Computer Simulation and Comparative Study on the Pervaporation Separation Characteristics of Sodium Alginate and Its Blend Membranes with Poly(vinyl alcohol) to Separate Aqueous Mixtures of 1,4-Dioxane or Tetrahydrofuran

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ABSTRACT: A comparative study on the pervaporation separation has been attempted for water + 1,4-dioxane and water + tetrahydrofuran mixtures using sodium alginate and blend membranes of sodium alginate with 5, 10, and 20 mass % of poly(vinyl alcohol). Pure sodium alginate membrane has a selectivity of 111 to water at 0.35-mol fraction of water in the feed mixture containing 1,4-dioxane while for water + tetrahydrofuran mixture, the membrane selectivity to water was 291 at 0.31-mol fraction of water in the feed mixture. Pervaporation results have been discussed using the solution–diffusion principles. Arrhenius activation parameters for diffusion and permeation have been computed from the temperature-dependent pervaporation results. Furthermore, experimental results have been analyzed using the complete mixing and plug flow models to compute membrane area as well as design parameters that are useful in scale-up operations. The plug flow model is more appropriate than the complete mixing model to analyze the pervaporation results. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1827–1840, 2004

Key words: diffusion; blend membranes; pervaporation; flux; selectivity

INTRODUCTION

The use of dense polymeric membranes in pervaporation (PV) separation of liquids has been quite well known in view of the potential advantages such as low-energy requirements, effective separation of azeotropes, ecofriendly nature, and easy operation of the technique[1–4] compared to distillation. Since PV is a diffusion-controlled process, solvent flux through the membrane is generally low, thereby making the process economically attractive particularly when the permeating species are minor constituents of the feed. In PV experiments, the recent trend is to develop compatible polymeric blends in which one polymer component provides the desired permeability characteristics, while the other improves the mechanical strength properties.[5,6] Composite membranes,[7,8] charged membranes,[9,10] polyion complex membranes,[11] copolymer,[12] and grafted copolymer membranes[13,14] have also been used in specific PV separation problems. Often, the goal of membrane modifications is to create either a material with enhanced barrier capabilities or one that exhibits a combination of high selectivity to a particular component of a mixture. These criteria reflect the prominent applications of newer polymers by the PV technique to separate the components of liquids from their mixtures.

Due to their abundant availability, biocompatibility, and commercial viability, natural polysaccharides have been used as membranes in PV separation studies.[15–22] Among these, sodium alginate (NaAlg) has good membrane forming properties[23,24] since it can be readily crosslinked with glutaraldehyde. However, to the best of our knowledge, we are not aware of the use of blend membranes of NaAlg with poly(vinyl alcohol) (PVA) in the PV separation of water + 1,4-dioxane and water + tetrahydrofuran (THF) mixtures. Therefore, we report here the experimental data on PV separation of membranes prepared from pure sodium alginate as well as its blends with 5, 10, and 20 mass % of PVA using glutaraldehyde as a crosslinking agent. These membranes have been used for a comparative

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PV separation study on water + 1,4-dioxane and water + THF mixtures. 1,4-Dioxane and THF are important solvents used in many chemical and pharmaceutical industries. Both are miscible with water in all proportions. 1,4-Dioxane forms an azeotrope at 0.33-mol fraction of water, while THF forms an azeotrope at 0.10-mol fraction of water. Therefore, dehydration of 1,4-dioxane or THF up to > 99% purity from their aqueous mixtures has been attempted by the PV technique.

The membrane performance was studied by calculating selectivity and permeation flux at 30, 40, and 50°C for pure NaAlg membrane at the azeotropic compositions of both the mixtures. Activation parameters have been evaluated and results have been discussed using the solution–diffusion principles.[25,26] Design parameters and membrane area requirements have been computed for the feed rate of 10 L/h at the feed composition of 0.55-mol fraction of water to achieve the final retentate concentration greater than 0.99-mol fraction of organics by using the Weller and Steiner theory[27] based on complete mixing and plug flow models. Programs were written to determine the minimum stripping concentration, permeate composition, stage cut (fraction of feed permeated through the membrane), and membrane area required for a given value of feed composition and the desired value of retentate (product) composition. A comparison of membrane performance has been attempted for the chosen aqueous-organic (1,4-dioxane or THF) mixtures.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (M_w = 125,000) was purchased from S. D. Fine Chemicals, Mumbai, India. Sodium alginate was purchased from Loba Chemicals, Mumbai, India. Solvents 1,4-dioxane, tetrahydrofuran, glutaraldehyde (GA), acetone, and hydrochloric acid (HCl) were purchased from S.D. Fine Chemicals, Mumbai, India. These were used without further purification. Double distilled water was used throughout the research work.

Membrane fabrication

A 5 mass % of stock solution of NaAlg was prepared in water. Stock solution (100 mL) was taken in a beaker and poured uniformly on a glass plate. Membranes were dried at room temperature for about 2–3 days. Casted membranes were crosslinked by immersion in a mixture of GA, HCl, acetone, and water. Membranes were kept in this mixture for 24 h and dried at ambient temperature. The blend membrane, NaAlg–PVA-5, was prepared by mixing 5 mass % of PVA solution with 95 mass % of NaAlg. Similarly, by taking 10 and 20 mass % of PVA with 90 and 80 mass % of NaAlg, we have prepared two other blend membranes designated, respectively, as NaAlg–PVA-10 and NaAlg–PVA-20. Blend membrane casting and crosslinking procedures remained the same for both pure NaAlg and its blends.

Pervaporation experiments

Pervaporation experiments were performed in an apparatus designed indigenously as explained before.[14,28] The effective surface area of the membrane was 32.43 cm^2 with a diameter of 6.4 cm and a volume capacity of 250 cm^3. The test membrane was equilibrated for 3 h with the feed mixture before starting the PV experiment. PV experiments were performed with the feed mixtures containing 0.35–0.83 mol fraction of water for water + 1,4-dioxane mixtures and 0.31–0.80 for water + THF mixtures. Depleted solvent mixture in the feed compartment was enriched by adding a required amount of fresh solvent mixture. The collected permeate composition in the trap was estimated by refractometry at 30°C using an Atago refractometer (model 3T, Tokyo, Japan) and by comparing the data with the previously determined graph of refractive index versus mixture composition at 30°C.

For mixtures containing lower composition (i.e., < 0.35-mol fraction) of water for water + 1,4-dioxane and < 0.30-mol fraction for water + THF mixture, the analysis was done by using a Nucon Gas Chromatograph (model 5765) with a Thermal Conductivity Detector (TCD) equipped with a Tenax packed column of 1/8-in. i.d. having 2 m length. The oven temperature was maintained at 70°C (isothermal) while the injector and detector temperatures were maintained at 150°C. The sample injection volume was 1 μL. Pure hydrogen was used as a carrier gas at a pressure of 1 kg/cm^2. The GC response was calibrated for the column and for known compositions of water + 1,4-dioxane and water + THF mixtures. Calibration factors were fed into the GC software to obtain the analysis for unknown samples.

RESULTS AND DISCUSSION

Membrane performance

In the present investigation, four membranes have been developed: pure NaAlg and three blend membranes of NaAlg with 5, 10, and 20 mass % of PVA. Membrane performance was studied by calculating pervaporation flux, J_P and selectivity, α, using respectively,

$$J_P = \frac{W_P}{At} \tag{1}$$

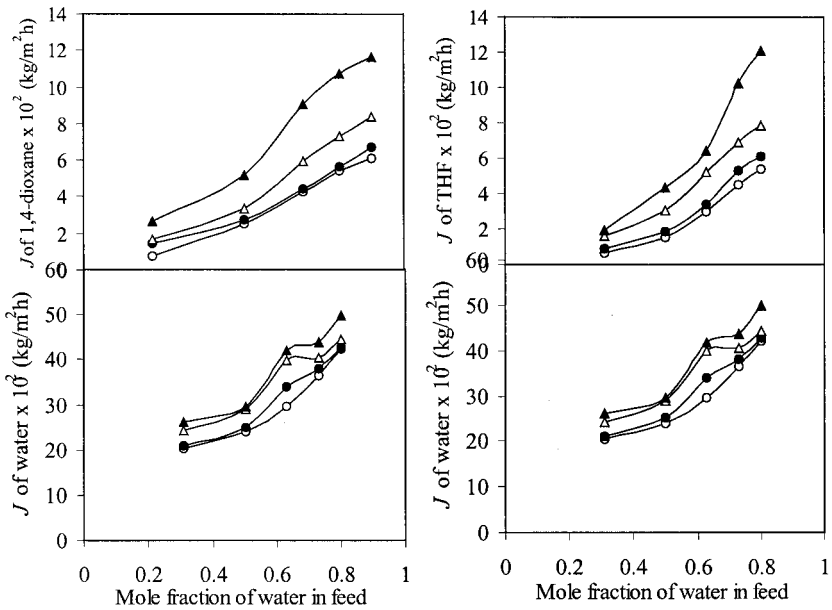

Figure 1 Water and organic component flux versus mole fraction of water in feed at 30°C. ▲, NaAlg–PVA-20; △, NaAlg–PVA-10; ●, NaAlg–PVA-5; ○, pure NaAlg.

$$\alpha = \frac{P_w/P_o}{F_w/F_o} \tag{2}$$

where W_p is mass of the permeate, A is area of the membrane in contact with the feed mixture, t is time, P_w and P_o are mole fractions of water and organic component (1,4-dioxane or THF) in the permeate; F_w and F_o are the respective mole fractions in the feed mixture (i.e., water and organics).

The results of flux for water, 1,4-dioxane, and THF at 30°C studied in both the binary mixtures are compared in Figure 1 for all the membranes. In both the mixtures, flux values are higher for water than for any of the organic components (1,4-dioxane or THF). Comparatively, water flux is much higher in case of water + THF mixture than in water + 1,4-dioxane mixture. In both mixtures, flux values increase with increasing amount of water in the feed mixture and with increasing amount of PVA in the blend membranes. This suggests the permeation of a large number of water molecules due to the increased hydrophilic nature of the membranes with the increasing amount of PVA in the membranes. The composition of water and organic component (1,4-dioxane or THF) in permeate versus mole fraction of water in the feed displayed in Figure 2 shows a decreasing trend for water with an increasing amount of water in the feed, while for 1,4-dioxane or THF, these values increase. Water composition in the permeate being higher than either 1,4-dioxane or THF suggests the water-selective nature of the membranes.

Selectivity data displayed in Figure 3 for water + 1,4-dioxane and water + THF mixtures exhibit a systematic decrease with increasing amount of water in the feed for all the membranes. However, pure NaAlg membrane has a selectivity of 111 at 0.35-mol fraction of water in the feed mixture containing 1,4-dioxane, whereas for the water + THF mixture, the membrane selectivity is about three times higher. With an increasing amount of water in the feed, membranes swell due to the plasticization effect, thereby resulting in a coupled transport of 1,4-dioxane or THF molecules along with water molecules. At a lower composition of water, membrane swelling is smaller, thus allowing more of water molecules to transport. For both the binary mixtures, pure NaAlg membrane exhibits the highest selectivity with the lowest flux.

NaAlg membranes have been used earlier for the PV separation of water–organic mixtures. For instance, Uragami and Saito[19] used the alginic acid membranes for the PV separation of ethanol + water mixtures. Mochizuki et al.[29] studied the relationship between permselectivity of alginic acid membranes and its solid-state structure as well as the effect of counter cations on membrane performance. Yeom and Lee[20] prepared the NaAlg dense membranes crosslinked with GA by solution method and used in the PV separation of water + ethanol mixtures containing 0.47–0.78 mol fraction of ethanol in the temperature range of 40–80°C. When membranes were prepared using a higher amount of GA, both flux and separation factors were reduced, probably due to the more crosslinked structure. Yeom and Lee[21] also developed the blend membranes of NaAlg with flexible PVA for the PV separation of water + ethanol mixtures. The rigid NaAlg membrane showed a drastic

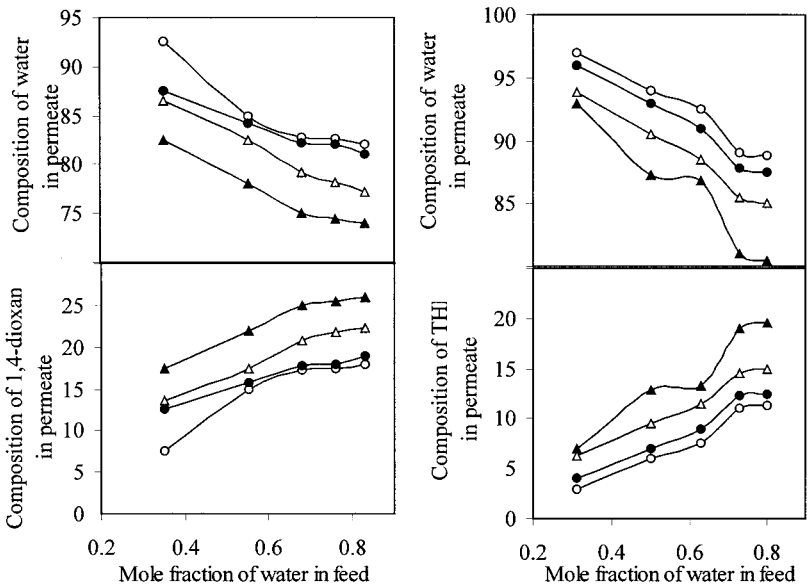

Figure 2 Composition of water and organic component in permeate versus mole fraction of water in feed at 30°C. Symbols are the same as in Figure 1.

decline in flux with an increase in selectivity due to relaxation of the polymeric chains, whereas the flexible PVA membrane helped to retain the consistent membrane performance during PV experiments. A number of authors have used various combinations of NaAlg membranes either in the blended forms or in the composite forms for the PV separation of aqueous–organic mixtures.[22,30,31] In all these studies, selectivity and flux of the membrane increased with increasing temperature and water content of the feed mixture. The crosslinked NaAlg composite membrane with PVA has shown much lower selectivity to water.

In a previous study[32] from our laboratory, we have been successful in increasing the membrane performance of NaAlg by blending it with PVA for dehydrating isopropanol. Permeation flux increased with an increasing amount of PVA, while the separation selectivity decreased. The highest selectivity of 356 was observed for pure NaAlg at 0.27-mol fraction of water, whereas a highest flux of 26×10^{-2} kg/m^{2}h was observed with pure PVA membrane at 0.69-mol fraction of water. Blend membranes of NaAlg with polyacrylamide-*grafted*-guar gum have also been prepared[33] and used for the PV separation of acetic acid + water and isopropanol + water mixtures. These blend membranes have shown good PV performance in terms of flux and selectivity compared to pure NaAlg membrane. A highest selectivity of 891 was observed with the lowest flux value of 4.3×10^{-2} kg/m^{2}h for a 50 : 50 % blend membrane of NaAlg with polyacrylamide-*grafted*-guar gum. However, selectivity of pure NaAlg membrane was lower, i.e., 441, compared to the blend membranes. We have also studied the PV separation of water + 1,4-dioxane mixture[34] by using the grafted membranes of polyacrylamide with NaAlg. The 92% grafted copolymer membrane gave the highest permeation flux of 52.3 $\times 10^{-2}$ kg/m^{2}h, while pure NaAlg membrane gave

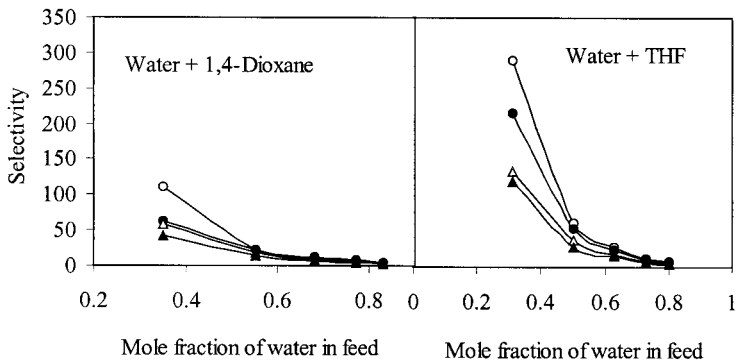

Figure 3 Selectivity versus mole fraction of water in feed at 30°C. Symbols are the same as in Figure 1.

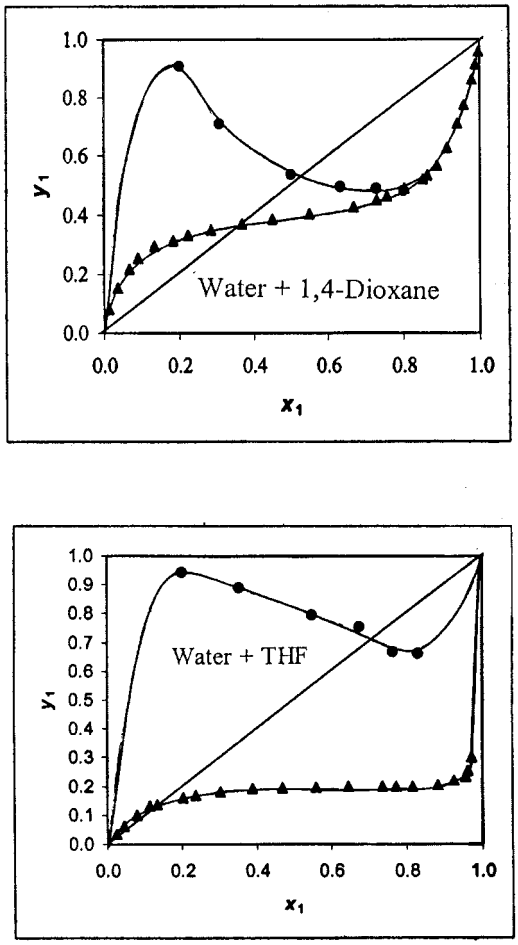

Figure 4 Comparison of vapor liquid equilibrium curve. ▲, with PV data; ●, for water (1) + 1,4-dioxane (2) and water + THF mixtures at 30°C.

only 19.5×10^{-2} kg/m^{2}h at 0.92-mol fraction of water in the feed. The reason for higher selectivity exhibited[34] by NaAlg was due to the addition of 10 mass % of polyethylene glycol (PEG-200) as a plasticizer and 5 mass % of PVA, which helped to optimize the membrane performance. However, selectivity of NaAlg was 351 at 0.35-mol fraction of water compared to blend membranes at 30°C. In the present work, pure NaAlg gave the highest selectivity of 111.

Comparison of PV data with VLE data

A comparison of PV separation data with the published results[35,36] obtained from the vapor–liquid equilibrium (VLE) technique for water + 1,4-dioxane and water + THF mixtures is made in Figure 4. Since VLE data for these systems are not available at 303.15 K, the literature data chosen for comparison were those obtained at temperatures as close as possible to 303.15 K. The azeotropic point for water + 1,4-dioxane mixture at 303.15 K, estimated on the basis of all other literature VLE data, is $x_1 = 0.37$, while water + THF forms an azeotrope at $x_1 = 0.10$. It may be noted that azeotropic points are weakly dependent on temperature and, hence, separation of water from such mixtures by distillation is not easy due to low relative volatility of the mixture. The PV curve falls well above the azeotropic compositions, indicating that the membrane acts as a third phase, which selectively allows water molecules to pass through due to its preferential affinity towards water molecules. Thus, the PV technique has overcome the azeotropic barrier. At higher compositions of water in the liquid phase, the PV curve cuts the diagonal line at 0.55-mol fraction of water in the liquid phase for water + 1,4-dioxane and at $x_1 = 0.68$ for water + THF mixture. In azeotropic distillation, usually, a small amount of entrainer (generally, hazardous organic compound) is added as a third phase to break the azeotrope, thus making the process less ecofriendly. In the present research, the membrane acts as a third phase making the process environmentally cleaner.

Diffusion coefficients

Diffusion in the PV process occurs due to a concentration gradient. This solution–diffusion model provides the following transport equation for the PV process.[30]

$$J_i = P_i[p_{i(\text{feed})} - p_{i(\text{permeate})}] = \frac{D_i}{h}[C_{i(\text{feed})} - C_{i(\text{permeate})}] \quad (3)$$

Here, $C_{i(\text{feed})}$ and $C_{i(\text{permeate})}$ are, respectively, the composition of liquids in feed and permeate sides. Computed values of D_i (where the subscript i stands for water or organic component) at 30°C are displayed in Figure 5. Values of D for water increase with an increasing amount of water in the feed due to creation of extra free volume in the membranes. Also, the values of D increase systematically with an increasing amount of PVA in the blend membranes at all the feed water compositions. It may be noted that values of D for 1,4-dioxane or THF are smaller by an order of magnitude than water. However, diffusion coefficients of THF are slightly smaller than those of 1,4-dioxane.

Arrhenius parameters

Temperature dependence of total flux, flux for water, 1,4-dioxane, and THF, selectivity, and compositions of water, 1,4-dioxane, and THF in permeate for pure NaAlg membrane at $x_1 = 0.35$ and $x_1 = 0.31$, respectively, for mixtures of water + 1,4-dioxane and water + THF are presented in Table I. Total flux increases with increasing temperature, whereas a reverse trend is observed for selectivity. This can be explained by

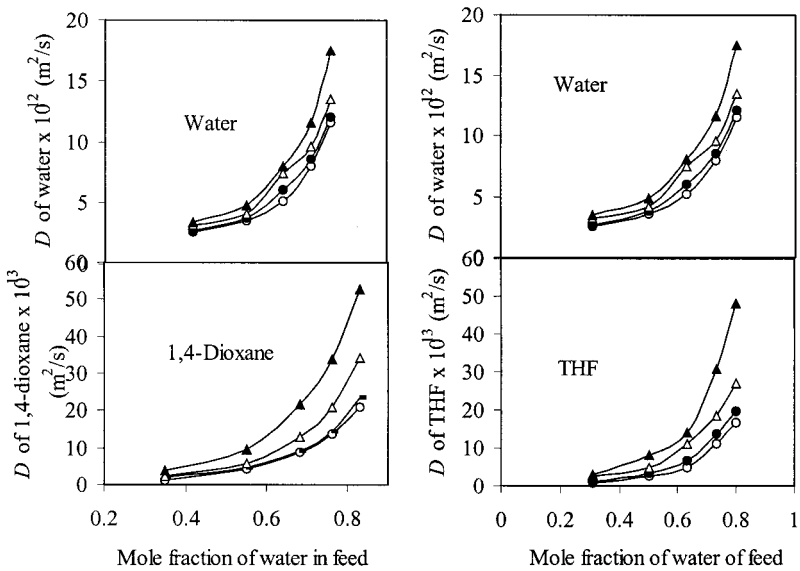

Figure 5 Plots of diffusion coefficients of water and organic versus mole fraction of water in feed at 30°C. Symbols are the same as in Figure 1.

the free volume theory of Fujita et al.[37] Total flux data have been fitted to the Arrhenius equation to obtain the activation parameters

$$J_P = J_{P0}\exp(-E_P/RT) \tag{4}$$

where E_P is activation energy for permeation, J_{P0} is permeation rate constant, R is gas constant, and T is temperature in Kelvin. The E_P values have been calculated from the slopes of straight lines of Arrhenius plots (not shown graphically) by the least squares method. These data are presented in Table II. Lower activation energy values observed for water compared to 1,4-dioxane or THF support the water-selective nature of the membranes. For a positive value of activation energy, permeation flux increases with increasing temperature, but selectivity decreases. The faster moving water molecules have lower activation energy than the slower moving 1,4-dioxane or THF. Similarly, activation energy, E_D for diffusion can be computed as

$$D_i = D_{i0}\exp(-E_D/RT) \tag{5}$$

where i represents water or organic component of the mixture. Arrhenius plots of log D_i versus 1,000/T are linear for both water and organic components (1,4-dioxane and THF), but these plots are not displayed. Using the values of E_P and E_D, heat of sorption values was calculated as ΔH_S ($\cong E_P - E_D$); these results are also included in Table II. Negative ΔH_S values suggest endothermic sorption process.

Temperature dependency of α was also studied by employing the equation proposed by Ping et al.[13]

$$Y_w = \frac{1}{1 + (J_o/J_w)\exp(-(E_o + E_w)/RT)} \tag{6}$$

TABLE I
Pervaporation Data of Pure NaAlg Membrane at Different Temperatures at 0.35-Mole Fraction of Water in the Feed Mixture for Water + 1,4-dioxane and 0.31-Mole Fraction of Water + THF Mixtures

Temperature (°C)	Total flux × 10^2 (kg/m^{2}h)	Selectivity	Mass % of water in permeate	Mass % of organics in permeate	Water flux × 10^2 (kg/m^{2}h)	Organic component flux × 10^2 (kg/m^{2}h)
Water + 1,4-Dioxane						
30	10.6	111.00	92.50	7.50	9.78	0.79
40	11.0	72.81	89.00	11.00	9.79	1.20
50	11.7	47.25	84.00	16.00	9.81	1.86
Water + THF						
30	20.9	291.00	97.00	3.00	20.29	0.63
40	22.4	267.92	96.75	3.25	21.63	0.73
50	24.9	257.67	96.63	3.37	24.06	0.84

TABLE II
Permeation and Diffusion Activation Energies, Heat of Sorption of Water, and Energy Difference Values for Pure NaAlg Membranes

Activation parameters	Water	1,4-Dioxane	Water	THF
E_P (kJ/mol) eq. (4)	0.1249	34.855	6.92	11.72
E_D (kJ/mol) eq. (5)	12.087	46.51	7.34	105.1
ΔH_S (kJ/mol)	−11.962	−11.655	−0.42	−93.41
$E_D - E_w$ (kJ/mol)	34.730		4.796	

where Y_w is water composition in the permeate, J_w and J_o are the permeation fluxes; E_w and E_o are the Arrhenius activation energies for water and organic components (1,4-dioxane or THF), respectively, at the average energy level. The positive value of $[E_o - E_w]$ is a clear indication that α decreases with increasing temperature, while the negative value indicates that α increases with increase of temperature. For all the membranes of this study and for both the mixtures, the difference $(E_o - E_w)$ is positive (see Table II), suggesting that α decreases with increasing temperature.

SIMULATION STUDIES

Membrane area requirement and design parameters

Based on the flow pattern of the feed and permeate streams, there are several mathematical models available to predict the performance of pilot and industrial scale PV separation membrane modules.[27,38–41] Weller and Steiner[27] proposed the mathematical equations for mass transfer analysis for complete mixing and plug flow models. We have used these models to simulate the PV process to obtain the required design parameters.

Complete mixing model

In the complete mixing case, design parameters, viz., ideal selectivity, α^* at the feed and outlet (retentate), 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, and membrane area, A for given values of feed concentration, and desired value of outlet concentration have been calculated. Ideal selectivity is given as

$$\alpha^* = \frac{K_A P_A^o}{K_B P_B^o} \tag{7}$$

Here, K_A is permeability of water at any value of x_A, K_B is permeability of organic component at any value of x_B $(= 1 - x_A)$; P_A^o and P_B^o are vapor pressures of water and organic component, respectively. Figure 6 displays the PV process for complete mixing case, wherein compartment (a) represents the upstream side through which feed enters and compartment (b) represents the downstream side where vacuum is applied. Concentration in the upstream side and at the outlet remains the same, but the feed enters at a flow rate, q_f and mole fraction, $x_A^f$of the faster permeating water. Dimensionless quantities, $K_A^1$and θ are defined as

$$K_A^1 = \frac{K_A(x_A)}{K_A(x_A = 1)} \tag{8}$$

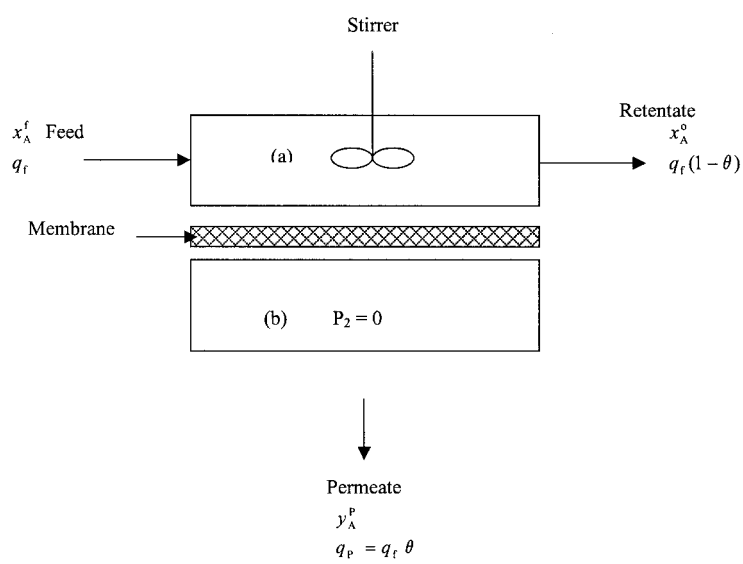

Figure 6 Complete mixing model for pervaporation process.

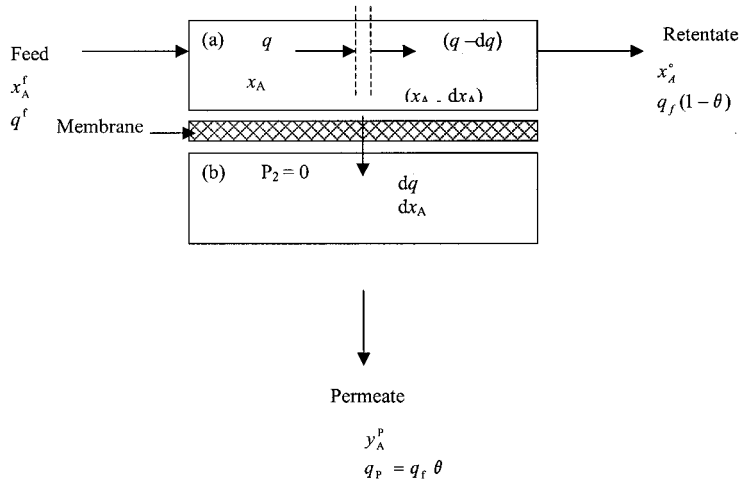

Figure 7 Plug flow model for pervaporation process.

$$\theta = \frac{q_P}{q_f} \tag{9}$$

where q_P is permeate flow rate. Using Fick's diffusion equation[42] for permeation rate, Q ($= q_P\, y_P$), we get

$$q_P y_P = \frac{K_A A(P_A^o x_A^o - P y_A^P)}{h} \tag{10}$$

Here, y_A^p is the mole fraction of the undesired component A (water) in permeate, A is membrane area exposed to the permeant molecules, h is membrane thickness, $x_A^o$is mole fraction of A in the outlet, and P is permeate pressure. Since the PV process involves a phase change from liquid to vapor due to the continuous application of vacuum on the downstream side, it is considered to be zero. Application of the material balance equation to the complete mixing case (see Fig. 6) for the binary mixture comprising A and B, we get

$$x_A^f = (1 - \theta)x_A^o + \theta y_A^P \tag{11}$$

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

$$A = S\left(\frac{q_f h}{K_A\,(x = 1)P_A^o}\right) \tag{12}$$

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

$$x_A^M = 1 - \frac{(1 - x_A^f)}{1 - \left(1 - \dfrac{1}{\alpha^*}\right)x_A^f} \tag{13}$$

The values of y_A^P and θ are, respectively, calculated in terms of experimental parameters using the equations

$$y_A^P = \frac{\alpha^* x_A^o}{(1 - x_A^o) + x_A^o \alpha^*} \tag{14}$$

and

$$\theta = \frac{x_A^f - x_A^o}{x_A^P - x_A^o} \tag{15}$$

Computer programs were written in C language (see Appendix) to calculate α^*, K_A^1 and $x_A^M$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 then ask for the values of membrane thickness, h and q_f, to give the output data of θ, S, and A.

Plug flow case

Figure 7 depicts the schematic sketch of the PV process for plug flow model (batch mixing) in which compartment (a) is the upstream side and compartment (b) is the downstream (permeate) side. Feed is introduced at a flow rate, q_f, and mole fraction, $x_A^f$for a stage cut, θ. Flow rate at the permeate side is θq_f and on the reject (retentate) side, it is $q_f(1 - \theta)$. In the plug flow model, there is no back mixing and, hence, concentrations inside the chamber and at the outlet are different, but are rapidly changing unlike in the complete mixing model. Thus, we consider a small elemental strip of differential area, dA for which transport equations are developed. As shown in Figure 7, x_A and q enter the elemental strip and come out of it as $(x_A - dx_A)$ and $(q - dq)$. Thus, dx_A and dq permeate through the membrane toward the downstream (permeate) side.

The permeation rate, qx_A of component (A) is given by

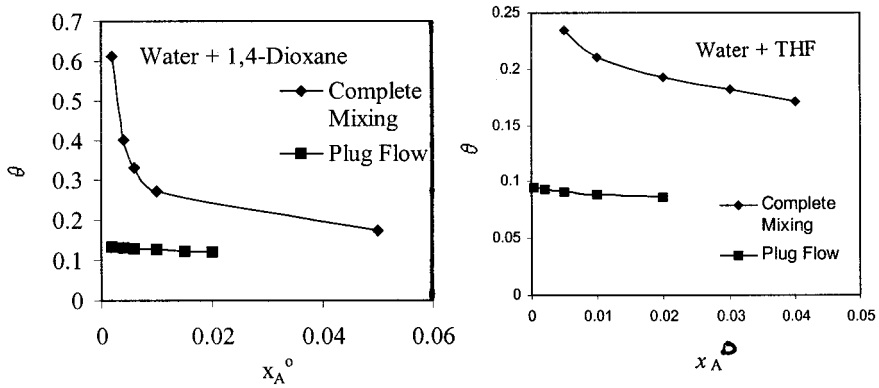

Figure 8 Variation of stage cut with desired retentate mole fraction for complete mixing and plug flow patterns with constant feed concentration ($x_A^f = 0.2$).

$$qx_A = -\frac{K_A A P_A^o x_A}{h} \tag{16}$$

All symbols of eq. (16) have the same meanings as before; the term, $P_A^o x_A$ is partial pressure of the mixture. Differentiating eq. (16) over an infinitesimal area, dA, for components A and B, followed by routine manipulations, we get the equation for differential flow rate as

$$q_f dq^1 = -\left[\frac{K_A P_A^o x_A}{h}\right] dA - \left[\frac{K_B P_B^o (1 - x_A)}{h}\right] dA \tag{17}$$

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

$$dq = d(q' q_f) = q_f dq' \tag{18}$$

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

$$\frac{dq'}{dx_A} = \frac{q'[x_A + (1 - x_A)/\alpha^*]}{x_A(1 - x_A)\left[1 - \frac{1}{\alpha^*}\right]} \tag{19}$$

After solving the above equations, an equation for membrane area can be derived to give

$$\frac{dS}{dx_A} = -\left[\frac{q'}{K' x_A (1 - x_A)\left(1 - \frac{1}{\alpha^*}\right)}\right] \tag{20}$$

To find y_A^p at the point when x_A reaches the final (minimum) stripping concentration, x_A^M, we have used eq. (14) in the program. The parameters α^* and K^1 are computed using the 2nd 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. Equations (14), (19), and (20) were integrated using the boundary conditions:

(a) $q' = 1, \quad S = 0 \quad \text{at} \quad x_A = x_A^f$ (initial conditions)

(b) $q' = 1 - \theta, \quad \text{and} \quad S = S \quad \text{at}$

$x_A = x_A^o$ (final conditions)

In a pervaporation experiment, the membrane is the most expensive component. PV experiments are often run at high temperatures and low permeate pressures to minimize the total membrane area since a trade-off exists between the membrane area and the energy consumption. We have used both complete mixing and plug flow models to calculate the membrane area and design parameters. Figures 8 and 9 display the comparison between complete mixing and plug flow models for varying desired retentate mole fraction of water at the constant feed mole fraction and vice versa, respectively. Stage cut values required for the complete mixing model are higher than those found for the plug flow model, suggesting the requirement of larger membrane area and energy consumption, besides greater losses of organic in the permeate. Figure 8 shows that, to achieve a retentate concentration of 0.002-mol fraction of water from the feed containing 0.20-mol fraction of the same liquid, stage cut required for complete mixing and plug flow models are higher for water + 1,4-dioxane mixtures compared to water + THF mixtures. Stage cut values for complete mixing model calculations are 0.61 and 0.23 respectively, in the case of water + 1,4-dioxane and water + THF mixtures, which are much higher than those observed for plug flow model (i.e., 0.13 and 0.09) to obtain a retentate concentration of 0.002-mol fraction of water. The difference between two flow patterns becomes

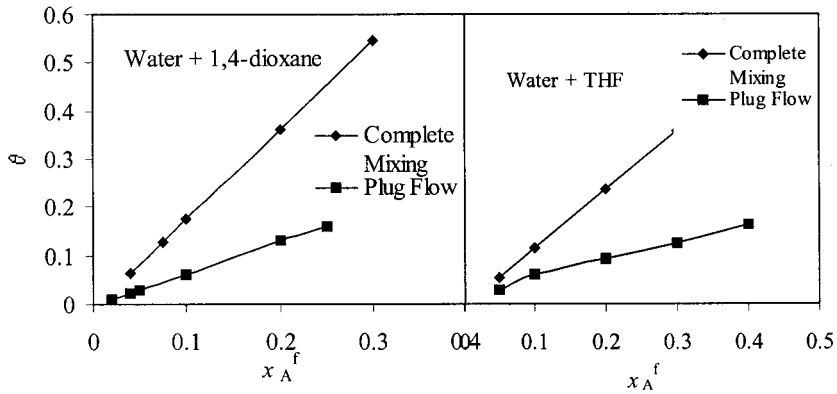

Figure 9 Variation of stage cut with mole fraction of water in feed (x_A^f) for constant desired retentate concentration (x_A^0 = 0.005).

narrower as the desirable retentate concentration of water is higher for both the mixtures (0.02-mol fraction or above).

Figure 9 shows the requirements of higher stage cuts for both the flow patterns with increasing mole fraction of water in the feed to achieve a final constant retentate water concentration of 0.005-mol fraction. Stage cut values for the plug flow case are reasonable, which range from approximately 0.01 to 0.16 for both the mixtures with the feed concentration increasing from 0.02 to 0.25-mol fraction for water + 1,4-dioxane and 0.02 to 0.40-mol fraction for water + THF mixtures. This difference between the flow models arises with increasing mole fraction of water in the feed.

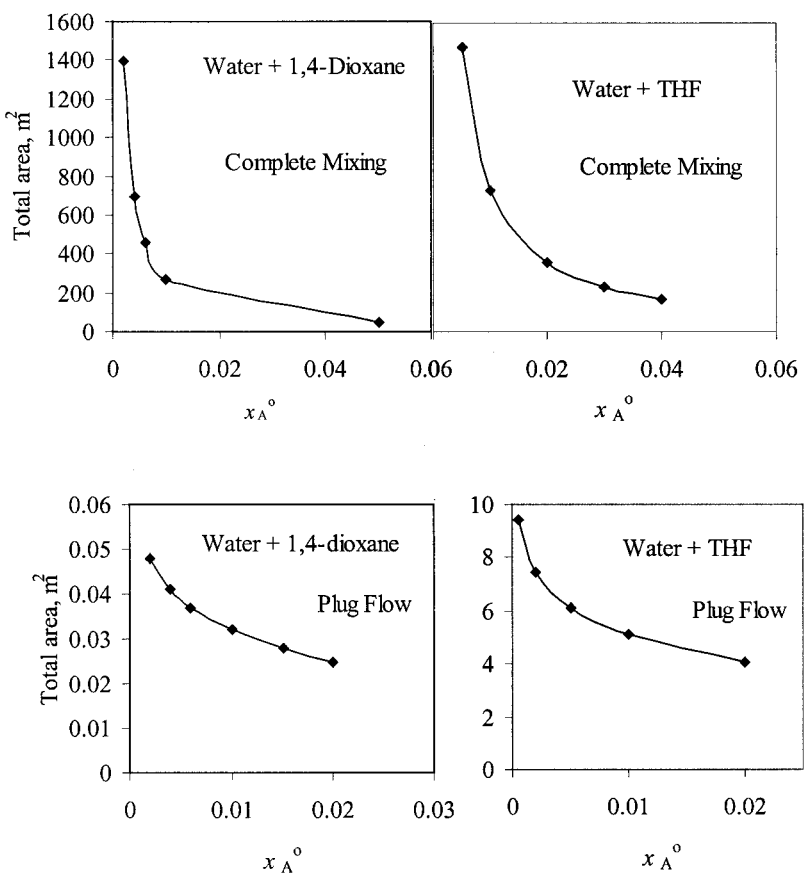

Figure 10 Comparison of total membrane area for complete mixing and plug flow models as a function of desired mole fraction of water in retentate with constant feed concentration (x_A^f = 0.2).

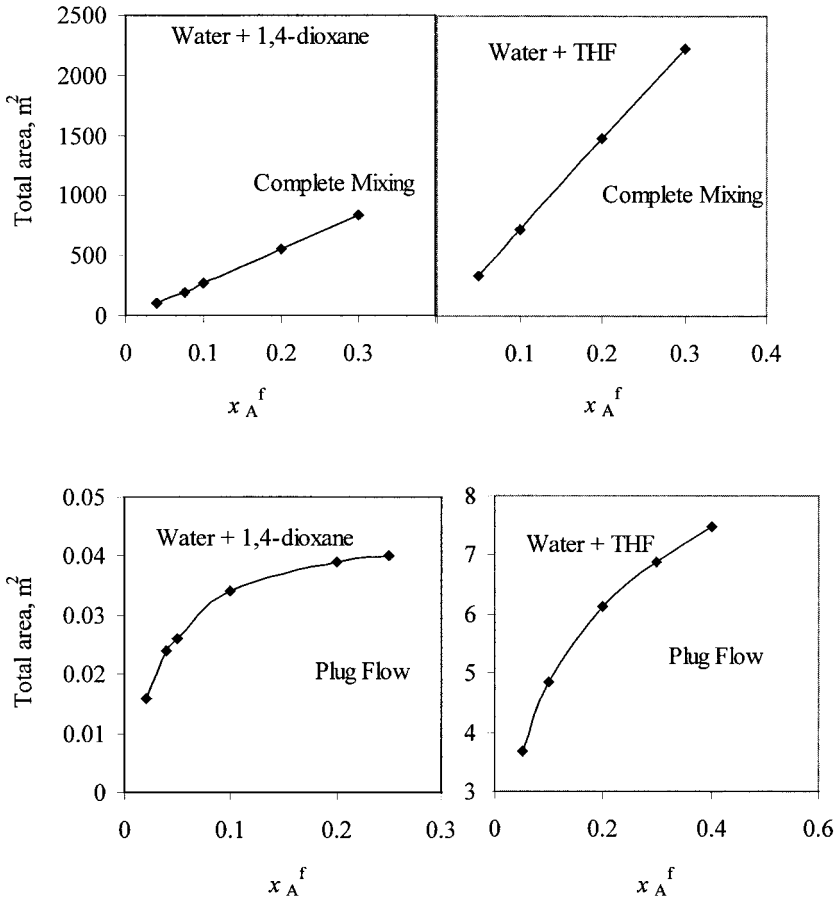

Figure 11 Comparison of total membrane area for complete mixing and plug flow molds as a function of desired mole fraction of water in retentate with constant feed concentration ($x^f_A = 0.2$).

Figures 10 and 11 describe the actual area requirements as a function of retentate and feed water concentrations assuming the feed flow rate of 1 L per hour for the membrane thickness of 40 μm (used in this study) and pure water permeability, K, of 7.411×10^{-7} $m^3 \cdot m/h \cdot m^2 \cdot atm$. The trends observed in Figures 10 and 11 expectedly show an opposite behavior for both the mixtures. The higher the water concentration in the retentate, the lower the desired organic product purity will be, which results in a lower membrane area requirement. Similarly, for greater feed water concentrations, a greater quantity of water must be removed, thus requiring greater area. Areas required for the complete mixing model were unrealistically high, revealing the limitations of this model for both the mixtures.

In Figure 10, the area was reduced from 1,480 to 160 m^2 for the complete mixing model in the water + THF mixture, while these values are reduced from 1,400 to 40 m^2 for water + 1,4-dioxane systems, which vary from 9.5 to 4.0 m^2 for the plug flow case for the water + THF mixture; however, these values are much higher then observed for the water + 1,4-dioxane mixture over the x^o_A range of 0.5 to 4 mol %. From Figure 11, it can be seen that, as the feed concentration increased from 5 to 30 mol %, the area required for complete mixing also increased from 350 to 2,200 m^2 and 100 to 900 m^2, respectively, for water + THF and water + 1,4-dioxane mixtures. However, in the plug flow model, these values are much higher for water + THF than observed for water + 1,4-dioxane mixtures and, at the same time, the increase is also lower than the complete mixing model.

CONCLUSION

The present study is an effort to compare the PV performance of pure sodium alginate and its blends with poly(vinyl alcohol) in the separation of aqueous mixtures of 1,4-dioxane or THF. The membrane performance was studied by calculating flux and selectivity at 30°C. The data suggest that pure NaAlg has shown a better PV performance than the blend membranes. Mathematical equations are developed to compute membrane area and design parameters using complete mixing and plug flow models. Simulated data using these models revealed that the plug flow model is more satisfactory than the complete mixing

case in predicting the membrane area as well as stage cut. Such parameters would be helpful in assessing the economics of the PV process. Values of stage cut and membrane area requirements for plug flow model are much smaller than those observed for the complete mixing model due to the greater driving force required for the separation. To achieve smaller values of desirable retentate water concentrations (($x_A^o \leq 0.01$), the total membrane area increases considerably for the complete mixing model, suggesting its limitation. The study also suggests the advantages of using the plug flow model with increasing stage cut values, but small cuts of 0.25 or less are to be preferred on a commercial-scale application. A membrane system designed and operated in plug flow case gives superior PV separation from that operated under complete mixing conditions.

NOMENCLATURE

α^* = Ideal selectivity
x_A^M = Minimum stripping constant
K^1 = Ratio of permeability of water at all values of mole fraction and that of pure water
y_A^P = Permeate concentration
θ = Stage cut (fraction of feed that has permeated through the membrane)
S = Dimensionless area
A = Membrane area
α = Selectivity
x_A = Mole fraction of water in feed
y_A = Mole fraction of water in permeate
K_A = Permeability of water at any value of x_A
K_B = Permeability of 1,4-dioxane or THF at any value of x_B ($= 1 - x_A$)
P_A^o and P_B^o = Vapor pressures of water and organic component
q_f = Feed flow rate
x_A^f = Mole fraction of the faster permeating component (water)
K_A^1 = Ratio of permeability of component (A) to that of component B
q_P = Permeate flow rate
y_A^P = Mole fraction of the undesired component A (water) in permeate
h = Membrane thickness
P = Permeate pressure
x_A^o = Mole fraction of A in the outlet
dq^1 = Dimensionless flow rate
J_P = Pervaporation flux
W_P = Mass of permeate
P_w and P_o = Mole fraction of water and organic component in permeate
F_w and F_o = Mole fraction of water and organic component in feed
C_w^P and C_W^F = Concentrations of permeate and feed
D = Diffusion coefficient
J_{P0} = Permeation rate constant
E_P = Activation energy for permeation
E_D = Activation energy for diffusion
E_w = Activation energy of water
R = Gas constant
T = Absolute temperature
ΔH_S = Heat of sorption

APPENDIX

Program for complete mixing case

```
#include <stdio.h>
#include <conio.h>
#include <math.h>
void main()
{
  double theta,xf,xo,yp,S,Ko,xm,A,t,p,qf;
  long double alphaxf,alpha,K1;
  printf("ln Enter the value of xf");
  scan("%lf",&xf);
  alphaxf=(306.04*xf*xf)- (542.44*xf)+241.93;
  printf("ln The value of alphaxf is %Lf",alphaxf);
  /*For calculating the value of selectivity at xf*/
  xm=1.0-(1.0-xf)/(1.0-(1.0–1.0/alphaxf)*xf;
  printf("ln The minimum stripping composition xm
    is %lf",xm);
  printf("ln Enter the value of xo"); /*xo should be
    greater than xm*/
  scanf("%lf",&xo);
  alpha=(306.04*xo*xo)-(542.44*xo)+241.93;
  /*Polynomial expression for alpha in terms of xo
    from trendline*/
  K1=(0.8221*xo*xo)-(0.0159*xo)+0.0929;
  printf("ln The values of alpha and K1 are %Lf %Lf",
    alpha,K1);
  /*Polynomial expression for reduced permeability
in xo from trendline*/
  yp=(alpha*xo)/((1-xo)+(xo*alpha));
  theta=(xf-xo)/(yp-xo);
  S=(yp*theta)/K1*xo);
  printf("ln Enter the values of t,Ko,qf");
  scanf("%lf%lf%lf",&t,&Ko,&qf);
  p=(0.0002*xo)+0.0416;
  A=(S*t*qf)/Ko*p);
  clrscr();
  printf("ln The final permeate composition in %lf",yp);
  printf("ln The stage cut is %lf",theta);
  printf("ln The dimensionless area required is
    %lf",S);
  printf("ln The total area in square meter required is
    %lf",A);
  getch();
  }
```

Program for plug flow case

```
#include <stdio.h>
#include <conio.h>
#include <math.h>
void main()
  {
  float q,S,yp=0.0,xf,xo,x,qf,SS,qq,d,dd,h,d1,d2,d3,d4,dd1,
    dd2,dd3,dd4,A=0.0;
  float  p=0.0444,alpha=0.0,alphaxf=0.0,xm,K1=0.0,
    theta=0.0,t,ko=7.411e-7;
  clrscr();
  q=1.0,S=0.0,h1.0e-5;
  printf("ln Enter the values of xf");
  scanf("%f",&xf);
  alphaxf=(306.04*xf*xf)-(542.44*xf)+241.93;
  printf("ln  The value of alphaxf is %f",alphaxf);
  /*For calculating the value of selectivity at xf*/
  xm=1.0–1.0xf)/1.0-(1.0–1.0/alphaxf)*xf);
  printf("ln  The minimum stripping composition xm
    is %f",xm);
  printf("ln Enter the value of xo"); /*xo should be
    greater than xm*/
  scanf("%f",&xo);
  x=xf;
  do
    {
    qq=q;
    SS=S;
    alpha=(306.04*x*x)-542.44*x)+241.93;
    K1=(0.8221*x*x)-(0.0159*x)+0.0929;
    d1=h*f1(q,x,alpha);
    dd1=h*f2(q,x,alpha,K1);
    q=qq+d1/2;
    S=SS+dd1/2;
    x=x+h/2;
    alpha=(306.04*x*x)-(542.44*x)+241.93;
    K1=(0.8221*x*x)-(0.0159*x)+0.0929;
    d2=h*f1(q,x,alpha);
    dd2=h*f1(q,x,alpha,K1);
    q=qq+d2/2;
    S=SS+dd2/2;
    alpha=(306.04*x*x)-(542.42*x)+241.93;
    K1=(0.8221*x*x)-(0.0159*x)+0.0929;
    d3=h*f1(q,x,alpha);
    dd3=h*f2(q,x,alpha,K1);
    x=x+h;
    q=qq+d3;
    S=SS+dd3;
    alpha=(306.04*x*x)-(542.44*x)+241.93;
    K1=(0.8221*x*x)-(0.0159*x)+0.0929;
    d4=h*f1(q,x,alpha);
    dd4=h*f2(q,x,alpha,K1);
    d=(d1+2.0*(d2+d3)+d4/6.0;
    dd=(dd1+2.0*(dd2+dd3)+dd4)/6.0;
    q=qq+d;
    S=SS+dd;
    }
  while(xxo);
  printf("ln  the value of xo is %f",xo);
  theta=1-q;
  printf("ln the  value  of  alpha  &  k1  is  %f  %f",
    alpha,K1);
  //yp=(xf-(1-theta)*xo)/theta;
  yp=(alpha*xo/1-xo))/(1+alpha*xo)/1-xo));
  printf("ln  Enter the values of t and qf");
  scanf("%f%f",&t,&qf);
  A=S*t*qf)/ko*p;
  printf("ln  The stage cut theta is %f",theta);
  printf("ln  The permeate composition is %f",yp);
  printf("ln  The dimensionless area S required is %f",S);
  printf("ln  The total area in square meters is %f",A);
  getch();
  }
  fl(q,x,alpha);
  float q,x,alpha;
  {
  float z;
  z=(q*(x+(1-x)/alpha))/x*(1-x)*(1-(1/alpha)));
  return(z);
  }
  f2(q,x,alpha,K1);
  float q,x,alpha,K1;
  {
  float z;
  zq/(K1*x*(1-x)*(1–1/alpha)));
  printf("ln the  value  of  k1  &  alpha  are
&f%f",K1,alpha);
  return(z);
  }
```

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