Synthesis and Characterization of Moisture-Cured Polyurethane Membranes and Their Applications in Pervaporation Separation of Ethyl Acetate/Water Azeotrope at 30°C

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ABSTRACT: NCO-terminated polyurethane membranes were prepared using diisocyanate, diol, and trimethylolpropane (TMP) using an NCO/OH ratio of 1.6 : 1. Prepolymer was chain-extended using cellulose acetate butyrate (CAB) in the ratios of 2 : 1, 4 : 1, and 3 : 1 of NCO/OH. Polyurethane (PU) membranes were characterized by differential scanning calorimeter (DSC) and thermogravimetry (TGA) to investigate their thermal properties. Equilibrium sorption studies were carried out at 30°C in water and ethyl acetate media as well as in their binary mixtures. The influence of CAB on pervaporation (PV) separation of an ethyl acetate/water (92/8, w/w, i.e., azeotropic composition) mixture was investigated. Membranes in this study showed a selectivity of 42.42 with a flux value of 0.187 kg/m/h for 3 : 1% NCO/OH containing PU membrane. In order to gain a more detailed picture of the molecular transport phenomenon, we performed the sorption gravimetric experiments at 30°, 35°, 40°, and 50°C to compute diffusion, swelling, sorption, and permeability coefficients of PU membranes in the azeotropic mixture of ethyl acetate and water. Activation parameters for diffusion and permeation were computed from the Arrhenius equation to understand the polymer/solvent interactions. Sorption trends and diffusion anomalies were established through an empirical equation after estimating the diffusion parameters. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3405–3414, 2007

Key words: polyurethane; pervaporation; azeotrope; membrane

INTRODUCTION

Polyurethane (PU) has a unique polymer chain structure and morphology comprising flexible soft segments (polyol) and rigid hard segments (diisocyanate and chain extender, i.e., diol and diamine). The nature and length of PU segments and their relative compositions constitute the principal factors affecting morphology, thereby controlling the properties of PU. However, the affinity of organic molecules can be increased by a judicial selection of polyol in PU. Thus, the properties of PU membrane depend on the soft/hard segmental distribution.[1] PUs, therefore, are attractive materials as membranes in pervaporation (PV) separation studies, since they are known to exhibit widely varying physicochemical properties, resulting from a two-phase morphology. Therefore, one can tailor the PV characteristics of a PU membrane to suit the requirements of a particular application.[2] Many researchers have found PUs to be more selective to aromatics than aliphatics.[3–5] Water-permselective PU membranes have been synthesized due to their good mechanical strength as well as chemical resistance and barrier properties.[6] Interpenetrating (IPN) membranes of hydrophilic PU with hydrophobic polystyrene (PS) have been studied to demonstrate their separation performances for a water/ethanol mixture.[7,8] Luo et al.[9] separated ethyl-tert butyl ether and ethanol mixtures from cellulose acetate butyrate (CAB) and cellulose acetate propionate blend membranes.

PUs are the most attractive materials to prepare PV membranes, since they can be synthesized by varying hard and soft segment structures that can affect their membrane performances depending on the matrix phase. Liquid permeation in PU is thus expected to vary with the chosen chain-extender as well as the hard segment concentration in addition to crosslink density of the PU. Transport of small molecules through the segmented PU has been found to occur in the elastomeric phase formed by soft segments.[10]

However, hard domains serve as the virtual crosslinks by providing junction points for soft segments. Reinforcing with fillers can influence the permeation process either by suppressing membrane swelling or by altering the path of the permeating molecules through the micro-voids. Therefore, polymer structure and separation properties can be investigated by studying its sorption properties, which are dependent on their physical and chemical structures. However, the driving force for molecular transport of liquids through dense polymeric membranes is greatly affected by their permeation characteristics.[11,12]

Compared to other traditional methods of separation, PV is by far the most cost-effective separation technique in addition to its simplicity and high selectivity. In recent years, PV has gained importance compared to conventional distillation because the process is environmentally benign. Polymeric membranes with high permselectivity have been used for the effective dehydration of alcohols, recovery of aromatic compounds, and separation of organic solvents.[13] The IPNs based on natural polymers have been used as PV membranes in order to improve the separation performance.[14] Linear cellulose esters have been used as semi-IPN matrices for the removal of ethanol; membranes with cellulose derivatives have shown large permeability and good mechanical strength properties without any loss of selectivity.[15] Cellulose is a highly crystalline polymer, which is insoluble in common solvents, but acetate, butyrate, and acetate butyrate substituted cellulosics are the thermoplasts that exhibit a single glass transition temperature, T_g, depending on the molecular weight.[16]

In order to understand the mechanism of diffusion at a microscopic level, it is important to investigate the polymer-penetrant interaction. Diffusion in polymers is a rather complex phenomenon and has been classified into three categories: 1) Fickian mode in which the rate of diffusion is much smaller than the polymer chain relaxation due to mechanical and structural modes of polymer-penetrant system; 2) non-Fickian, which refers to rapid penetrant diffusion as compared to relaxation and swelling kinetics; and 3) anomalous diffusion, in which diffusion and relaxation rates are comparable. Harogoppad and Aminabahvi[17] investigated the sorption trends and diffusion anomalies of a number of elastomers versus organic liquids. In an effort to understand the PV separation performance, we investigated the diffusion and sorption behaviors of ethyl acetate/water mixtures through PU membranes at 30°, 35°, 40°, and 50°C containing CAB in the ratios of 2 : 1, 4 : 1, and 3 : 1 of NCO/OH designated, respectively, PU-1, PU-2, and PU-3 polyurethanes. We report here the synthesis of PU membranes, whose performances were monitored by varying the percent CAB concentration on the PV separation of ethyl acetate/water mixture at the azeotropic composition. Membranes were cured at the atmospheric conditions for a period of 20 days. Differential scanning calorimetry (DSC) and thermogravimetric (TGA) techniques have been used to investigate thermal properties of PU membranes developed as a function of temperature.

Ethyl acetate is a key component in coffee aroma and it has also been identified as the most common ester in fruits. It is used as a solvent in many chemical and pharmaceutical industries and in the production of PU and epoxy resins. Ethyl acetate vapors are released into the atmosphere during manufacturing processes and their disposal is harmful to the environment. The loss of these substances to the atmosphere will lead to an adverse effect on air quality, thereby endangering the public health and hygiene. Therefore, separation of water from ethyl acetate is an important unit operation process in the chemical/engineering areas. Membranes in this study were tested for their PV performances to separate ethyl acetate/water azeotropes. Temperature variations of sorption and diffusion were studied to estimate the Arrhenius activation parameters for the diffusion and permeation processes to understand the transport phenomenon.

EXPERIMENTAL

Materials

Polypropylene glycol (PPG) (MW 1000) and trimethylolpropane (TMP) were procured from Aldrich (Milwaukee, WI). PPG was refluxed using the sulfur-free toluene at 50°C before use. CAB was purchased from Eastman (Rochester, NY) (MW 30,000). Toluene and ethyl acetate were purchased from S.D. Fine Chemicals (Mumbai, India). Toluene diisocyanate (TDI) with a purity >99.9% was purchased from Loba Chemicals (Mumbai, India). Methyl-isobutyl ketone (MIBK) was purchased from Ranbaxy (Mumbai, India).

Synthesis of moisture-cured polyurethane (MCPU)

PU was prepared by reacting PPG, TMP, and TDI with an NCO/OH ratio of 1.6 : 1 at 70°C for 8 h. The reaction was carried out in a 500-mL round-bottom flask equipped with a stirring motor connected to a CaCl$_2$ drying tube; the flask was placed in an oil bath at 70°C under an inert nitrogen atmosphere and stirred well. Diisocyanate was stirred for 1 h at 70°C. Diol along with TMP was added dropwise to diisocyanate and the mixture was allowed to react under a constant stirring condition for 8 h at the same temperature. Adding methyl-isobutyl ketone solvent controlled the viscosity of the reaction medium. The prepolymer formed was chain-extended with CAB before casting the films. The reaction Scheme 1 displays the formation of PU with CAB.
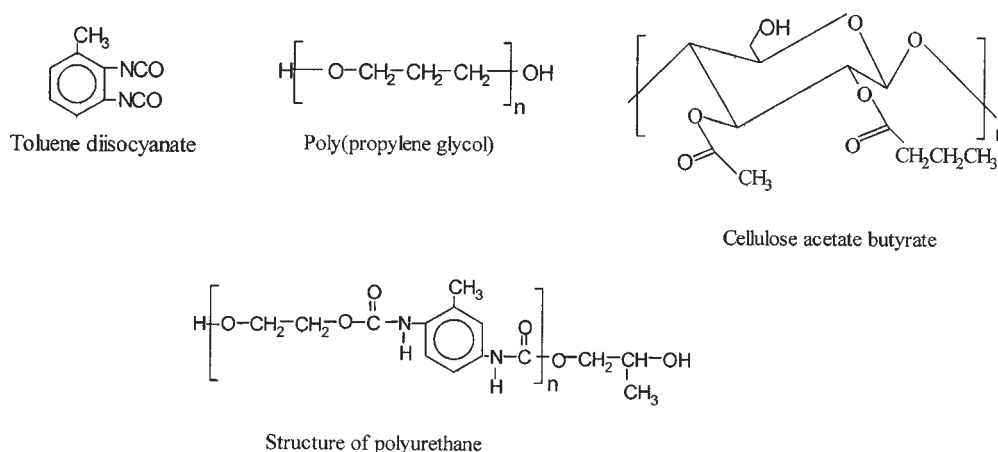
Scheme 1a
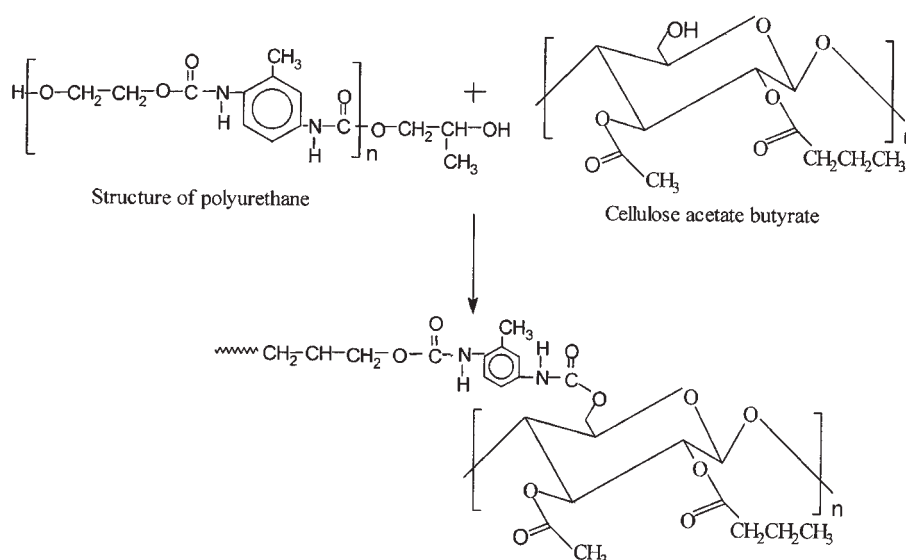
Scheme 1 Structural representation of polymers and monomers displaying the possible interaction between PU and CAB upon moisture curing.

Membrane preparation

Membranes were prepared by casting the resin solution on tinfoil mounted onto a glass plate by using the power-driven automatic applicator and left for 20 days at ambient temperature (30 ± 2°C at 40 ± 1% relative humidity) to complete the curing process. The cured membranes were placed in a clean mercury bath to amalgamate the tin substrate. The underside of the unsupported coating was cleaned of mercury or the amalgam adhering to it.[18]

Membrane characterization

Thermogravimetric analysis

The thermal stability and decomposition characteristics of the PU membranes were examined using a Mettler TGA/STA 851 (London, UK) instrument.

Samples were scanned between 30° and 600°C at a heating rate of 10°C/min and flushed with nitrogen gas at a flow rate of 20 mL/min.

Differential scanning calorimeter

DSC thermograms of the PU membranes were obtained on a Rheometric Scientific (Model DSC-SP, London, UK) instrument. Measurements were done over a temperature range of 50° to 400°C at a heating rate of 10°C/min in hermetically sealed aluminum pans.

Dynamic swelling

Dynamic and equilibrium swelling of the known weight of PU film (3 cm diameter) were performed at 30°, 35°, 40°, and 50°C maintained within an accuracy

TABLE I
Results of Diffusion Coefficient (D), Sorption Coefficient (S), and Permeation Coefficient (P) at Different Temperatures for Water/Ethyl Acetate Azeotrope

Membrane	Permeability coefficient (Barrer)*				Sorption coefficient $S \times 10^3$ cc (STP)/(cm^{3}cm Hg)				Diffusion coefficient $D \times 10^7$(cm^2/s)			
	30°C	35°C	40°C	50°C	30°C	35°C	40°C	50°C	30°C	35°C	40°C	50°C
PU-1	0.01	1.56	29.77	47.34	1.43	33.96	62.93	86.58	0.10	3.40	4.73	5.47
PU-2	25.85	28.87	238.44	355.11	62.00	78.25	277.9	409.58	4.17	3.69	8.58	8.67
PU-3	19.97	40.83	620.96	1131.25	38.34	65.02	311.1	444.5	5.21	6.28	19.96	25.45

of ±0.5°C in a thermostatically controlled oven (WTB binder, Model BD-53, Tuttilgen, Germany) until equilibrium was attained when immersed in an ethyl acetate/water azeotropic mixture. Membranes were taken out of the liquid environment periodically and weight measurements were taken immediately after carefully wiping the excess surface liquid droplets adhered to the surface of the films.

The same procedure was repeated at different temperatures to study the effect of temperature until equilibrium sorption was attained. During this period the total time spent by the membrane outside the solvent medium was kept to minimum (30–40 s) so as to minimize the experimental error due to solvent evaporation. This error was negligible when the time spent by the membrane outside the test bottle is compared to the time spent inside the solvent medium. Weight measurements were done on a digital Mettler microbalance (Model AE 240, Greifensee, Switzerland) sensitive to ±0.01 mg. Weight gain, Q_t, of the soaked PU membranes is expressed in mol % units (i.e., number of moles of solvent sorbed by 100 g of the polymer), which is calculated as[17]:

$$Q_t = \left(\frac{W_t - W_i}{W_i}\right)\frac{100}{M_s} \tag{1}$$

where W_t and W_i are, respectively, the weight gains at time, t, and initial weight; M_s is the molecular weight of the sorbed liquid. An increase in mol % of solvent by the PU membrane is a consequence of the distribution of solvent molecules, which will fill the available free volumes of the membrane matrix. Ultimately, equilibrium is attained when all the free volume spaces are completely filled up, i.e., no more increase in mol % takes place.

Since permeation of solvent molecules through the polymeric membrane occurs due to diffusion, which is controlled by the solvent sorption and, hence, the permeability coefficient, P, can be calculated as:

$$P = DS \tag{2}$$

where D is the diffusion coefficient and S is solubility, which is usually referred to as the sorption coefficient. The sorption coefficient is calculated using sorption data.[19]

The diffusion coefficient was computed from the sorption results using the equation[20]:

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \tag{3}$$

where θ is slope of the linear portion of the sorption curve, i.e., Q_t vs. $t^{1/2}$ before attainment of 60% equilibrium and h is the initial thickness of the membrane. Estimated values of D, S, and P are given in Table I. The results of percent sorption of PU membranes in water, ethyl acetate, and the azeotropic mixture of water and ethyl acetate are compared in Table II at different temperatures. The swelling coefficient, α_s, was calculated using the equation[21]:

$$\alpha_s = \left(\frac{M_\infty - M_0}{M_0}\right) \times 1/\rho_s \tag{4}$$

where M_∞ and M_0 are the masses of the swollen and dry membranes and ρ_s is density of the solvent media.

TABLE II
Comparison of Percent Sorption Results of PU Membranes in Different Media at Different Temperatures

Membrane	30°C	35°C	40°C	50°C
		Water		
PU-1	1.01	1.16	1.61	2.25
PU-2	1.32	1.89	2.98	3.02
PU-3	1.52	3.85	6.66	19.64
		Ethyl acetate		
PU-1	11.11	31.25	59.64	64.53
PU-2	20.55	69.69	113.7	114.32
PU-3	31.25	121.6	123.2	127.6
	Ethyl acetate/water azeotrope			
PU-1	25	54.14	70.96	82.5
PU-2	60.65	85.39	166.96	174
PU-3	87.01	119.6	178	194

TABLE III
Results of Swelling Coefficients at Different Temperatures for Azeotropic mixture

Membrane	Swelling coefficient (α_s)			
	30°C	35°C	40°C	50°C
PU-1	0.27	0.60	0.79	0.91
PU-2	0.67	0.95	1.85	2.0
PU-3	0.97	1.34	1.98	2.15

TABLE IV
Arrhenius Activation Parameters

Membrane	E_P (kJ/mol)	E_D (kJ/mol)	ΔH_S (kJ/mol)
PU-1	18.79	10.19	8.60
PU-2	52.46	17.35	35.11
PU-3	54.89	29.26	25.63

The results of the swelling coefficients at different temperatures for the azeotropic mixture are given in Table III.

From a consideration of the temperature dependence of P, D, and S, activation energies were estimated for diffusion and permeation processes using the Arrhenius relationship given in its general form[22]:

$$X = X_0 \exp^{-E_X/RT} \tag{5}$$

where X represents either P or D, E_X is the activation energy for permeation or diffusion, R is a molar gas constant, and T is the temperature in Kelvin. Arrhenius plots of log P vs. $1/T$ and log D vs. $1/T$ were constructed, but not displayed in order to minimize the number of figures. The results of activation parameters, i.e., E_D and E_P for diffusion and permeation processes, were computed by the method of least squares. These data are presented in Table IV.

Pervaporation studies

Pervaporation experiments were carried out on a 100-mL batch level instrument with an indigenously constructed manifold [Fig. 1(a)] operated at a vacuum level as low as 0.05 mmHg in the permeate line. The effective membrane area of the PV cell assembly [(Fig. 1(b)] is about 20 cm^2. Experimental details were provided previously.[23] Permeate samples were collected after about 3–4 h and tests were carried out at ambient temperature (30 ± 1°C). Collected permeate samples were weighed after attainment of the ambient temperature using a Sartorius electronic balance (accuracy, 10^{-4} g) to determine flux, j, and membrane selectivity, α, which is the ratio of permeability coefficients of water to that of ethyl acetate using the equations:

$$J_i = \frac{W_i}{At} \tag{6}$$

$$\alpha = \frac{y(1-x)}{x(1-y)} \tag{7}$$

Here, W_i represents the mass of water in permeate (kg), A is the membrane area (m^2), t is permeation time (h), y is the permeated (%) weight fraction of water, and x is the feed water (%) weight fraction.

FC   Feed Chamber
PS   Power Supply Unit
PV   Pervaporation
HC   Heating Coil
TW   Thermowell
DF   Dewar Flask
VP   Vacuum Pump
MG   Mcleod Gauge
CW   Cold Water(~5°C)

a) Manifold of lab-scale pervaporation system
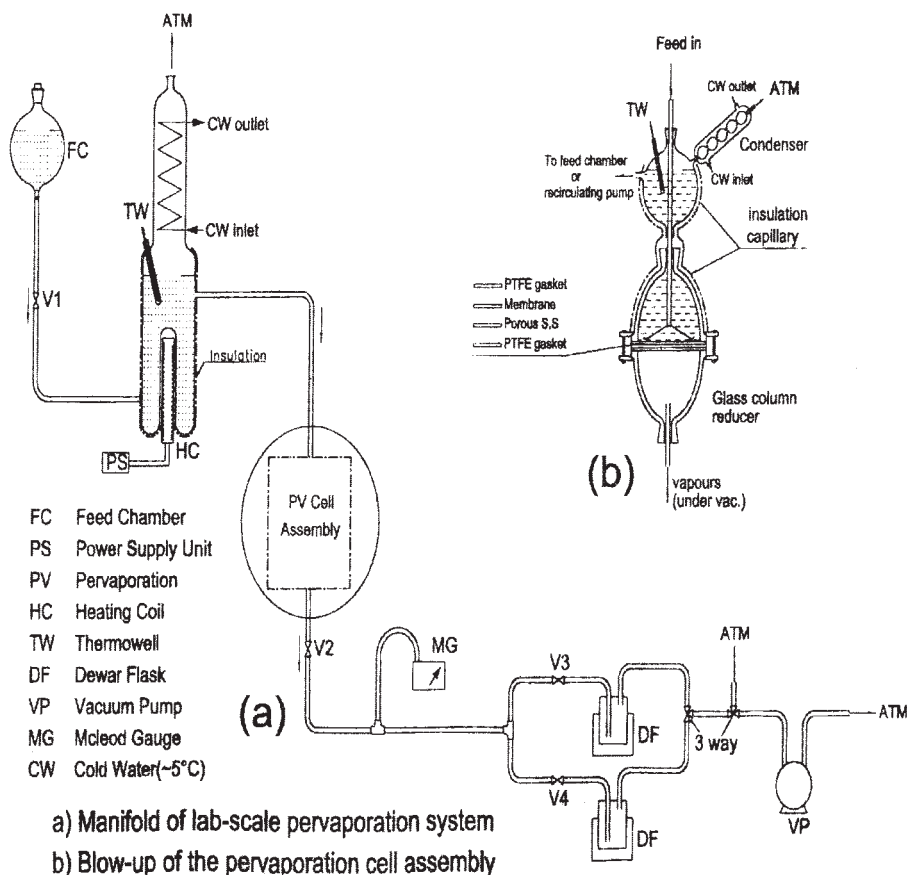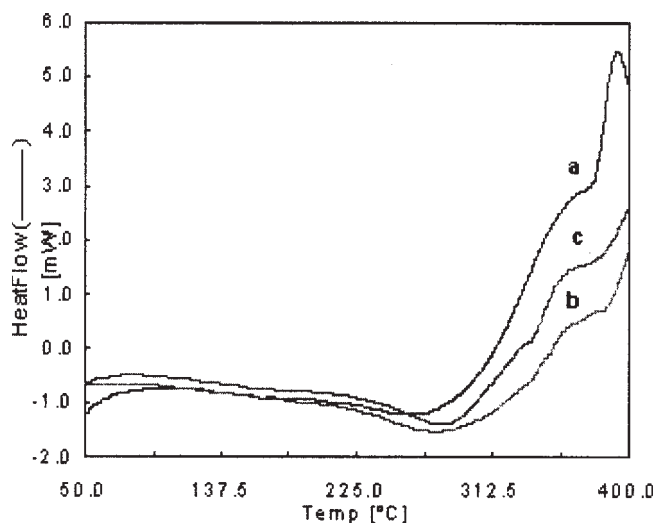b) Blow-up of the pervaporation cell assembly

Figure 1 Schematic representation of the laboratory prototype pervaporation unit.

Figure 2 DSC curves of (a) PU-3, (b) PU-2, and (c) PU-1 membranes.

Feed and permeate samples were analyzed using a Nucon Gas Chromatograph (GC, Model 5765, Mumbai, India) installed with a Thermal Conductivity Detector (TCD) and a packed column of 10% DEGS on a 80/100 Supelco port of 1/8″ ID and 2 m length. Details of these measurements have been provided previously.[24]

Often, the enrichment factor, β, calculated from Eq. (8), has been used to test the membrane performance.[14,15] This quantity is defined as:

$$\beta = C_w^p / C_w^F \qquad (8)$$

Here, C_w^p and C_w^F are the concentrations of water in the permeate and feed sides. The PV separation results are compiled in Table VI.

Diffusion coefficient

The transport of molecules in PV experiments has been explained by the solution–diffusion model,[12] since molecular transport in PV depends on the sorption and diffusion of liquid molecules through the barrier membrane and, hence, attempts have been made to compute the diffusion coefficients of liquids through such membranes. Diffusion in PV experiments occurs as a result of the concentration gradient, thereby creating a driving force across the membrane as a result of a pressure differential from high vacuum (lower pressure compared to feed side) on the permeate side. The diffusion coefficient, D_i, of solvent molecules was computed from the PV results using the equation[25,26]:

$$J_i = (D_i \times C_i)/h \qquad (9)$$

where C_i is the concentration of water or ethyl acetate in the feed mixture after completion of the PV process,

J_i is the flux of the transporting species i, and h is the membrane thickness. The computed values of D_i at 30°C are also included in Table VI.

RESULTS AND DISCUSSION

Differential scanning calorimeter

DSC analysis was carried out to evaluate T_g of the synthesized PUs. Figure 2 shows the DSC curves. It is of particular interest to study thermal transitions by varying the amount of CAB (see curve (a) of Fig. 2) for PU-3, which shows an endothermic peak at 268°C, while curve (b) for PU-2 shows an endothermic peak at 280°C. On the other hand, curve (c) for PU-1 shows an endothermic peak at 285°C. After the addition of chain extender, a decrease in crystallinity occurs, which reduces the T_g of PU; this exerted an influence on the transport properties of PU membranes. Generally, polymers with low T_g have a greater segmental mobility and, thus, will allow increased diffusivity of liquid molecules.[27]

Thermogravimetric analysis

The thermal behavior of all the PU membranes was examined to account for the effects of CAB content of the PU matrix. TGA curves and decomposition characteristics of PU membranes are shown in Fig. 3, where curve (a) exhibits a single stage weight loss at 260°C followed by a final decomposition at 460°C; curve (b) exhibits two-stage weight losses around 270–350°C and 360–445°C, followed by a final decomposition of the membrane; curve (c) also exhibits
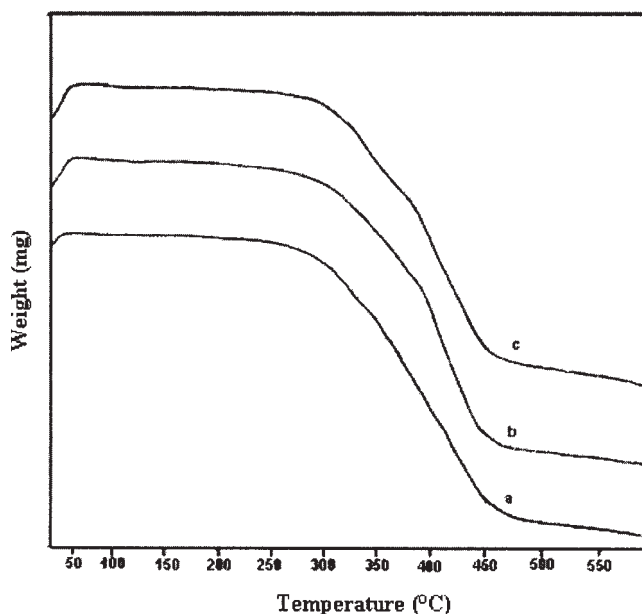
Figure 3 TGA thermograms of (a) PU-1, (b) PU-2, and (c) PU-3 membranes.

two-stage weight losses from 275–360°C followed by a final decomposition at 450°C. However, the initial weight loss is attributed to the splitting of the main polymer chain before its final decomposition; thus, an increase in thermal stability of the membrane was observed as percent CAB in PU increases.

Sorption phenomenon

It has been customary to understand the PV results in terms of sorption, diffusion, and permeation of liquid molecules through the barrier membranes. To explore these concepts further, we performed sorption experiments on PU membranes of this study in water, ethyl acetate, and water/ethyl acetate azeotropic media at different temperatures. The results of S, P, and D for different membranes for water/ethyl acetate azeotrope are presented in Table I at different temperatures. It was noticed that with increasing temperature from 30° to 50°C the values of S, P, and D increase systematically for all the PU membranes. In a similar manner, with increasing CAB content of the PU the results of S, P, and D increase, indicating that both temperature and concentration of CAB in the PU matrix show a systematic effect on the membrane transport properties due to expansion of the PU chains. With increasing concentration of CAB in PU, the preferential interactions will increase, leading to increased swelling because ethyl acetate is likely to interact more preferentially with the hard segment part of the PU chain than the water molecules.

The results of percent sorption of PU membranes in different media, i.e., pure water, pure ethyl acetate, and their azeotropic mixture are presented in Table II. Here also, the percent sorption data show trends varying with respect to the nature of the liquid media and temperature. For instance, with increasing temperature, percent sorption for water increases; such an increase is considerable in the case of the PU-3 membrane (which contains a higher amount of CAB) than either the PU-1 or PU-2 membranes. The sorption data of ethyl acetate are considerably higher than water as well as the water/ethyl acetate azeotropic mixture. The temperature dependency of sorption follows the same patterns as those of the S, D, and P results for all the PU membranes.

The results of α_s presented in Table III indicate the extent of increase in swelling of PU membranes as a function of temperature. These data follow the same trends as those of percent sorption data. The temperature-dependent data clearly indicates that with increasing temperature from 30° to 50°C the α_s values also increase systematically. Notice that the α_s values increase systematically with increasing CAB contents of the PU membranes. The Arrhenius activation parameters for permeation, E_P, and diffusion, E_D, given in Table IV, also increase systematically with an

amount of CAB present in PU matrices. A higher value of E_P of 54.89 kJ/mol for the PU-3 membrane is indicative of the fact that more energy is required for the diffusing molecule to cross over the energy barrier as per the Eyring's theory of activation energy. Similarly, the diffusion activation energy, E_D, of 29.26 kJ/mol observed for PU-3 is much higher than those of PU-1 and PU-2 membranes for the same reasons. The heat of sorption values, i.e., $\Delta H_s = (E_P - E_D)$ are positive, suggesting an endothermic sorption process (Henry's type sorption mode). Notice that these values do not follow any systematic trend with the
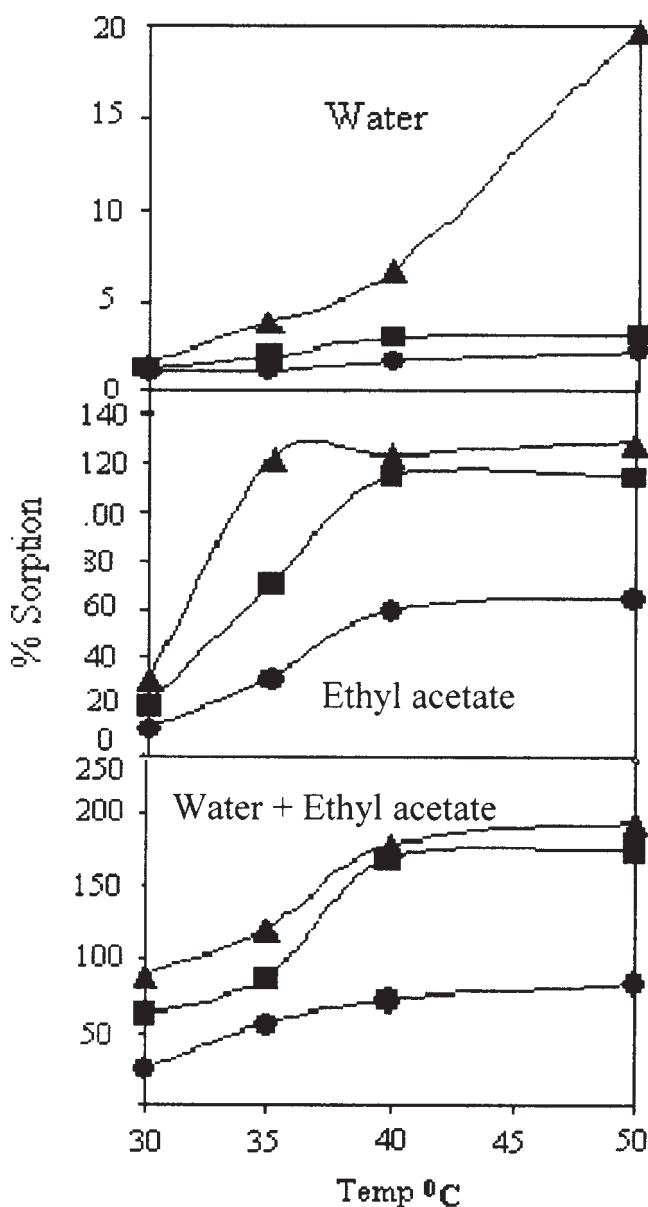
Figure 4 Percent sorption of membranes at equilibrium in (a) water for (▲) PU-3, (■) PU-2, and (●) PU-1 membranes; (b) in ethyl acetate for (▲) PU-3, (■) PU-2, and (●) PU-1 membranes; and (c) in ethyl acetate/water at azeotropic concentration for (▲) PU-3, (■) PU-2, and (●) PU-1 membranes.
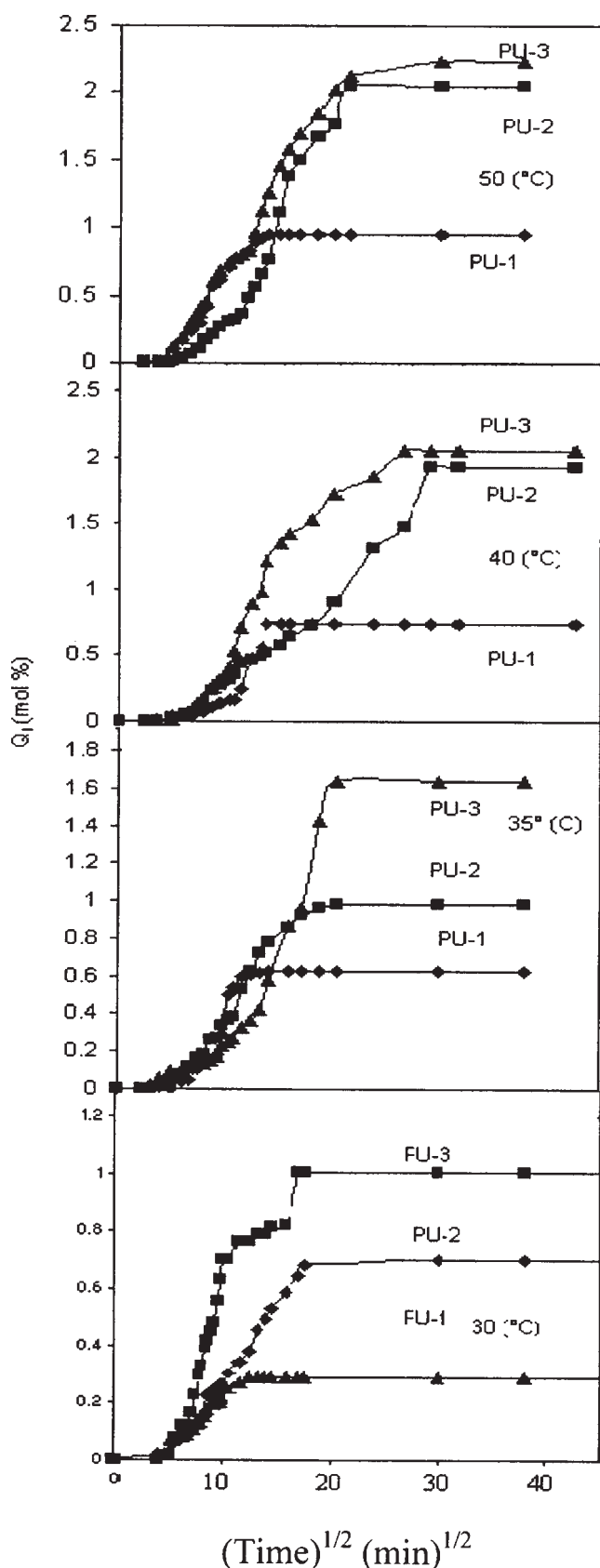
Figure 5 Mol % sorption plots for PU-1, PU-2, and PU-3 membranes at 30°, 35°, 40°, and 50°C.

concentration of CAB in the PU matrix; however, these data support the S, P, and D results discussed above.

The sorption curves in different media for different PU membranes displayed in Figure 4 suggest increasing non-Fickian trends (sigmoidal shapes) for the azeotropic mixture as well as ethyl acetate compared to pure water. For water, the percent sorption curves for PU-3 membrane increase considerably due to the molecular interactions as a result of high-level CAB containing PU membrane, whereas for PU-1 and PU-2 membranes the increase in percent sorption is not so considerable and the curves vary almost linearly for ethyl acetate due to higher preferential interactions between CAB of PU. However, at lower contents of CAB in the PU matrix, the increase in percent sorption is not as significant. Similar effects are seen even with the azeotropic mixture, indicating that water has the least interaction with the PU membrane than with either ethyl acetate or the azeotropic mixture. This further suggests that temperature has a significant effect on the morphological changes of the PU membranes. Notice that the percent equilibrium sorption of the membranes vary differently with the temperature in all the media tested, as shown in Figure 5. The mol% sorption trends as well as other transport parameters (S, P, and D) follow similar sequences for the PU membranes, i.e., PU-3 > PU-2 > PU-1, but the difference in equilibrium sorption diminishes at higher temperatures (40°C and 50°C), indicating increased interactions of PU membranes at higher temperatures; this also suggests that Case-II type transport is operative in the present systems. Also notice that equilibrium sorption was attained quite rapidly at higher temperatures. The overshoot effect was observed initially only in the case of PU-3 membrane in the presence of ethyl acetate due to a slower PU chain relaxation process.

Notice that diffusion coefficients calculated from Eq. (3), i.e., before the completion of 60% equilibrium sorption, are quite different from those computed from Eq. (9) due to different processes (see Tables I, VI). However, these data cannot be compared on an absolute scale due to the fact that the experimental setup used and the systems chosen for the study are different in both processes. In order to ascertain the mechanism of liquid diffusion through the PU

TABLE V
Analysis of Sorption Data at Different Temperatures (a)

Temp (°C)	n			$k.10^4$		
	PU-1	PU-2	PU-3	PU-1	PU-2	PU-3
30	1.036	1.141	1.476	0.666	1.998	5.518
35	1.758	1.310	1.029	1.416	7.587	1.428
40	1.401	1.178	1.629	5.394	6.586	1.167
50	1.514	1.501	1.115	4.958	1.313	1.521

TABLE VI
Pervaporation Data and Diffusion Coefficients of Membranes for Ethyl Acetate + Water Feed Mixtures
at Azeotropic Composition (Membrane Thickness, 100 μm)

Membrane	Feed water composition (wt %)	Permeate water composition (wt %)	α	J (kg/m^2. h)	β	Diffusion coefficient (m^2/s)	
						Water $\times$ (10^9)	Eac[a] $\times$ (10^{10})
PU-1	6.58	44.42	11.34	0.152	6.75	2.53	1.71
PU-2	7.52	54.24	14.59	0.176	7.22	3.22	1.98
PU-3	7.52	77.47	42.42	0.187	10.31	3.45	2.10

membranes, we analyzed the mol % sorption data using an empirical equation of the type[26]:

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \qquad (10)$$

where Q_t and Q_∞ are mol % uptake values at time, t, and at equilibrium (infinity), respectively; k and n are the system parameters that depend on the structural characteristics of the PU. These values offer valuable information about the nature of interactions between the liquid components and the PU membranes. Values of k and n have been estimated by the method of regression analysis by fitting $\log(Q_t/Q_\infty)$ vs. $\log t$. The value of n indicates the type and nature of the diffusion mechanism. In this study, it was found that n values varied from 1 to 1.7, indicating the relaxation-controlled Case-II type transport. However, no systematic trends are observed for the values of n and k as shown in Table V for the three types of PU membranes studied in this work.

Pervaporation performance of the PU membranes

Table VI shows the PV performance results of the PU membranes. It is observed that the membrane performance got better with increasing percent CAB content of the PU matrix. Flux and selectivity values for PU-1, PU-2, and PU-3 membranes were determined for the feed azeotropic concentration of 98/2 (wt %) of

Figure 6 Effect of CAB on PV performance (at membrane thickness 100 μm, permeate pressure 1 mmHg).

the water/ethyl acetate mixture. With increasing percent of CAB concentration in the PU matrix, selectivity increased to 4-fold, i.e., from 11.34 to 42.42, along with a slight increase in flux from 0.152 to 0.187 kg/m . h (see Fig. 6). The results of diffusion coefficients for water increased from 2.53×10^{-9} to 3.45×10^{-9} m^2/s for the azeotropic mixture, but for ethyl acetate, D values increased from 1.708×10^{-10} to 2.101×10^{-10} m^2/s, suggesting a systematic increase in D with an increasing amount of CAB in the PU matrix. This also suggests the increasing interactions between PU membranes and liquid components as shown in Table V. Notice that the values of the enrichment factor, β, for water also increases systematically from 6.75 to 10.31, following the same trends as those of the α, J, and D results discussed above.

CONCLUSIONS

In the present study, polyurethane membranes containing different amounts of CAB as the chain extender were prepared and their membrane properties were investigated for PV dehydration of ethyl acetate to achieve a separation up to 77.47%, indicating the usefulness and applicability of the PU membranes developed in pervaporation separation problems. Considering the good compromise between flux and selectivity values, the PU-3 membrane exhibited reasonable flux and selectivity to water. The PU membranes of this study have an adequate thermal, mechanical, and chemical stability to withstand the PV experimental conditions. Sorption experiments were performed to compute diffusion, permeation, and swelling coefficients; their dependencies were investigated with reference to percent CAB concentrations of MCPU membranes. It was found that temperature showed a systematic effect on diffusion and permeability for all the PU membranes developed. Activation energies for permeation, E_P, and diffusion, E_D, were estimated using the Arrhenius relationship. Solvent uptake by the PU membranes increased with increasing temperature as well as the CAB content of the PU matrix. Diffusion kinetics followed Case-II Fickian transport due to the relaxation-controlled transport of liquids through the PU membranes of this study.
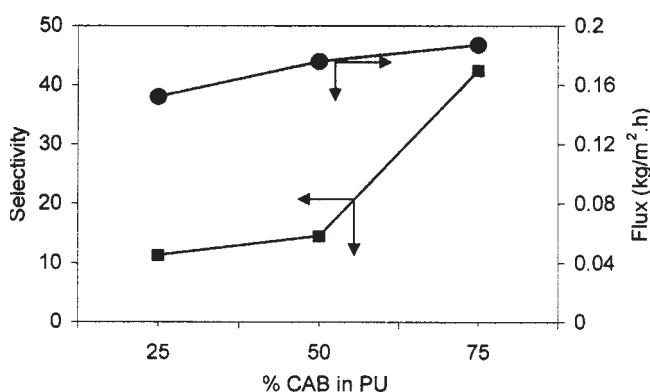
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