Chemical Engineering Journal 149 (2009) 153–161

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Removal of tetrahydrofuran (THF) from water by pervaporation using homo and blend polymeric membranes

S. Ray, N.R. Singha, S.K. Ray*

Department of Polymer Science & Technology, University of Calcutta, 92, A.P.C. Road, Kolkata 700009, India

ARTICLE INFO

Article history:
Received 30 April 2008
Received in revised form
30 September 2008
Accepted 9 October 2008

Keywords:
VOC
Pervaporation
Flux
Separation factor
Permeation factor
Blend
Morphology

ABSTRACT

Pervaporation (PV) membranes have been made from some homopolymers like unplasticized polyvinyl chloride (UPVC), plasticized PVC (PPVC), polystyrene (PSTY) and blends of UPVC and PSTY in different compositions. The morphology of the blend membranes was characterized by scanning electron microscopy (SEM). Sorption and pervaporation of tetrahydrofuran (THF) with different concentrations (0.44–11.3 wt.%) in water were studied under various conditions like feed concentration, temperature etc. Permeation factor and activation energy as a function of feed concentration were also studied in this work. For 0.44 wt.% of THF in feed at 30 °C the used membranes were found to show the following trend of flux i.e. PPVC(13.18 g/m^2 h) > PSTY(10.38 g/m^2 h) > Blend-5(8.51 g/m^2 h) > UPVC(4.79 g/m^2 h) while separation factor showed the opposite trend i.e. UPVC(170.28) > Blend-5(127.80)> PSTY(89.81)> PPVC-5(81.65). UPVC with its close packed structure showed highest separation factor while presence of polar DOP loosen its matrix and thus, UPVC showed highest flux. PSTY contains some free void space because of its aromatacity and showed lower selectivity than Blend-5 membrane. Among the various blend membranes, THF selectivity decreases while flux increases with increasing amount of PSTY and Blend-5 containing 5 wt.% styrene showed good balance of flux and selectivity.

1. Introduction

Pervaporation (PV) is a membrane process involving separation of liquid mixtures through a dense membrane. In PV, separation of the desired component is achieved by its preferential sorption and diffusion through the membrane under reduced pressure which creates a chemical potential gradient in the liquid phase. The selectivity of the membrane is the determining factor [1] in the relative flow of the different components. In recent years extensive research work is going on PV for separation of traces of organic waste [2] or volatile organic components (VOC) [3]. A good many number of applications exist for pervaporative removal or recovery of VOCs from water. Pervaporation can be efficiently applied for recovery of VOCs with medium to high volatility in the concentration range of 200–50,000 ppm. These VOCs are normally more hydrophobic than acetone with Henry's coefficient greater than 2 at./mol fraction [4]. If the aqueous stream is very dilute, pollution control is the principal economic driving force. In this case the objective of PV is to remove this trace amount of VOCs from the industrial wastewaters, allowing the water to be discharged to the sewer and concentrating the VOCs in a small-volume stream that can be sent to a hazardous water treater. Without a treatment system such as PV, the entire waste stream would have to be trucked off site which could demand considerable transport cost. Like most of the membrane processes the cost of PV increase linearly with increasing system size, whereas processes such as stream stripping scale to the 0.6–0.7 power. This makes PV most competitive for small to medium-sized stream for removal of highly volatile VOCs like tetrahydrofuran (THF).

Separation of highly volatile organic like THF is industrially very important. The aqueous solution of THF is encountered in many a chemical processes [5]. THF react readily with oxygen on contact with air producing an unstable hydroperoxide. Distillation of peroxide containing THF increases the peroxide concentration, resulting in a serious risk of explosion [6]. THF also forms an azeotrope with water and the mixture of THF–water needs separation during manufacture of THF [5]. Pervaporation can be suitably used for separation of this THF–water mixtures by choosing a highly selective membrane. Most of the membranes used for VOC removal or recovery are organophilic, mainly crosslinked rubber membranes. The problem of using organophilic rubber membranes is that they give high flux at the cost of selectivity [7]. Thus, glassy membranes are also being tried as they give high selectivity with low flux [8]. However, glassy polymers are hard and brittle with restricted chain mobility. Most of the glassy polymers are characterized with high T_g and very little void space

---

* Corresponding author. Tel.: +91 33 2350 8386; fax: +91 33 351 9755.
E-mail address: samitcu2@yahoo.co.in (S.K. Ray).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.10.013

Nomenclature

Di	diffusion coefficient of THF (m^2/s)
D_{i0}	diffusion coefficient of THF at infinite dilution (m^2/s)
D_j	diffusion coefficient of water (m^2/s)
D_{j0}	diffusion coefficient of water at infinite dilution (m^2/s)
i	ith component (THF)
j	jth component (water)
J	total flux ($kg/m^2\,s$)
J_i	THF flux ($kg/m^2\,s$)
Jj	water flux ($kg/m^2\,s$)
L	thickness of membrane (m)
W_{im}	membrane phase THF mass fraction (−)
W_{jm}	membrane phase water mass fraction (−)

Greek symbols

α	separation factor (−)
β	coupling parameter of water (−)
γ	coupling parameter of THF (−)
ρ	membrane density (kg/m^3)

(0.2–10%) within its structure [9]. Therefore, diffusion in glassy polymers is more complex compared to that in rubbery polymers. In fact, transport of liquid through glassy polymer occurs with state transition from glassy to the rubbery state due to increased mobility of its long chain by the selective permeant. The diffusion is non-Fickian case-II transport [10] as also evidenced by diffusional Deborah number being close to unity for glassy polymer [10]. The choice of glassy membranes is based on relative solubility parameters of the membrane polymer with respect to the component to be separated. Thus, in most of the works copolymers or blend polymers have been used where one polymer or copolymer moiety has solubility in the component to be separated while the other polymer or copolymer moiety is insoluble in that selectively permeating component. In this case the insoluble part of the membrane gives the mechanical integrity of the membrane while the organophilic part would give permeability. However, for waste treatment the component to be separated is present in very low concentration in the feed mixtures. Thus, it is quite likely that if the homopolymer which is soluble in that component to be separated is used as a membrane material, high flux and selectivity would be obtained as the other component is insoluble in the membrane material. In the present study thus for separation of THF from aqueous waste membrane was prepared from unplasticized polyvinyl chloride (UPVC),polystyrene (PSTY), plasticized PVC (PPVC) with three different doses of dioctyl phthalate (DOP) plasticizers and also blends of UPVC and PSTY in three different compositions.

2. Experimental

2.1. Preparation of PV membrane

For removal of THF from water PV membranes were prepared from UPVC, PSTY, PPVC and blends of PSTY and UPVC. The UPVC with *K* value of 65 was kindly supplied by Reliance Industries, Mumbai, while the general purpose grade PSTY (weight average molecular weight around 100k, polydispersity index, 2.5)was supplied by ABS Bayer Ltd., Baroda.

2.2. Preparation of polymer solution

The homopolymer UPVC and PSTY was dissolved in THF (each with ∼5 wt.% solution) using a magnetic stirrer till a clear viscous solution was obtained. PPVC with three different doses of DOP (PPVC-5, PPVC-10 and PPVC-20 containing 5 wt.%, 10 wt.% and 20 wt.% DOP, respectively) and the three blends of UPVC and PS Blend-5, Blend-10 and Blend-20 containing 5 wt.%, 10 wt.% and 20 wt.% PSTY, respectively) were made in a similar way by solution blending in THF.

2.3. Membrane casting

The homogeneous polymer solutions were cast on a smooth and clean 12 in. × 6 in. glass plate and air dried overnight at ambient condition. The glass plate containing the membrane material was dried in a vacuum oven at 45 °C for 3 h. The membranes were then peeled out from the glass plate by immersing in cold water. The membrane thickness for the copolymers were maintained at ∼30 μm. The thickness was measured by Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

2.4. Membrane characterization

Apart from physical parameters like feed concentration, temperature and permeate pressure, pervaporative transport through a membrane also depends on nature of the polymer used for making the membrane. For a homogeneous polymer its polarity and molecular weight influences the transport properties while for a membrane made by blending two polymers or doping one polymer with a chemical, the pervaporative transport is not only influenced by the nature of its constituent polymers or chemical but also compatibility of the blend. For a poor blend membrane with coarse morphology, selectivity falls rapidly due to increased free volume of the membranes. Thus, characterization of blend and plasticized membranes are very important to understand the nature of compatibility as it influences the pervaporative transport properties. The homopolymer UPVC and PSTY were used as obtained and thus these two membrane polymers were not characterized.

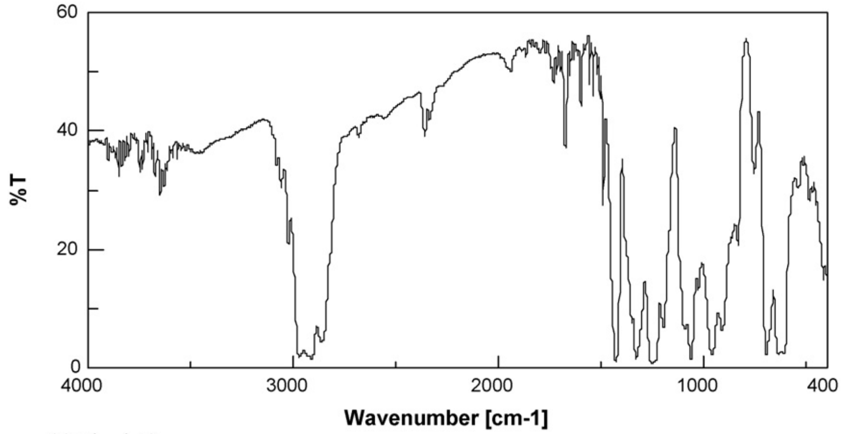
The PPVC membranes made by doping pure UPVC with different doses of DOP plasticizers and the UPVC–PSTY blend membranes made by solution blending of the two polymers at different compositions were characterized by the following methods.

2.4.1. Studies of FTIR spectra

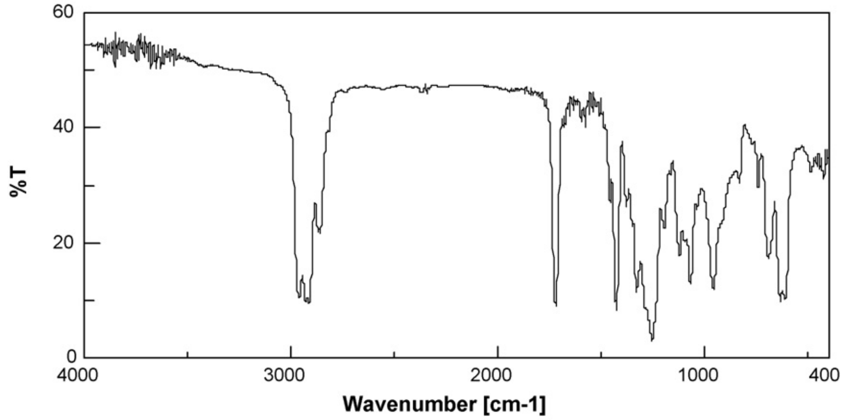
The FTIR spectra of different copolymer membranes were recorded on a Jasco (FT/IR-460 plus, Jasco Corporation, Japan) FTIR spectroscope using a thin film (10 μ) of the polymer.

2.4.2. Surface morphology of the blend membranes by scanning electron microscopy (SEM)

SEM is carried out to characterize a polymer blend in terms of its morphology. SEM was used for the UPVC–PSTY blend membranes to observe its surfaces as well as bulk morphology with micrographs obtained by collecting secondary electrons emitted upon bombarding the polymer blends with high energy electrons. For getting bulk morphology, the polymer samples were annealed in liquid nitrogen and then fractured. However, the membranes of the polymer blend obtained from its homogeneous solution always give a dense featureless micrograph. Thus, to get an idea about compatibility of PSTY and UPVC in the blend, the PSTY phase was etched with one of its solvent which is nonsolvent to UPVC i.e. the blend membranes were etched in a soxlet apparatus with cyclohexane to etch PSTY from the blend. As the PSTY phase leaves the



(a) Blend-10



(b) PPVC-10

Fig. 1. FTIR spectra of Blend-10 and PPVC-10 membranes.

blend it leaves the voids equaling its domain size in the blend. The membrane samples were coated with gold (Au). The surface morphology of the membranes were observed by using SEM (Scanning Microscope, model no. JSM-5200, made by JEOL, Japan) with the accelerating voltage set to 15 kV.

2.4.3. Glass transition temperature (T_g)

T_g was measured by a Differential Scanning Calarometry Analyzer (DSC822^e Mettler Toledo, Switzerland). The temperature range for these experiments was 30–125 °C at scanning rate of 10 °C/min.

2.4.4. Mechanical strength

The tensile strength and elongation at break of the polymer film was determined by an Instron-Tensile tester (Instron 4301, Instron Limited., England). The experiment was performed according to ASTM D 882-97.

2.5. Sorption studies

2.5.1. Sorption isotherm

Membranes of known weights were immersed in different known concentrations of THF in water and were allowed to equilibrate for 96 h at 30 °C. These membranes were taken out from the solutions and weighed after the superfluous liquid was wiped out with tissue paper. The increment in weight is equal to the total weight of THF and water sorbed by the membrane.

2.5.2. Sorption selectivity

The amount of water sorbed by the membranes was analyzed by Karl Fischer titration. From the total sorption weight and corresponding water content (weight) of the membrane, sorption selectivity of the membrane for THF was calculated from the following equation

$$\alpha_S = \frac{((1 - y_{\text{water}})/y_{\text{water}})}{((1 - x_{\text{water}})/x_{\text{water}})} \tag{1}$$

where y_i and x_i are weight fraction of component i (water) in membrane and feed, respectively.

2.6. Permeation studies

PV experiments were carried out in a batch stirred and jacketed cell [11] with adjustable downstream pressure that was maintained at 1 mmHg. Effective membrane area in contact with the feed solution was 19.635 cm^2 and the feed compartment volume was 150 cm^3. The membrane was first conditioned in the feed mixture to be separated and then mounted in the cell. The vacuum was then pumped out on the downstream side. The THF–water mixtures in contact with the membrane was allowed to equilibrate for around 3 h for the first experiment and 1 h for the subsequent experiments with collected in traps immersed in liquid nitrogen. The PV experiment was performed at a constant temperature by circulating constant temperature water around the jacket of the PV cell. The composition of the permeant was analyzed by an Abbe type Refractometer.

The permeation selectivity of THF was calculated from a similar type of equation as sorption selectivity.

3. Results and discussion

3.1. Characterization of the membranes

3.1.1. Studies of FTIR spectra

Chemical modification of a polymer may be evaluated by FTIR spectroscopy in that the resulting functional groups/bonds may be detected by its stretching or bending vibration through FTIR. Though no chemical bond is formed between the constituent polymers in a physical blend, specific interaction of these polymers if any, in the blend can be evaluated in terms of shifting of the absorption bands of the polymers. However, no shifting of any band occurs for the UPVC–PSTY blends in comparison to UPVC or PSTY. The FTIR of Blend-10 is shown in Fig. 1(a) It is clearly observed from this figure that all the absorption bands due to PSTY or UPVC [12] remain unaltered in the Blend-10. The other two blends also showed similar type of FTIR signifying no specific interaction of UPVC and PSTY in its blend. The FTIR of PPVC-10 is shown in Fig. 1(b) where the band at 1717 cm^{-1} corresponds to carbonyl peak of DOP. With increase in doses of DOP from PPVC-5 to PPVC-20 the intensity of carbonyl peak increases as evidenced by the increasing peak ratios [3] shown in Table 1.

3.1.2. Morphology of the blend membranes by SEM

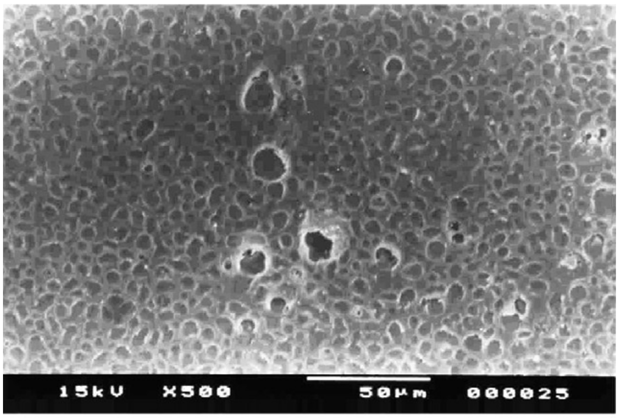
The SEMS of the three different blends are shown in Fig. 2(a)–(c). From these figures it is observed that PSTY phase was well dispersed in the UPVC matrix with almost equal domain sizes. As expected, with increase in wt.% of PSTY, the number of voids increases from Blend-5 to Blend-20 and the morphology become gradually coarser affecting separation potential of the membranes. It is also interesting to note that bi-continuous phase as generally observed for these kind of blend [13] is also seen in the SEMs.

3.1.3. Glass transition temperatures (T_g)

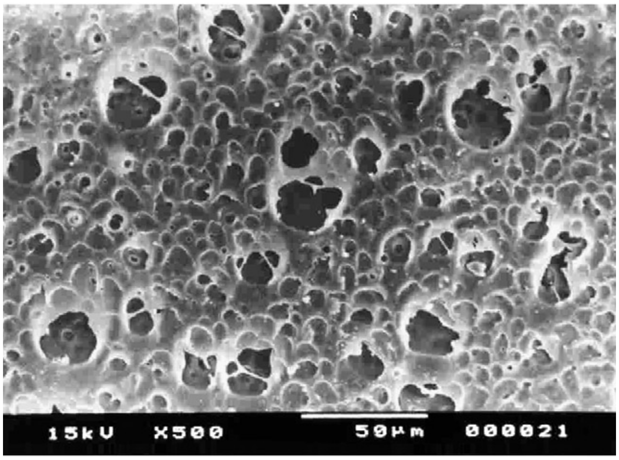
Glass transition temperature affects pervaporative transport in that a decrease in glass transition temperature will result in segmental motion at lower temperature and hence increased flux at lower temperature. With increase in wt.% of DOP in the PPVC from PPVC-5 to PPVC-20 glass transition temperature decreases due to increased plasticization which promotes segmental motion of PVC at a lower temperature. The DSC curve of PPVC-5 is shown in Fig. 3(a). Similar types of curves with different T_gs were also obtained with other two PPVC membranes. Miscible blend shows a single composition dependent T_g while a two phase blend shows two different T_g corresponding to the same of the two different phases [14]. The UPVC–PSTY blend showed two different T_g as shown in the DSC curve of Blend-5 in Fig. 3(b). Similar kind of DSC curves with two distinct T_g were also observed for the other two blends. The T_gs of the PPVC and UPVC–PSTY blends are given in Table 1.

3.1.4. Mechanical properties

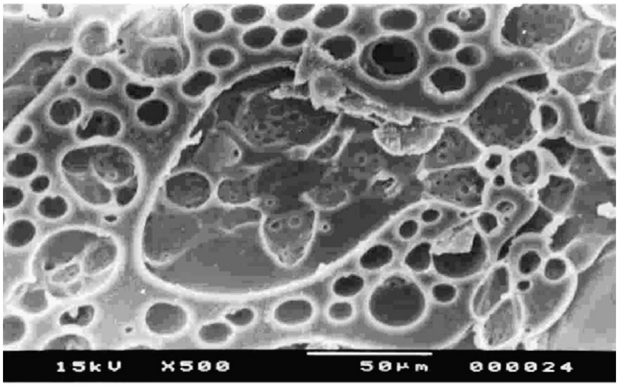
The tensile strength (T.S) and elongation at break (E.A.B) of all the membranes are shown in Table 1. The high degree of mechanical integrity of UPVC and PSTY membranes are reflected by its high tensile strength. The low E.A.B of PSTY may be ascribed to its stiffness due to aromaticity. The compatibility of UPVC and PSTY in the blend membranes is clearly characterized by its T.S and E.A.B values. The decrease of both T.S and E.A.B with increasing amount of PSTY in the blend signifies increasing immiscibility of UPVC and PSTY phase. Poor stress transfer between the phases of the immiscible blend [14] causes fall of its tensile properties.



(a) Blend-5



(b) Blend-10



(c) Blend-20

Fig. 2. SEM of blend membranes.

3.2. Sorption studies

3.2.1. Sorption isotherm

Sorption isotherm of UPVC, PSTY, Blend-5 and PPVC-5 membranes at 30 °C are shown in Fig. 4(a). The other two blend and PPVC membranes show similar isotherm as Blend-5 or PPVC-5. Like sorption in pure water (0 wt.% THF or 100 wt.% water) sorption in pure THF was not studied as the membranes would collapse

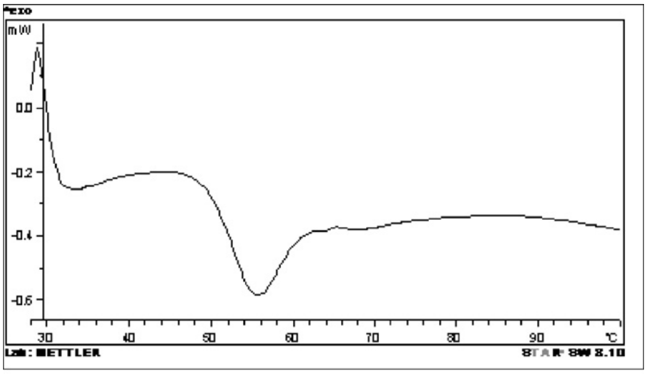
Table 1
Physical Properties of different polymers/blends.

Name of the polymers/blends	Tensile strength (MPa)	Elongation at break (%)	$C{=}O/{-}CH_2{}^-$ peak ratio	Glass transition temperature (°C) (T_g)
UPVC	43.56	48.64	–	70
PS	35.89	3.89	–	108
Blend-5	40.26	37.45	–	70, 108
Blend-10	38.76	34.65	–	70, 108
Blend-20	33.69	31.86	–	70, 108
PPVC-5	36.24	71.4	2.6679	56
PPVC-10	29.57	89.5	1.8738	44
PPVC-20	22.34	105.65	0.7649	40

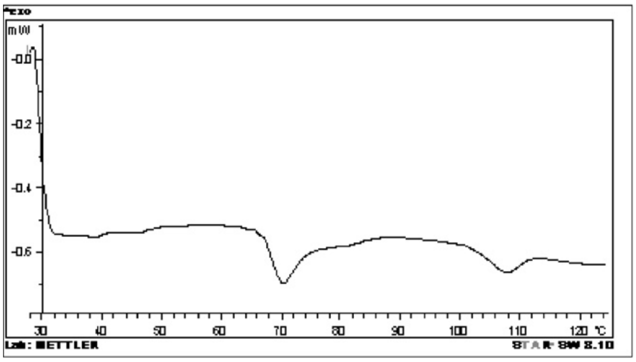
in pure THF. These sorption isotherms of Fig. 4(a) closely resemble Roger's Type-I sorption obeying Henry's law [15]. From this figure it is also observed that for the same feed concentration, initially for very low concentration of THF in water the isotherms of all the membranes are very close. However, with increasing feed concentration of THF these isotherms differ from one another and show the following order of sorption for both THF and water.

PPVC – 5 > UPVC > Blend – 5 > PSTY

The presence of DOP plasticizer may have caused maximum sorption by softening the otherwise stiff UPVC matrix. It also increases its free volume. The higher concentration of THF in feed also promotes greater extent of sorption by swelling the THF selective membranes. The higher sorption of UPVC than that of PSTY may be ascribed to its closer solubility parameter value with respect to THF [16]. Among the three blend and PPVC membranes, similar sorption behavior is observed i.e. for the same feed concentration of THF in feed, total sorption increases with increasing wt.% of DOP or PSTY in the PPVC or blend membranes.



(a) PPVC-5



(b) Blend-5

Fig. 3. D.S.C. curves of Blend-5 and PPVC-5 membranes.

3.2.2. *Sorption selectivity*

Fig. 4(b) shows the variation of sorption selectivity for THF of PPVC-5, UPVC, Blend-5 and PSTY membranes with feed concentration of THF. From this figure it is observed that sorption selectivity for THF decreases exponentially with feed concentration of THF.

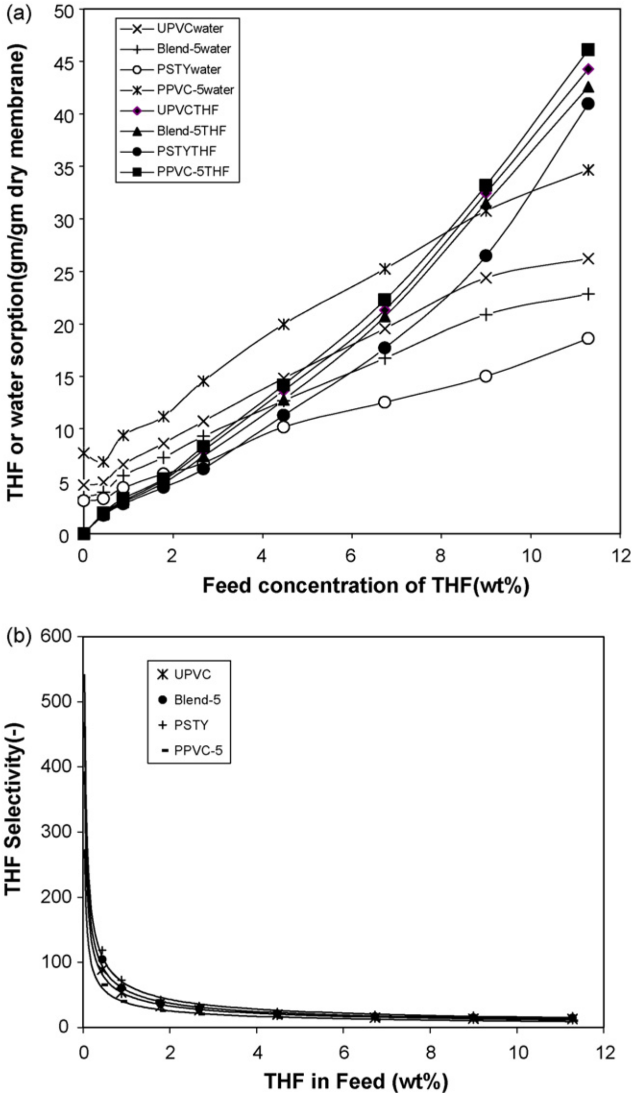


Fig. 4. (a) Variation of THF and water sorption with feed concentration of THF at 30 °C. (b) Variation of THF selectivity with feed concentration of THF at 30 °C.

From this figure it is also observed that for the same feed concentration of THF sorption selectivity of THF follows the reverse trend of total sorption i.e.

$$\text{PPVC} - 5 < \text{UPVC} < \text{Blend} - 5 < \text{PSTY}$$

The highest sorption selectivity of PSTY may be explained in terms of its highest hydrophobicity. Among all the membranes, PSTY with aromaticity absorbs minimum amount of water for all the used feed concentrations as also seen in Fig. 4(a)

3.3. Permeation studies

3.3.1. Effect of feed concentration on THF separation

Fig. 5(a) shows the variation of wt.% of THF in the permeate against wt.% of THF in the feed for THF separation from its mixture with water with the two homopolymers i.e. UPVC, PSTY, one plasticized PVC namely PPVC-5 and one blend namely Blend-5 membranes at 30 °C. It appears from this McCabe-Thiele type *xy* diagrams that these membranes show measurable permeation separation characteristics over the concentration range of 0–11.3 wt.% THF in feed without any pervaporative azeotrope. It is also interesting to note that for the same feed concentration the separation characteristic of the membranes has the following trend:$\text{UPVC} > \text{Blend} - 5 > \text{PSTY} > \text{PPVC} - 5$

This trend is different from the trend of sorption selectivity i.e. PSTY membrane shows lower permeation separation of THF though it showed highest sorption selectivity. The higher permeation separation characteristic of UPVC may be explained in terms of its structure. The unplasticized PVC has a semicrystalline closed packed structure with limited permeability properties [17,18]. The restricted permeation through UPVC matrix probably gives highest separation characteristic for UPVC membrane. Doping with plasticizer DOP was carried out with an objective of getting facilitated transport of THF through organophilic DOP which is miscible with THF. However, presence of DOP in PPVC was found to cause loosening of its matrix with the result of lowering in separation characteristic for THF. Further, the polarity of DOP also caused permeation of more water in comparison to UPVC as evidenced by lower separation characteristic of PPVC membrane than the UPVC membrane. In a similar way, the presence of aromatic ring in PSTY creates appreciable free volumes resulting in poor separation characteristic of the membrane. It also deserves mentioning that PSTY is more amorphous than UPVC signifying higher permeability through this membrane. This apart, UPVC is closer than PSTY in terms of solubility parameter value with respect to the same of THF. The lowest separation characteristic of Blend-5 may be due to presence of PSTY in UPVC matrix as in the two phase blend of Blend-5 containing a large amount of free volume for permeation of both water and THF. Among the PPVC and blend membranes separation characteristic for THF increases from PPVC/Blend-20 to 5 with decreasing amount of DOP/PSTY in the blend.

3.3.2. Effect of feed temperature on separation characteristic of the membranes

The effect of feed temperature on separation characteristic of homo UPVC membrane is shown in Fig. 5(b). Similar kind of separation characteristic at different temperatures was also obtained for the other membranes. From these it is observed that for all the membranes separation characteristic decreases with increase in temperature. This may be due to increased permeation of both water and THF at higher temperature.

3.3.3. Effect of feed concentration on flux and separation factor

The effect of feed concentration of THF on THF flux and selectivity is shown for PPVC-5, PSTY, Blend-5 and UPVC membranes in Fig. 5(c). Among the blend and PPVC membranes only Blend-5 and PPVC-5 has been shown in this figure. The other two blend and PPVC membranes showed similar type of trend. From this Fig. 6(a), it is observed that with increase in feed concentration of THF its flux increases linearly for all the membranes with the following order PPVC-5 > PSTY > Blend-5 > UPVC. Quite reasonably, the separation factor of the membranes which follows a power trend has the opposite order. This trend may be ascribed to increasing extent of restriction in permeation through the membrane from PPVC to UPVC.

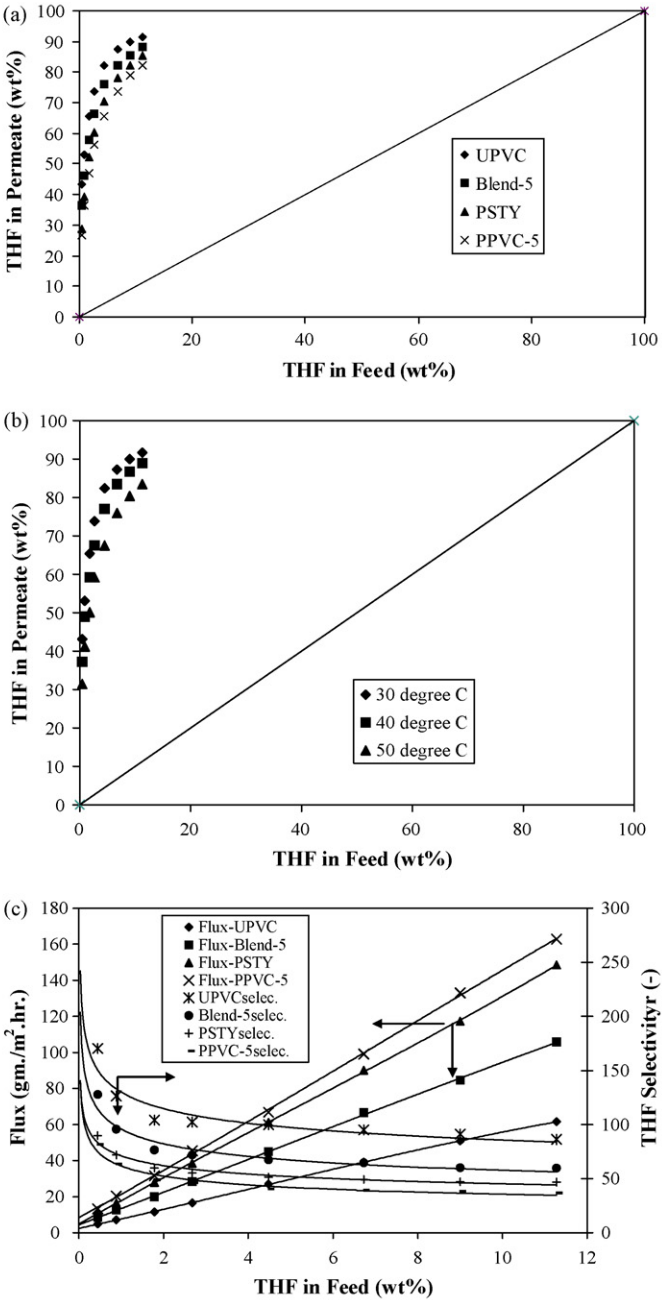


Fig. 5. (a) Variation of Permeate conc. of THF with its feed concentration at 30 °C. (b) Variation of Permeate concentration of THF with its feed concentration for UPVC membrane at different temperatures. (c) Variation of THF Flux and Selectivity with its feed conc. at 30 °C.

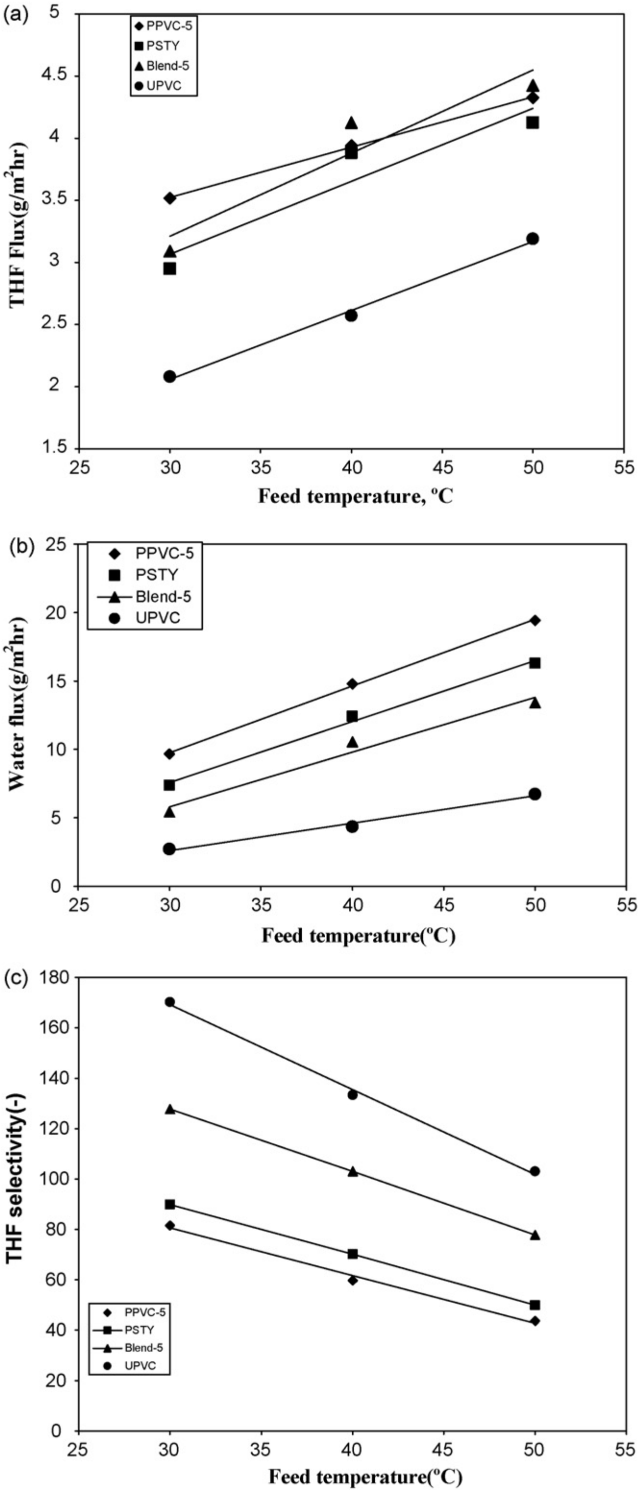


Fig. 6. (a) Variation of THF Flux with feed temperature for 0.44 wt.% THF in water. (b) Variation of water flux with temperature. Feed concentration 0.44 wt.% THF in water. (c) Variation of THF selectivity with temperature for 0.44 wt.% THF in feed.

3.3.4. *Effect of feed temperature on flux and separation factor*

The variation of THF and water flux with feed temperature for all the used membranes at 0.44 wt.% feed concentration of THF are shown in Fig. 6(a) and (b), respectively. Similar kind of trend lines was also obtained at other feed concentration of THF. From Fig. 6(a) and (b) it is observed that both THF and water flux increase linearly with temperature with regression coefficient >0.99 for all these linear trend lines. It is also observed that the rate of increase (slope of the linear trend line) of flux with temperature for water (Fig. 6(b)) is much higher than that for THF (Fig. 6(a)). Hence, with increase in temperature THF selectivity decreases as shown in Fig. 6(c). At higher temperature small water molecule diffuses faster resulting in higher rate of flux with temperature. Thus, THF selectivity decreases linearly with temperature.

3.3.5. *Effect of feed concentration on activation energy*

Activation energy for sorption and permeation of all the membranes at different feed concentrations of THF in water were obtained from the Arrhenius type plot of logarithmic of total sorption and flux, respectively, against inverse of absolute temperature. For each of these linear plots by best fit method the values of regression coefficient were close to unity as shown in Fig. 7(a) for UPVC, Blend-5, PPVC-5 and PSTY membranes. The effect of feed concentration of THF on activation energy for sorption and permeation for these membranes are shown in Fig. 7(b). Similar kind of trend lines was obtained for the other two PPVC and 'Blend' membranes. From this figure, it is observed that the activation energy for sorption and permeation decreases linearly with increase in feed concentration of THF due to plasticization of the organophilic membranes by THF. It is also observed from the figure that for the same feed concentration, activation energies of the various membranes show the following trend PPVC-5 > PSTY >Blend-5 > UPVC The change of flux or sorption with temperature is highest in PPVC membrane due to increased solubility of DOP in PVC matrix at higher temperature resulting in more loosening of its structure and hence increased flux and sorption.

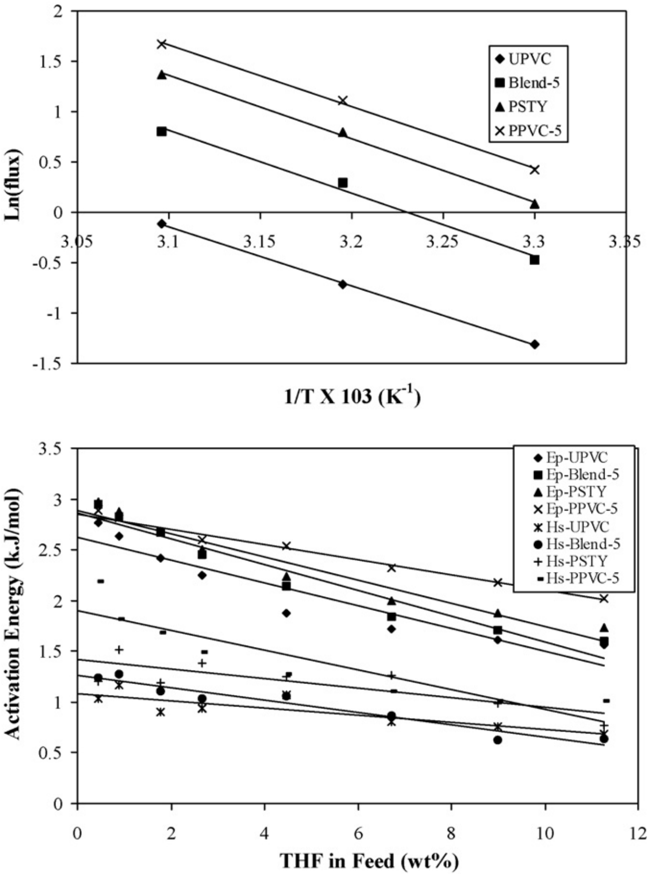


Fig. 7. (a) Estimation of activation energy for permeation by Arrhenius plot. (b) Variation of activation energy with feed concentration of THF.

3.3.6. *Model calculation of theoretical flux and diffusion coefficient*

In a binary system with a non porous dense membrane pervaporative flux for *i*th component can be described by Fick's first law as,

$$J_i = -\left(\frac{\rho_m D_i}{1 - W_{\mathrm{im}}}\right)\frac{dW_{\mathrm{im}}}{dl} \tag{2}$$

For very small W_{im}, the above equation reduces to,

$$J_i = -\rho_m D_i \frac{dW_{\mathrm{im}}}{dl} \tag{3}$$

However, diffusion coefficient depends on the concentration of the permeating components in the membrane and their mutual coupling effect. For components *i* and *j* the diffusion coefficient can be expressed as [19],

$$D_i = D_{i0}\exp(W_{\mathrm{im}} + \beta W_{\mathrm{jm}}) \tag{4}$$

$$D_j = D_{j0}\exp(W_{\mathrm{jm}} + \gamma W_{\mathrm{im}}) \tag{5}$$

Substituting Eq. (5) in Eq. (3) results in

$$J_i = -\rho_m D_{i0}\exp(W_{\mathrm{im}} + \beta W_{\mathrm{jm}})\frac{dW_{\mathrm{im}}}{dl} \tag{6}$$

Integrating Eq. (7) over the membrane thickness results in total flux of *i*th component through the membrane.

$$\int_0^L J_i dl = -\rho_m D_{i0}\int_{W_{\mathrm{imf}}}^{W_{\mathrm{imp}}} \exp(W_{\mathrm{im}} + \beta W_{\mathrm{jm}}) dW_{\mathrm{im}} \tag{7}$$

For the present system both THF and water will influence the transport of each other.

Ignoring the very low concentration of the permeating component on the downstream side (because of very low pressure on this side), Eq. (7) reduces to

$$J_i = \frac{D_{i0}\rho_m}{L}[\exp(W_{\mathrm{im}} + \beta W_{\mathrm{jm}}) - 1] \tag{8}$$

Similarly for *j*th component (say water)

$$J_j = \frac{D_{j0}\rho_m}{L}[\exp(W_{\mathrm{jm}} + \gamma W_{\mathrm{im}}) - 1] \tag{9}$$

The density and thickness of the membranes were found experimentally. From the sorption experiments W_{im} and W_{jm} and from permeation data J_i and J_j were obtained. By a linear regression of these permeation and sorption data and comparing these regressed equations with Eqs. (8) and (9), diffusion coefficients at infinite dilution were calculated. The values of plasticization coefficients β and γ were adjusted so as to make the predicted flux as close as possible to experimental flux maintaining regression coefficient close to unity. The values of diffusion coefficients at infinite dilutions for both THF and water at various feed temperatures are given in Table 2. The parity plot of experimental and theoretical flux of THF for all the membranes at 30 °C and UPVC membrane at three different temperatures i.e. 30,40 and 50 °C is shown in Fig. 8(a) and (b), respectively. The validity of the generalized model [20] for the present system is quite satisfactory from the closeness of the theoretical and experimental flux data as shown in the above figure. Similar types of parity plots were also obtained for other membranes.

Table 2
Diffusion coefficients of THF ($D_{0,\mathrm{THF}}$) and water ($D_{0,\mathrm{water}}$) through all the membranes at infinite dilution.

Name of the membranes	$D_{0,\mathrm{THF}}$ (m^2/s) × 10^{11}	$D_{0,\mathrm{Water}}$ (m^2/s) × 10^{13}
At 30 °C feed temperature		
UPVC	0.143	0.3676
Blend-5	0.2326	0.8929
PSTY	0.27	1.43
PPVC-5	0.455	2.0
At 40 °C feed temperature		
UPVC	0.25	0.714
Blend-5	0.3226	1.87
PSTY	0.40	2.899
PPVC-5	0.781	3.922
At 50 °C feed temperature		
UPVC	0.345	1.28
Blend-5	0.4545	3.333
PSTY	0.658	5.0
PPVC-5	1.49	6.67

3.3.7. *Effect of feed concentration on permeation Factor*

Permeation ratio quantifies the effect of one component on the permeation rate of the other component. Huang and Lin [21] defined this permeation ratio (θ) as a measure of the deviation of the actual permeation rate(J_{expt}) from the ideal rate(J^0) to explain interactions between membrane polymer and permeants. Thus,

$$\theta_i = -\frac{J_{i\,\mathrm{expt\ \ at\ \ }x\mathrm{\ \ conc.}}}{J^0_{i\ \ \mathrm{expt\ \ at\ \ }x\mathrm{\ \ conc.}}} \tag{10}$$

$$J^0_{i(\mathrm{at}\ \ x\ \ \mathrm{conc.})} = J^0_{(\mathrm{pure}\ \ i)}x_i \tag{11}$$

where *i* denote '*i*th' component in the binary mixture, *x* is the weight fraction in feed mixture, superscript 0, denotes ideal permeation.

It is quite clear from Eq. (10) that a value of θ_i greater than unity amounts to positive coupling effect of the other component (*j*) on

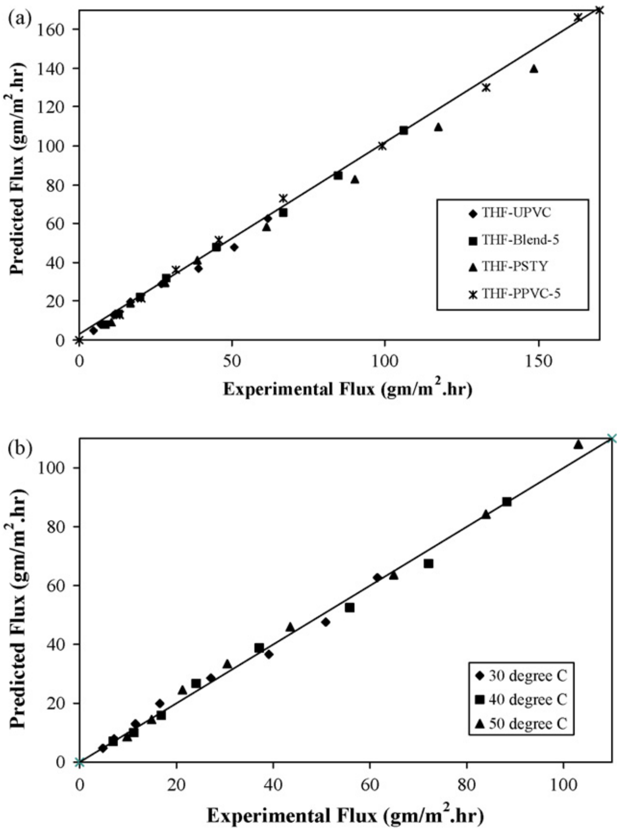


Fig. 8. (a) Parity plot of experimental and predicted water flux for different membranes at 30 °C. (b) Parity plot of THF for UPVC membrane at different temperatures.

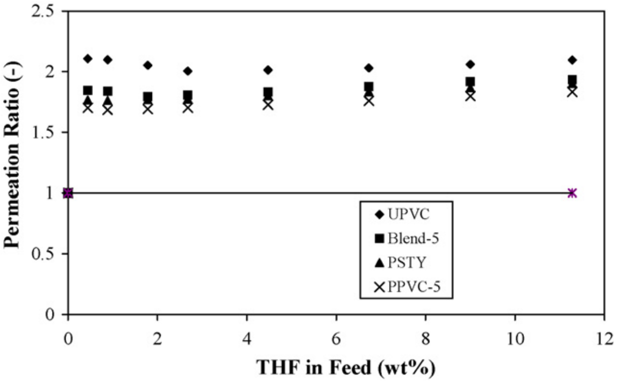


Fig. 9. Variation of permeation ratio with feed conc. of THF at 30 °C.

permeation rate of *i*th component. The variation of permeation factor of water with respect to feed concentration of THF is shown in Fig. 9 for UPVC, Blend-5, PPVC-5 and PSTY membranes. Similar kind of trend lines were obtained for the other two blend and PPVC membranes. The organophilic THF selective membranes swelled too much to sustain pure THF permeability and hence, permeation factor for THF could not be measured. From this figure, it is observed that permeation factor of water exceeds its ideal value for even very low feed concentration of THF indicating strong positive coupling effect of THF on permeation rate of water. It is also observed from this figure that for the same feed concentration of THF the coupling effect shows the following order i.e.

$$\text{UPVC} > \text{Blend} - 5 > \text{PSTY} > \text{PPVC} - 5$$

This may be ascribed to THF selectivity of the membrane which follows the same trend. The effect of THF on water flux i.e. permeation factor of water increases as the membranes become increasingly THF selective in the above order.

4. Conclusion

Pervaporative removal of volatile organic like THF demands a membrane of good mechanical strength and high selectivity for THF. In the present work instead of conventional rubbery membranes, glassy membranes have been used for separation of THF from water. Unlike elastomeric membranes, the pervaporation membranes made from solution casting of high molecular weight homo UPVC, PSTY, three blends of these two homopolymers and three PPVC showed very high THF selectivity with reasonable flux over the entire concentration range of 0–11.5 wt.% THF in feed. The activation energy for sorption and permeation was found to decrease linearly with increase in feed concentration of THF. Diffusion coefficient of both water and THF at infinite dilution were obtained by using a generalized model. THF was also found to show strong influence on permeation of water as shown in terms of high permeation factor for water. All the membranes showed comparable performance in terms of both flux and THF selectivity and these membranes would be very useful for removal of VOC like THF present in very low concentration in water.

Acknowledgements

The authors are grateful to University Grant Commission (U.G.C.) and Council for Scientific and Industrial Research (C.S.I.R.), Govt. of India for sponsoring this work.

References

[1] H.L. Flemming, C.S. Slater, Pervaporation–definition and background, in: W.S.W. Ho, K.K. Sirkar (Eds.), Membrane Handbook, VaNostrandReinhold, 1992, p. 113.
[2] K.W. Boddeker, G. Bengtson, Selective pervaporation of organics from water, in: R.Y.M. Huang (Ed.), Pervaporation Membrane Separation Processes, Elsevier, Amsterdam, 1991, p. 452.
[3] S. Ray, S.K. Ray, Effect of copolymer type and composition on separation characteristics of pervaporation membranes – a case study with separation of acetone–water mixtures, J. Membr. Sci. 270 (2006) 73–87.
[4] R.W. Baker, Membrane Technology and Applications, John Wiley and Sons, Ltd., West Sussex, England, 2004.
[5] G. Cox, R.W. Baker, Pervapooration for the treatment of small volume VOC-contaminated waste water stream, Ind. Waste Water 6 (1998) 35.
[6] H. Muller, Tetrahydrofuran, in: B. Elvers, S. Hawkins, W. Russey (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, vol. A26, VCH Verlagsgesellschaft mbH, D-69451, Weinheim (Federal Republic of Germany), 1995, pp. 221–226.
[7] S. Ray, S.K. Ray, Separation of organic mixtures by pervaporation using crosslinked rubber membranes, J. Membr. Sci. 270 (2006) 132–145.
[8] S. Ray, S.K. Ray, Dehydration of tetrahydrofuran (THF) by highly selective pervaporation membrane, Sep. Purifi. Technol. 50 (2006) 156–160.
[9] S.G. George, S. Thomas, Transport phenomena through polymeric systems, Prog. Polym. Sci. 26 (2001) 985–1017.
[10] N.A. Peppas, J.L. Sinclair, Anomalous transport of penetrants in glassy polymers, Colloid Polym. Sci. 261 (1983) 404–408.
[11] S. Ray, S.K. Ray, Dehydration of acetic acid, alcohols, and acetone by pervaporation using acrylonitrile-maleic anhydride copolymer membrane, Sep. Sci. Technol. 40 (2005) 1583–1596.
[12] M.M. Colemuni, C. Painter, Infrared-absorption spectroscopy, in: H.F. Mark (Ed.), Encyclopedia of Polymer Science and Engineering, vol. 8, John Wiley and Sons, New York, 1992, pp. 69–101.
[13] T. Inoue, Morphology of polymer blends, in: L.A. Utracki (Ed.), Polymer Blends Handbook, vol. 1, Kluwer Academic Publishers, AH Dordrecht, The Netherlands, 2002, p. 562 (chapter 8).
[14] D.R. Paul, J.W. Barlow, H. Keskulla, Polymer blends, in: H.F. Mark (Ed.), Encyclopedia of Polymer Science and Engineering, vol.12, John Wiley and Sons, New York, 1992, pp. 399–461.
[15] C.E. Roger, Permeation of gases and vapors in polymers, in: J. Comyn (Ed.), Polymer Permeability, Elsevier Applied Science, New York, 1985, p. 32.
[16] E.A. Grulke, Solubility parameter values, in: J. Brandrup, E.H. Immergut, E.A. Grulke (Eds.), Polymer Hand Book, 4th ed., John Wiley and Sons. Inc., New York, U.S.A., 1999, pp. V/59–V/66.
[17] W.A. Combellick, Barrier polymers, in: H.F. Mark (Ed.), Encyclopedia of Polymer Science and Engineering, vol. 2, John Wiley and Sons, New York, 1992, pp. 176–192.
[18] J. Brydson, Vinyl chloride polymers, in: Plastic Materials, 7th ed., Butterworth Heinemann, Oxford, 1999, pp. 311–362.
[19] R.A. Rautenbach, C.M. Herion, A.A. Asfour, A.E. Bemquerer, Bo. Costa, Investigation of mass transport in asymmetric pervaporation membranes, J. Membr. Sci. 36 (1988) 445.
[20] S. Marx, P.V. Gryp, H. Neomagus, R. Everson, K. Keizer, Pervaporation separation of methanol from methanol/*tert*-amyl methyl ether mixtures with a commercial membrane, J. Membr. Sci. 209 (2002) 353–362.
[21] R.Y.M. Huang, V.J.C. Lin, Separation of liquid mixtures by using polymer membranes. I. Permeation of binary organic liquid mixtures through polyethylene, J. Appl. Polym. Sci. 12 (1968) 2615–2631.