Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Dehydration of 2-Butanol by Pervaporation Through Blend Membranes of Chitosan and Hydroxy Ethyl Cellulose

S. Sridhar[a]; Dhanuja Ganga[a]; B. Smitha[a]; M. Ramakrishna[a]
[a] Membrane Separations Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Hyderabad, India

To cite this Article Sridhar, S. , Ganga, Dhanuja , Smitha, B. and Ramakrishna, M.(2005) 'Dehydration of 2-Butanol by Pervaporation Through Blend Membranes of Chitosan and Hydroxy Ethyl Cellulose', Separation Science and Technology, 40: 14, 2889 — 2908

To link to this Article: DOI: 10.1080/01496390500333186

URL: http://dx.doi.org/10.1080/01496390500333186

Separation Science and Technology, 40: 2889–2908, 2005
Copyright © Taylor & Francis, Inc.
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500333186

Dehydration of 2-Butanol by Pervaporation Through Blend Membranes of Chitosan and Hydroxy Ethyl Cellulose

S. Sridhar, Dhanuja Ganga, B. Smitha, and M. Ramakrishna
Membrane Separations Group, Chemical Engineering Division,
Indian Institute of Chemical Technology, Hyderabad, India

Abstract: Blend membranes of chitosan (CS) and hydroxyethylcellulose (HEC) were synthesized and cross-linked with glutaraldehyde for the separation of 2-butanol/water mixtures. The blends were characterized by fourier transform infrared (FTIR) spectroscopy and wide-angled X-ray diffraction (WAXD) to assess the intermolecular interactions and occurrence of cross-linking, respectively. The pervaporation performance was evaluated by varying experimental parameters such as feed composition, membrane thickness, and permeate pressure and found to be promising. Sorption studies were conducted to evaluate affinity and degree of swelling of both the unmodified and cross-linked blend membranes in pure as well as binary mixtures of the two liquids. The blends were found to have good potential for breaking the aqueous azeotrope of 2-butanol (77 wt.%). Upon cross-linking, the blend membranes exhibited a substantial improvement in performance. Amongst the various blend combinations used for the dehydration studies, the membrane constituting 70 wt.% of CS and 30 wt.% HEC yielded a flux of 2.1 $\text{kg/m}^2 \cdot \text{h} \cdot 10\,\mu\text{m}$ and a selectivity of 554, which was optimum.

Keywords: Pervaporation, chitosan/hydroxyethylcellulose blend, 2-butanol/water mixture, membrane characterization

Received 25 January 2005, Accepted 1 September 2005
IICT Communication No: 051016

Address correspondence to S. Sridhar, Membrane Separations Group, Chemical Engineering Division, Indian Institute of Chemical Technology, Uppal Road, Hyderabad 500007, India. Tel.: 040-27160123-2394; E-mail: sridhar11in@yahoo.com

INTRODUCTION

Pervaporation (PV) is an attractive separation process which has been successfully utilized in separating azeotropic mixtures since it can overcome the limitations of vapor-liquid equilibrium (1). Pervaporation has proven to be highly efficient for dehydration of organic solvents and alcohols, separation of heat-sensitive products and even isomeric mixtures (2, 3). Pervaporation separation mechanism is based on the differences in sorption and diffusion properties of the permeating components (4, 5). Therefore membranes used for dehydration are prepared from polymers having polar functional groups or moieties, which can attract water molecules.

The effectiveness of the dehydration process is governed by the chemical nature and structure of the membrane material (6). The membrane should also show excellent mechanical stability in aqueous environment besides sufficient affinity to water so that water can be preferentially absorbed and transported at a rapid rate.

Researchers worldwide have focused on usage of biopolymers for dehydration applications. One prominently used biopolymer used is chitosan, which is the deacetylated form of chitin, the second most abundant polymer in nature after cellulose (7, 8). Chitosan (CS) has both reactive amino and hydroxyl groups that can participate in chemical reactions resulting in salt formation (9). These hydrophilic groups are considered to play an important role in preferential water sorption and diffusion through the chitosan membrane (10, 11). Chitosan membranes have been extensively studied for the dehydration of alcohols and other industrial solvents like dimethyl sulphoxide and ethylene glycol.

Hydroxyethylcellulose (HEC) is a non-ionic water-soluble cellulose ether which is compatible with a wide range of water soluble polymers (12, 13). HEC is used as a thickener in latex paints and paper finishes (12). However, reports on usage of this membrane in pervaporation applications are few (14–16).

2-butanol of high-purity finds major application in varnish, dye, and paint industry. Chitosan and HEC are hydrophilic polymers capable of selectively permeating water from aqueous-organic solutions. The purpose of blending them is for obtaining better separation properties compared to the individual polymers. Chitosan is a cationic polymer possessing $-NH_2$ groups whereas HEC is a neutral polymer, which has $-OH$ groups. It is expected that there could be some interaction between the amino and hydroxyl groups. The preparation of this blend is easily feasibly since both polymers dissolve readily in the same solvent, which is aqueous acetic acid. Moreover, highly homogeneous blends can be prepared in varying ratios of the respective polymers. Hence in the current study, attention is focused on the applicability of unmodified and cross-linked blend membranes of CS/HEC for dehydrating 2-butanol/water mixtures. The effect of chitosan concentration on degree of swelling and pervaporation performance of blend membrane is studied. The ideal blending ratio that yields high flux and selectivity also forms a key part of the study.

EXPERIMENTAL

Materials

Chitosan, of 84% degree of deacetylation, having viscosity average molecular weight 500000, was purchased locally. HEC, having a viscosity average molecular weight of 150000, was purchased from PIDILITE Industries Ltd., Mumbai, India. Other chemicals such as 2-butanol, iso-propanol, HCl and glutaraldehyde were purchased from s.d. Fine Chemicals, Mumbai, India. Glacial acetic acid was purchased from Loba Chemie, Mumbai. Distilled water (conductivity = 0.02 S/cm) which was used for the preparation of feed solution was generated in the laboratory itself.

Preparation of Membranes

One wt.% of CS and HEC solutions were prepared in 2% v/v aqueous solution of acetic acid separately and the solutions were filtered to remove undissolved matter. Membranes were prepared by solution casting and solvent evaporation method. Sample blends were designated as CS/HEC (CS wt.%)/(HEC wt.%). For example, CS/HEC90/10 represents the membrane containing 90 wt.% chitosan and 10 wt.% HEC. Similarly, membranes with other blend ratios were prepared. The blend solution was then stirred for a period of 0.5 h for homogeneity and kept aside for 1 h to obtain a bubble-free solution which was cast on to a clean glass plate and evaporated to dryness in atmosphere at room temperature to obtain dense nonporous membrane. These membranes were cross-linked in a bath containing iso-propanol/water mixture (90% v/v) with 5 vol% glutaraldehyde as the cross-linking agent and 1 vol% hydrochloric acid as a catalyst. After 2 h of cross-linking, the membranes were washed with deionized water for 4–5 h followed by vacuum drying for a period of 8 h at elevated temperature (100°C) in a closed oven to remove the remaining traces of solvent. Table 1 gives the designations of various blend membranes synthesized in the study.

Pervaporation Procedure

Experiments were carried out on a 100 mL batch level with an indigenously constructed Pervaporation manifold (Fig. 1) operated at a vacuum as low as 0.05 mmHg in the permeate line. The membrane area in the pervaporation cell assembly was approximately 20 cm^2. The experimental procedure is

Table 1. Designation of membranes synthesized and their blending ratio

Sl. no	Designation	Composition of blend (wt.%)
1	CS/HEC (9 : 1)	90 wt.% of CS and 10 wt.% of HEC
2	CS/HEC (7 : 3)	70 wt.% of CS and 30 wt.% of HEC
3	CS/HEC (1 : 1)	50 wt.% of CS and 50 wt.% of HEC

described in detail elsewhere (17). Permeate was collected for a duration of 8–10 h. Tests were carried out at room temperature (30 ± 2°C) and repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed after allowing it to attain room temperature in a Sartorius electronic balance (accuracy: 10^{-4} g) to determine the flux and then analyzed by gas chromatography to evaluate the membrane selectivity.

Flux and Selectivity Equations

In pervaporation the flux J of a given species, say faster permeating component i of a binary liquid mixture comprising of i (water) and j (2-Butanol), is given by

$$J_i = \frac{W_i}{At}$$

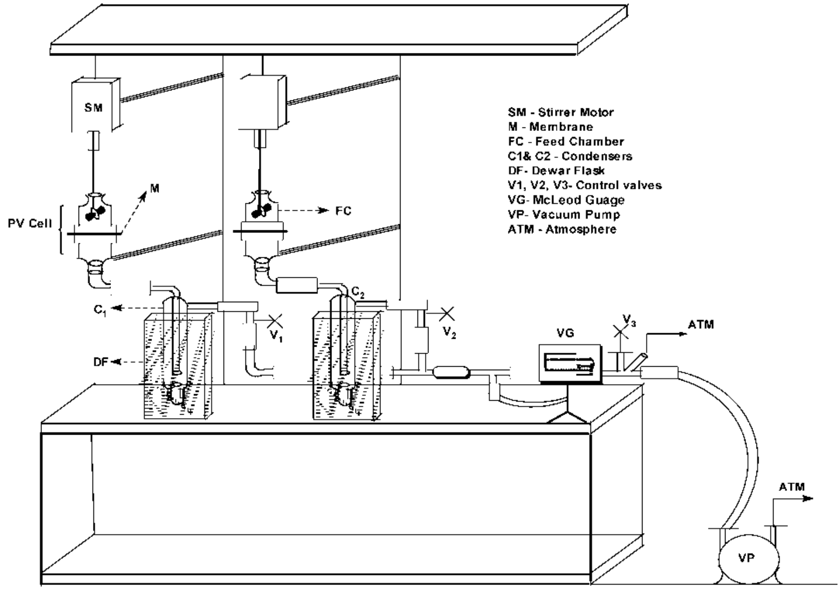


Figure 1. Schematic of laboratory pervaporation setup.

where W_i represents the mass of water in permeate (kg), A is the membrane area (m^2), and t represents the evaluation time (h). In the present study, though different membrane thicknesses were utilized, the flux has been normalized and reported for thickness of 10 μm.

The membrane selectivity is the ratio of permeability coefficients of water and 2-butanol and can be calculated from their respective concentrations in feed and permeate as given below

$$\alpha = \frac{y(1-x)}{x(1-y)}$$

where x and y represent the feed and permeate concentrations of the faster permeating component i, which is water in the present case.

Quite often, pervaporation separation index (PSI) is used to describe the overall performance of a membrane for a selected feed mixture. This can be calculated from the product of water flux, j_i, and selectivity, α.

$$PSI = J_i * \alpha$$

Permeance and Permeability Equations

Permeance of the membrane for component i is given by

$$Q_i = \frac{J_i}{(P_{i,feed}^{vapor} - n_{i,permeate} P_{Permeate})}$$

where

Q_i = permeance of the membrane for component i
J_i = partial permeate flux of component i
$P_{i,feed}^{vapor}$ = the equilibrium partial vapor pressure of I in the feed
n_i = mole fraction of I in the permeate
$P_{permeate}$ = permeate pressure

whereas permeability is the product of permeance and membrane thickness

$$K_i = Q_i * \text{membrane thickness } (\mu\text{m}).$$

Analytical Procedure

The feed and permeate samples were analyzed using a Nucon Gas Chromatograph (GC Model 5765) installed with Thermal Conductivity Detector (TCD) and packed column of 10% Diethylene glycol sebacate (DEGS) on 80/100 Supelcoport of 1/8 in ID and 2 m length. The oven temperature was maintained at 70°C (isothermal) while the injector and detector temperatures were maintained at 150°C each. The sample injection size was 1 μL and pure hydrogen was used as the carrier gas at a pressure of 1 kg/cm^2. The GC response was calibrated for their particular column and conditions with known compositions of 2-butanol-water mixtures, and the calibration factors were fed into the software to obtain correct analysis for unknown samples.

Membrane Characterization

XRD Analysis

A Siemens D 5000 powder X-ray diffractometer was used to study the solid-state morphology in powdered form. X-rays of 1.5406 Å wavelengths were generated by a CuK source. The X-ray diffractograms of CS, HEC, unmodified and cross-linked blend membranes of CS/HEC are shown in Figs. 2–4. The angle of diffraction was varied from 2° to 60° to identify the changes in the crystal structure and intermolecular distances between the intersegmental chains after cross-linking.

FTIR Studies

The FTIR spectra of the homopolymers, CS/HEC blend and cross-linked blend membranes were scanned using Nicolet-740, Perkin-Elmer-283B FTIR Spectrometer. These spectra are shown in Figs. 5 and 6.

Swelling Characteristics

Interactions of the polymer blends with the two liquids present in the feed mixture was determined by sorption studies (Table 2). Weighed samples of circular pieces of the polymer films (3-cm dia.) were soaked in pure water, 2-butanol as well as their binary mixtures. The films were taken out after different soaking periods and quickly weighed after carefully wiping out excess liquid to estimate the amount absorbed at the particular time "*t*". The films were then quickly placed back in the solvent. The process was repeated until the films attained steady state as indicated by constant weight after a certain period of soaking time. The degree of swelling was calculated from the equation:

$$\text{Degree of swelling} = Ms/Md$$

where

Ms = mass of the swollen polymer in g
Md = mass of the dry polymer in g

The percentage sorption was calculated from the equation:

$$\%\ \text{Sorption} = \frac{Ms - Md}{Md} * 100$$

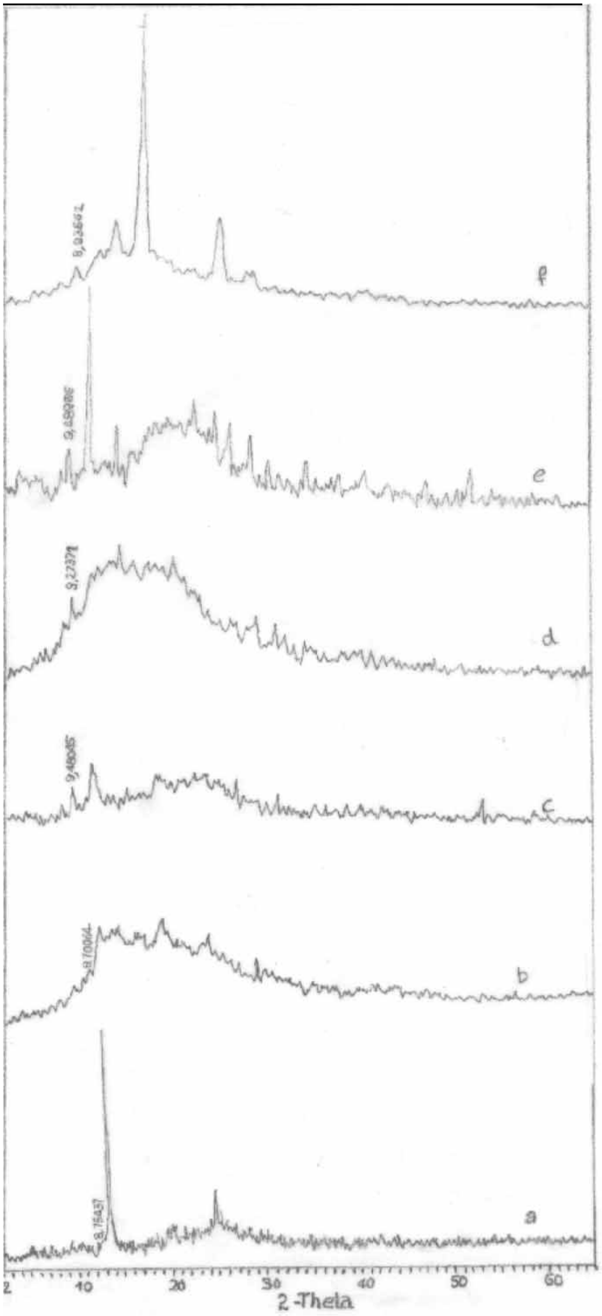


Figure 2. XRD spectra of (a) 9 : 1 CS/HEC unmodified blend, (b) 9 : 1 cross-linked blend, (c) 7 : 3 CS/HEC unmodified blend, (d) 7 : 3 cross-linked blend, (e) 1 : 1 CS/HEC unmodified blend, (f) 1 : 1 cross-linked blend.

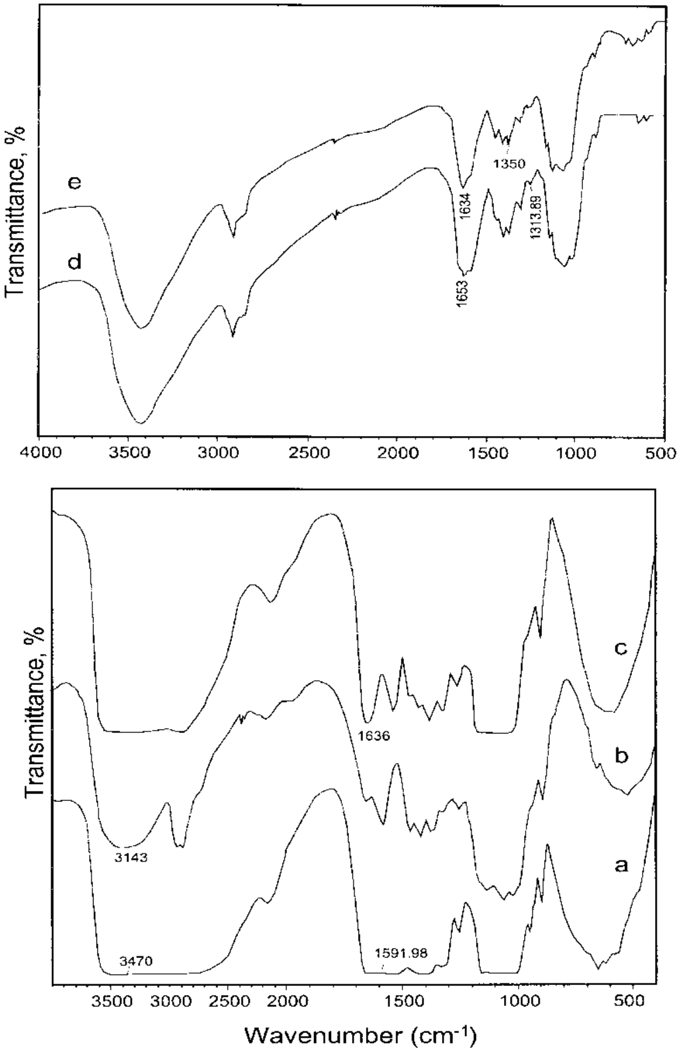


Figure 3. FTIR spectra of (a) CS, (b) HEC, (c) 9 : 1 unmodified membrane, (d) 7 : 3 unmodified membrane, (e) 1 : 1 unmodified blend membrane.

Determination of Ion Exchange Capacity

In order to determine the effect of cross-linking on the blend, the ion exchange capacity (IEC) of the blend was estimated. IEC indicates the number of groups present before and after cross-linking which gives an idea of the extent of cross-linking. The ion exchange capacity (IEC) indicates the number of milli-equivalents of ions in 1 g of the dry polymer. To determine the ion

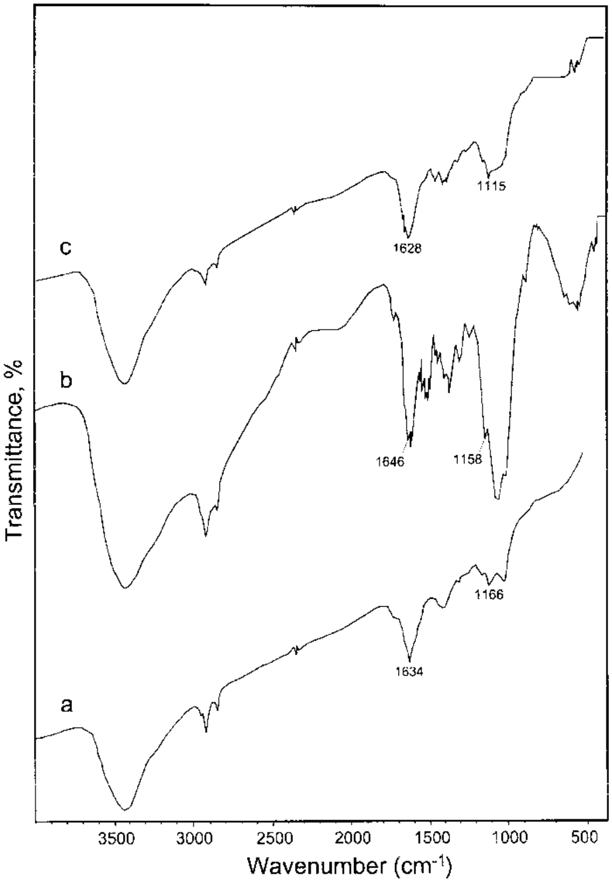


Figure 4. FTIR spectra of (a) 9 : 1 cross-linked membrane, (b) 7 : 3 cross-linked membrane, (c) 1 : 1 cross-linked membrane.

exchange capacity, the specimens of similar weight were soaked in 50 mL of 0.01 N sodium hydroxide solution for 12 h at ambient temperature. Then, 10 mL of this per sample solution were titrated with 0.01 N sulfuric acid. The sample was regenerated with 1 N hydrochloric acid, washed and dried to obtain constant weight. The IEC was calculated according to the equation:

$$\mathrm{IEC} = \mathrm{B} - \mathrm{P} * 0.01 * 5/\mathrm{m}$$

where:

IEC: Ion exchange capacity

B: Amount of sulphuric acid used to neutralize blank sample

P: Amount of sulphuric acid used to neutralize the pervaporation membranes

0.01: Normality of sulphuric acid

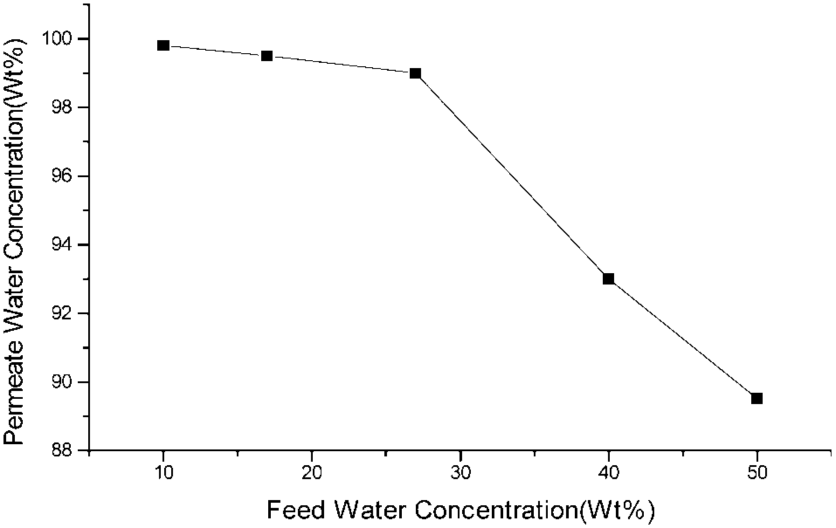


Figure 5. Feed water composition vs. permeate water concentration for 7 : 3 CS/HEC cross-linked blend membrane for different feed compositions (50 μm, 0.5 mm Hg, 40°C).

5: Factor corresponding to the ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration

m: Sample mass in gms

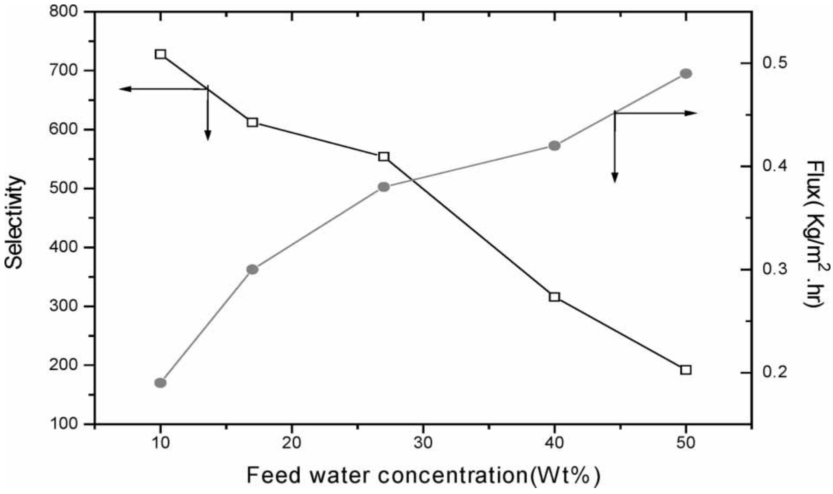


Figure 6. Effect of feed water concentration on pervaporation performance of 7 : 3 cross-linked membrane (50 μm, 0.5 mmHg, 40°C).

Table 2. Water sorption characteristics of unmodified and modified membranes of different blending ratios

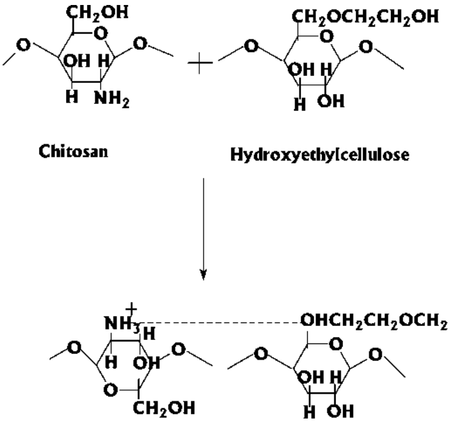
		% Sorption		
Sl. no	Polymer blend	9 : 1	7 : 3	1 : 1
1	Unmodified	141	112	102
2	Cross-linked	82	61.46	32

RESULTS AND DISCUSSION

Blend membranes of CS/HEC were chosen for dehydrating 2-butanol/water mixture on the basis of the close proximity of Hansen's solubility parameter value ($43.04\,J^{1/2}/cm^{3/2}$) (18) of chitosan polymer to that of water ($47.9\,J^{1/2}/cm^{3/2}$) (19) as well as its good mechanical strength and chemical resistance. It was observed that the blend membrane formed on mixing the two homopolymers exhibited considerable swelling but remained insoluble in water. This nonsolubility of the blend can be due to the formation of a weak force of interaction resulting on blending the two homopolymers. Scheme 1 shows the possible interaction between CS and HEC.

The blends were then cross-linked with glutaraldehyde (GA) to reduce the extent of swelling. During the cross-linking reaction, the amino group of chitosan interacts with the aldehyde groups of GA resulting in the formation of imine linkages, whereas the hydroxyl group of HEC interacts with aldehyde group of GA, resulting in the formation of acetal linkages. Scheme 2 shows a mechanism representing the cross-linking reaction occurring between GA and CS/HEC blend. To evaluate the extent of cross-linking and the possibility of formation of homolinks (20), the membranes were analyzed for their ion exchange capacity (IEC) to estimate the number of functional groups present before and after cross-linking.

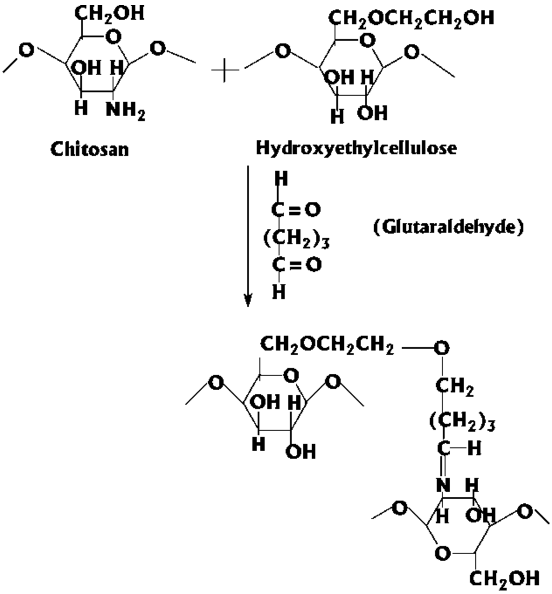
The amount of residual amine and hydroxyl groups present after cross-linking was estimated from the IEC studies. It was noted that unmodified blend showed an IEC of 0.74 meq/g whereas the cross-linked blend membrane exhibited an IEC of 0.69 meq/g. The IEC, which is equivalent to the total number of free amino groups (considering the fact that amino groups in the blend are more reactive when compared to hydroxyl groups), decreased after cross-linking (21). This shows that almost 93% of the amine groups present in the unmodified blend have now formed cross-links with GA, and there are still a few amine and hydroxyl groups left for sorption and diffusion of water molecules through the blend, thereby excluding the possibility of formation of the homolinks.



Scheme 1. Weak forces of attraction between CS/HEC.

Effect of Blending Ratio

The homopolymers viz., CS and HEC were mixed in various ratios to obtain blend membranes. It was noted that an increase in the HEC content in the blend renders the membrane brittle as evidenced by the membrane stability test. The stability of the membrane was assessed by bending the film. The



Scheme 2. Covalent cross-linking of CS/HEC.

membrane is considered stable if its mechanical strength is restored after bending it, i.e., it does not break upon bending. The mechanical weakness, introduced by the addition of HEC as a component has a profound effect as its content in the blend increases. Hence, various blending ratios of chitosan to hydroxyethylcellulose were studied among which only three mechanically stable blends were considered for pervaporation studies.

Membrane Characterization

XRD Studies

The XRD spectra of unmodified and cross-linked blends of CS and HEC are shown in Fig. 2. The change in the crystal structure and the effective d-spacing of the blend before and after cross-linking were studied using XRD studies.

From the spectra of CS/HEC (1 : 1) blend (Fig. 2e) and crosslinked CS/HEC (1 : 1) blend (Fig. 2f), one peak at $2\theta = 10^\circ$ corresponding to crystal 1 (22) is evidenced. This crystal peak, which is responsible for separation, as it corresponds to functional groups such as $-NH_2$ and $-OH$ (23), has undergone significant change after cross-linking. A reduction in the d_{eff} value from 9.48 (at $2\theta = 10^\circ$) for un-cross-linked blend to 8.93 (at $2\theta = 10^\circ$) for cross-linked blend is an indication of shrinkage in cell size or intersegmental spacing, which could improve the selective permeation property of the membrane (24). Similarly, the XRD spectra's of unmodified and cross-linked 7 : 3 blend and 9 : 1 blend showed a similar reduction in the effective d-spacing, thereby confirming the occurrence of cross-linking.

FTIR Studies

Figures 5 and 6 show the FTIR spectra of the homopolymers, i.e., CS and HEC in comparison with their blends. The FTIR spectra of chitosan (Fig. 3a) shows the prominent peaks of hydroxyl and amide at 3470 and 1591 cm^{-1}, respectively. Figure 3b represents the spectra of HEC. The characteristic O–H stretching peak in HEC can be noted at 3413 cm^{-1}. Figure 3c–e shows additional peaks in the range 1660–1610 cm^{-1} and 1350–1260 cm^{-1}. The formation of new peaks can be assigned to the NH_3^+ deformation in CS besides –CO stretching and –OH deformation in HEC occurring on blending the two hompolymers. Hence, a weak force of attraction between chitosan and hydroxyethylcellulose is observed on blending.

On cross-linking the blend with glutaraldehyde, the formation of imine linkage $-C{=}N-$) resulting on interaction between chitosan and glutaraldehyde and acetal linkage (C–O–C) due to the reaction between glutaraldehyde and HEC, is likely (25). The FTIR spectra of the cross-linked blends (Fig. 4a–c) shows prominent peaks in the range 1690–1590 cm^{-1}. These peaks can be attributed to (–C=N–) linkage. On the other hand, peaks in the range 1050–1150 cm^{-1} correspond to acetal linkages.

Hence, it can be said that glutaraldehyde acts as a cross-linking agent to both chitosan and HEC. The FTIR spectra agrees well with the model structure proposed for cross-linking CS/HEC blends with glutaraldehyde.

Sorption Studies

From Table 2, it was also found that the cross-linked membrane showed a high degree of sorption in pure water (61.46%) but relatively negligible sorption (1.2%) in pure 2-butanol. The preferential affinity of the blend for water makes it selective to water permeation. The percent sorption correspondingly rises with an increase in the feed water concentration resulting in enhanced flux. However, increased swelling has a negative impact on membrane selectivity since the swollen and plasticized upstream membrane layer allows some 2-butanol molecules also to escape into the permeate side along with water.

Pervaporation Studies

Pervaporation studies for dehydrating 2-butanol-water mixtures were carried out using blend membranes of CS and HEC. Table 3 shows the performance of unmodified and cross-linked blend membranes for azeotropic composition of 2-butanol/water mixture. All the membranes (both unmodified and cross-linked) were of uniform thickness and the permeate pressure was maintained at 0.5 mmHg.

From the table it can be noted that the unmodified blend membranes exhibited higher fluxes but poor selectivities. On the other hand, the cross-linked membranes exhibited reasonably high fluxes and good selectivities. This shows that cross-linking brings the polymer chains in close proximity with each other, thereby enhancing the permeation of one component to provide high selectivity.

Table 3. Flux and selectivity of unmodified and cross-linked blend membranes of different blending ratios for azeotropic feed composition (77 wt.% 2-butanol)

Sl. no	Pervaporation charactersitics	Unmodified blend			Cross-linked blend		
		9 : 1	7 : 3	1 : 1	9 : 1	7 : 3	1 : 1
1	Flux (kg/m^2 · h · 10μm)	4.56	3.41	1.15	2.9	2.1	0.25
2	Selectivity	9	18.82	21	104	554	601
3	Pervaporation seperation index (PSI)	41.04	64.17	24.15	301.6	1163.4	150.25

From the table it can also be noted that among the cross-linked blends, the blend containing 70 wt.% of CS and 30 wt.% of HEC showed optimum flux and selectivity and highest PSI. With the increase in the content of HEC [CS/HEC (1 : 1)], the interaction between the two homopolymers tends to become stronger, which gets strengthened further on cross-linking with GA, thereby reducing the membrane flux to a considerable level. On the other hand, cross-linked membranes constituting lower HEC content exhibited higher swelling, resulting in a drop of selectivity. Hence further pervaporation studies were conducted using 7 : 3 CS/HEC cross-linked blend.

Effect of Feed Composition

The variation of pervaporation performance over a wide range of feed mixtures at 30°C was investigated using both the unmodified and cross-linked blend membranes. For this study, the membrane thickness and permeate pressure were kept constant at 50 μm and 0.5 mmHg, respectively. The pervaporation performance of CS/HEC membrane cross-linked with glutaraldehyde was investigated for varying feed compositions comprising of 10 wt.% to 50 wt.% water, keeping other operating parameters such as permeate pressure and membrane thickness constant.

With an increase in the feed water concentration from 10 wt.% to 30 wt.%, the variation in the permeate water concentration is found to be negligible and with a further increment in the water concentration from 30 wt.% to 50 wt.%, a drop in permeate water concentration from 99.2 to 87.2 wt.% is clearly evidenced as seen in Fig. 5.

Figure 6 shows the variation of flux and selectivity of the blend membrane with varying feed water concentration. Expectedly, a rise in the feed concentration of water produced an increase in the water flux from 1.2 to 2.65 $kg/m^2 \cdot h \cdot 10\ \mu m$. Mass transport through the hydrophilic blend membrane occurs by solution diffusion mechanism (26). In addition to the sorption data for binary feed mixtures presented in Table 3, it was also found that the cross-linked membrane showed a high degree of sorption in pure water 61.46% but relatively negligible sorption (0.2%) in pure 2-butanol. The preferential affinity of the membrane toward water causes swelling, which allows rapid permeation of feed molecules. The degree of swelling correspondingly rises with an increase in the feed water concentration resulting in enhanced flux. However, increased swelling has a negative impact on membrane selectivity since the swollen and plasticized upstream membrane layer allows some 2-butanol molecules also to escape into the permeate side along with water. Therefore, the permeate water concentration was found to reduce from 99.4 wt.% and 89.52 wt.% indicating a drop in selectivity from 728 to a lower value of 192 over the same feed concentration range of 10–50% water. However, it is worth mentioning that the membrane showed promising results for dehydrating feeds having 10–30 wt.% water. Moreover, the azeotropic composition of (77 wt.% 2-butanol) was easily broken by pervaporation since a comparable high flux of $2.1\,\mathrm{kg/m^2 \cdot h \cdot 10\,\mu m}$ and selectivity of 554 was obtained using 7 : 3 membrane. The permeance and permeability values calculated from flux and membrane thickness are tabulated in Table 4.

Effect of Membrane Thickness

The effect of varying membrane thickness on separation performance was studied at constant feed composition (azeotropic) and permeate pressure (0.5 mmHg) by synthesizing membranes of thickness ranging from 30 μm to 120 μm. With an increase in the membrane thickness a gradual reduction in the flux from 0.57 to $0.025\,\mathrm{kg/m^2 \cdot h}$ can be clearly evidenced from Fig. 7. Though the availability of polar groups enhances with an increase in the thickness, flux decreases since diffusion becomes increasingly retarded as the feed molecules have to travel a greater distance to reach the permeate side. With an increase in membrane thickness from 25 μm to 120 μm the selectivity increased from 428 to 612 correspondingly. In pervaporation process, the upstream layer of the membrane is swollen and plasticized due to absorption of feed liquid and allows unrestricted transport of feed components. In contrast, the downstream layer is virtually dry due to continuous evacuation in the permeate side and therefore this layer forms the restrictive barrier which allows only interacting and smaller sized molecules such as water to pass through. It is expected that the thickness of the dry layer would increase with an increase in the overall membrane thickness resulting in improved selectivity as observed in the present case.

Effect of Permeate Pressure

The permeate pressure was varied from 0.5 to 10 mm Hg to study the permeation characteristics at a constant membrane thickness of 50 μm and

Table 4. Permeance and permeability of 2-Butanol and water for 7 : 3 cross-linked membrane

Sl. no	Concentration of 2-butanol in feed (wt.%)	Permeance of 2-butanol (GPU)	Permeance of water (GPU)	Permeability of 2-butanol (Barrer)	Permeability of water (Barrer)
1	90	0.02632	5.68	1.316	284
2	80	0.21	90976	10.5	498.8
3	73	0.486	11.6	24.3	580
4	60	1.045	12.4	52.5	620
5	50	1.994	14.13	99.7	701.5

GPU: 10^{-6} [Cm^3 (STP)]/[cm$^2 \cdot$ § CmHg].
Barrer: 10^{-10} [Cm^3 (STP)]/[cm$^2 \cdot$ § CmHg].

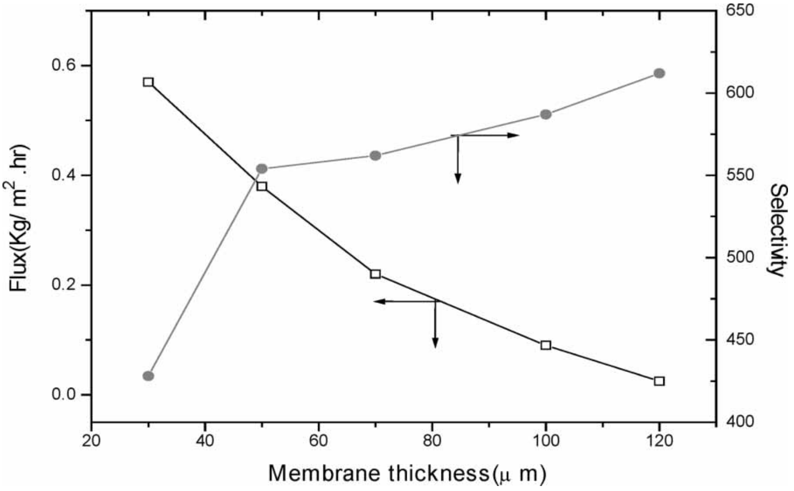


Figure 7. Effect of membrane thickness on pervaporation performance of 7 : 3 cross-linked membrane (0.5 mmHg, 40°C).

azeotropic feed composition. At lower pressures (high vacuum) the influence of the driving force on the diffusing molecules in the membrane is high and will result in the components being swept out immediately from the permeate side resulting in high mass transfer rates. Figure 8 shows that the membrane exhibits considerable lowering of flux from 1.9 to 0.183 kg/ $m^2 \cdot h \cdot 10\,\mu m$ as well as a reduction in selectivity from 554 to 28, with an

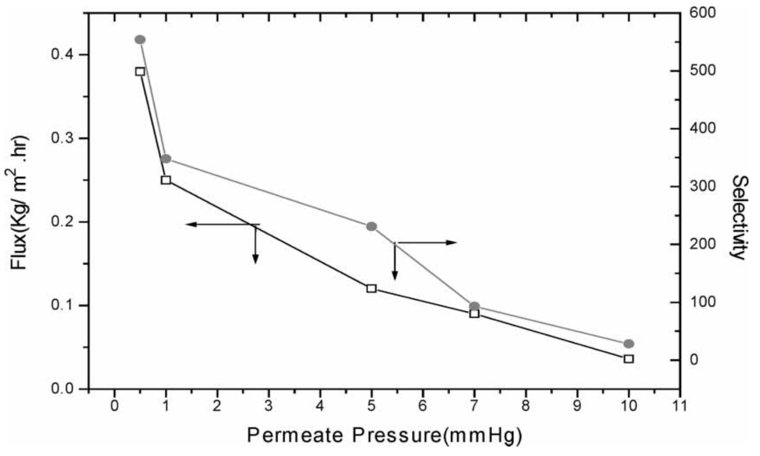


Figure 8. Effect of permeate pressure on pervaporation performance of 7 : 3 cross-linked membrane (50 μm, 40°C).

increase in permeate pressure from 0.5 mmHg to 10 mmHg. Under high vacuum conditions (lower pressures) diffusion through the membrane is the rate determining step of the pervaporation process, and the diffusing water molecules experience larger driving force, which enhances the desorption rate at the downstream side. Lower vacuums reduce the driving force, thus slowing the desorption of molecules. In such cases the relative volatilities of the two components of the mixture govern the separation factor of the membrane. 2-Butanol being more volatile (B.P. 98°C) than water permeates competitively with the latter, thus lowering membrane selectivity.

CONCLUSIONS

Blend membranes were prepared from chitosan and hydroxyethylcellulose by mixing the respective polymer solutions in different weight ratios. These membranes were then cross-linked using glutaraldehyde. FTIR characterization and ion exchange capacity studies confirmed the occurrence of cross-linking resulting on blending the two polymers. The reduction in the effective d-spacing as well as the amorphous nature of the cross-linked blend was confirmed by XRD studies. Moderate water sorption (40–60%) of the blends with no significant effect on mechanical stability was attained on cross-linking the CS/HEC blend.

The cross-linked blends appeared to be more promising for dehydration of 2-butanol/water mixtures compared to unmodified blends. Among the cross-linked blends synthesized in this study, CS/HEC (7 : 3) appears more suitable for 2-butanol dehydration, considering its optimum pervaporation characteristics. Varying thickness showed a considerable effect on the flux with negligible effect on selectivity. Lower permeate pressures resulted in a reduction in both the flux and selectivity.

REFERENCES

1. Kirk-Othmer (1984) *Encyclopedia of Chemical Technology*, 3rd ed.; Wiley Interscience: USA; Vol. 4, 338–345.
2. U.S. Department of Energy, Membrane separation systems – a research need assessment, US DOE Rep. no. DE 90-011770, Washington, DC, Apr' 90.
3. Baker, R.W., Cussler, E.L., Eykamp, W., Koros, W.J., Riley, R.L., and Strathmann, H. (1991) *Membrane Separation Systems Recent Developments and Future Directions*; Noyes Data Corp: Park Ridge, NJ.
4. Noble, R.D. and Stern, S.A. (1995) *Membrane Separation Technology Principles and Applications*; Elsevier: Amsterdam; Vol. 2, 143–204.
5. Hwang, S.T. and Kammermeyer, K. (1975) *Pervaporation, in Membranes in Separations, Techniques of Chemistry*; John Wiley and Sons: New York, Vol. VII, Chap. VII, 99–123.

6. Huang, R.Y.M., eds. (1991) *Pervaporation Membrane Separation Process*; Elsevier: Amsterdam.
7. Huang, R.Y.M. and Feng, X. (1996) Pervaporation with chitosan membranes I. Separation of water from ethylene glycol by a chitosan/polysulfone composite membrane. *J. Membr. Sci.*, 116: 67.
8. Urgami, T., Matsuda, H., Okuno, and Miyata, T. (1994) Structure of chemically modified membranes and their characteristics of permeation and separation of aqueous ethanol solutions. *J. Membr. Sci.*, 88: 243–251.
9. Uragami, T. and Takigawa, K. (1990) Permeation and separation characteristics of ethanol-water mixtures through chitosan derivative membranes by pervaporation and evapomeation. *Polymer*, 31: 668–672.
10. Lee, Y.M., Nan, S.Y., and Woo, D.J. (1997) Pervaporation of ionically surface crosslinked chitosan composite membranes for water-alcohol mixtures. *J. Membr. Sci.*, 133: 103–110.
11. Hara, M., ed. (1993) Chapter 4. *Polyelectrolytes, Science and Technology*; Marcel Dekker: New York.
12. Nicholson, M.D. and Merritt, F.M. (1985) Cellulose ethers. In *Cellulose Chemistry and its Applications*; Nevell, T.P. and Zeronian, S.H., eds.; Ellis Horwood: U.K., 363–383.
13. Savge, A.B. and Ethers, C. (1971) Part V. *Cellulose & Cellulose Derivatives*; Bikales, N.M. and Segal, L., eds.; Wiley: USA.
14. Chanachai, A., Jiraratananon, R., Uttapap, D., Moon, G.Y., Anderson, W.A., and Huang, R.Y.M. (2000) Pervaporation with chitosan/hydroxyethylcellulose (CS/HEC) blended membranes: I. Effect of operating conditions. *J. Membr. Sci.*, 166 (2): 271–280.
15. Jiraratananon, R., Chanachai, A., Huang, R.Y.M., and Uttapap, D. (2002) Pervaporation dehydration of ethanol–water mixtures with chitosan/hydroxyethylcellulose composite membranes: I. Effect of operating conditions. *J. Membr. Sci.*, 195 (2): 143–151.
16. Jiraratananon, R., Chanachai, A., and Huang, R.Y.M. (2002) Pervaporation dehydration of ethanol-water mixtures with chitosan/hydroxyethylcellulose (CS/HEC) composite membranes: II. Analysis of mass-transport. *J. Membr. Sci*, 199 (1–2): 211–222.
17. Sridhar, S., Ravindra, R., and Khan, AA. (2000) Recovery of monomethyl hydrazine liquid propellant by pervaporation technique. *Ind. Eng. Chem. Res.*, 39: 2485.
18. Ravindra, R., Kameswara Rao, K., and Khan, AA. (1998) Solubility parameter of chitin/chitosan. *Carbohydr. Polym.*, 36: 121.
19. Barton, A.F.M., ed. (1983) *CRC Handbook of Solubility Parameters and Other Cohesive Parameters*; CRC Press: Boca Raton, Florida.
20. Kurita, K. (2001) Controlled functionalization of polysaccharide chitin. *Prog. Polym. Sci.*, 26: 1921–1971.
21. Keiji, I. and Yoshio, N. (2002) Fundamental adsorption properties of chitosan gel particles prepared by suspension evaporation method. *J. Appl. Polym. Sci.*, 86 (4): 901–906.
22. Samuels, R.J. (1981) Solid state characterization of the structure of chitosan films. *J. Poly. Sci. Polym. Phys.*, 19: 1081.
23. Ge Cui, Y. and Jiang, W. (2000) The effect of structure on pervaporation of chitosan membrane. *J. Membr. Sci.*, 165: 75–81.

24. Charati, G., Houde, A.Y., Kulkarni, S.S., and Kulkarni, M.G. (1991) Transport of gases in aromatic polyesters: Correlation with WAXD studies. *J. Polym. Sci. Polym. Phys.*, 29: 921.
25. Sridhar, S., Susheela, G., Jayasimha Reddy, G., and Khan, A.A. (2001) Cross-linked chitosan membranes: Characterization and study of dimethylhydrazine dehydration by pervaporation. *Polymer International*, 50: 1156–1161.
26. Wijmans, J.G. and Baker, R.W. (1995) The solution-diffusion model: A review. *J. Membr. Sci.*, 107: 1.