Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.698812

48 (2012) 191–198
October

Pervaporative separation of isopropyl alcohol/water mixtures: effects of the operation conditions

Nilüfer Durmaz Hilmioglu[a,*], Sema Tulbentci[b]

[a]*Department of Chemical Engineering, Engineering Faculty, Kocaeli University, 41380 Kocaeli, Turkey*
Tel. +90 262 303 35 45; Fax: +90 262 303 30 03; email: niluferh@kocaeli.edu.tr
[b]*Istanbul Technical University, Chemical and Metallurgical Faculty, Chemical Engineering Department, Maslak 34469, Istanbul, Turkey*

Received 15 September 2011; Accepted 30 April 2012

ABSTRACT

Isopropyl alcohol/water mixture was separated by an environmentally friendly membrane process: pervaporation. Pervaporation experiments were carried out with a polymer blend membranes of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) at different temperatures. PVA/PAA cross-linked membranes were prepared with different blend ratios. The influence of PVA/PAA ratio and of liquid mixture composition were investigated. The apparent activation energies were calculated at different temperatures. With increasing PAA content in the membranes fluxes decreased and selectivities increased. The flux increased with increasing operation temperature, as selectivity decreased. The studies showed that isopropylalcohol/water mixtures can be separated by pervaporation which is an energy efficient technology using the prepared membranes.

Keywords: Pervaporation; Isopropyl alcohol; Water; Poly(vinyl alcohol); Poly(acrylic acid); Apparent activation energy

1. Introduction

Alternative solvents have been searched by the oilseed industry to replace hexane which is toxic. Because of high oil solubility isopropy lalcohol (IPA) is the most suitable solvent. But oil solubility of IPA reduces at high water content near azeotropic point. This problem can be hanged up by using pervaporation which is a membrane process [1].

Membrane separation technology has been regarded as one of the most promising energy-saving processes. Pervaporation is considered as one of the most suitable separation technology among the membrane processes. It is applicable to the separation of azeotropic mixtures [2].

Pervaporation has been increased interest in the recent years because of its high separation efficiency and flux rates coupled with potential savings in energy costs, and it is environmentally friendly membrane proces [3].

The three applications of pervaporation are dehydration of solvents, water purification and organic/organic separations. Ethanol and isopropanol dehydration plants

---

*Corresponding author.

are the only processes installed on a large commercial scale. Some applications exist for removing or recovering VOCs from water. Organic/organic separations are efficient when combined with distillation in a hybrid process [4].

Research studies on pervaporation have been continued. Ethanol/water separations by pervaporation have been still investigated as the first main topic by researchers [5–8]. The other dehydration applications by pervaporation are water removal from solutions such as caprolactam, 1,4-dioxane, tetrahydrofuran [9,10]. Separation of dissolved organics (VOCs) from water by pervaporation is second main research topics [11,12]. Organic/organic mixtures are the third research area for pervaporation [13,14].

In the literature, the operating costs of different processes are compared. The hybrid systems combining distillation and pervaporation which is used for the azeotropic point have the lowest costs. There is a decrease in operating costs of approximately 53% compared to the azeotropic distillation which uses benzene as entranier that has extra cost [15]. Therefore, the studies should be played emphasis on membrane development for separation of IPA/water azeotropic mixtures by pervaporation.

Researchers concentrated on the development of membrane materials. Poly(vinyl alcohol) (PVA) is the object of pervaporation researchers even though PVA composite membrane material known as GFT membrane has been commercialized. Because of its high permselective characteristics, poly(vinyl alcohol) is still used for dehydration of alcohols by pervaporation, but it has poor stability in aqueous solutions. The stability of PVA is improved in aqueous mixtures by crystallization or cross-linking [16–24].

In this study, a polymer blend membranes of poly(vinyl alcohol) and poly(acrylic acid) were prepared by cross-linking and evaluated to separate IPA/water mixtures by pervaporation. Influence of blend composition, and feed composition at 40 °C were published in the previous study [25]. The influence of temperature on the pervaporation fluxes and pervaporation selectivities were investigated in this study for 50 °C and 60 °C. The apparent activation energies were calculated for PAA (5–20 wt.%) and water concentrations (5–20 wt.%) at 40, 50, 60 °C.

2. Experimental

2.1. Materials and methods

2.1.1. Materials

Isopropyl alcohol, poly(vinyl alcohol), poly(acrylic acid) were analytical grade. PVA (hydrolyzed 99%) with molecular weight of 89,000–98,000 and PAA with molecular weight of 2000 from Aldrich were used for preparing membranes.

2.1.2. Membrane preparation

The membranes were prepared in our laboratory, according to method described by Rhim et al. [18] and Gref et al. [21]. The procedure was reported in the previous work [25].

The membrane preparation procedure was presented shortly as following. PVA and PAA solutions were mixed together by varying composition to form a homogeneous solution for 24 h at room temperature. The blended homogeneous membranes were cast onto a glass plate. Then, the membranes were allowed for drying in air at room temperature. The dried blended membranes were peeled off after 2–3 days, and cross-linked in a nitrogen convection oven at 150 °C for 1 h by heating.

The esterification reaction between the carboxylic acid group in PAA and the hydroxyl group in PVA occurs. The PVA/PAA ratio was changed from 95/5 to 80/20. Because of brittleness, the membrane with a PVA/PAA ratio of 75/25 could not be tested.

2.2. Pervaporation experiments

Pervaporation experiments were carried out at different PVA/PAA ratios, different liquid feed mixture compositions, and different temperatures. The influence of temperature on the pervaporation fluxes and pervaporation selectivities were investigated at 50 °C and 60 °C.

The pervaporation cell and the pervaporation apparatus used in the experiments were such as given in the other article [25]. The pervaporation test procedure was presented briefly as following. The membrane was installed in the pervaporation cell. The effective membrane diameter was 6 cm. The feed temperature was kept constant at ±0.1 °C. The feed liquid was circulated through the pervaporation cell from a feed tank by a pump with a rate of 2 l/h. The pressure at the downstream side was kept approximately 10 mbar within ±1 mbar by a vacuum pump. The permeate was condensed in liquid nitrogen traps. The composition of the collected permeate was determined by GC (TCD Chromosorb 101).

The pervaporation properties are characterized by the flux J and the selectivity α. Fluxes were determined by measuring the weight of liquid collected in the cold traps for every 1 h at the steady state conditions which were reached 4 h later. The flux was normalized by dividing membrane thickness which were 35–45 μm.

The pervaporation selectivity is defined by the following equation:

$$a = \left(y_{\text{water}} / y_{\text{ipa}}\right) / \left(x_{\text{water}} / x_{\text{ipa}}\right) \tag{1}$$

where x and y represent the weight fractions in the feed and in the pervaporate, respectively. Indices water and ipa refer to the more permeated component, and the less permeated one, respectively.

The reproducibilities of fluxes and selectivities were within ±2%.

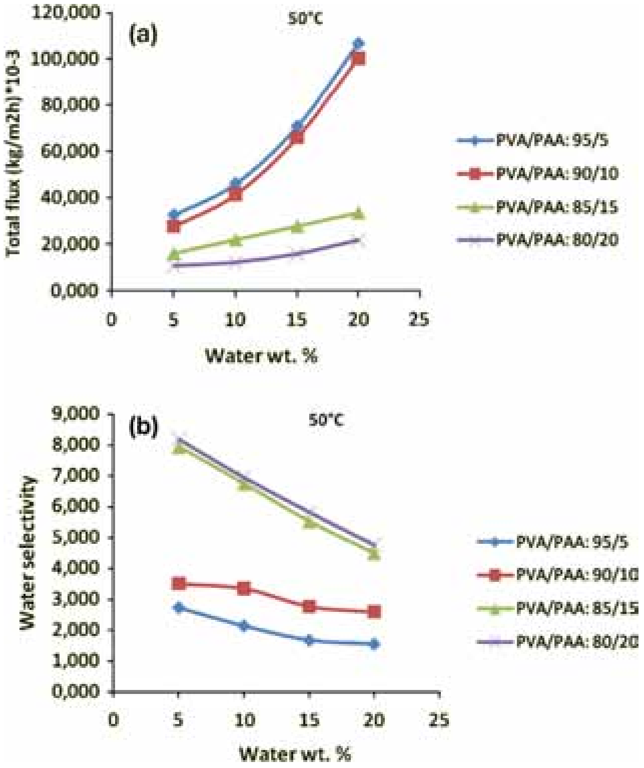

Fig. 1. The effect of the feed composition on the pervaporation flux (a) and selectivity (b) of IPA/water mixtures for various PVA/PAA ratios of the membranes at 50 °C.

3. Results and discussion

3.1. Influence of concentration

Pervaporation data for the IPA/water binary system at 50 °C are given in Fig. 1a and b for PAA (5–20 wt.%) and water concentration (5–20 wt.%).

A strong effect of the feed mixture concentration on the pervaporation performance was observed.

The total flux increased as the water concentration increased. The swelling tests which were given in the previous study [25] showed that, because of the higher swelling degree in higher water concentration, polymer chains become more flexible and this causes easier penetration of all components.

Degree of swelling values at 40 °C are also given in Table 1 [25].

There is normally a relation exists between the flux and selectivity. The selectivities were higher at lower concentrations of water. The sharp decrease in the separation factors with high concentrations of water is due to the facilitated transport of IPA by membrane swelling induced by sorption of excess water.

The interaction between the components and the membrane becomes stronger at lower concentration, therefore polymer segments form hydrogen bonding with water molecule and selectivity increases with decreasing water concentration of feed mixtures.

As a result, because of the plasticization effect, the total flux increased as the water concentration in the feed increased while the selectivity decreased [26,27].

3.2. Influence of PVA/PAA ratio

Pervaporation data for the IPA/water binary system at 60 °C are given in Fig. 2a and b for PAA (5–20 wt.%) and water concentration (5–20 wt.%).

Table 1
Degree of swelling (%) for water concentration (5–20 wt.%) and PAA (5–20 wt.%) at 40 °C [25]

T: 40 °C	Degree of swelling (%)											
Water wt.%	PVA/PAA: 95/5			PVA/PAA: 90/10			PVA/PAA: 85/15			PVA/PAA: 80/20		
	Total %	Water %	IPA %	Total %	Water %	IPA %	Total %	Water %	IPA %	Total %	Water %	IPA %
0	10.59	0.00	10.59	6.59	0.00	6.59	3.62	0.00	3.62	2.15	0	2.15
15	13.17	2.92	10.25	8.12	2.79	5.33	7.47	3.16	4.31	5.83	2.70	3.13
35	22.69	10.47	12.22	17.65	10.36	7.29	13.94	9.11	4.83	11.18	7.57	3.61
55	37.36	23.38	13.98	30.05	21.12	8.93	23.25	17.04	6.21	18.23	14.10	4.13
90	61.01	55.75	5.26	51.96	48.14	3.82	38.7	36.42	2.15	29.13	27.90	1.23
100	64.84	64.84	0.00	53.72	53.72	0.00	42.44	42.44	0.00	34.69	34.69	0

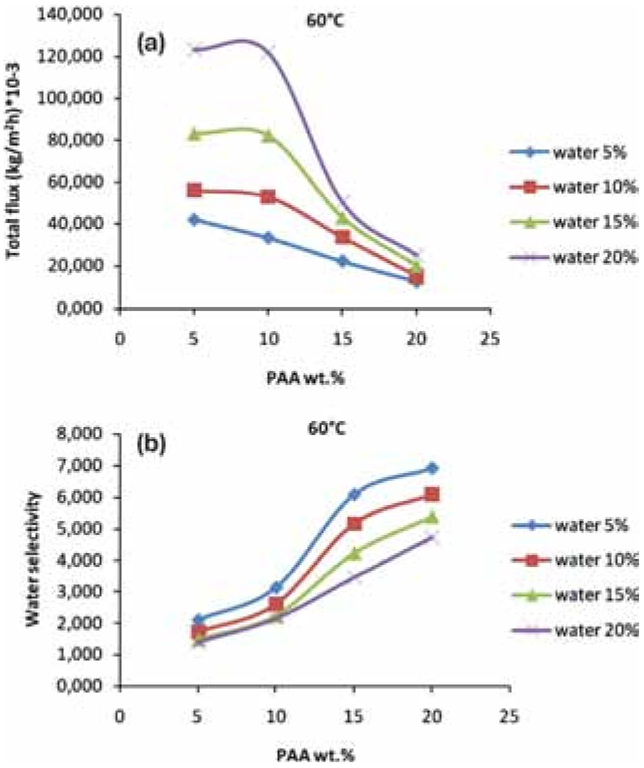

Fig. 2. The effect of the cross-linking agent on the pervaporation flux (a) and selectivity (b) of IPA/water mixtures for various water concentrations of the feed mixtures at 60 °C.

Pervaporation experiments show that pervaporation characteristics can be controlled with adjusting PVA/PAA ratio in the membranes.

As the amount of PAA content which is the cross-linking agent in the membrane increases, the flux decreases. This is natural that the flux decreases because of the more cross-linking effect, membrane network forms more compact.

According to the swelling tests which were given in the previous study [25] and given in Table 1, the decreasing flux with increasing PAA content can be caused by a lower swelling of the membranes. This showed that the cross-linking portions in the membranes increase with an increase in the PAA cross-linking agent. This can be a proof that the cross-linking reactions progressed properly.

Since PAA can preferentially interact with water which has more polarity, the pervaporation selectivities increase with the increasing PAA cross-linking agent. When the amount of PAA is more added because of the less chain mobility, there could exist the unreacted carboxylic acid groups in PAA. This free carboxylic acid group forms the hydrogen bonding with water molecule in the feed mixture and this interaction causes selectivity increasing.

As a conclusion, as the cross-linking agent in the membrane increases, cross-linking degree also increases. Therefore, swelling decreases. Because the membrane acts as a perm-selective medium, preferential sorption increases. Since polymer segment mobility decreases with cross-linking, the diffusion channels become more narrow for penetrants, and smaller permeant which interacts the membrane diffuses more selectively. This causes lower flux and higher selectivity [18,24].

3.3. *Influence of temperature*

The temperature effects of the pervaporation data are given as flux values in Fig. 3a–d and as selectivity values in Fig. 4a–d for water concentration (5–20 wt.%) and PAA (5–20 wt.%). Water selectivity and total flux were calculated at temperatures 50 °C and 60 °C. The flux and selectivity values at 40 °C are given in Table 2 [25].

The total flux is plotted in logarithmic scale as a function of reciprocal temperature in the figures. Figures show that there is an Arrhenius type relationship between the fluxes and operation temperature.

An Arhenius type relationship is given bythe following equation [26]:

$$J = J_0 \exp\left(-E_\mathrm{p} / RT\right) \tag{2}$$

where J_0 is the pre-exponential factor, E_p is the overall activation energy for permeation, RT is the usual energy term.

Calculated apparent activation energy values are given in Table 3 for water concentrations (5–20 wt.%) and PAA (5–20 wt.%).

The apparent activation energy is calculated from the slope of Fig. 3a–d and Eq. (2). They were found at around 19.33 kJ/kmol–16.610 kJ/kmol for PAA (5–20 wt.%) and water concentration (10 wt.%). These results explain flux decreasing while PAA ratio increasing. With increasing PAA content, activation energy which is necessary for transport increases, diffusion becomes more difficult and permeation decreases also.

The apparent activation energy were calculated as 18.755–16.583 kJ/kmol for water concentration (5–20 wt.%) and PAA (5 wt.%). These results explain flux increasing while water concentration in the feed increasing. With increasing water concentration, activation energy which is necessary for transport decreases, diffusion becomes easier and permeation is also increases.

The flux (J) increases gradually with the feed temperature. In pervaporation, the dependence of diffusivity on temperature is generally described by an Arrhenius type exponential law with the apparent activation energy for diffusion. When activation energy is a positive, diffusivity

Table 2
Pervaporation data (flux and selectivity) for water concentration (5–20 wt.%) and PAA (5–20 wt.%) at 40 °C [25]

T: 40°C	Flux (*J*) (kg/m^2 h) × 10^{-3}			
Water wt.%	PVA/PAA: 95/5	PVA/PAA: 90/10	PVA/PAA: 85/15	PVA/PAA: 80/20
5	27.167	23.886	10.545	8.842
10	35.917	36.543	13.341	10.289
15	55.194	47.943	16.704	11.789
20	84.000	71.771	20.659	13.316
	Selectivity ($\alpha_{\text{Water/IPA}}$)			
	PVA/PAA: 95/5	PVA/PAA: 90/10	PVA/PAA: 85/15	PVA/PAA: 80/20
5	2.917	3.916	8.412	9.567
10	2.310	3.782	7.147	8.123
15	1.936	3.347	5.849	6.911
20	1.931	3.172	4.767	5.633

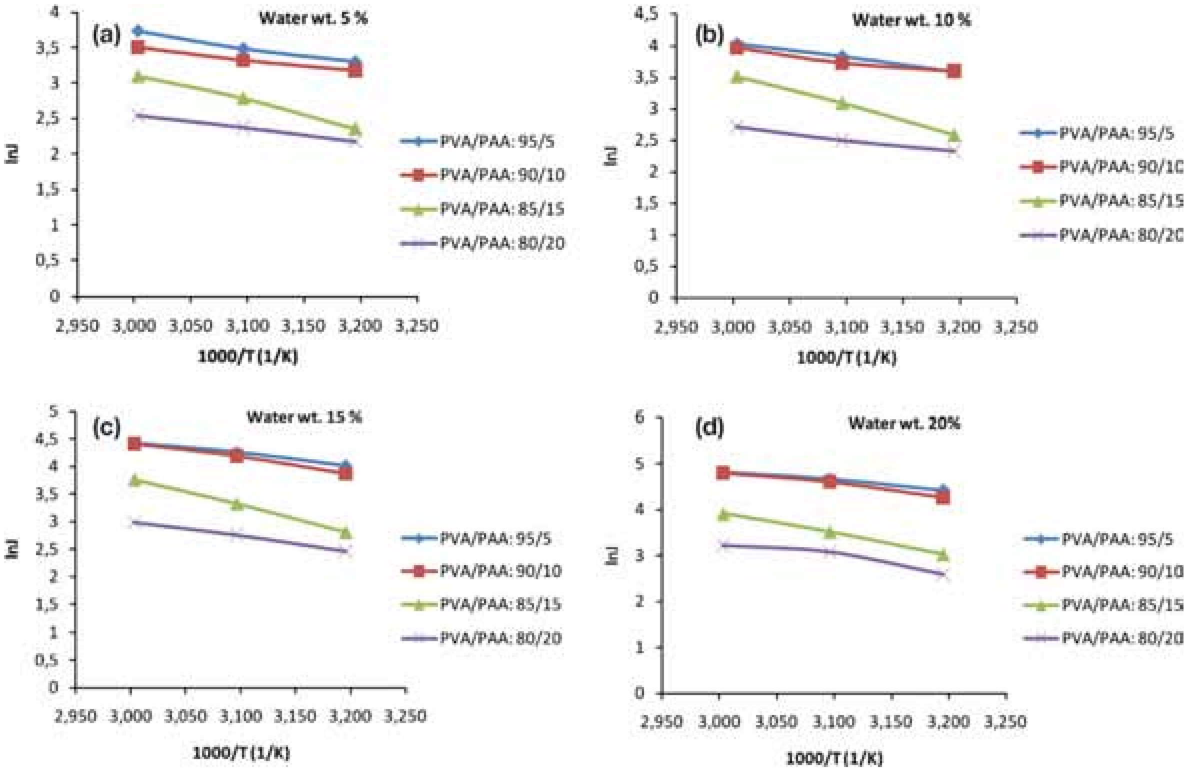

Fig. 3. The effect of the temperature on flux of various PVA/PAA membranes at 40, 50, 60 °C for water 5 wt.% (a), 10 wt.% (b), 15 wt.% (c), 20 wt.% (d).

increases with temperature. The flux may increase many times for each 10 °C temprature increment.

In addition to the enhanced diffusivity, the driving force for the mass trasfer increases with temperature also. The driving force is given by the difference in partial vapor pressure of the permeants between the feed side and the permeate side. The vapor pressure at the feed side increases as the feed temperature increases,

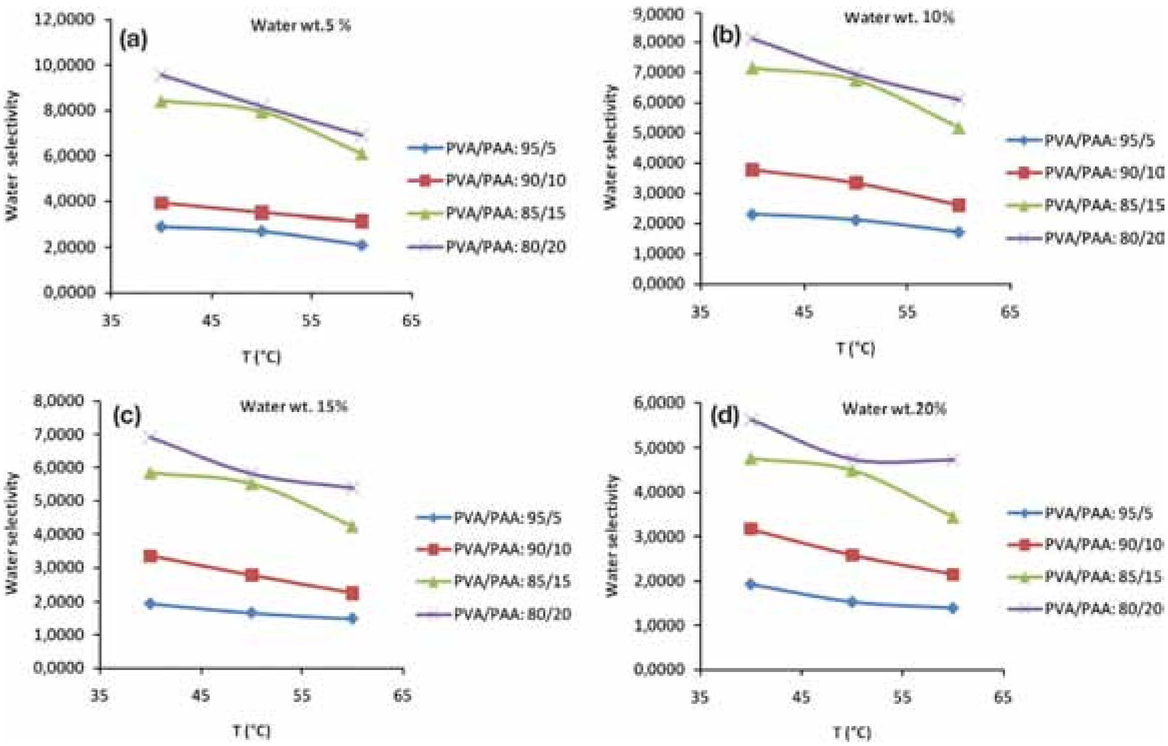

Fig. 4. The effect of the temperature on selectivity of various PVA/PAA membranes at 40, 50, 60 °C for water 5 wt.% (a), 10 wt.% (b), 15 wt.% (c), 20 wt.% (d).

while the vapor pressure at the permeate side is not affected by the feed temperature. Therefore, the driving force increases with the operation temperature.

The selectivity decreases with the temperature. It is hardly affected by the temperature, in most cases a small decrease of selectivity is found with increasing temperature. The interaction between the components and the membrane becomes stronger at lower temperature, therefore polymer segments form hydrogen bonding with water molecule and selectivity increases with decreasing temperature [3,26].

Table 3
Calculated apparent activation energy (E_p) values for water water concentration (5–20 wt.%) and PAA (5–20 wt.%)

PAA %	E_p (kJ/kmol)			
	Water wt.%: 5	Water wt.%: 10	Water wt.%: 15	Water wt.%: 20
5	18.755	19.433	17.898	16.583
10	14.359	15.983	23.473	22.893
15	32.218	40.006	40.924	38.541
20	15.553	16.610	22.754	27.349

3.4. Comparison of pervaporation performance data with the literature

The fluxes and selectivities of PVA membranes for the separation of IPA/water azeotropic mixtures and other mixtures were reported in the literature. PVA/PAA cross-linked membranes were tested for IPA/water in this study.

Table 4 compares the pervaporation performance of the various membranes used in the pervaporation of IPA/water mixtures. Table 5 compares the pervaporation performance of PVA/PAA membranes for different mixtures.

Pervaporation performances of the tested membranes for IPA/water mixtures could be acceptable values.

4. Conclusions

Membranes of a polymer blend of poly(vinyl alcohol) and poly(acrylic acid) that had been cross-linked were evaluated for the separation of IPA/water mixtures. Tested membranes were water selective.

The flux values were 8.842 kg/m^2 h × 10^{-3} at 40 °C [25], 10.737 kg/m^2 h × 10^{-3} and 12.658 kg/m^2 h × 10^{-3} at 50 °C and 60 °C, respectively for PAA (20 wt.%) and water concentration (5 wt.%).

Table 4
Comparison of pervaporation performance of different membranes for IPA/water mixtures

Feed composition (water wt.%)	Membrane	Operating temperature (°C)	Flux[a] (g/m^2 h)	Selectivity[a]	Reference
20	PVA cross-linked by 3 trimesoyl chloride	60	320	275	[30]
10	PVA cross-linked by sulfur-sucinic acid	70	206	1969	[29]
25	PVA cross-linked by amic acid	40	Partial flux of water: 400	50	[31]
20	PVA cross-linked by glutaraldehyde	60	250	180	[32]
12.3	PVA cross-linked by glutaraldehyde	40	79.75	45.23	[33]
5	PVA/PAA = 80/20	40	8.842	9.567	This study

[a] Flux and selectivity data were read from plots.

Table 5
Comparison of pervaporation performance of of PVA/PAA membranes for different mixtures

Feed mixture	Feed concentration	Membrane	Operating temperature (°C)	Flux[a] (g/m^{2}h)	Selectivity[b]	Reference
Dimethyl carbonate/methanol	Methanol (70 wt.%)	PVA/PAA (blend) = 90/10	70	510	2.8	[34]
Dimethyl carbonate/methanol	Methanol (70 wt.%)	PAA/PVA (blend) = 70/30	60	577	13	[35]
Methyl tert-butyl ether/methanol	Methanol (30 wt.%)	PAA/PVA (blend)= 0.26	30	6,2	48	[36]
Acetic acid/water	Water (10 wt. %)	PVA/PAA = 75/25	30	5,6	795	[37]
Phenol/water	Water (20 wt. %)	PVA/PAA = 80/20	30	70	3580	[38]
IPA/water	Water (5 wt. %)	PVA/PAA = 80/20	40	8.842	9.567	This study

[a]Flux and selectivity data were read from plots.

The selectivities were 9.567 at 40 °C [25], 8.185 and 6.919 at 50 °C and 60 °C, respectively, for PAA (20 wt.%) and water concentration (5 wt.%).

Results imply that an optimal pervaporation performance may be obtained by adjusting the operation conditions. Prepared membranes could have the potentials to break the azeotrope of IPA/water.

Pervaporation process is feasible technically in the separation of IPA/water azeotropic mixtures. Development of proper membranes could improve also the feasibility of pervaporation process commercially.

Symbols

E_p	activation energy
J	flux (kg/m^2 h)
J_0	pre-exponential factor
R	ideal gas constant (8.3145 kJ/kmol K)
T	absolute temperature (K)
x	weight fractions of the component in the feed
y	weight fractions of the component in the pervaporate
α	pervaporation selectivity

References

[1] S.S. Koseoglu and E. Hernandez, Oppurtunities for pervaporation, Proceedings of Seventh International Conference on Pervaporation Processes in the Chemical Industry, Bakish Materials Corporation, Nevada, 1995. pp.263–269.

[2] M. Yoshikawa, T. Matsuura and D. Cooney, Studies on the state of permeant in the membrane and its effect on pervaporation phenomena. J. Appl. Polym. Sci., 42 (1991) 1417–1421.

[3] R.Y.M. Huang, Pervaporation Membrane Separation Processes, Elsevier, The Netherlands 1991, pp.243, 271–272.

[4] R.W. Baker, Membrane Technology and Applications, 2nd ed., Wiley, England 2004, pp. 372.

[5] B.V. Di Carlo, J.C. Gottifredi and A.C. Habert, Pervaporation through composite membranes with plasma treatment of porous support. Desal. Water Treat., 27 (2011) 135–140.

[6] J. Wang, T. Yoshioka, M. Kanezashi and T. Tsuru, Prediction of pervaporation performance of aqueous ethanol solutions based on single gas permeation. Desal. Water Treat., 17 (2010) 106–112.

[7] S. Araki, T. Satoh, H. Doi, H. Yano and Y. Miyake, Properties of amino-functionalized silica membranes for the dehydration of water/ethanol mixtures. Desal. Water Treat., 7 (2009) 12–17.

[8] A. El-Gendi, D. Roizard, J. Grignard and E. Favre, Investigations of rubbery copolyimides for the preparation of asymmetric pervaporation membranes. Desal. Water Treat., 14 (2010) 67–77.

[9] Q. Li, P. Yu, T. Zhu, L. Zhang, Q. Li and Y. Luo, Pevaporation performance of crosslinked PVA and chitosan membranes for dehydration of caprolactam solution. Desal. Water Treat., 16 (2010) 304–312.

[10] M.B. Patil, R.S. Veerapur, S.D. Bhat, C.D. Madhusoodana and T.M. Aminabhavi, Hybrid composite membranes of sodium alginate for pervaporation dehydration of 1,4-dioxane and tetrahydrofuran. Desal. Water Treat., 3 (2009) 11–20.

[11] D. Jeong, J. Oh, I. Yum and Y. Lee, Removal of VOCs from their aqueous solution by pervaporation with PDMS-zeolite composite membrane. Desal. Water Treat., 17 (2010) 242–247.

[12] J. Xu and A. Ito, Removal of VOCs from water by pervaporation with a hollow-fiber silicone rubber membrane module. Desal. Water Treat., 17 (2010) 135–142.

[13] A.Y. Pulyalina, G.A. Polotskaya, I.G. Suschenko, T.K. Meleshko, L.M. Kalyuzhnaya and A.M. Toikka, Pervaporation membrane based on composite of polyimide with polyaniline or its copolymer. Desal. Water Treat., 14 (2010) 158–164.

[14] G.A. Polotskaya, A.V. Penkova, Z. Pientka and A.M. Toikka, Polymer membranes modified by fullerene C_{60} for pervaporation of organic mixtures. Desal. and Water Treat., 14 (2010) 83–88.

[15] V.V. Hoof, L.V. den Abeele, A. Buekenhoudt, C. Dotremont and R. Leysen, Economic comparison between azeotropic distillation and different hybrid systems combining distillation with pervaporation for the dehydration of isopropanol. Sep. Purif. Technol., 37 (2004) 33–49.

[16] S. Xiao, X. Feng and R.Y.M. Huang, Investigation of sorption properties and pervaporation behaviors under different operating conditions for trimesoyl chloride-crosslinked PVA membranes. J. Membr. Sci., 302 (2007) 36–44.

[17] S. Xiao, R.Y.M. Huang and X. Feng, Preparation properties of trimesoyl chloride crosslinked poly(vinyl alcohol) membranes for pervaporation dehydration of isopropanol. J. Membr. Sci., 286 (2006) 245–254.

[18] J.W. Rhim, M.Y. Sohn, H.J. Joo and K.H. Lee, Pervaporation separation of binary organic–aqueous liquid mixtures using crosslinked PVA membranes. I. Characterization of the reaction between PVA and PAA, J. Appl. Polym. Sci., 50 (1993) 679–684.

[19] C.K. Yeom and R.Y.M. Huang, Pervaporation separation of aqeous mixtures using crosslinked poly(vinyl alcohol). I. Characterization of the reaction between PVA and amic acid. Die Angewandte Makromolekulare Chemie, 184 (1991) 27–40.

[20] K.J. Kim, S.B. Lee and N.W. Han, Effects of the degree of crosslinking on properties of poly(vinyl alcohol) membranes. Polym. J., 25 (12) (1993) 1295–1302.

[21] R. Gref, Q.T. Nguyen, P. Schaetzel and J. Neel, Transport properties of poly(vinyl alcohol) membranes of different degrees of crystallinity. I. Pervaporation results. J. Appl. Polym. Sci., 49 (1993) 209–218.

[22] Z. Yuzhong, Z. Keda and X. Jiping, Prefential sorption of modified PVA membrane in Pervaporation. J. Membr. Sci., 80 (1993) 297–308.

[23] H.C. Park, Separation of alcohols from organic liquid mixtures by pervaporation, PhD Thesis, Twente University, Netherlands 1993. p.68–88.

[24] .W. Rhim and Y.K. Kim, Pervaporation separation of MTBE–methanol mixtures using cross-linked PVA membranes. J. Appl. Polym. Sci., 75 (2000) 1699–1707.

[25] N. Durmaz Hilmioglu and S. Tulbentci, Separation of IPA/water mixtures by pervaporation: sorption and pervaporation results. Vacuum, 72 (2004) 35–40.

[26] S. Zereshki, A. Figoli, S.S. Madaeni, S. Simone, M. Esmailinezhad and E. Drioli, Pervaporation separation of MeOH/MTBEE mixtures with modified PEEK membrane: effect of operating conditions. J. Membr. Sci., 371 (2011) 1–9.

[27] S. Cao, Y. Shi and G. Chen, Pervaporation separation of MeOH/MTBE through CTA membrane. J. Appl. Polym. Sci.,, 71 (1999) 377-386.

[28] H.C. Park, N.E. Ramaker, M.H.V. Mulder and C.A. Smolders, Separation of MTBE-methanol mixtures by pervaporation. Sep. Sci. Technol., 30 (1995) 419–433.

[29] J.W. Rhim, C.K. Yeom and S.W. Kim, Modification of poly(vinyl alcohol) membranes using sulfur–succinic acid and its application to pervaporation separation of water–alcohol mixtures. J. Appl. Polym. Sci.,, 68 (1998) 1717–1723.

[30] S. Xiao, R.Y.M. Huang and X. Feng, Preparation and properties of trimesoyl chloride crosslinked poly(vinyl alcohol) membranes for pervaporation dehydration of isopropanol. J. Membr. Sci., 286 (2006) 245–254.

[31] C.H. Lee and W.H. Hong, Influene of different degrees of hydrolysis of poly(vinyl alcohol) membrane on transport properties in pervaporation of IPA/water mixture. J. Membr. Sci., 135 (1997) 187–193.

[32] J. Yu, C.H. Lee and W.H. Hong, Performances of crosslinked asymmetric poly(vinyl alcohol) membranes for isopropanol dehydration by pervaporation. Chem. Eng. Process., 41 (2002) 693–698.

[33] P. Das, S.K. Ray, S.B. Kuila, H.S. Samanta and N.R. Singha, Systematic choice of crosslinker and filler for pervaporation membrane: a case study with dehydration of isopropyl alcohol–water mixtures by polyvinyl alcohol membranes. Sep. Purif. Technol., 81 (2011) 159–173.

[34] L. Wang, J. Li, Y. Lin and C. Chen, Crosslinked poly(vinyl alcohol) membranes for separation of dimethyl carbonate/methanol mixtures by pervaporation. Chem. Eng. J., 146 (2009) 71–78.

[35] L. Wang, J. Li, Y. Lin and C. Chen, Separation of dimethyl carbonate/methanol mixtures by pervaporation with poly(acrylic acid)/poly(vinyl alcohol) blend membranes. J. Membr. Sci., 305 (2007) 238–246.

[36] G. Gozzelino, Pervaporation of methanol/methyl-*t*-butyl ether mixtures through poly(vinyl alcohol)/poly(acrylic acid) blend membranes. Sep. Sci. Technol., 40 (2005) 2265–2276.

[37] J.W. Rhim, S.W. Yoon, S.W. Kim and K.H. Lee, Pervaporation separation and swelling measurement of acetic acid–water mixtures using crosslinked pva membranes. J. Appl. Polym. Sci., 63 (1997) 521–527.

[38] J.W. Rhim, M.Y. Sohn and K.H. Lee, Pervaporation separation of binary organic-aqueous liquid mixtures using cross-linked pva membranes. II. Phenol–water mixtures. J. Appl. Polym. Sci., 52 (1994) 1217–1222.