

Pervaporation Separation of Isopropanol–Water Mixtures Using Mixed Matrix Blend Membranes of Poly(vinyl alcohol)/Poly(vinyl pyrrolidone) Loaded with Phosphomolybdic Acid

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Received 14 July 2010; accepted 11 November 2010

DOI 10.1002/app.33791

Published online 23 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Mixed matrix membranes of poly(vinyl alcohol) and poly(vinyl pyrrolidone) blends were prepared by loading with phosphomolybdic acid (PMA) and their pervaporation (PV) properties were investigated for the PV separation of isopropanol. Membrane performance shown a dependence on the extent of PMA loading. The 4 wt % PMA-loaded blend membrane had the highest separation factor of 29991, which declined considerably at higher loading. The flux of 4 wt % PMA-loaded membrane was lower than that of nascent blend membrane.

Feed water composition and temperature influenced the PV performance. Solubility selectivity was higher than diffusion selectivity. Degree of swelling was smaller after PMA loading exhibiting better separation ability. The PV results were analyzed using the Flory-Huggins theory and sorption was dominated by Langmuir's mode. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 711–719, 2011

Key words: pervaporation; phosphomolybdic acid; PVA/PVP blend; isopropanol–water mixture

INTRODUCTION

Isopropanol (IPA) is widely used as a solvent in pharmaceutical industry as well as in many chemical processes such as acetone production, solvent extraction, and in the manufacturing of hydrogen peroxide. High purity grade IPA is required as a cleansing agent in semiconductor and electronic industries.^{1–3} Azeotropic composition of IPA with water is 12.2%, which makes it difficult to separate from water by the conventional distillation without recourse to carcinogenic benzene as an entrainer.⁴ Alternatively, membrane-based pervaporation (PV) separation offers high separation efficiency along with high energy savings.^{5–8}

Blends of poly(vinyl alcohol), PVA and poly(vinyl pyrrolidone), PVP are miscible in all proportions and then when loaded with phosphomolybdic acid (PMA) offered better PV performances for ethanol dehydration.⁹ Herein, we report the PV separation performance of the same membranes for IPA–water mixtures. The effect of PMA loading on swelling

and PV separation was investigated. The results were analyzed using Flory-Huggins theory¹⁰ to estimate binary interaction parameters. The sorption, diffusion, and permeation parameters have been estimated in the temperature interval of 30–60°C. Arrhenius parameters evaluated from these data have been used to discuss the temperature effects on the separation abilities of the membranes for IPA dehydration.

EXPERIMENTAL

Materials

Poly(vinyl pyrrolidone), $M_w = 40,000$ was purchased from SRL, Mumbai, India. Poly(vinyl alcohol) of $M_w = 125,000$, PMA, glutaraldehyde (GA) and IPA were all purchased from s.d. fine Chemicals, Mumbai, India. All the chemicals were of reagent grade samples and were used without further purification. Double-distilled water was used throughout the study.

Membrane preparation

Blend membranes of PVA/PVP were prepared by solution casting method by separately dissolving 6 g of PVA or PVP in 100 mL of distilled water at 90°C⁹ and by mixing them volumetrically 9 : 1. The

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Contract grant sponsor: University Grants Commission, New Delhi, India; contract grant number: 37-336/2009(SR).

mixture was stirred for 30 min to afford homogeneous solution and filtered to remove any suspended particles. *In situ* crosslinking was done by adding 0.3 mL of GA to the above solution and the resulting solution was cast into membrane onto a clean glass plate in a dust-free environment; the membranes were dried at ambient temperature (30°C) and peeled off from the glass plate. Similarly, the mixed matrix membranes were fabricated by mixing 4, 8, or 12 wt % of PMA with respect to weight of blend polymer under vigorous stirring. Membranes thus prepared were designated as: M-0 for virgin blend of PVA/PVP (0.2 mL of concentrated HCl as a catalyst was used for crosslinking). The PMA-filled membranes containing 4 wt %, 8 wt %, and 12 wt % were designated as: M-4, M-8, and M-12, respectively.

Swelling and sorption studies

Swelling experiments were performed gravimetrically at 30°C for IPA/water mixture with variable water compositions of 10, 20, 30, and 40 wt %. Initial masses of the circularly cut (dia = 3 cm) membranes were taken by placing them on a single-pan digital microbalance (model AE 240, Mettler, Switzerland) sensitive to ± 0.01 mg. Samples were placed inside the specially designed airtight test bottles containing 30 cm³ of the test solvent and were placed in hot-air oven maintained at the constant desired temperature. Dry membranes were equilibrated by soaking in different compositions of the feed mixture in a sealed vessel at 30°C for 48 h. Swollen membranes were weighed immediately after carefully blotting them on a digital single pan microbalance. Sorbed liquids were recovered in a liquid nitrogen trap by desorbing the equilibrated sample in the purge and trap apparatus, which were analyzed by gas chromatography (Model: Ultima-2100, Netel India, Mumbai, India). The % degree of swelling, DS was calculated as:

$$DS(\%) = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \quad (1)$$

where W_s and W_d are weights of the swollen and dry membranes, respectively.

Sorption selectivity, α_s , was calculated as explained before.⁹

$$\alpha_s = \left(\frac{M_w}{M_I} \right) \times \left(\frac{F_I}{F_w} \right) \quad (2)$$

The diffusion selectivity, α_d , was calculated using the solution-diffusion theory⁷:

$$\alpha_d = \frac{\beta}{\alpha_s} \quad (3)$$

where β and α_s refer to separation factor and sorption selectivity, respectively.

Pervaporation experiment

PV experiments were performed in an indigenously built stainless steel apparatus described elsewhere,¹¹ which includes a cell of membrane area of 26.43 cm² and a feed volume of 200 cm³. The feed stock solution was maintained at a constant temperature controlled thermostatically using a water jacket. The cell consists of an efficient three-blade stirrer powered by a DC motor. The feed mixture was stirred at 200 rpm speed by maintaining the downstream pressure at 5 mbar using a vacuum pump (Model: ED-21, Hindhivac, Bangalore, India).

Before starting the PV experiment, test membrane was equilibrated for 3 h with the feed mixture and after establishment of steady state equilibrium, liquid permeate was collected and condensed in traps under liquid nitrogen atmosphere. Permeate was collected up to 8–10 h, and tests were carried out at the required constant temperatures. Collected permeate was weighed after attainment of the ambient temperature using a digital microbalance sensitive to ± 0.01 mg to determine flux and was analyzed by gas chromatography. The flux, J and separation factor, β , were calculated using:

$$J_i = \frac{W_i}{A \times t} \quad (\text{kg/m}^2 \text{ h}) \quad (4)$$

where i for water refers to moving component of the mixture, and W_i is weight of permeate (kg), A is effective area of the membrane (m²), and t is permeation time (h).

Separation factor, β being the ratio of permeability coefficient of water to IPA, was calculated using respective concentrations of the components in the feed and permeate as:

$$\beta = \left(\frac{P_w}{P_I} \right) \times \left(\frac{F_I}{F_w} \right) \quad (5)$$

where P_w and P_I are wt % of water and IPA in permeate, F_w and F_I are wt % of water and IPA in the feed, respectively. In PV experiments, even after continuously using the membranes for up to 8 h, they all remained in-tact without breakage, and hence, the same membranes were used for repeated PV runs.

RESULTS AND DISCUSSION

Characterization of membranes

Thickness of both pure blend membranes and mixed matrix membranes was around 50 ± 3 μm . The Fourier

Transform Infra Red (FTIR) of PMA and PMA-loaded blend membranes have been discussed before.^{9,12,13} X-ray diffraction data support the existence of free volume for a reduction in separation factor and increase of flux¹⁴; also, the presence of PMA in the blend reduced the crystallinity of the matrix. The Scanning Electron Microscope (SEM) images indicated uniform distribution of filler particles, facilitating higher water transport. The chain mobility in terms of glass transitions were studied before⁹ using dynamic mechanical thermal analysis and differential scanning technique.⁹

Pervaporation performance

Effect of added filler

Figure 1 displays the result of flux and separation factor at 30°C for all the membranes at 10 wt % water composition, a value almost close to azeotropic composition, i.e., 12.2% of water. For nascent blend membrane (M-0), separation factor is 312, which increased to 29,991 for M-4 membrane. Further increasing PMA loading, separation factor decreased to 12848 for M-8 and 8172 for M-12 membranes. Such a rapid decrease in separation factor at higher concentration of PMA is due to change of pore texture in the mixed matrix membranes and because of increase in void volume of the membrane phase after incorporating PMA particles. Possibly also, at high concentration of PMA particles, the leaching out of the particles might have taken place, making the membranes moiré brittle and less prone to water transport.

Notice that the flux of M-4 is lower than M-0 as well as M-8 and M-12 membranes, indicating the unfavorable trade off between flux and separation factor, a formidable task to achieve in PV separation. This may be because of the linear polymer clusters in M-4 might have resulted in a high density of func-

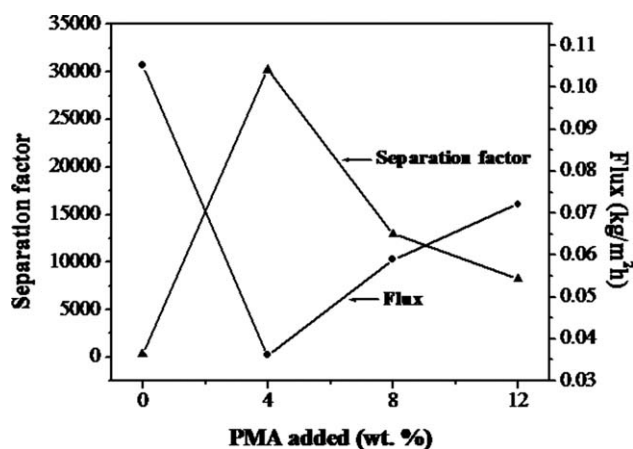


Figure 1 Effect of PMA content on PV performance at 30°C using 10 wt % feed water composition.

TABLE I
Effect of Added PMA Particles on Sorption and Diffusion Selectivities at 30°C Using 10 wt % Feed Water

Membranes	β	α_s expt.	α_s calc.	α_d
M-0	312	26	24	12.2
M-4	29,991	267	262	112
M-8	12,848	198	193	64.8
M-12	8172	166	161	49.1

tional groups of PMA, since it has higher separation factor than M-8 and M-12. Also, resistance to molecular diffusion and tortuosity of the diffusion pathway, resulting from lower degree of swelling did not change at higher PMA content. Similar results were observed by Wang et al.,¹⁵ in case of polyimide/Sodium Dodecyl Sulfate (SDS)-clay modified membranes used for the PV separation of water-ethanol mixture.

Following the principles of solution-diffusion model,⁷ permeability coefficient, β , is the product of solubility and diffusivity, is expressed as a product of sorption selectivity and diffusion selectivity. To test this empirical hypothesis, we have computed the values of sorption selectivity and diffusion selectivity using eqs. (2) and (3), respectively. As per data given in Table I, sorption selectivity is quite higher than diffusion selectivity, supporting higher transport of water than IPA, indicating that sorption process dominates the PV behavior. Notice that separation factor exhibits the same trend similar to sorption selectivity and diffusion selectivity. Also, M-4 exhibits higher sorption selectivity than all other membranes.

Influence of feed water composition

In this work, the overall PV performance of the blend mixed matrix membranes was investigated in comparison to the nascent blend membranes of PVP and PVA. The PV performance data as a function of feed water composition given in Table II suggest that for the unfilled M-0 membrane, % degree of swelling is considerably higher than observed for M-4. For both M-0 and M-4, degree of swelling increased considerably with increasing feed water composition (10–40 wt %). Conversely, separation factor declined considerably with increasing water composition. Thus, addition of PMA plays an important role to increase the membrane performance.

The presence of filler particles would make the transport path more tortuous as well as help to increase crosslink density with a reduction in membrane swelling. Higher water concentration of the feed results in more sorption of water in the membrane, high preferential interaction, increased

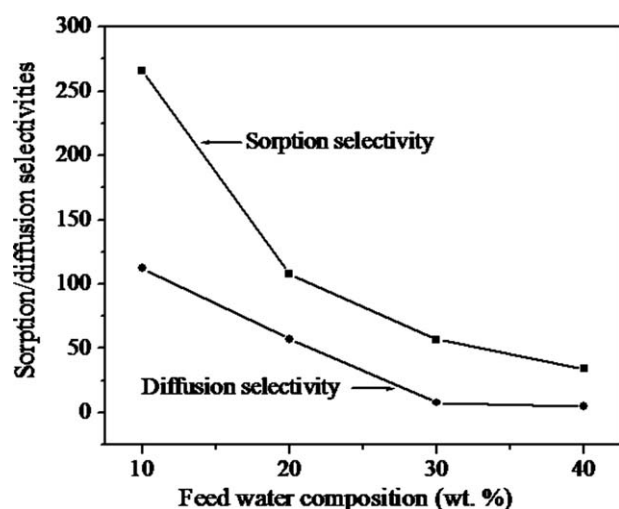


Figure 2 Sorption selectivity (α_s) and diffusion selectivity (α_d) of M-4 membrane at different feed water compositions at 30°C.

swelling, more open structure, and high IPA diffusion (bigger molecule, thus giving lower separation factor with a higher flux). Thus, for M-0, the observed lower separation factor to water is due to the retardation of blend polymer molecular chain motion in the presence of PMA particles, resulting in a lesser degree of swelling for M-4 than M-0 membrane. At 10 wt % water in the feed, the β value is 29,991 for M-4, which shows the effect of added PMA particles.

The data analysis indicates that the physico-chemical nature of the blend polymer in the presence of PMA particles might have changed. Heteropolyacids are like mineral acids having protons in the protected environment, allowing them to interact with hydroxyl groups of the blend polymer as well as water molecules, consequently reducing the fractional free volume channels in the bulk of the polymer matrix, due to reduced degree of swelling. With increasing feed water composition, more of water molecules are sorbed by PMA particles due to induced plasticization of the membrane polymer as

a result of increased chain mobility. This fact can be satisfactorily explained as per the solution-diffusion principles.

To test the above hypothesis, we have calculated solubility and diffusion selectivities for M-4 at varying feed water compositions. These results are displayed in Figure 2, wherein water is preferentially sorbed compared with IPA. We observe a drastic reduction in sorption selectivity from 10 wt % water-containing feed mixture to 20 wt % of water, which levels off at higher water compositions. The diffusion selectivity values at all compositions of feed water decline systematically from 10 to 30 wt % and later levels off. Because the driving force for permeation is chemical potential gradient between two faces of the membrane, the driving force is quasi-equal to the component chemical potential at the upstream side (in the feed composition) of the membrane for PV separation to take place at high vacuum, due to negligible chemical potential in the downstream side. However, chemical potential gradient varies slightly with the feed water composition from 10 to 40 wt %, whereas a greater decrease in sorption selectivity is observed compared with diffusion selectivity.

PMA exhibits pseudo-liquid phase behavior, wherein polar water molecules will enter into the bulk phase by expanding or contracting the distance between Keggin type of anions in the crystal lattice. Thus, lesser number of IPA molecules are sorbed onto the membrane surface without actually entering into the bulk due to higher propensity of H-bond formation between PMA protons and water existing as guarded protons viz., H_3O^+ or $H_5O_2^+$.^{16,17} With increasing feed water composition (10–40 wt %), more of water molecules are replaced with lesser number of IPA molecules for protonation to take place. After the protonation, IPA in the pseudo-liquid phase of PMA with its reduced size will permeate through the membrane, thereby affording high flux with a reduced separation factor. Thus, our results demonstrate the positive effect played by PMA

TABLE II
Effect of Feed Water Composition on Degree of Swelling, Flux, and PV Selectivity of M-0 and M-4

Membranes	Water in feed (wt %)	DS (%)	J (kg/m ² h)	β
M-0	10	59.3	0.105	312
	20	117.3	0.169	93
	30	171.7	0.200	29
	40	222.2	0.228	11
M-4	10	36.2	0.036	29991
	20	89.9	0.109	5710
	30	138.6	0.137	226
	40	194.4	0.164	88

TABLE III
Effect of Temperature on Flux, Separation Factor, and Diffusion Coefficients of 10 wt % Feed Water for M-4

Temp. (°C)	J (kg/m ² h)	β	D (cm ² /s)	
			Water	IPA
30	0.036	29,991	3.42×10^{-8}	3.79×10^{-12}
40	0.154	11,241	1.48×10^{-7}	4.32×10^{-11}
50	0.187	1130	1.79×10^{-7}	5.18×10^{-10}
60	0.222	400	2.10×10^{-7}	1.71×10^{-9}

particles after loading into PVA/PVP blend membrane to enhance its performance over that of the unfilled PVA/PVP blend membrane.

Diffusion coefficient and temperature effects

The concentration-independent diffusion coefficient, D_i of the permeating molecules was calculated using the Fick's diffusion equation¹⁸:

$$J_i = -D_i \left(\frac{dC_i}{dx} \right) \quad (6)$$

where J_i is permeation flux/unit area (kg/m² s), D_i is diffusion coefficient (m²/s), C_i is concentration of permeate (kg/m³), subscript i stands for water or IPA, and x is diffusion path length. For simplicity, we assume that the concentration profile along the diffusion pathway is linear, and hence, concentration-independent, D_i can be calculated as:

$$D_i = \frac{J_i h}{C_i} \quad (7)$$

where h is membrane thickness (50 μ m, in this study).

Calculated D of water and IPA between 30°C and 60°C compiled in Table III show an increase in flux with a decrease in separation factor, β . The D values of water are quite higher than those of IPA, supporting the water-selective nature of the membranes. The D values of water and IPA increased with increasing temperature. The activation parameters were evaluated for M-4 at 10 wt % water using the Arrhenius relationship for both permeation and diffusion processes as:

$$X = X_o \exp \left(\frac{-E_a}{RT} \right) \quad (8)$$

where X represents diffusion coefficient, D or permeation flux, J_p , X_o is a constant representing the pre-exponential factors, D_o or J_o , and E_a represents activation energy of permeation or diffusion, whereas RT is the usual energy term.

Arrhenius plots of $\ln J$ versus $1/T$ and $\ln D$ versus $1/T$ displayed in Figure 3(A,B) for permeation flux and diffusion, respectively, exhibit linear trends, suggesting that permeability and diffusivity follow the Arrhenius rule. From the least-squares fit of the linear plots, activation energies of permeability (E_p) and diffusivity (E_d) have been estimated. Permeation activation energy value of water (E_{pw}) is 45.1 kJ/mol, which is close to 45.7 kJ/mol for total activation energy (E_p), whereas activation energy of IPA (E_{pIPA}) is 172.5 kJ/mol, which is significantly higher than E_p (45.7 kJ/mol). Total activation energy for diffusion (E_d) is 45.9 kJ/mol, diffusion activation energy of water (E_{dw}) is 45.6 kJ/mol, whereas that of IPA (E_{do}) is 171.9 kJ/mol, suggesting that both permeating and diffusing molecules require higher activation energies to affect the molecular transport of liquids through the barrier membranes. Notice that $E_d > E_p$, yet the difference is not significant, indicating that both permeation and diffusion processes are contributing to the overall PV process. Using the values of E_p and E_d , the heat of sorption, ΔH_s was calculated as:

$$\Delta H_s = E_p - E_d \quad (9)$$

The resulting ΔH_s is negative (−0.2 kJ/mol), suggesting that the mode of transport is originated from Langmuir's sorption, which requires the pre-existence of a site in which sorption occurs by hole-filling mechanism, giving an exothermic contribution.¹⁸

Comparison of E_p values of the M-4 with other membranes reported earlier for IPA dehydration is displayed in Table IV. The E_p values for AlPO₄-5 (20 wt %)-filled NaAlg, NaAlg-charcoal-10, NaAlg-2, NaAlg-PVA-5, PVA/PMMA, and M-4 membranes are 11.9, 19.1, 24.9, 25.6, 36.5, and 35.6 kJ/mol, respectively. Higher values of E_p suggest higher membrane selectivity to water.

Thermodynamic analysis of pervaporation

A detailed thermodynamic analysis of sorption in terms of PV performance is attempted here based on

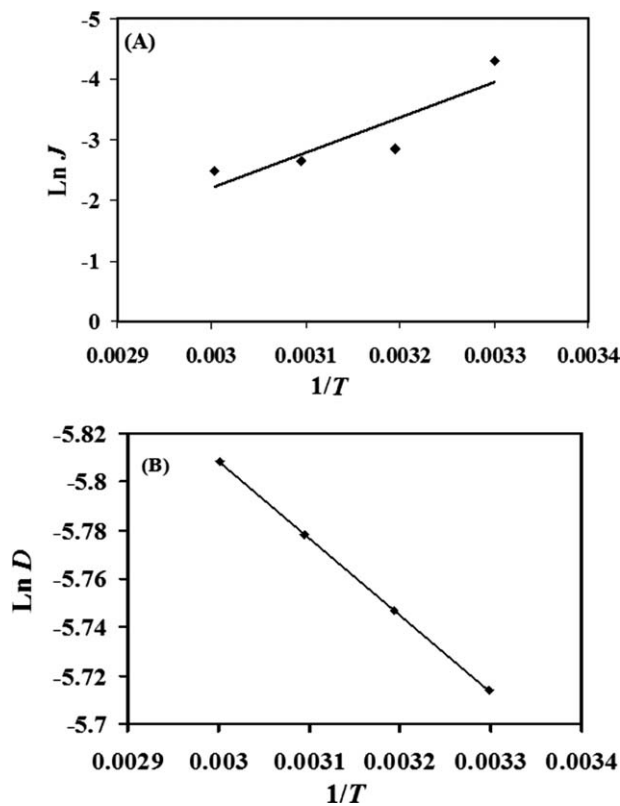


Figure 3 Arrhenius plot (A) $\ln J$ vs. $1/T$ and (B) $\ln D$ vs. $1/T$ for M-4 membrane.

Flory-Huggins theory.^{19–21} Thermodynamic equation for sorption selectivity, α_s , of a three-component system is given as:

$$\begin{aligned} \ln \alpha_s &= \ln \left(\frac{\Phi_1}{\Phi_2} \right) - \ln \left(\frac{v_1}{v_2} \right) \\ &= \left(\frac{V_1}{V_2} - 1 \right) \ln \left(\frac{\Phi_2}{v_2} \right) - \chi_{12}(\Phi_2 - \Phi_1) - \chi_{12}(v_1 - v_2) \\ &\quad - \Phi_P \left(\chi_{1P} - \frac{V_1}{V_2} \chi_{2P} \right) \end{aligned} \quad (10)$$

Here, Φ_i is volume fraction of the i th-component in the swollen polymer membrane, v_i is volume fraction of the i th-component in the external liquid

phase, and V_i is the respective molar volume(s). Subscripts 1, 2, and P refer to water, IPA, and polymer, respectively. The values of V_i at 30°C for water and IPA were taken from the literature,²² whereas volume fraction, ϕ_P of the polymer in the swollen state was calculated as²³:

$$\Phi_P = \left[1 + \frac{\rho_P}{\rho_S} \left(\frac{M_a}{M_b} \right) - \left(\frac{\rho_P}{\rho_S} \right) \right]^{-1} \quad (11)$$

where ρ_P and ρ_S are densities of the polymer and solvent, respectively; M_b and M_a are the masses of polymer before and after swelling. Density of the polymer was measured by benzene displacement method using a specific gravity bottle. Initially, the benzene-filled bottle and empty bottle weights were taken. Then, a weighed quantity of polymer was introduced into the bottle. Excess benzene was then wiped off using a soft filter paper and masses of the bottle along with benzene and polymer was taken. Volume of the polymer was used to calculate the density of polymer; molar volume of water + IPA mixture was calculated using²⁴:

$$V = \frac{(x_1 M_1 + x_2 M_2)}{\rho_m} \quad (12)$$

where x_1 and x_2 are mole fractions of components 1 and 2, respectively, of the mixture, M_1 and M_2 are the corresponding molecular weights, and ρ_m is density of water + IPA mixture.

Interaction parameter, χ_{12} between water and IPA was calculated using²⁴:

$$\chi_{12} = \frac{\{x_1 \ln(x_1/v_1) + x_2 \ln(x_2/v_2) + (\Delta G^E/RT)\}}{x_1 v_2} \quad (13)$$

where ΔG^E (J mol^{-1}) is excess Gibbs free energy of mixing, R is gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), and T is absolute temperature (K). Values of ΔG^E were calculated using activity coefficients, γ as:

$$\Delta G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (14)$$

TABLE IV
Comparison of E_p Values with Literature

Membranes	Feed water composition (wt %)	E_p (kJ/mol)	Reference
AlPO ₄ -5 (20 wt %)-filled NaAlg	12.6	11.9	30
NaAlg-charcoal	12.2	19.1	18
NaAlg	10	24.9	31
NaAlg-PVA	20	25.6	32
PVA/PMMA	10	36.5	33
M-4	10	45.7	This work

TABLE V
Selectivity Values, Permeances of Water, IPA, and Total Permeance of M-4 Membrane at Various Temperatures

Temp. (°C)	α_{ij}	J_i (g/m ² h kPa)	J_j (g/m ² h kPa)	Total permeance (g/m ² h kPa)
30	2342	1.93	0.03	1.96
40	889	9.54	0.42	9.96
50	90	13.05	5.56	18.6
60	32	17.15	19.9	37.0

In the absence of direct experimental data on γ_1 and γ_2 , we have used van Laar equation at 30°C to compute activity coefficient, γ_i of component, i in the mixture as:

$$\ln \gamma_i = A_{ij} \left(\frac{A_{ji}x_j}{A_{ij}x_i + A_{ji}x_j} \right)^2 \quad (15)$$

van Laar parameters, A_{ij} for water and A_{ji} for IPA were taken from the literature.²⁵

The polymer-solvent interaction parameter, χ_{iP} , was calculated as¹⁹:

$$\chi_{iP} = \frac{V_i(\delta_P - \delta_i)^2}{RT} \quad (16)$$

where δ_i is solubility parameter of the i th-component. Solubility parameters of polymer, water, and IPA were taken from the literature,²² but solubility parameter, δ of the blend was calculated using the additivity relationship:

$$\delta = w_1\delta_1 + w_2\delta_2 \quad (17)$$

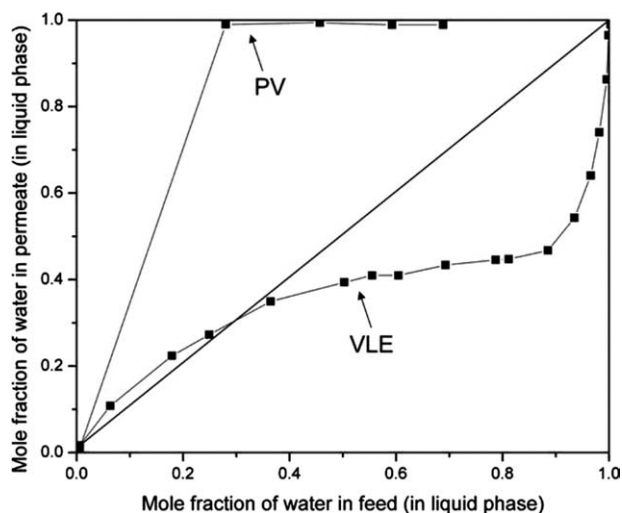


Figure 4 Comparison of vapor-liquid equilibrium curve with PV data for water-IPA mixtures.

Here, w_1 and w_2 are weight fractions, δ_1 and δ_2 are solubility parameters of PVA and PVP, respectively. These data were fitted into eq. (10) to compute sorption selectivity, α_s .

Experimental and theoretical values of sorption selectivity for all the PMA-loaded blend membranes are also compared in Table I, which suggest a good agreement and hence, one can conclude that the thermodynamic treatment based on Flory-Huggins theory can be successfully used to explain the PV separation phenomenon.

Effect of driving force and permeation

Effect of driving force and permeation due to interactions between feed liquid components is important in PV dehydration. To explain this effect, we have chosen M-4 membrane. Permeation rate, J as per Wijmans and Baker theory can be written as²⁶:

$$J_i = (p_i^f - p_i^p) \frac{P_i}{h} \quad (18)$$

$$J_j = (p_j^f - p_j^p) \frac{P_j}{h} \quad (19)$$

where the superscripts f and p refer to feed and permeate, respectively; p_i and p_j are partial vapor pressures of water and IPA, respectively; P_i and P_j are the corresponding membrane permeability coefficients of water and IPA that are the product of diffusion (D_{ij}) and solubility coefficients (S_{ij}). Diffusion and solubility coefficients are calculated as before²⁷; h is thickness of the membrane, whereas P_i/h and P_j/h are the permeances of water and IPA, respectively. The relationship between partial vapor pressure (p_{ij}^f), molar concentration of water (x_i), IPA (x_j), and activity coefficients of the individual components of the feed mixture obtained from van Laar eq. (15) are now written as:

$$p_i^f = x_i\gamma_i p_i^s \quad (20)$$

$$p_j^f = x_j\gamma_j p_j^s \quad (21)$$

Saturated vapor pressures of water (p_i^s) and IPA (p_j^s) were calculated using the Antoine equation:

$$\log p_{ij}^o = \frac{A - B}{T + C} \quad (22)$$

where p_{ij}^o are vapor pressures of water and IPA, respectively; A , B , and C are Antoine constants taken from the literature,²⁸ T is temperature in Kelvin. By considering the activity coefficient and molar concentrations of individual component, the saturated vapor pressure of water and IPA were calculated as:

$$P_i^s = x_i \gamma_i p_i^o \quad (23)$$

$$p_j^s = x_j \gamma_j p_j^o \quad (24)$$

Combining eqs. (18)–(24), we get:

$$J_i = \left(\frac{P_i}{h} \right) (x_i \gamma_i p_i^s - p_i^p) \quad (25)$$

$$J_j = \left(\frac{P_j}{h} \right) (x_j \gamma_j p_j^s - p_j^p) \quad (26)$$

The membrane selectivity, α_{ij} , was calculated as per Baker et al.,²⁹ and for a binary mixture, selectivity is the ratio of permeabilities or permeances of components, i and j through the membrane and is calculated as:

$$\alpha_{ij} = \frac{(P_i/h)}{(P_j/h)} \quad (27)$$

Permeances of water and IPA with respect to feed temperature for M-4 membrane displayed in Table V, suggest that water permeance is higher than IPA, because PMA is hydrophilic. Thus, PMA-loaded PVA/PVP matrix is well suited for PV separation of water from IPA.

Because the conventional distillation has drawbacks for azeotropic separation and hence, PV separation has better advantages as shown in Figure 4, typically for M-4 compared with vapor–liquid equilibrium curve obtained from distillation.³⁴ PV separation has thus a better option to conventional distillation to break the IPA–water azeotrope as the membrane acts as a third phase.

CONCLUSIONS

This work assesses the validity of PMA-loaded PVA/PVP blend matrix membranes for the PV dehydration of IPA. The high membrane performance was observed for 4 wt % PMA loaded membrane compared to higher loadings. Solubility selectivity being higher than diffusion selectivity,

suggests that separation is dominated by solubility. Flory-Huggins theory enabled to satisfactorily explain the thermodynamic processes involved in PV separation. With increasing feed water composition, membrane performance affected markedly in accordance with the swelling results, which also supports the findings of increase of separation factor with a decrease in flux. The near azeotropic composition of water-IPA mixture (10 wt % feed water) could be efficiently separated using the water-selective M-4 membrane that exhibited significantly lower activation energies for water than IPA with a negative heat of sorption. Furthermore, sorption is dominated by the Langmuir's mode of sorption.

T.M.A. thanks the CSIR [21(0760)/09/EMR-II], New Delhi, India for awarding CSIR Emeritus Scientist.

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