

Separation of Ethylene Glycol–Water Mixtures with Composite Poly(vinyl alcohol)–Polypropylene Membranes

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ABSTRACT: Composite membranes consisting of a cross-linked poly(vinyl alcohol)(PVA) active layer on top of a porous polypropylene (PP) support were prepared with glutaraldehyde as a crosslinking reagent. The degree of crosslinking and the thickness of the active layer were determined with attenuated total reflection–Fourier transform infrared spectroscopy and scanning electron microscopy, respectively. The membranes were used in the pervaporation dehydration of ethylene glycol (EG)–water mixtures. The effects of the crosslinker content and operational conditions, including feed EG concentration and operating tem-

perature, on the permeation flux and selectivity of the PVA–PP composite membranes were investigated. We observed that the dehydration of a 80 wt % EG mixture at temperature of 60°C, a feed flow rate of 1.5 L/min, and a vacuum pressure of 10 mmHg could be effectively performed, and a moderate permeation flux and a high separation factor were obtained, that is, 0.91 kg m⁻² h⁻¹ and 1021, respectively. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1704–1710, 2011

Key words: EG/water mixtures; glutaraldehyde; Pervaporation; PVA/PP composite membrane

INTRODUCTION

Ethylene glycol (EG) is an important chemical widely used as a nonvolatile antifreeze and coolant and as an intermediate in the manufacturing of polyesters. At present, the main commercial route of EG production is the direct oxidation of ethylene to ethylene oxide followed by the hydrolysis of ethylene oxide.¹ In the hydrolysis reaction, excess water is added to ethylene oxide to increase the EG content and decrease the diethylene glycol and triethylene glycol contents in the product. When the molar ratio of water to ethylene oxide is about 22 : 1 in the reaction column, the product has the maximum content of EG and contains about 86 wt % water.² The excess water is removed from the hydrolysis product by multistage evaporation, and the EG-enriched product is then dehydrated in another distillation unit. Although EG and water do not form an azeotrope over the entire composition range, the separation of water from EG by distillation has been proven to be costly because high-pressure steam is required for reboiling because of the high boiling point of EG (198°C). In fact, EG–water separation by

distillation is ranked as the eighth most energy-intensive distillation operation in chemical industries.³

Pervaporation (PV) is an attractive alternative conventional separation processes for liquid mixtures. PV is the selective evaporation of one component in a liquid mixture by a membrane that is in direct contact with the mixture. This process depends on the fact that certain membranes permit the selective permeation of different species in a mixture and produce a permeate stream enriched in the preferentially permeating species. It is the selective permeability of the membrane that forms the basis of separation. A successful PV membrane needs primarily to be made from the proper materials and via appropriate procedures. PV is expected to provide an energy-efficient alternative. In PV, only a small fraction of the feed that permeates through the membrane vaporizes. Moreover, PV can be operated at temperatures lower than distillation; this makes it possible to use waste heat as the heat of vaporization needed for PV.⁴

Well-known applications of PV are the dehydration of ethanol, 2-propanol, acetic acid, and other chemical solvents. The dehydration of EG is relatively a new topic and has attracted significant interest from researchers.⁵

Almost all industrially important PV membranes are composites in which a selective layer is deposited on a porous support layer.⁶ Some composite polymeric membranes have been tried by early researchers for the separation of EG–water mixtures,

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including chitosan–polysulfone composite membranes,⁶ crosslinked poly(vinyl alcohol)(PVA)–poly(ether sulfone) composite membranes,⁷ PVA–polyacrylonitrile composite membranes,⁸ surface crosslinked chitosan–poly(ether sulfone) composite membranes,⁹ and crosslinked PVA–poly(sulfone) composite membranes.¹⁰

In this study, the separation of EG–water mixtures by PV through a novel PVA–polypropylene (PP) composite membrane was performed. At first, the preparation of some composite membranes with PVA as separating layer were conducted with different polymer materials (e.g., cellulose acetate (CA), polyamide (PA), Polyvinyl difluoride (PVDF), PP) as supporting layers. It was discovered that PVA solution is difficult to cast onto porous membranes of CA, PA, and PVDF, but it could be uniformly cast onto a porous membrane of PP.

Favorable properties, such as a high hydrophilicity, facile film-forming ability, good chemical and mechanical stability, and low manufacturing cost, make PVA an attractive membrane material for the PV dehydration of organic aqueous solutions. However, because of the large amount of hydroxyl groups (ca. 38%), PVA is not stable in aqueous solutions and has to be modified by techniques such as crosslinking, blending, hybridization, or grafting. Among them, crosslinking is very simple and effective because the degree of crosslinking and, thus, the hydrophilicity/hydrophobicity can be tuned conveniently by changes in the crosslinker concentration and crosslinking time.¹¹ Hence, crosslinked PVA can be an appropriate membrane material for the PV dehydration of EG aqueous solutions.

EXPERIMENTAL

Materials

PVA (98%, molecular weight = 145,000) and glutaraldehyde (GA, 50 wt %) were purchased from Merck (Darmstadt, Germany). PP was purchased from Membrana (Wuppertal, Germany); PP Accurel 2E, nominal pore size = 0.2 μm , membrane thickness = 165 μm]. EG (purity >99.8 wt %) was supplied by Arak Petrochemical Co. (Arak, Iran). Deionized water was used in all of the experiments.

Membrane preparation

PVA (5 g) was dissolved in 95 g of distilled water at 100°C. A certain amount of GA was then added to the solution. The solution was gently stirred for 2 h at room temperature, and the resulting homogeneous solution was then cast onto a PP porous substrate with the aid of a casting knife. The membranes were allowed to dry at room temperature for

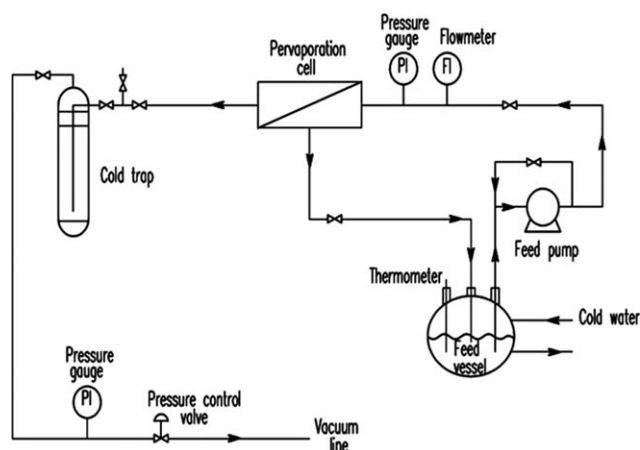


Figure 1 Schematic diagram of the experimental setup for PV.

24 h. The dried membranes were peeled off and heated in the oven. The crosslinking reaction time was 1 h at 150°C.¹² The GA content was also varied (0.1–0.4 mL).

Membrane characterization

To characterize the chemical composition of a membrane before and after crosslinking, attenuated total reflection (ATR)–Fourier transform infrared (FTIR) spectroscopy (Shimadzu model 8400S, Tokyo, Japan) was used. The infrared spectra of uncrosslinked (not treated with heat) and crosslinked membranes were obtained within a midrange (400–4000 cm^{-1}) at 25°C. The membrane morphology was examined with a scanning electron microscope (Philips model XL30, Eindhoven, Holland). Cross sections of the composite membranes were observed by scanning electron microscopy (SEM) after they were broken in liquid nitrogen. The membranes were then coated with gold before observation.

PV experiments

Figure 1 presents a schematic diagram of the setup for the PV experiments. The effective membrane area (A) was 10.4 cm^2 . EG–water mixtures were used as the feed. The feed solution was circulated by a pump with a flow rate of 1.5 L/min from the feed tank, which had a capacity of 5 L, to the PV cell, and the retentate was recycled back to the feed tank. The vacuum in the permeate side was maintained (10 mmHg) with a vacuum pump. The permeate was collected in a cold trap at -35°C . The operating temperature (T) was controlled with water circulation in coils. We determined the permeation rate gravimetrically by measuring the quantity of permeate sample collected over a given period of time. The compositions of the feed and the permeate

were measured with an accurate refractometer (2WAJ, Tokyo, Japan).

The separation performance of the membranes was evaluated on the basis of the total permeation flux (J) and separation factor (α):

$$J = \frac{Q}{At} \quad (1)$$

$$\alpha = \frac{Y_w(1 - X_w)}{X_w(1 - Y_w)} \quad (2)$$

where Q is the weight of the permeate (kg), t is the operating time (h), and Y_w and X_w are the weight fractions of water in the permeate and in the feed, respectively. Usually, there is a tradeoff between these two factors; that is, when one factor increases, the other decreases. The pervaporation separation index (PSI) is an overall measure of the membrane performance and is expressed as product of the selectivity and J , as follows:¹³

$$PSI = J(\alpha - 1) \quad (3)$$

The results for the PV dehydration of EG–water mixtures were found reproducible, and the errors were less than 5.0%.

Swelling measurement experiments

Weighted samples of circular pieces of crosslinked polymer films (crosslinked PVA layers, 1.8 cm in diameter) were soaked in EG–water mixtures. The films were taken out after different soaking periods and quickly weighed to determine the amount absorbed at the particular time after we carefully wiped off excess liquid. The films were then quickly placed back into the mixtures. The process was repeated until the films attained their steady-state weights after a certain period of soaking (24 h). The degree of swelling was calculated as follows:

$$\text{Degree of swelling} = \frac{W_s - W_d}{W_d} \times 100 \quad (4)$$

where W_s is mass of the swollen polymer and W_d is the mass of the dry polymer.

RESULTS AND DISCUSSION

ATR–FTIR analysis

The FTIR spectra of the uncrosslinked and crosslinked membranes are shown in Figure 2. The PVA membranes showed absorption peaks at 3300–3400 cm^{-1} for the hydroxyl (–OH) groups. A reduction in the absorption peak intensity was observed for

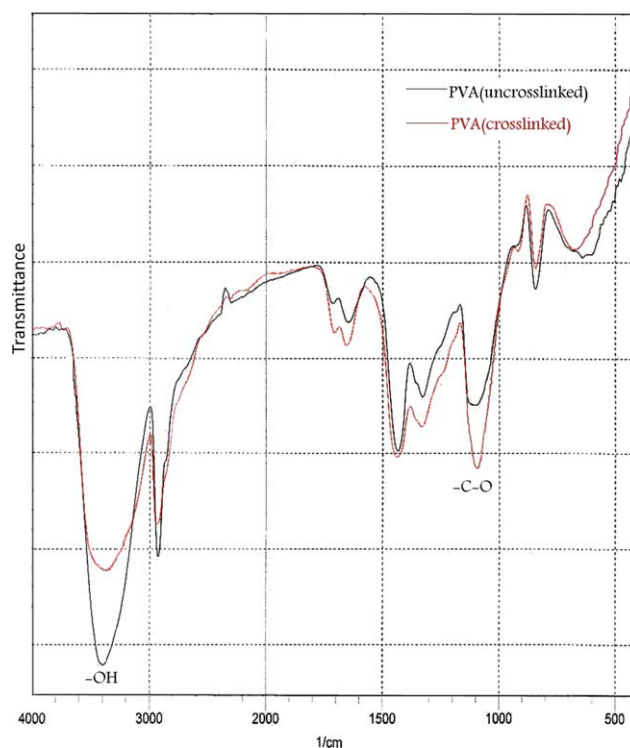


Figure 2 ATR–FTIR spectra of the PVA–PP and crosslinked PVA (GA 0.2 mL)–PP membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the crosslinked PVA membrane; this indicated that the number of the hydroxyl groups decreased after crosslinking. The absorption peaks at 1600–1800 and 1100 cm^{-1} corresponded to the acetal and ether groups, respectively, in the PVA membrane¹³ and reflected the crosslinking of the PVA membrane.

SEM analysis

Figure 3 shows structure of the composite membrane with selective PVA layers supported by the PP substrate. An interface was observed between PVA and PP. The top PVA layer was found to be free of defects or cracks, and the SEM analysis showed that the thickness of the PVA active layer was $7 \pm 2 \mu\text{m}$.

Effect of the crosslinker content

The effect of the GA content in the polymer solution on the PV performance of the crosslinked PVA membranes was investigated, and the results are presented in Figure 4. A mixture of 80 wt % EG was used as the feed at 60°C. We observed that J decreased with increasing GA content, and the highest α was obtained at a GA content of 0.2 mL. This phenomenon could be tentatively explained as follows: crosslinking changed not only the polymer structure but also the physicochemical nature of the

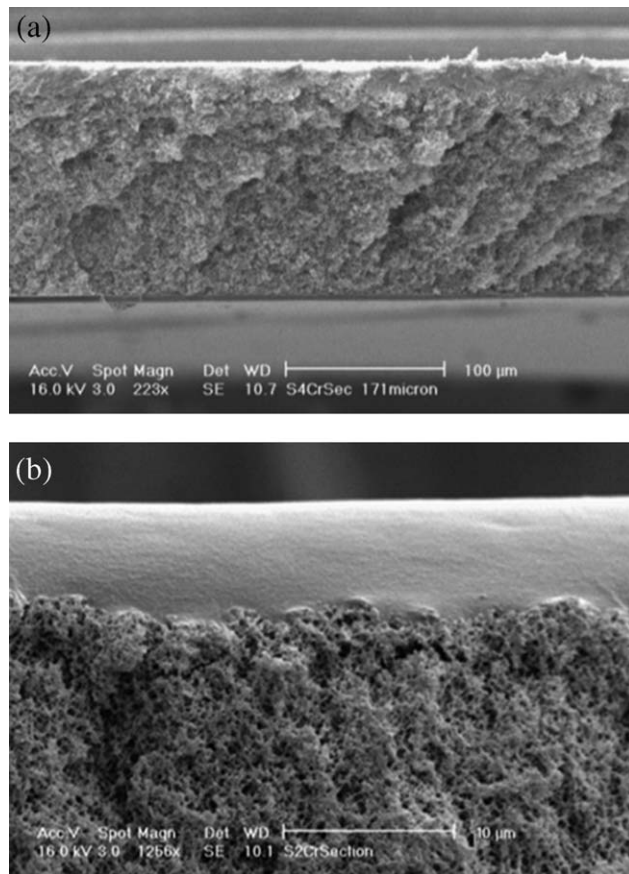


Figure 3 SEM analysis of the composite membrane.

membrane. As the GA content increased, the membrane hydrophobicity increased.¹¹ When the GA content was lower than 0.2 mL, the membrane swelling resulted in a lower selectivity. However, when the GA content was greater than 0.2 mL, the increased hydrophobicity of the membrane and the compact crosslinking structure decreased the membrane selectivity toward water; this led to the simultaneous reduction of α and J .

Effect of the feed composition

The effect of the EG concentration on J and α of the membranes was also studied. Figure 5 illustrates the total flux as a function of the EG concentration. As observed, an increase in the EG concentration in the feed decreased J . The flux reduction may have been due to the fact that at high EG concentrations, the water driving force was reduced.² The reduction rate was higher at lower EG concentrations, and this was attributed to the plasticization effect of water, which was a dominant factor that caused more swelling of the membrane at higher water concentrations.

The swelling degree of the PVA-PP composite membranes is presented in Figure 6. As observed, the swelling degree of the PVA-PP composite membranes decreased with increasing water

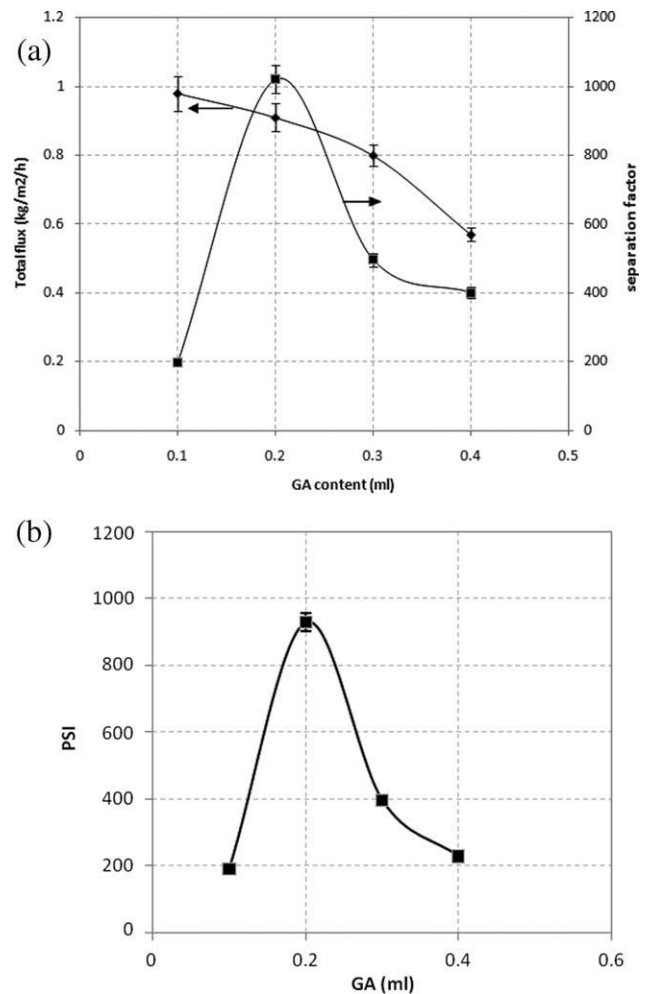


Figure 4 Effect of the GA content on the PV performance of the PVA-PP membranes (80 wt % EG in the feed at 60°C).

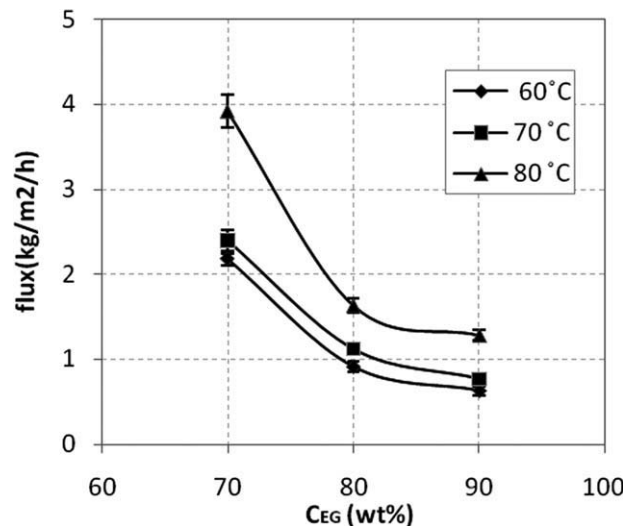


Figure 5 Effect of EG composition (C_{EG}) in the feed on the total flux.

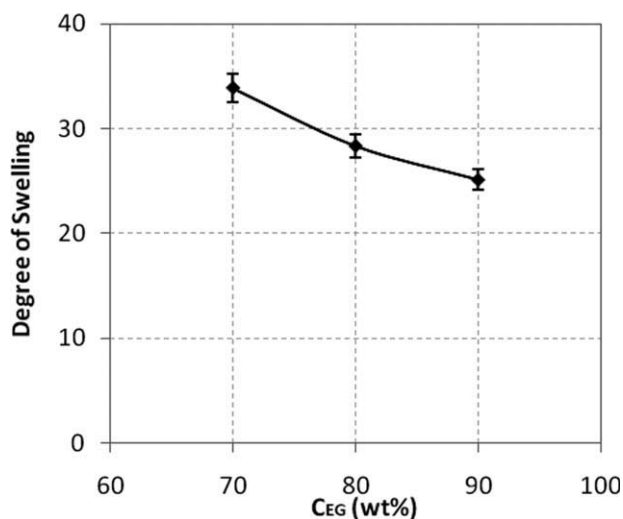


Figure 6 Effect of EG composition (C_{EG}) in the feed on the swelling degree of the PVA-PP composite membrane at 60 °C.

concentration in the feed. The absorbed water, which acted as a plasticizer in the PVA-PP composite membranes, lost the compact structure of the polymer chains and, consequently, reduced the permeation resistance.¹¹ Generally, the more swollen membranes had less selectivity because the swollen and plasticized upstream membrane layer allowed more EG molecules to escape into the permeate side. However, as shown in Figure 7, α of the composite membranes reached a maximum value of 1021 at 80 wt % EG concentration in the feed. With increasing EG concentration from 70 to 80 wt %, the transport of EG molecules was substantially inhibited and a higher selectivity toward water was obtained. This abnormal phenomenon was attributed to the influence of a coupling effect between EG and water.¹¹ A similar behavior was observed by Guo et al.¹⁴

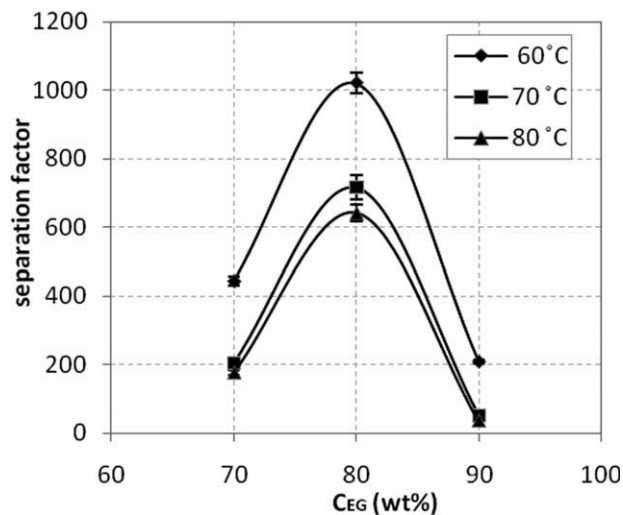


Figure 7 Effect of EG composition (C_{EG}) in the feed on α .

Effect of the feed temperature

The effect of T on the PV performance was also investigated over a temperature range of 60–90°C, with a constant feed flow rate (1.5 L/min). The experimental results are presented in Figure 8. With increasing temperature from 60 to 80°C, J increased, and α decreased. As the temperature increased, the polymer chain mobility and fractional free volume increased. Consequently, the transport of bulkier EG molecules, along with water molecules, was enhanced; this led to a higher J and a lower α .

From another point of view, it can be said that an increase in the temperature increased the saturated vapor pressure of the permeating species; this resulted in a higher driving force for mass transport through the membrane. As a result, J increased with increasing temperature. At elevated temperatures, a higher saturated vapor pressure of EG allowed EG to vaporize more easily, and this remarkably

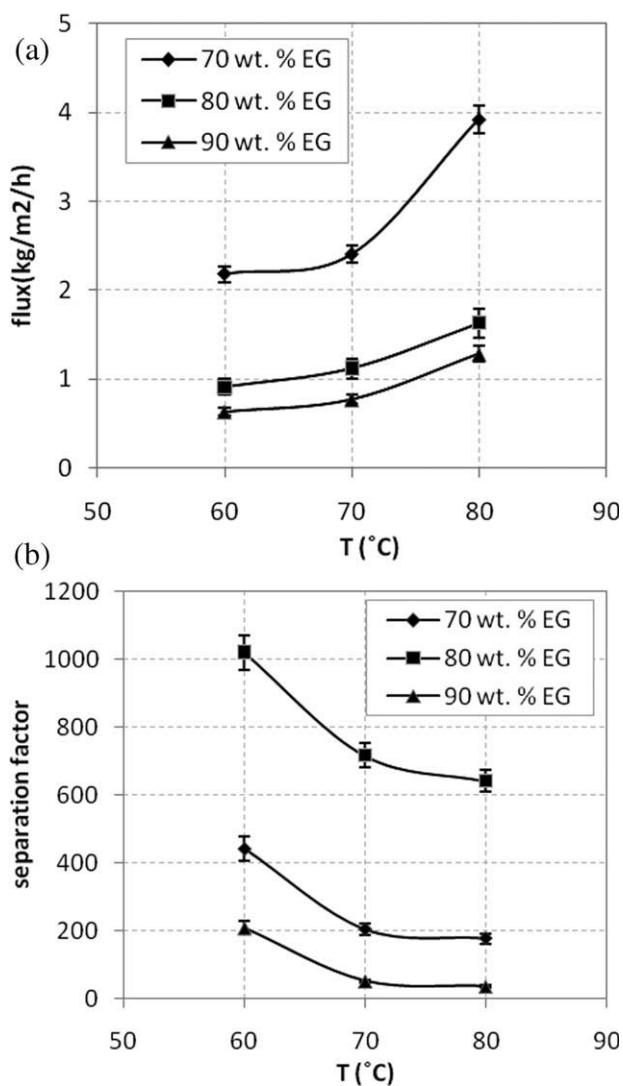


Figure 8 Effect of the feed temperature on α and J .

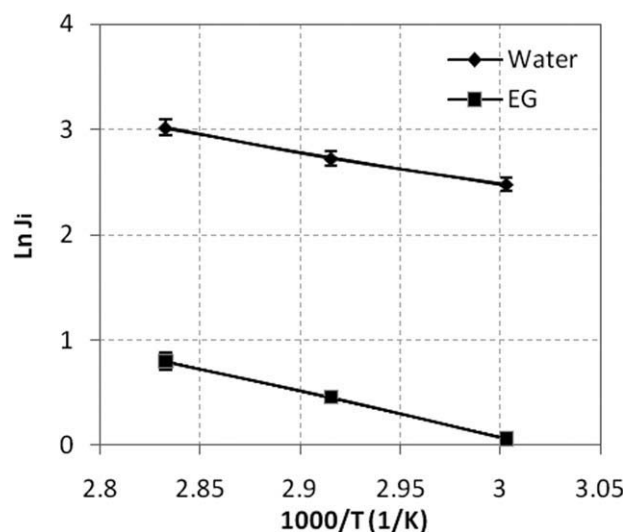


Figure 9 Arrhenius plots of J_i through the PVA–PP membrane at 80 wt % EG in the feed and 1.5 L/min feed flow rate.

decreased α . In addition, the feed viscosity had a major impact on the transport resistance. At a temperature of 60°C, the viscosities of water and EG were 0.46 and 5 cP, Although at 80°C, they were 0.35 and 2.85 cP, respectively. The viscosity of the liquids had a significant effect on the Re (Reynolds) number. As observed, increasing temperature had a more significant effect on the viscosity of EG than that of water. As a result, this may have resulted in considerable variations in the membrane performance. It can be said that an increase in the temperature increased the Re number and, consequently J , and decreased α .²

We also used the dependences of the water and EG fluxes on the temperature to calculate the activation energies by fitting the results to the Arrhenius equation:¹⁰

$$J_i = J_{i0} \exp(-E_{pi}/RT) \quad (5)$$

where J_i is the permeation flux of component i , J_{i0} is the permeation flux constant, E_{pi} is the apparent activation energy of the permeating component i , R is the gas constant, and T is the operating temperature (K).

Figure 9 shows an Arrhenius plot ($\ln J_i$ vs $1/T$) for water and EG through the PVA–PP membrane. The two calculated values of the activation energies were 26.3 and 35.1 kJ/mol for water and EG, respectively. On the basis of the solution–diffusion mechanism, the activation energy for permeation was a summation of the heat of sorption and the activation energy for diffusion (E_D). E_D is the energy needed for diffusion to start, and its value was, thus, positive. The sorption process, on the other hand, is often exothermic. The positive values of E_{pi} showed that the positive values of E_D overweighed the negative values of heat of sorption.¹⁵

Comparison of the PV performance for EG dehydration

A comparison between the published data in the literature and data the obtained in this study, as presented in Table I, showed that the performance of the synthesized PVA–PP composite membrane was better than the other membranes except one.¹¹ As

TABLE I
Comparison of the Experimental Data with the Reference z' Data for the PV of EG–Water Mixture

Membrane	Flux (kg m ⁻² h ⁻¹)	α	(C _{EG}) _F *(wt %)	T(°C)	PSI	Reference
Chitosan/PS	0.30	104	90	35	31.20	6
PVA/PES	0.38	402	83	80	152.76	7
GFT1001	0.22	1116	90	75	245.52	8
GFT1000	0.06	141	90	75	8.46	8
PAAM/PVA IPN	0.14	96	80	30	13.44	3
PAAc/PVA (30/70) IPN	0.48	196	80	30	94.08	3
Chitosan/PES	1.13	796	80	80	899.48	9
SPEEK	0.67	1100	80	70	737.00	16
PVA–GPTMS/TEOS	0.06	714	80	70	42.84	17
Cs–PAAc	0.22	105	80	70	23.10	18
PVA–silica nanocomposite	0.07	311	80	70	21.77	19
PVA/(GA15)	1.29	5509	80	70	7106.61	11
P-CS	0.15	130	80	70	19.50	20
PVA/PES	0.43	438	80	70	187.03	13
PVA/PS	0.36	987	90	60	355.32	14
PVA/PP	0.91	1021	80	60	928.2	This study

* EG composition in the feed.

PAAM: poly(acryl amide), IPN: interpenetrating polymer network, GFT: crosslinked PVA/PAN composite membrane, PES: poly(ether sulfone), SPEEK: sulfonated poly(ether ether ketone), GPTMS: glycidylxypropyltrimethoxysilane, TEOS: tetraethoxysilane, CsPAAc: chitosan-poly(acrylic acid), PAAc: poly (acrylic acid), PS: poly(sulfone), P-CS: phosphorylated-chitosan, GA15: the volume ratio of GA is 15 vol %.

observed, the PSI value of the PVA–PP composite membrane was higher than the other membranes. The membrane synthesized by Guo et al.¹⁴ had an extraordinary PSI value; however, our efforts to duplicate their procedure failed several times.

CONCLUSIONS

The PV performance of synthesized PVA–PP composite membranes for the dehydration of EG at different feed concentrations and temperatures was investigated. The best PVA–PP composite membrane was prepared when the PVA active layer was cross-linked with 0.2 mL of GA (50 wt %). The effects of the operating conditions, including the feed concentration and feed temperature on the PV performances of the membranes were investigated. The synthesized crosslinked PVA–PP composite membrane had the highest α of 1021 with a J of $0.91 \text{ kg m}^{-2} \text{ h}^{-1}$. The results obtained demonstrate the successful performance of the synthesized composite PVA–PP membrane for the dehydration of the EG–water mixtures.

References

1. Forkner, M. W.; Robson, J. H.; Snellings, W. M.; Kroschwitz, J. I.; Howe-Grant, M. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1994; Vol. 12.
2. Nik, O. G.; Mohebl, A.; Mohammadi, T. *Chem Eng Technol* 2006, 29, 1340.
3. Burshe, M. C.; Sawant, S. B.; Joshi, J. B.; Pangarkar, V. G. *Sep Purif Technol* 1998, 13, 47.
4. Baker, R. W.; Cussler, E. L.; Eykamp, W.; Koros, W. J.; Riley, R. L.; Strathmann, H.; *Membrane Separation Systems*, Wiley: Park Ridge, NJ, 1991.
5. Chapman, P. D.; Oliveira, T.; Livingston, A. G.; Li, K. *J Membr Sci* 2008, 318, 5.
6. Feng, X.; Huang, R. Y. M. *J Membr Sci* 1996, 116, 67.
7. Chen, F. R.; Chen, H. F. *J Membr Sci* 1996, 109, 247.
8. Jehle, W.; Staneff, T.; Wagner, B.; Steinwandel, J. *J Membr Sci* 1995, 102, 9.
9. Nam, S. Y.; Lee, Y. M. *J Membr Sci* 1999, 153, 155.
10. Hyder, M. N.; Huang, R. Y. M.; Chen, P. *J Membr Sci* 2009, 326, 363.
11. Guo, R.; Hu, C.; Li, B.; Jiang, Z. *J Membr Sci* 2007, 289, 191.
12. Durmaz-Hilmioglu, N.; Yildirim, A. E.; Sakaoglu, A. S.; Tulbentci, S. *Chem Eng Proc* 2001, 40, 263.
13. Hyder, M. N.; Huang, R. Y. M.; Chen, P. *J Membr Sci* 2008, 318, 387.
14. Guo, R.; Fang, X.; Wu, H.; Jiang, Z. *J Membr Sci* 2008, 322, 32.
15. Du, J. R.; Chakma, A.; Feng, X. *Sep Purif Technol* 2008, 64, 63.
16. Huang, R. Y. M.; Shao, P.; Feng, X.; Anderson, W. A. *Ind Eng Chem Res* 2002, 41, 2957.
17. Guo, R.; Hu, C.; Pan, F.; Wu, H.; Jiang, Z. *J Membr Sci* 2006, 281, 454.
18. Hu, C.; Li, B.; Guo, R.; Wu, H.; Jiang, Z. *Sep Purif Technol* 2007, 55, 327.
19. Guo, R.; Ma, X.; Hu, C.; Jiang, Z. *Polymer* 2007, 48, 2939.
20. Rao, P. S.; Sridhar, S.; Wey, M. Y.; Krishnaiah, A. *Ind Eng Chem Res* 2007, 46, 2155.