rapid decrease in the average pore size on the membrane surface which resulted in an abrupt change in the surface morphology of the membrane. The change in morphology has resulted in better membrane performance in terms of the solute separation where rejection rates of 75% is achievable. The results showed that the presence

of about 10 to 13% methanol in the casting solution formulation resulted in better membranes produced.

SYMBOLS

f	– salt separation.
C_{A3}	– concentration of sodium chloride in the permeate.
C_{A1}	– concentration of sodium chloride in the feed.
A	– pure water permeability constant ($\text{g}\cdot\text{mol H}_2\text{O}/\text{cm}^2\cdot\text{s}\cdot\text{atm}$).
PWP	– pure water permeability through effective area of membrane surface, ($\text{l}/\text{hr}/\text{m}^2$).
PR	– product rate through effective area of membrane surface ($\text{l}/\text{hr}/\text{m}^2$).
M_w	– molecular weight of water.
S	– effective membrane area (cm^2).
P	– operating pressure (atm).
NB	– solvent water flux through membrane ($\text{g}\cdot\text{mol}/\text{cm}^2\cdot\text{s}$).
N_A	– solute flux through membrane ($\text{g}\cdot\text{mol}/\text{cm}^2\cdot\text{s}$).
X_{A1}, X_{A2}, X_{A3}	– mole fraction of feed solution, concentrated boundary solution and product solution respectively.
c_1, c_2, c_3	– molar density of feed solution, concentrated boundary solution and product solution respectively. ($\text{g}\cdot\text{mol}/\text{cm}^3$).
π	– osmotic pressure of solution (atm).
$(D_{AM}/K\delta)$	– solute transport parameter for sodium chloride (cm/s).
k	– mass transfer coefficient on the high pressure side of membrane (cm/s).

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