

Pervaporation Separation of Water-Isopropanol Mixtures Using Polymeric Membranes: Modeling and Simulation Aspects

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ABSTRACT: Pervaporation technique was used to separate water + isopropanol azeotropic mixtures at 30°C using pure sodium alginate, pure poly(vinyl alcohol), and blend membranes of sodium alginate containing 10 and 20 mass % of poly(vinyl alcohol). The membrane performance was studied by calculating flux, selectivity, pervaporation separation index, and enrichment factor. Pure sodium alginate membrane gave the highest pervaporation separation index for all compositions of water. Pervaporation experiments were carried out for 10 mass % containing water + isopropanol mixture at 30, 40, and 50°C. The Arrhenius activation

parameters were computed. The PV results have been analyzed by considering complete mixing and plug flow models. Design parameters, like membrane area, permeate concentrations, flux, stage cut, separation selectivity, etc., have been calculated for different feed compositions of water in the mixture. Results are explained in terms of sorption-diffusion principles. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1143–1153, 2005

Key words: pervaporation; sodium alginate; poly(vinyl alcohol); membrane; modeling

INTRODUCTION

Analysis of mass transfer in polymeric materials undergoing phase transition (liquid to vapor) has been of great interest to polymer scientists and chemical engineers. Prominent examples include the use of polymeric membranes in liquid separation problems by pervaporation (PV) technique, where low-energy requirements make it attractive compared to other processes like distillation.^{1–5} In PV applications, it is desirable to employ polymeric blends in which one component provides the desired permeability characteristics, while the other improves mechanical properties. Often, materials with enhanced barrier capabilities that exhibit a combination of high selectivity to a particular component of the binary mixture are required. The PV process offers advantages over con-

ventional distillation due to low energy requirements in effectively separating azeotropes, simple modular design, and its eco-friendly nature. In PV experiments, flux through membranes is generally low and hence, the process is economically feasible when the permeating molecules are minor constituents of the feed mixture.

In the earlier literature, different types of membranes made from natural polymers^{6–12} have been used in PV separation studies.⁴ However, due to abundant availability, biocompatibility, and commercial viability, sodium alginate (NaAlg) has been used to separate aqueous–organic mixtures.^{13–20} The advantages of using NaAlg are that it can be readily crosslinked with glutaraldehyde to impart mechanical strength and good permeability characteristics when blended with another hydrophilic polymer like poly(vinyl alcohol), PVA. In the present article, PV separation characteristics have been studied for pure NaAlg, pure PVA, and blend membranes of NaAlg with PVA for mixtures containing 10 to 50 mass % of water in isopropanol. Water-isopropanol mixture forms an azeotrope at 0.30 mol fraction of water and hence, dehydration of isopropanol up to > 99% purity can be difficult. The membrane performance was studied by computing selectivity, permeation flux, and pervaporation separation index (*PSI*). Temperature dependencies of these quantities have been investi-

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gated at 30, 40, and 50°C by selecting the membrane that gives the highest *PSI*. Programs were written to determine the minimum stripping concentration, permeate composition, stage cut (fraction of feed that has permeated through the membrane), dimensionless area, and the membrane area required for a given value of feed concentration and the desired value of retentate (product) concentration. Results of this study have been explained in terms of sorption-diffusion principles.

EXPERIMENTAL PROCEDURES

Materials

Poly(vinyl alcohol), PVA (mol. wt. 125,000) is a widely used hydrophilic polymer in PV separation studies.⁵ Its solubility and hydrophilicity can be varied depending upon the extent of hydrolysis of PVA. Hydroxy groups of PVA react readily with aldehydes and thus, it can be crosslinked easily with formaldehyde or glutaraldehyde (GA). In this study, GA was used as crosslinking agent to fabricate the membranes. PVA was purchased from s. d. Fine Chemicals, Mumbai, India. Sodium alginate was purchased from Loba Chemicals, Mumbai, India. Isopropanol, acetone, and hydrochloric acid were purchased from s. d. Fine Chemicals, Mumbai, India. Hydrochloric acid was used as a promoter in the crosslinking medium. Double distilled water was used throughout the research work.

Membrane fabrication

Stock solution (100 mL) of sodium alginate (5 mass % in water) was prepared in a beaker and poured uniformly on a clean glass plate. Membranes were dried at room temperature for 2–3 days. Casted membranes were crosslinked by immersing in a mixture of GA, HCl, acetone, and water after trial experiments to optimize the membrane properties. Membranes were kept in this mixture for 24 h and dried at ambient temperature. Sodium alginate membrane thus prepared is designated as M-1. Blend membrane (M-2) was prepared by mixing 10 mass % of solutions of PVA with 90 mass % of NaAlg. Similarly, by taking 20 mass % of PVA with 80 mass % of NaAlg, we have prepared another blend membrane designated as M-3. Pure PVA membrane requires *in situ* crosslinking because it swells more in the crosslinking medium. Therefore, crosslinking of PVA was done by adding 0.5 mL of 1N HCl and 0.5 mL of GA and stirring for 45 min before casting. We have to monitor the solution in such a way that it should not form the gel. Pure PVA membrane prepared was designated as M-4.

Pervaporation separation experiments

Pervaporation separation experiments were performed in an apparatus designed indigenously.²¹ The

PV apparatus consists of a stirred stainless steel cell having an effective membrane surface area of 28.27 cm² with a diameter of 6.0 cm, and volume capacity of the cell is 250 mL. Temperature of the feed mixture is kept constant using a thermostatic water jacket. The PV cell is provided with an efficient three-blade stirrer powered by a DC motor in the feed compartment. Turbulent flows were obtained even at low rotation of the stirrer, that is, below 200-rpm speed. Mass transfer limitations due to concentration polarization are negligible. The downstream side of the PV apparatus was evacuated using a vacuum pump (Toshniwal, Mumbai, India) at the vacuum pressure of 10 Torr. The test membrane was equilibrated for 2 h with the feed mixture before starting the PV experiment. After the establishment of steady state, liquid permeate was collected in traps immersed in liquid nitrogen. Permeate was condensed in liquid nitrogen traps.

PV experiments were performed for the feed mixtures ranging from 10 to 50 mass % of water. Depleted water and make-up water for the next composition was enriched continuously by adding the required amount of fresh water and further allowed to stand for 1 h to attain equilibrium. Mass of permeate collected in the trap was taken and its composition was determined by measuring refractive index of the mixture using a refractometer. Refractive index data for different compositions of water + isopropanol mixtures at 30°C were measured using an Abbe refractometer (Atago, model 3T, Tokyo, Japan).

RESULTS AND DISCUSSION

Membrane performance

Separation by PV occurs due to solution/diffusion processes,²² wherein permeation is controlled by solubility and diffusivity of the liquid permeants through the membrane. Permeation of a mixture through the membrane involves: (1) transport of molecules from the bulk liquid phase to the feed membrane interface, (2) preferential sorption of molecules at the feed-membrane interface (upstream), (3) diffusion of molecules through the membrane, and (4) desorption of molecules at the membrane-permeate interface. Solubility is a thermodynamic quantity, whereas diffusivity is a mass transfer quantity. Both solubility and diffusivity affect membrane selectivity towards a particular component. However, flux and selectivity of the diffusing molecules judge the membrane performance. The driving force for water transport through a dense membrane represents the gradient of chemical potential of the water on feed and permeate sides of the membrane. However, external mass transfer limitations may impose additional resistance to transport of molecules.

The set of parameters used to describe the performance of the PV process are: flux, J_p , selectivity, α ,

TABLE I
Pervaporation Data of Water + Isopropanol (IPA) Mixtures for Different Membranes at 30°C

| Mass % of water in feed | Total flux $\times 10^2$ kg/m ² · h | Selectivity | Mass % of water in permeate | Mass % of IPA in permeate | Water flux $\times 10^2$ kg/m ² · h | IPA flux $\times 10^2$ kg/m ² · h | <i>PSI</i> |
|---|---|-------------|--------------------------------|------------------------------|---|---|------------|
| Pure Na-Alginate membrane (M-1) | | | | | | | |
| 10 | 6.770 | 652.8 | 98.64 | 1.360 | 6.678 | 0.092 | 43.59 |
| 20 | 12.43 | 229.9 | 98.24 | 1.710 | 12.21 | 0.220 | 28.07 |
| 30 | 17.04 | 127.3 | 98.20 | 1.800 | 16.73 | 0.310 | 21.29 |
| 40 | 24.07 | 38.39 | 96.24 | 3.760 | 23.16 | 0.910 | 8.890 |
| 50 | 35.34 | 25.04 | 96.16 | 3.840 | 33.98 | 1.357 | 8.510 |
| Blend membrane of Na-Alginate (90%) + PVA (10%) (M-2) | | | | | | | |
| 10 | 6.880 | 579.2 | 98.47 | 1.530 | 6.770 | 0.110 | 39.21 |
| 20 | 12.95 | 167.7 | 97.67 | 2.330 | 12.65 | 0.300 | 21.21 |
| 30 | 17.12 | 81.60 | 97.22 | 2.780 | 16.64 | 0.480 | 13.58 |
| 40 | 24.59 | 51.69 | 97.18 | 2.820 | 23.89 | 0.700 | 12.35 |
| 50 | 39.72 | 31.89 | 96.96 | 3.040 | 38.51 | 1.210 | 12.28 |
| Blend membrane of Na-Alginate (80%) + PVA (20%) (M-3) | | | | | | | |
| 10 | 8.177 | 230.4 | 96.24 | 3.760 | 7.869 | 0.308 | 18.13 |
| 20 | 18.21 | 60.51 | 93.80 | 6.200 | 17.08 | 1.134 | 10.33 |
| 30 | 23.71 | 21.57 | 90.24 | 9.760 | 21.39 | 2.320 | 4.610 |
| 40 | 24.89 | 9.034 | 85.76 | 14.24 | 21.34 | 3.550 | 1.930 |
| 50 | 31.17 | 5.631 | 84.92 | 15.08 | 26.47 | 4.703 | 1.490 |
| Pure poly(vinyl alcohol) membrane (M-4) | | | | | | | |
| 10 | 10.66 | 77.29 | 89.57 | 10.43 | 9.548 | 1.112 | 7.380 |
| 20 | 24.43 | 29.90 | 88.20 | 11.80 | 21.55 | 2.880 | 6.440 |
| 30 | 36.54 | 16.51 | 87.62 | 12.38 | 32.01 | 4.527 | 5.280 |
| 40 | 42.85 | 8.795 | 85.43 | 14.57 | 36.61 | 6.242 | 3.220 |
| 50 | 47.09 | 5.506 | 84.63 | 15.37 | 39.85 | 7.240 | 2.190 |

pervaporation separation index, *PSI*, and enrichment factor, β . Flux is the permeate flow rate per unit membrane area per unit time for a given membrane thickness, which is calculated as

$$J_p = W_p / At \quad (1)$$

where W_p is mass of the permeate, A is effective area of the membrane, and t is time. Selectivity and enrichment factor describe the ability of the membrane to separate water and isopropanol in the liquid feed. On the other hand, *PSI* describes the overall performance of the membrane for a selected feed mixture. These quantities are calculated as follows:

$$\alpha = (P_W F_{IPA}) / (P_{IPA} F_W) \quad (2)$$

Here, P_W and P_{IPA} are mass % of water and isopropanol in permeate, respectively; F_W and F_{IPA} are mass % of water and isopropanol in the feed, respectively. The *PSI* and β values are calculated as follows:

$$PSI = J_w \alpha \quad (3)$$

$$\beta = C_w^p / C_w^f \quad (4)$$

where C_w^p is the concentration of permeate and C_w^f is the concentration of feed.

In dilute solutions, the concentration of solvent is close to unity since selectivity will be close to β . Calculated values of total flux, selectivity, mass % of water in permeate, mass % of isopropanol in permeate, water flux, isopropanol flux, and *PSI* for all membranes are presented in Table I as a function of mass % of water in the feed. Average data of only three sets of independent measurements are presented. It is observed that total flux of all the membranes increases with increasing amount of water in the feed as well as with increasing amount of PVA in the blend membranes. For blend membranes (M-2 and M-3) as well as for pure PVA membrane (M-4), total flux values are higher than those observed for pure NaAlg (M-1) membrane. Of all the membranes, PVA exhibits the highest total flux values. This is attributed to the hydrophilic nature of PVA, which absorbs more water molecules when compared to pure NaAlg membrane.

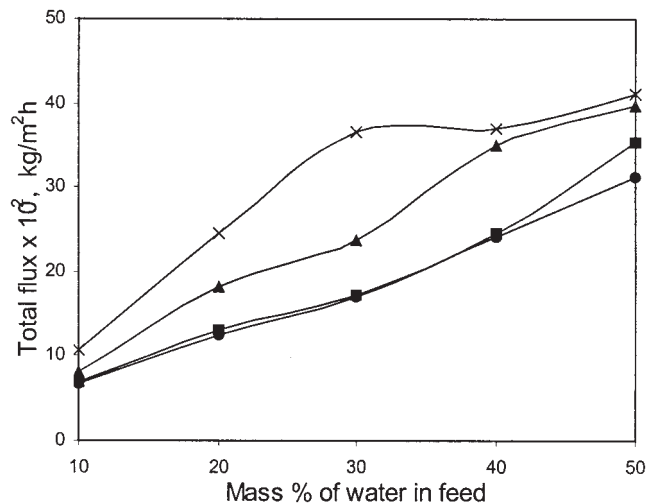


Figure 1 Plot of total flux versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

Flux values of water and isopropanol increase from pure NaAlg to blend membranes as well as pure PVA membrane. The flux values are quite higher for water than observed for isopropanol by almost an order of magnitude, indicating the hydrophilic nature of the membranes fabricated in the present study. Plots of total flux, water flux, and isopropanol flux at 30°C are displayed in Figures 1–3. Water + isopropanol mixture has an azeotropic composition at 0.30 mol % of water; thus, their separation by simple distillation is not easy due to their close relative volatility, as shown in Figure 4. Notice that the PV curve is well above the

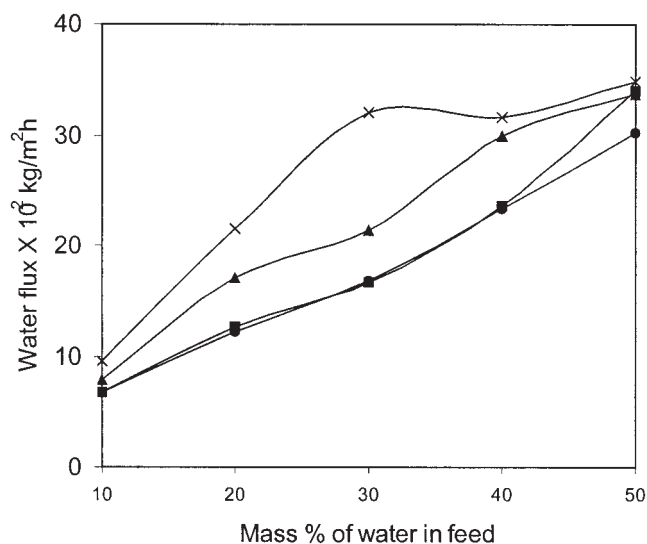


Figure 2 Plot of water flux versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

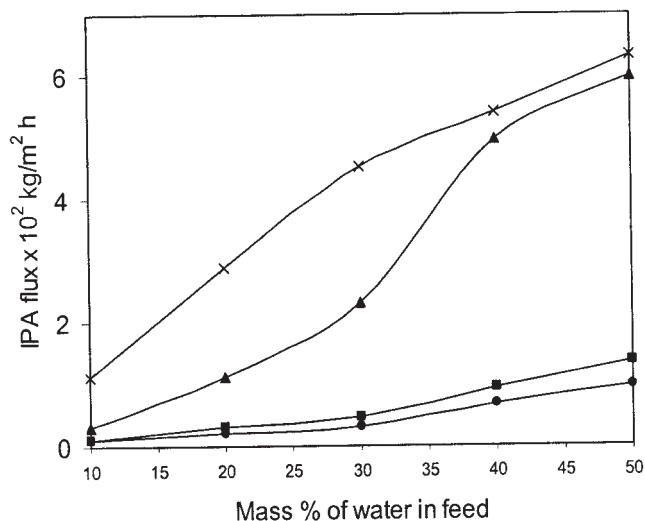


Figure 3 Plot of isopropanol flux versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

VLE²³ curve without crossing the equilibrium (diagonal) line, suggesting that the azeotrope can be broken by the membrane acting as a third phase, which has a more preferential affinity to water than the isopropanol.

At higher water concentration, the membrane swells considerably, causing plasticization of the polymer matrix and thereby resulting in a coupling effect between the solvent and water molecules. Since the membrane does not swell at a lower concentration of water, there is a minimum coupling effect, which can be understood in terms of solvent–solvent and membrane–solvent interactions. For instance, in a ternary system (polymer membrane plus binary mixtures of

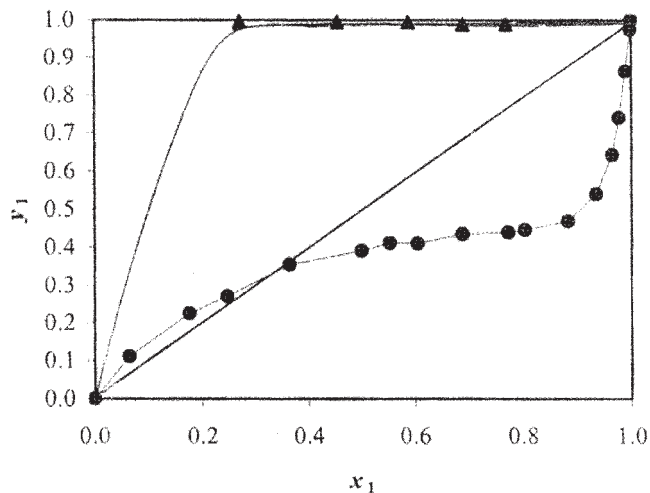


Figure 4 Comparison of PV curve (▲) with vapor liquid equilibrium curve (●) for water + isopropanol mixture.

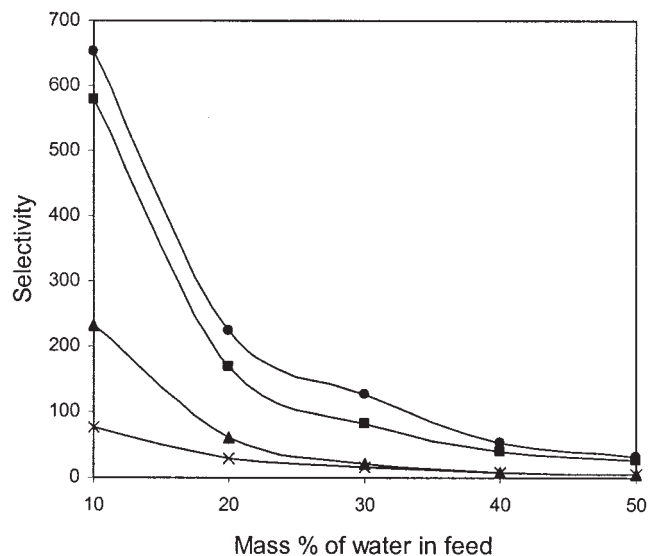


Figure 5 Plot of water selectivity versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

isopropanol and water), it is important to understand the nature of inter and intramolecular interactions between components of the mixture as well as individual and combined interactions of the mixed solvent media with the membrane. In the present study, the membrane preferentially interacts with water molecules more than those of isopropanol.

Results of selectivity (included in Table I and displayed in Fig. 5) indicate that selectivity is highest (i.e., 652.8) at 10 mass % of water in the feed for all membranes. However, selectivity decreases with an increasing amount of water in the feed mixture. Blending of NaAlg with an increasing amount of PVA resulted in a dramatic decrease of selectivity, that is, 5.5% for pure PVA membrane (M-4) for the mixture containing 50 mass % of water. The mass % of water in permeate is higher than isopropanol for all the membranes, particularly higher for M-1 membrane. This indicates the water selective nature of the membranes. PVA (hydrophilic) attracts more water molecules than NaAlg membrane and hence, flux for all membranes increases with an increasing amount of water in the feed as well as with an increasing amount of PVA in the blend, but a reverse trend is observed for selectivity. With an increasing amount of water in the feed, due to higher swelling of the membrane, water molecules might have transported along with some of the isopropanol molecules.

Following the approach by Huang,⁵ the membrane performance was studied by calculating *PSI* (see Table I and Fig. 6). It was observed that *PSI* for NaAlg membrane is highest (43.59) at 10 mass % of water in the feed mixture, but these data decrease systemati-

cally with increasing composition of water in the feed mixture. For 10 mass % PVA containing blend membrane, *PSI* values are almost identical to pure NaAlg membrane. At higher composition of water in the blend membrane (M-2), *PSI* values have improved slightly. On the other hand, with 20 mass % PVA containing blend membrane, *PSI* values decrease considerably, suggesting that next to pure NaAlg, optimum *PSI* values can be achieved for 20 mass % PVA containing blend membrane. However, with the pure PVA membrane (M-4), somewhat reasonably better values of *PSI* were observed when compared to M-3 membrane.

Results of β_W of water versus composition of water in the feed mixture displayed in Figure 7 exhibit trends almost similar to those of selectivity (Fig. 5). The β_W values of water decrease systematically with increasing water composition in the feed mixture. The plots of enrichment factor for isopropanol follow a reverse trend, that is, these increase with increasing composition of water in the feed for all membranes (Fig. 8). Mass % of water and isopropanol in permeate versus mass % of water in the feed mixture, displayed, respectively, in Figures 9 and 10, follow the same general trends as those of *PSI* and β values. Both *PSI* and β values at 10 mass % of water are higher in the feed mixture than those observed at higher compositions of water in the feed mixture, indicating the efficiency of pure NaAlg membrane to dehydrate water-isopropanol mixture.

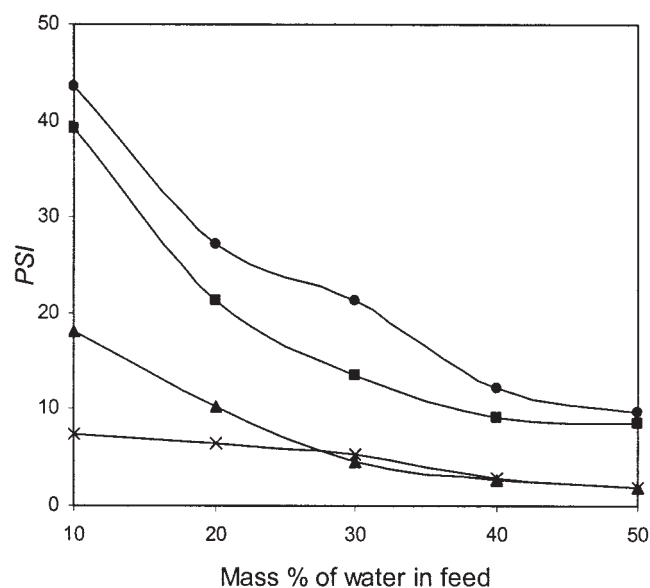


Figure 6 Plot of *PSI* versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

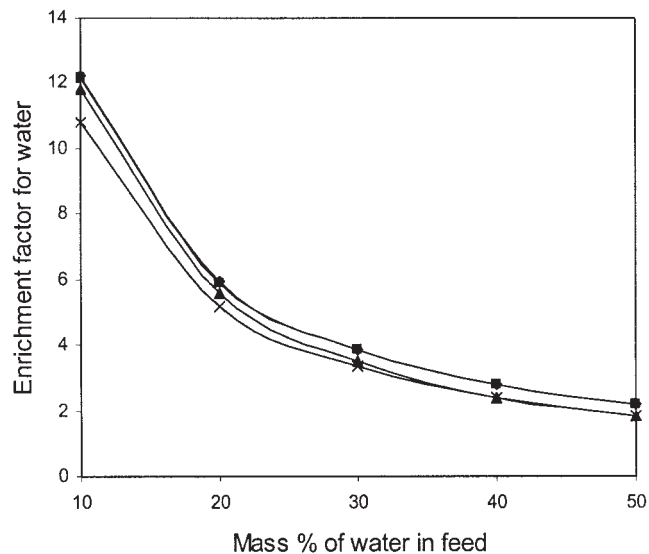


Figure 7 Plot of water enrichment factor versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

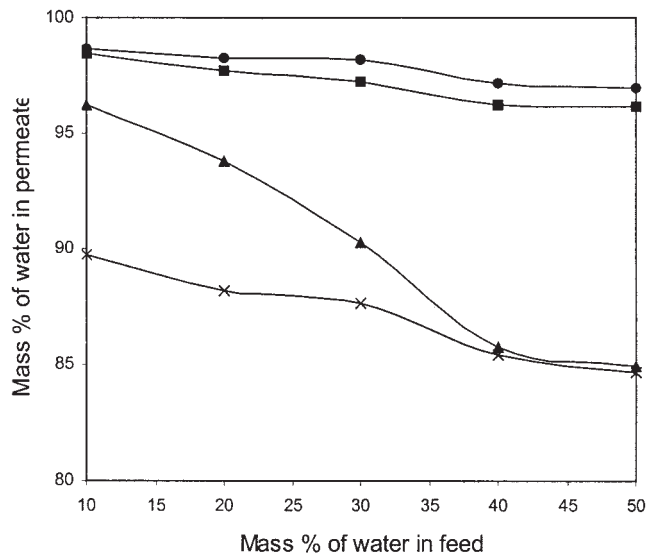


Figure 9 Plot of mass % of water in permeate versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

Diffusion coefficients

Since diffusion in PV experiments occurs due to concentration gradient, we have calculated diffusion coefficients, D_i , of solvent mixtures through the membrane using Fick's first law of diffusion.²⁴

$$J_i = (D_i/h)[C_{i(\text{feed})} - C_{i(\text{permeate})}] \quad (5)$$

Here, D_i is assumed to be constant across the effective membrane thickness, h ; $C_{i(\text{feed})}$ and $C_{i(\text{permeate})}$ are, respectively, compositions of liquids present in feed and permeate. The computed values of D_i (where subscript i stands for water or isopropanol) at 30°C are presented in Table II. As expected, diffusion coefficients of water increase considerably with increasing amount of water in the feed mixture for all the membranes, suggesting their water-selective nature. An

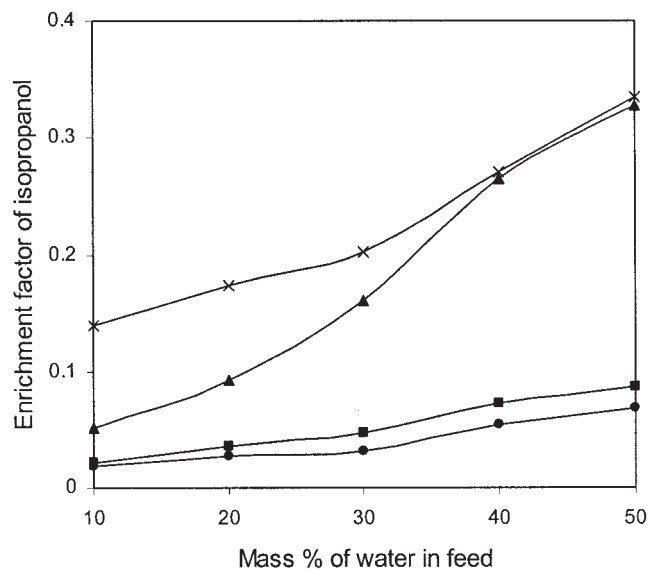


Figure 8 Plot of isopropanol enrichment factor versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

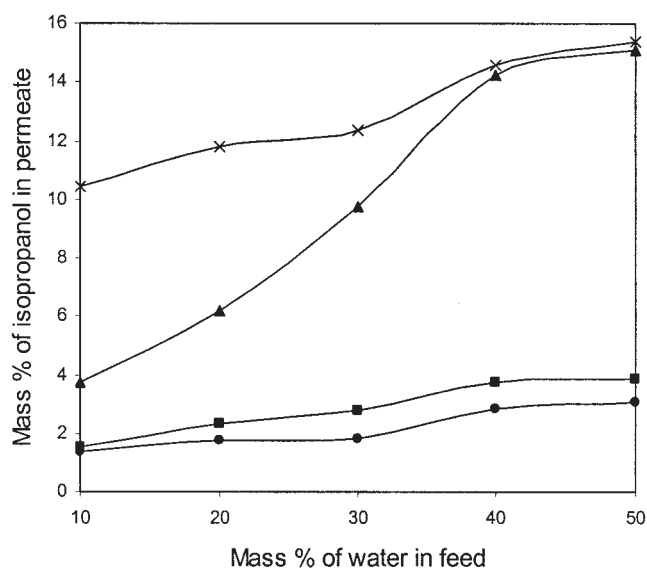


Figure 10 Plot of mass % of isopropanol in permeate versus mass % of water in feed at 30°C. Symbols: × - Neat PVA (M-4), ▲ - blend of NaAlg + 20% PVA (M-3), ■ - blend of NaAlg + 10% PVA (M-2), ● - Pure NaAlg (M-1).

TABLE II
Diffusion Coefficients of Water (D_w) and Isopropanol (D_{IPA}) for Different Membranes as a Function of Mass % of Water in the Feed at 30°C

| Mass % of water in feed | $D_w \times 10^{12}$ (m ² /s) | | | | $D_{IPA} \times 10^{13}$ (m ² /s) | | | |
|----------------------------|--|-------|-------|-------|--|-------|-------|-------|
| | M-1 | M-2 | M-3 | M-4 | M-1 | M-2 | M-3 | M-4 |
| 10 | 0.616 | 0.647 | 0.752 | 1.006 | 0.108 | 0.133 | 0.373 | 1.486 |
| 20 | 1.251 | 1.308 | 1.877 | 2.602 | 0.286 | 3.931 | 1.580 | 4.406 |
| 30 | 1.918 | 1.940 | 2.833 | 4.463 | 0.450 | 7.092 | 3.895 | 7.999 |
| 40 | 3.165 | 3.203 | 3.682 | 6.367 | 1.576 | 1.190 | 7.763 | 13.76 |
| 50 | 5.541 | 6.161 | 5.879 | 8.932 | 2.805 | 2.453 | 13.23 | 20.56 |

increase in water content is dramatic at higher compositions of water in the feed mixture when compared to lower water content. This effect is attributed to the creation of extra free volume of the membrane matrix due to the plasticization effect, as well as more water molecules present within the pores of the membrane matrix.

Even though diffusion coefficients of isopropanol are quite smaller than those observed for water, these data show a considerable increase with increasing amount of water in the feed mixture. As regards the nature of membranes, diffusion values show a systematic trend, that is, with increasing mass % of PVA, D values also increase systematically from M-1 to M-4 membranes. In the case of isopropanol, D values increase systematically from M-1 to M-4 membranes, suggesting that molecular transport increases with increasing amount of PVA in the blend membranes, and particularly, more so with the pure PVA membrane.

Effect of temperature

Temperature of the feed mixture in PV experiments was varied between 30°C (room temperature) and 50°C, keeping all the other parameters like feed concentration (10 mass %) and permeate pressure (10 Torr) constant. This was done only for pure NaAlg membrane at 10 mass % of water containing feed mixture. These results are summarized in Table III and displayed in Figure 11. As expected, the PV flux increased steadily with increasing temperature due to enhanced vapor pressure and mobility (activity) of the transporting molecules. According to the free volume theory,²⁵ an increase in temperature increases the ther-

mal mobility of polymeric chains and generates extra free volume in the polymeric matrix, thereby enhancing the sorption and diffusion rates of the permeant molecules. An increase in polymer free volume makes the membrane more permeable, but less discriminative to permeation of the penetrant molecules. Consequently, permeation fluxes of both isopropanol and water are enhanced, leading to increased permeate flux with a decrease in selectivity.

Temperature dependence of pervaporation flux and selectivity for the feed mixture containing 10 mass % of water presented in Table III have been used to compute the activation parameters by fitting the results to the Arrhenius equation:

$$J_p = J_{p0} \exp(-E_p/RT) \quad (6)$$

Here, E_p is the activation energy of permeation, J_{p0} is the permeation rate constant, R is the gas constant, and T is temperature in Kelvin. If the activation energy is positive, then permeation flux increases with increasing temperature, a generally observed phenomenon in PV experiments. However, the driving force for mass transport, which represents the concentration gradient resulting from the difference in partial vapor pressure between the feed and the permeate, increases with increasing temperature.

As the feed temperature increases, vapor pressure in the feed compartment also increases, but vapor pressure at the permeate side will not be affected, resulting in an increase of driving force at higher temperatures. Arrhenius plots of $\ln J_p$ versus $1/T$ for both water and isopropanol fluxes (not displayed to minimize the number of graphs) are linear, signifying

TABLE III
Pervaporation Data of Pure Sodium Alginate Membrane (M-1) at Different Temperatures for 10 Mass % of Water in the Feed Mixture

| Temp. °C | Total flux $\times 10^2$ kg/m ² h | Selectivity | Mass % of water in permeate | Mass % of IPA in permeate | Water flux $\times 10^2$ kg/m ² h | IPA flux $\times 10^2$ kg/m ² h |
|----------|---|-------------|--------------------------------|------------------------------|---|---|
| 30 | 6.770 | 652.8 | 98.64 | 1.360 | 6.678 | 0.092 |
| 40 | 8.700 | 546.6 | 98.38 | 1.620 | 8.560 | 0.140 |
| 50 | 10.11 | 491.0 | 98.20 | 1.800 | 9.928 | 0.182 |

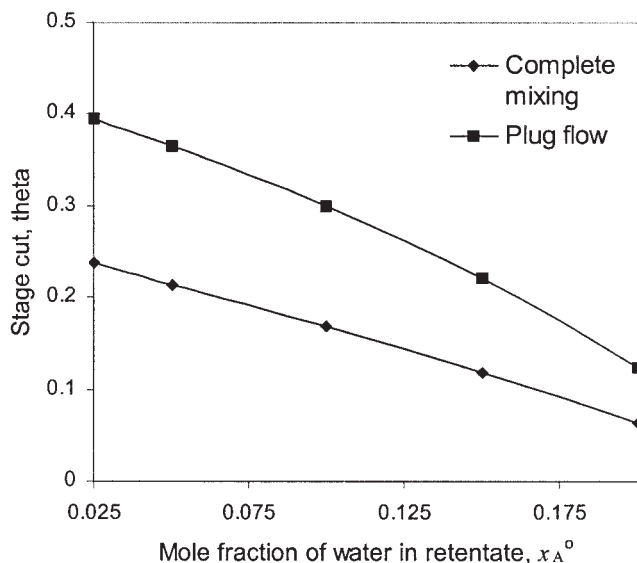


Figure 11 Variation of stage cut with desired retentate mole fraction for complete mixing and plug flow patterns with constant feed concentrations ($x_A^f = 0.25$).

that the temperature dependence of the total permeation flux follows the Arrhenius trend. Apparent activation energy data for permeation, E_P calculated from the slopes of the straight lines of the Arrhenius plots using the least squares method, is presented in Table IV.

In a similar manner, results of mass transport due to activated diffusion have been fitted to the Arrhenius equation of the type:

$$D_i = D_{i0} \exp(-E_D/RT) \quad (7)$$

Here, E_D is the energy of activation for diffusion, and i represents water or isopropanol. Arrhenius plots of $\ln D_i$ versus $1/T$ (not displayed) for water and isopropanol are also linear in the temperature range studied, suggesting the validity of the Arrhenius equation. Heat of sorption data calculated using: $\Delta H_S (= E_P - E_D)$ are also included in Table IV. The ΔH_S values for both water and isopropanol are negative, suggesting the endothermicity of the sorption process.

TABLE IV
Permeation and Diffusion Activation Energies, Heat of Sorption of Water, and Energy Difference Values of the Membranes

| Parameters | Pure sodium alginate membrane (M-1) for | |
|-----------------------|---|-------------|
| | Water | Isopropanol |
| E_P (kJ/mol) | 16.150 | 27.725 |
| E_D (kJ/mol) | 16.311 | 28.008 |
| ΔH_S (kJ/mol) | -0.1620 | -0.2830 |

MODELING AND SIMULATION STUDIES

During the selective transport of liquids through a membrane, liquid concentration is distributed in every continuous phase of the polymer matrix. Distribution is particularly pronounced when the permeation rate and the channel width are small, but selectivity of the membrane and the fraction of recovery are large. The mathematical analysis developed earlier by Weller and Steiner²⁶ based on complete mixing and plug flow models has been applied to the PV process.

Complete mixing case

We have computed ideal selectivity at feed and outlet (retentate), α^* , minimum stripping concentration, x_A^M , ratio of permeability of water at all values of mole fraction and that of pure water, K^1 , permeate concentration, y_A^p , stage cut (fraction of feed that has permeated through the membrane), θ , dimensionless area, S , and membrane area, A , for the given values of feed concentration and the desired value of outlet concentration, based on the complete mixing model and plug flow models of Weller and Steiner²⁶ as described before.²⁰ Defining selectivity, α , as:

$$\alpha = \left(\frac{y_A}{1 - y_A} \right) \left(\frac{1 - x_A}{x_A} \right) \quad (8)$$

where x_A is the mole fraction of water in the feed and y_A is the mole fraction of water in the permeate, ideal selectivity is calculated as:

$$\alpha^* = \frac{K_A P_A^o}{K_B P_B^o} \quad (9)$$

where K_A is the permeability of water at any value of x_A ; K_B is the permeability of isopropanol at any value of $x_B (= 1 - x_A)$; and P_A^o and P_B^o are vapor pressures of water and isopropanol, respectively. Defining dimensionless quantities, K_A^1 , as the ratio of the permeability of component A in the mixture to that of the permeability of pure component A and stage cut, θ , as the fraction of feed that has permeated through the membrane, we may write as

$$K_A^1 = \frac{K_A(x_A)}{K_A(x_A = 1)} \quad (10)$$

$$\theta = \frac{q_p}{q_f} \quad (11)$$

where q_p is the permeate flow rate. Using Fick's diffusion equation²⁴ for permeation rate, $Q (= q_p y_p)$, we get

$$q_P y_P = \frac{K_A A (P_A^o x_A^o - P y_A^p)}{h} \quad (12)$$

Here, y_A^p is the mole fraction of the undesired component A (water) in permeate, A is the membrane area exposed to the permeant molecules, h is the membrane thickness, x_A^o is the mole fraction of A in the outlet, and P is the permeate pressure. Considering the permeate pressure as zero on the downstream side of the membrane, we can apply the material balance equation to the complete mixing case for the mixture comprising A and B to get

$$x_A^f = (1 - \theta)x_A^o + \theta y_A^p \quad (13)$$

where x_A^f is the feed composition. Total membrane area is calculated from the dimensionless area, S , as:

$$A = S \left(\frac{q_f h}{K_A (x = 1) P_A^o} \right) \quad (14)$$

The minimum stripping concentration, x_A^M for a given value of x_A^f is given as:

$$x_A^M = 1 - \frac{(1 - x_A^f)}{1 - \left(1 - \frac{1}{\alpha^*}\right) x_A^f} \quad (15)$$

Values of y_A^p and θ are, respectively, calculated as:

$$y_A^p = \frac{\alpha^* x_A^o}{(1 - x_A^o) + x_A^o \alpha^*} \quad (16)$$

and

$$\theta = \frac{x_A^f - x_A^o}{x_A^p - x_A^o} \quad (17)$$

Computer programs were written in C language to calculate α^* , K_A^1 , x_A^M , and y_A^p of water in the outlet by inputting the values of x_A^f and the feed value of $x_A^o > x_A^M$ to calculate α^* . The program will ask for membrane thickness, h , and q_f to give output data of θ , S , and A .

Plug flow case

The feed enters at a flow rate, q_i , mole fraction, x_A^f , and stage cut, θ . Flow rate at the permeate side is θq_f and on the reject (retentate) side, it becomes $q_f(1 - \theta)$. In the plug flow case, there is no back mixing and hence, concentration inside the chamber and at the outlet is different, which is rapidly changing unlike the complete mixing case. Therefore, considering a small differential area, dA , the transport equation becomes

$$q x_A = - \frac{K_A A P_A^o x_A}{h} \quad (18)$$

The term $P_A^o x_A$ is partial pressure of the mixture. Differentiating eq. (18) over an infinitesimal area, dA , for components A and B, followed by routine manipulations, we get the equation for differential flow rate as

$$q_f dq^1 = - \left[\frac{K_A P_A^o x_A}{h} \right] dA - \left[\frac{K_B P_B^o (1 - x_A)}{h} \right] dA \quad (19)$$

Since $q'_f = q/q_f$, the differential form of the equation is given as

$$dq = d(q' q_f) = q_f dq' \quad (20)$$

Here, q_f is a constant. Further simplification gives the final working equation for flow rate:

$$\frac{dq^1}{dx_A} = \frac{q^1 [x_A + (1 - x_A)/\alpha^*]}{x_A(1 - x_A) \left[1 - \frac{1}{\alpha^*} \right]} \quad (21)$$

After solving the above equations, the equation for the membrane area can be derived as

$$\frac{dS}{dx_A} = - \left[\frac{q^1}{K^1 x_A (1 - x_A) \left(1 - \frac{1}{\alpha^*} \right)} \right] \quad (22)$$

To find y_A^p at the point when x_A reaches the final (minimum) stripping concentration, x_A^M we have used eq. (16) in the program. The parameters α^* and K^1 are computed using the second degree polynomial equation in x_A obtained by fitting the trend lines using Microsoft Excel to the curves by plotting α^* values versus feed water mole fraction (x_A) and K^1 versus x_A , respectively, from the experimental data. Values of α^* and K^1 will change with every step in the Runge-Kutta algorithm due to changing x_A values. Eqs. (16), (21), and (22) were integrated using the boundary conditions:

- (a) $q^1 = 1$, $S = 0$ at $x_A = x_A^f$ (initial conditions)
- (b) $q^1 = 1 - \theta$, and $S = S$ at $x_A = x_A^o$ (final conditions)

On a commercial scale, a major portion of the capital investment for PV is membrane. However, the effective area can be minimized by not only developing a membrane with high flux and selectivity, but also by choosing optimum operating conditions, including the patterns of feed and permeate flow, flow rate, stage cut, feed temperature, and extent of vacuum applied in the permeate chamber. The most significant quantity obtained by simulation is the dimensionless membrane area from which the actual area require-

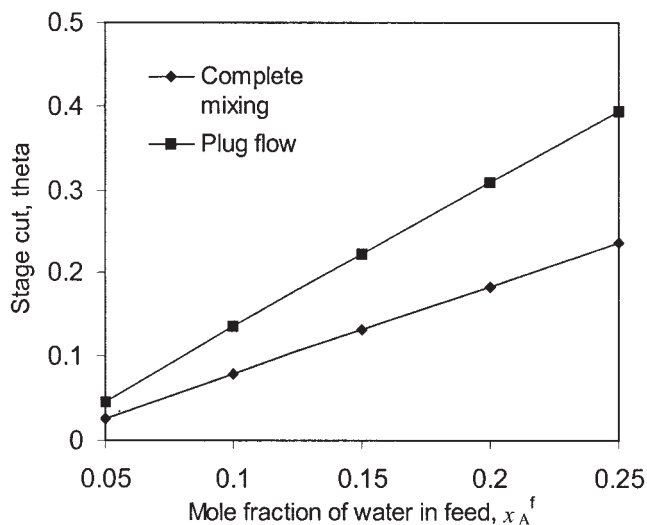


Figure 12 Variation of stage cut with mole fraction of water in feed for constant desired retentate concentration ($x_A^o = 0.025$).

ment can be obtained by using known values of feed flow rate, membrane thickness, and permeability coefficient. Among the two modes of flow patterns possible in commercial PV systems, the plug flow pattern is quite efficient when compared to the complete mixing case.

Simulated plots for constant desired retentate water concentrations with varying feed compositions and *vice versa* are given in Figures 11–14. Expectedly, membrane area increased by increasing the values of stage cut and feed water concentration, as well as for decreasing values of desirable retentate concentration. Figure 11 describes the effect of the increasing concentration of water desired in the retentate for stripping a constant feed concentration of 25 mol % of water. For an increase of x_A^o from 2.5 mol % to 20% (corresponding to a decreasing product purity of 97.5 to 80 mol % of IPA), the stage cut decreased from 0.237 to 0.063 for the complete mix-

ing case, whereas somewhat higher values of 0.395 to 0.123 for the plug flow case are observed. As shown in Figure 12, to achieve a constant value of 2.5 mol % of water in the retentate from the feed having water concentration ranging from 5 mol % to 25 mol %, stage cuts for the plug flow case were found to be in the range of 0.046–0.394, which were more than half of the requirement for complete mixing.

Figures 13 and 14 describe the actual area requirements as a function of retentate and feed water concentrations, assuming a feed flow rate of 25 lit/h, membrane thickness of 30 μm , and pure water permeability ($K_{x=1}$) of 7.411×10^{-7} . The trends observed in Figures 13 and 14 have expectedly shown the opposite behavior because the greater the water concentration to be found in the retentate, the lower is the desired isopropanol product purity and the lower will be the membrane area requirement. Similarly, for greater feed water concentration, more quantity of water has to be removed, thereby requiring a greater membrane area. The area required for the complete mixing model is unrealistically high, revealing the limitations of this model. In Figure 13, the area is reduced from 1548 to 96 m^2 for the complete mixing case and from 353 to 81.5 m^2 for the plug flow case over the x_A^o range of 2.5 to 20 mol %. From Figure 14, it is seen that as the feed concentration increased from 5 to 25 mol %, the total area required for the complete mixing model went up to 1548 m^2 from 172 m^2 , whereas for the plug flow case, it increased from 120 to 353 m^2 .

To make an economic estimation of the PV process, a program was run based on the plug flow model for a flow rate of 10 lit/h and all calculations were done based on the presently available market data. For the design purpose, we have used 0.30 mol fraction of water in the feed mixture, which is the azeotropic concentration of isopropanol with water. The outlet composition is 99% of isopropanol, and the total membrane area obtained is 55.55 m^2 for a membrane thickness of 10 μm . A stage cut

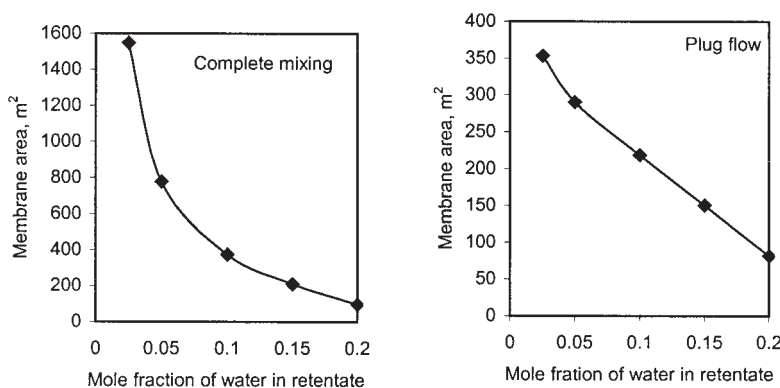


Figure 13 Comparison of total membrane area for complete mixing and plug flow models as a function of desired mole fraction of water in retentate with constant feed concentration ($x_A^f = 0.25$).

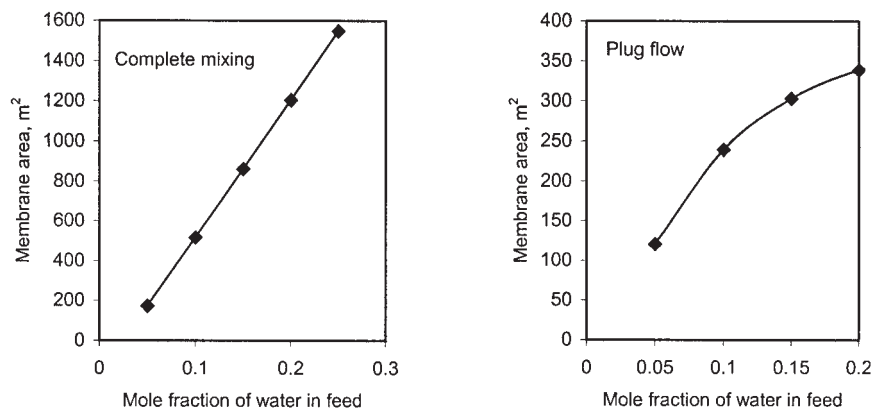


Figure 14 Comparison of total membrane area for complete mixing and plug flow model as a function of desired mole fraction of water in feed with constant feed concentration ($x_A^o = 0.025$).

value of 0.492 and permeate mole fraction of 0.938 were found. The membrane is applied in the plate module of 25 plates each of 2.25 m².

CONCLUSIONS

It was shown that recovery of a small concentration of isopropanol from water is possible with pure sodium alginate membrane since it breaks the azeotrope. Selectivity decreased at higher concentrations of water in the feed mixture due to increased plasticization (swelling). Variation of the temperature from 30° to 50°C revealed that 30°C appears to be the optimum condition for PV separation of water + isopropanol mixtures. Selectivity for water was as high as 652.8 for the 10% water containing mixture. Further, it was shown that it is economical to carry out the PV experiment at ambient temperature (30°C) because any increase in flux and savings in energy could compensate selectivity. A comparison of vapor liquid equilibrium data with the experimental pervaporation data revealed that pervaporation has succeeded in breaking the azeotropic mixture formed at mole fraction of 0.30 of water. Even though the present study has demonstrated the application of design models for both continuous and batch types of modes, the plug flow model appears to be vital for the simulation of a pilot or large-scale PV plant. Computations of model equations indicate that since the observed membrane area is very high due to low flux, this may be the main limitation of the PV method. Therefore, the development of new membranes exhibiting high flux and high selectivity are required with decreased membrane area to give a low payback period for developing the PV process on a commercial scale.

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References

- Aminabhavi, T. M.; Khinnavar, R. S.; Harogoppad, S. B.; Aithal, U. S.; Nguyen, Q. T.; Hansen, K. C. *J Macromol Sci-Rev Macromol Chem Phys* 1994, 34, 139.
- Dutta, B. K.; Sikdar, S. K. *AIChE J* 1991, 37, 581.
- Rautenbach, R.; Albrecht, R. *J Membr Sci* 1985, 25, 25.
- Feng, X.; Huang, R. Y. M. *Ind Eng Chem Res* 1997, 35, 1048.
- Huang, R. Y. M., Ed. *Pervaporation Membrane Processes*; Elsevier: Amsterdam, 1991; p. 25.
- Okuno, H.; Urugami, T. *Polymer* 1992, 33, 1459.
- Bhat, N. V.; Wavhal, D. S. *J Appl Polym Sci* 2000, 76, 258.
- Huang, R. Y. M.; Moon, G. Y.; Pal, R. *J Membr Sci* 2001, 184, 1.
- Jiratananon, R.; Chanachai, A.; Huang, R. Y. M.; Uttapap, D. *J Membr Sci* 2002, 195, 143.
- Urugami, T.; Saito, M. *Sep Sci Technol* 1989, 24, 541.
- Yeom, C. K.; Lee, K. H. *J Appl Polym Sci* 1998, 67, 209.
- Yeom, C. K.; Lee, K. H. *J Appl Polym Sci* 1998, 67, 949.
- Toti, U. S.; Karidurganavar, M. Y.; Soppimath, K. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2002, 83, 259.
- Toti, U. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2002, 85, 2014.
- Kurkuri, M. D.; Kumbar, S. G.; Aminabhavi, T. M. *J Appl Polym Sci* 2002, 86, 272.
- Kurkuri, M. D.; Toti, U. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2002, 86, 3642.
- Kurkuri, M. D.; Aminabhavi, T. M. *J Appl Polym Sci* 2003, 89, 300.
- Toti, U. S.; Aminabhavi, T. M. *J Membr Sci* 2004, 228, 198.
- Toti, U. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2004, 92, 2030.
- Aminabhavi, T. M.; Vijaya Kumar Naidu, B.; Sridhar, S. *J Appl Polym Sci*, 2004, 94, 1827.
- Aminabhavi, T. M.; Naik, H. G. *J Appl Polym Sci* 2002, 83, 244.
- Wijmans, J. G.; Baker, R. W. *J Membr Sci* 1995, 107, 1.
- Udovenko, V. V.; Mazanko, T. F. *Zh Fiz Khim* 1967, 41, 1615.
- Crank, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford, 1975; 2nd ed.
- Fujita, H.; Kishimoto, A.; Matsumoto, K. M. *Trans Faraday Soc* 1970, 56, 424.
- Weller, S.; Steiner, W. A. *Chem Eng Prog* 1950, 46, 585.