This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

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

Separation of Toluene-Methanol Mixtures by Pervaporation Using Semi-IPN Polymer Membranes

N. R. Singha[a]; S. K. Ray[a]
[a] Department of Polymer Science and Technology, University of Calcutta, Kolkata, India

Online publication date: 29 November 2010

To cite this Article Singha, N. R. and Ray, S. K.(2010) 'Separation of Toluene-Methanol Mixtures by Pervaporation Using Semi-IPN Polymer Membranes', Separation Science and Technology, 45: 16, 2298 — 2307

To link to this Article: DOI: 10.1080/01496395.2010.504680

URL: http://dx.doi.org/10.1080/01496395.2010.504680

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Separation Science and Technology, 45: 2298–2307, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.504680

Separation of Toluene-Methanol Mixtures by Pervaporation Using Semi-IPN Polymer Membranes

N. R. Singha and S. K. Ray
Department of Polymer Science and Technology, University of Calcutta, Kolkata, India

Polyvinyl alcohol (PVOH) has been chemically modified by polymerizing hydroxyethylmethacrylate (HEMA) in aqueous solution of PVOH and finally crosslinking PVOH with glutaraldehyde to produce a semi-interpenetrating network (SIPN) membrane. Accordingly, three such SIPN membranes, namely SIPNI, SIPNII, and SIPNIII were synthesized with different weight ratio of PVOH: HEMA i.e., 1:0.25 (SIPNI), 1:0.50 (SIPNII), and 1:0.75 (SIPNIII). These SIPN membranes were used for pervaporative separation of methanol from its mixtures with toluene. The flux and methanol selectivity of these SIPN membranes were found to be much higher than conventional PVOH membrane crosslinked with glutaraldehyde. Among the three membranes, SIPNIII with 75 wt% HEMA incorporation shows optimum performance in terms of flux and methanol selectivity. The permeability of the membranes was also found to increase with increase in HEMA content in PVOH matrix. The novelty of the work lies in synthesis and characterization of a new kind of membrane and its potential for selective removal of methanol from its mixtures with toluene.

Keywords dehydration; pervaporation; polyvinyl alcohol; semi-IPN

Downloaded At: 08:37 25 January 2011

INTRODUCTION

Pervaporation (PV) is a membrane process where separation of a binary liquid mixture through a dense membrane is achieved by preferential sorption and diffusion of one component through the membrane under reduced pressure. PV is carried out at low temperature and the membrane can be reused with minimum environmental emission of the treated chemicals. Thus, in terms of energy and material consumption as well as environmental emission, PV is an ideal example of process intensification. The major field of pervaporative separation is the dehydration of organic using a hydrophilic membrane or for the removal of organics from water using an organophilic membrane. However, for the separation of organic-organic mixtures neither of these hydrophilic or organophilic membranes can be used. In this case a suitable membrane selection is based on the closeness of the solubility parameter value of the desired permeate with the membrane material (1). PV is widely tried for the separation of toluene-methanol mixtures (2–13). This aromatic-aliphatic mixture is used in many pharmaceutical and petrochemical industries. For conventional separation of this mixture alcohol is first extracted with water followed by distillation of alcohol-water mixtures. This two-step separation process increases the operation cost and energy consumption. Further, toluene–methanol mixture forms an azeotropic solution at a composition of 32% (w/w) toluene at a constant pressure of 101.3 kPa. As an alternative candidate a single step separation process like pervaporation would be very effective provided a highly aromatic (toluene) or methanol selective membrane is available. Various filled and unfilled elastomeric (2–4) as well as glassy membranes (5–7) were tried as aromatic selective membrane for the separation of toluene from its mixtures with methanol. However, for selective permeation of methanol from its mixtures with toluene, hydrophilic membrane is to be used as methanol is similar to water in polarity (8). Various hydrophilic membranes like membranes made from polyacrylonitrile (9), polyvinyl alcohol, cellulose acetate, cellulose triacetate, cellophane (10), polyimide (11), Y-zeolite (12), blend of polypyrrole–hexafluorophosphate (13), polyacrylic acid-polyvinyl alcohols (14) have been tried for the removal of methanol from its mixtures with toluene. Thus, in one of our earlier studies, polyvinyl alcohol (PVOH) was chemically modified by allowing copolymerization of (acrylic acid-co-hydroxy ethyl methacrylate) in the matrix of PVOH followed by crosslinking with glutaraldehyde (15). The membranes made from these interpenetrating network [IPN] polymers were used for dehydration of isopropyl alcohol (15) and also for the removal of methanol from its mixtures with toluene (16). In the present work hydroxyethylmethacrylate (HEMA) was polymerized in the matrix of PVOH followed by crosslinking of PVOH with glutaraldehyde to produce a semi-interpenetrating network (SIPN) polymer. The membrane made from this polymer possesses the mechanical integrity of PVOH along with added hydrophilicity due to the presence of polyHEMA in its matrix. These membranes have been used for the separation of methanol from its mixtures with toluene over the concentration range of

---

Received 6 January 2010; accepted 24 June 2010.

Address correspondence to Dr. S. K. Ray, Polymer Science and Technology, 92, A.P.C. Road, Kolkata, India. Tel.: 91-033-23508386; Fax: 91-033, 351. E-mail: samitcu2@yahoo.co.in

Downloaded At: 08:37 25 January 2011

1.8–18.5 wt% methanol in toluene. Earlier, these membranes have been used for dehydration of dioxane (17) with high water selectivity.

EXPERIMENTAL

Material

High purity analytical grade toluene and methanol used for this study were purchased from E. Marck, Mumbai. The monomer, i.e., hydroxyethylmethacrylate (HEMA), was synthesis grade and procured from S.D. Fine Chemicals, Mumbai. The monomer was used as obtained. Potassium persulfate and sodium metabisulfide was used as a redox initiator pair for the polymerization reaction. Polyvinyl alcohol (PVOH) of number average molecular weight 1,25,000 and hydrolysis% of 98–99 was obtained from S.D. Fine Chemicals, Mumbai and used as obtained.

Synthesis of PVOH – PolyHEMA Semi IPN (SIPN)

Synthesis of PVOH – PolyHEMA Semi interpenetrating network polymer (SIPN) with three different weight ratios of HEMA: PVOH i.e., 0.25:1, 0.50:1, and 0.75:1, termed as SIPNI, SIPNII, and SIPNIII, respectively, was carried out by solution polymerization in a three-necked reactor at 60°C for approximately 3 hrs using ammonium persulfate and sodium metabisulfide (each, 0.5 wt% of the total monomer weight) as a redox pair of initiators. The reactor was fitted with a stirrer, a thermometer pocket, and a condenser. At first, around 5 wt% PVOH solutions were made in a 250 ml glass beaker by gradual addition of the required amount of PVOH to boiling water at several intervals with constant stirring to obtain a viscous clear PVOH solution. Required amounts of HEMA were then added and the reaction mixture was added to the three-neck flask placed on a constant temperature bath. Temperature was raised to 60°C and aqueous solution of initiators (0.5 wt% of monomer HEMA) was added to the reactor. After polymerization for approximately 3 hours the viscous polymer solution was taken out from the reactor and precipitated in ethanol to remove polyHEMA if any, (which is soluble in ethanol) from the reaction mixtures. The polymer was dried at ambient temperature in a vacuum oven and redissolved in water.

Croslinking and Casting of Membranes from SIPN

The aqueous solution (~5 wt%) of the resulting SIPN as well as polyvinyl alcohol (PVOH) was mixed with 0.4 ml of glutaraldehyde (25% aqueous solution in water), 0.2 ml concentrated sulfuric acid, 0.6 ml glacial acetic acid, and 0.4 ml methanol for 2 wt% crosslinking of PVOH (18). The Membrane was prepared by casting this aqueous solution of the SIPN with an applicator on a clean and smooth glass plate. It was kept overnight at room temperature and then dried at 60°C for 2 hrs under vacuum. Subsequently, the membrane was annealed at 80°C for an additional 6 hrs under vacuum. The thickness of the membranes made from PVOH and SIPN was maintained at ~ 50 μm. The thickness was measured by Test Method ASTM D 374 using a standard dead weight thickness gauge (Baker, Type J17).

Membrane Characterization

The resulting membranes were characterized with XRD and SEM. Characterization of the membranes with mechanical properties, DSC and TGA, were reported elsewhere (17).

X-Ray Diffraction

Wide angle X-ray diffraction profile of the SIPN membranes (sample thickness 50 micron) were studied at room temperature with a diffractometer (model: X'Pert PRO. made by PANalytical B.V., The Netherlands) using Ni-filtered Cu Ka radiation (l = 1.5418 Å) and a scanning rate of 0.005 deg (2θ)/s). The angle of diffraction was varied from 2–72 degree to study the comparative change of the crystallinity in terms of the relative intensity of diffraction for the three SIPN membranes.

Scanning Electron Microscopy (SEM)

The three membrane samples were coated with gold (Au). The morphology of the membranes were observed by using SEM (Scanning electron Microscope, model no. S3400 N, VP SEM, Type-II, made by Hitachi, Japan) with the accelerating voltage set to 10 kV.

Sorption Study

Total Sorption

Sorption studies of methanol-toluene mixtures with these SIPN membranes were carried out taking different known concentrations of methanol-toluene mixtures. Membranes of known weights (around 1 gm thick membrane sample) were immersed in solution of different known concentrations of these organic mixtures and were allowed to equilibrate for 96 hours at 30°C. Each sample was weighed periodically until no weight change was observed. 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 these solvents sorbed by the membranes.

Sorption Selectivity

Sorption selectivity of the membranes was determined by a method reported elsewhere (17). For this the sorped sample was heated under vacuum and the vapor coming out of the thick sorped membranes was freezed and collected in the cold trap immersed in liquid nitrogen. The amount of methanol sorped by the membranes was obtained by analyzing the composition of the liquefied vapor from the cold trap

Downloaded At: 08:37 25 January 2011

by an Abbe type Refractometer (model no. AR600, MISCO, USA) at 30°C temperatures for all the samples. From the total sorption weight and corresponding methanol content (weight) of the membrane, sorption selectivity (α_s) of the membrane for methanol was calculated from the following equation

$$\alpha_s = \frac{\dfrac{y_{m\ \text{methanol}}}{y_{m\ \text{toluene}}}}{\dfrac{x_{f\ \text{methanol}}}{x_{f\ \text{toluene}}}} \tag{1}$$

Here y_{mi} and x_{fi} denotes membrane phase and feed concentration of component 'i'.

Permeation Study

Pervaporation Experiment

Permeation studies with these SIPN membranes were carried out by Pervaporation experiments in a batch stirred cell reported elsewhere (1). Effective membrane area (A) in contact with the feed mixture was $19.6\,\text{cm}^2$ and the feed compartment volume was $150.0\,\text{cm}^3$. The methanol-toluene mixtures in contact with the membrane were allowed to equilibrate for around 3 hours for the first experiment and one hour for the subsequent experiments with different feed compositions. When the steady state was reached the permeate was collected in traps immersed in liquid nitrogen. Permeation flux (J) was calculated by dividing the amount of total permeate (W) by the time (t) of experiment and area (A) of the membrane from Eq. (2)

$$J = \frac{W}{At} \tag{2}$$

The permeation selectivity (α_{pv}) of the membranes was calculated from a similar kind of equation like sorption selectivity (Eq. (1)). The performance of the membrane was also evaluated in terms of the permeation separation index (PSI) and enrichment factor (β) as obtained from the following Eqs. (3 and 4) respectively.

$$\text{PSI} = J_{\text{methanol}}(\alpha_{\text{PV}} - 1) \tag{3}$$

$$\beta = \frac{y_{\text{methanol}}}{x_{\text{tmethanol}}} \tag{4}$$

Here J_{methanol} is methanol flux, y_i and x_i are permeate and feed concentration of component 'i'.

RESULTS AND DISCUSSION

Membrane Characterization

Membrane Characterization by XRD Studies

The crystallinity of atactic polyvinyl alcohol arises from extensive hydrogen bonding by the small hydroxyl groups occupying d and l sites in an atactic chain within a single crystal lattice. As this PVOH is crosslinked, relative peak intensity also decreases due to loss in crystallinity. From the figure it is observed that for the same 2theta, SIPNI shows the highest peak intensity followed by SIPNII and SIPNIII. Polymerization of HEMA in the matrix of PVOH reduces the extent of hydrogen bonding and hence crystallinity resulting in the above trend of peak intensity.

Membrane Characterization by Scanning Electron Microscopy (SEM)

SEM studies of the three SIPN membranes are shown in Figs. 2a,b,c, respectively. SEM of a pure polymer like PVOH always gives a dense feature. SEM is usually carried out for a polymer blend to evaluate the extent of compatibility in terms of the morphology of the blend. The poorer the compatibility, the coarser is the morphology. IPN is different from a blend in that due to interpenetration of the constituent polymers the extent of compatibility is very high in a IPN. Thus, much higher magnification is required (higher than those used for conventional blend) for getting the morphology of an IPN through SEM. Hence, SEM of the membranes was carried out at 10 KV with 10 K magnification (5 micron) to get the morphology of the constituent polymers. In semi-IPNs (SIPN), the size and shape of the polymer II domains (i.e., polyHEMA) are controlled by the cross-link density of polymer I (PVOH) and the relative proportions of the two polymers (18). Close examination of Figs. 2a,b,c suggests that with an increasing amount of polymer-II domain, i.e., polyHEMA, the morphology becomes coarser from SIPNI to SIPNIII. The microphase separation of PVOH and polyHEMA is maximum in SIPNIII resulting in needle like morphology (19,20).

Sorption Study

Total Sorption and Sorption Selectivity

Figure 3 shows the variation of the total sorption and the sorption selectivity of methanol for all the membranes

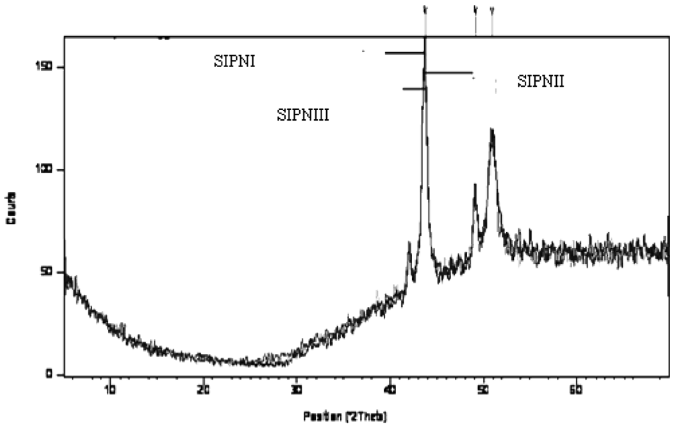
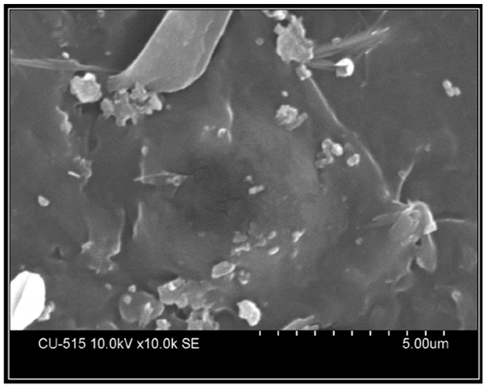
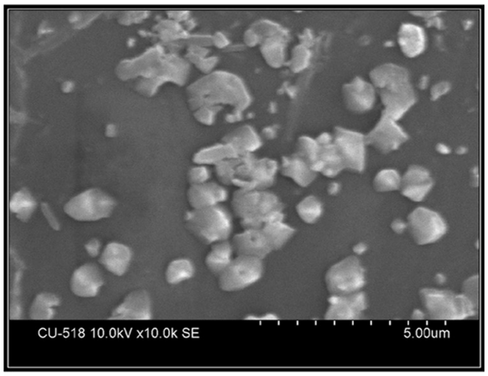


FIG. 1. XRD of SIPN membranes.

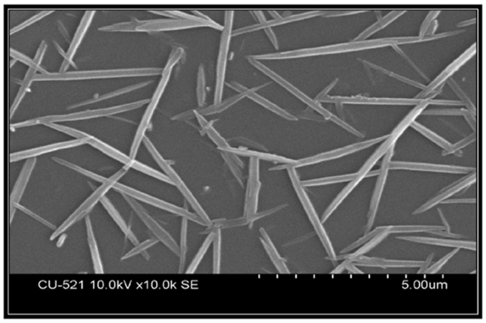
Downloaded At: 08:37 25 January 2011



(a) SIPNI



(b) SIPNII



(c) SIPNIII

FIG. 2. SEM of SIPN membranes. 2a SIPNI, 2b. SIPNII, 2c. SIPNIII.

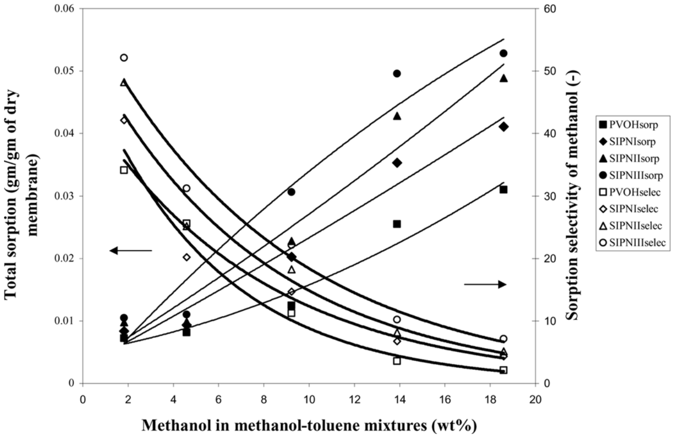


FIG. 3. Sorption isotherms and sorption slelectivity of methanol at 30°. ■ PVOHsorp; ■ SIPNIsorp; ▲ SIPNIIsorp; ● SIPNIIIsorp; □ PVOHsel; ◇ SIPNIsel; △ SIPNIIsel; ○ SIPNIIIsel.

with feed concentration of methanol at 30°C. It is observed from the figure that the total sorption increases almost linearly with the feed concentration of methanol. It is also observed that for the same feed concentration, SIPNIII with maximum amount of polyHEMA shows the highest total sorption while PVOH which is crosslinked with glutaraldehyde but not chemically modified with HEMA shows the lowest total sorption. As the wt% of HEMA increases from PVOH (0% polyHEMA) to SIPNIII (75% polyHEMA), the total sorption increases due to increasing extent of hydrophilicity in the membranes(17). It is also observed that at a lower range of feed concentration (up to around 5 wt%) the sorption isotherm of all the membranes are very close to one another. However, at higher feed concentration of methanol the difference in total sorption for these membranes are quite high and above around 10 wt% methanol in feed the increment is extensive due to plasticization of the hydrophilic and hence methanol-selective membranes by methanol.

Permeation Study

Effect of Feed Concentration on Methanol Separation

The PV experiments were carried out at five different feed concentrations of methanol in toluene i.e., 1.83, 4.58, 9.21, 13.88, and 18.59 wt% methanol in toluene. The PV performance of PVOH and the three SIPN membranes, i.e., SIPNI, SIPNII, and SIPNIII at these five feed concentrations of methanol are shown in Table 1 in terms of total flux (Table 1a), permeate concentration of methanol (Table 1b), and methanol selectivity (Table 1c) at 30°C. Figure 4 shows the variation of wt% of methanol in the permeate against the wt% of methanol in the feed for all of the five feed concentrations at 30°C. Similar kinds of relationships were also observed at the two other PV temperatures, i.e., at 40 and 50°C. It appears from Table 1 and these McCabe-Thiele type xy diagrams that all the membranes show measurable separation characteristics for methanol over the concentration range studied without any pervaporative azeotrope. It is also observed from the figure and the table that all the four membranes show high methanol concentration in the permeate. Among these four membranes, methanol concentration in the permeate increases in the following order SIPNIII>SIPNII>SIPNI>>PVOH.

It is interesting to note that the SIPN membranes show higher permeate concentration of methanol than the conventional PVOH membrane crosslinked with glutaraldehyde.

TABLE 1
Variation of performance of the membranes (membrane thickness 50 micron) with feed concentration of methanol at 30°C

Feed concentration of methanol wt%	PVOH	SIPNI	SIPNII	SIPNIII
(a) Total flux (g/m^{2}h)				
1.8307	13.90	22	28	35
4.5887	14.06	26.40	38	42
9.217	18.64	32	47	56
13.886	24.19	38	58	76
18.596	33.65	42	72	96
(b) Permeate concentration of methanol (wt%)				
1.8307	88	90	92.7	93.05
4.5887	88.50	89.76	92	92.41
9.217	78	88.82	91.94	92.35
13.886	73	88.23	91.88	92.29
18.596	71.50	88.24	91.58	92.17
(c) Methanol selectivity (–)				
1.8307	393	482.6	681.54	718.92
4.5887	160	182.35	239.11	253.21
9.217	34	78.27	112.37	118.95
13.886	16.7	46.5	70.19	74.27
18.596	10.98	31.06	47.66	51.57

Incorporation of hydrophilic polyHEMA in PVOH matrix increases methanol affinity of the membranes. Thus, with an increasing amount of polyHEMA from PVOH (0 wt%) to SIPNIII (75 wt%) methanol affinity of the membranes increases in the above order.

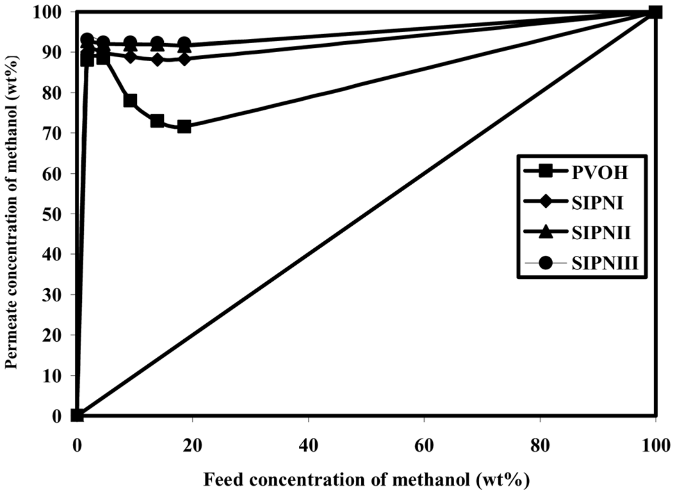


FIG. 4. Variation of permeate concentration of methanol with its feed concentration at 30°C ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII.

Effect of Feed Concentration on Flux and Permeation Selectivity

The effect of feed concentration of methanol on methanol and toluene partial flux and permeation selectivity at 30°C are shown in Figs. 5 and 6 respectively. The partial methanol and toluene flux was calculated from the permeate concentration of methanol and total flux. A similar kind of relationship was also observed at the other two temperatures of PV experiments, i.e., at 40 and 50°C. From Fig. 5 it is observed that both methanol and toluene flux increases linearly with feed concentration in the following order-SIPNIII>SIPNII>SIPNI>>PVOH.

The increasing order of flux from SIPNI to SIPNIII may be ascribed to decreasing extent of crystallinity from SIPNI to SIPNIII. Incorporation of the hydrophilic polyHEMA, not only increases the affinity for methanol but also void space in these SIPN membranes because of loss in crystallinity. Thus, flux increases from SIPNI to SIPNIII. The much lower methanol flux of PVOH in comparison to the SIPN membranes may be due to its high degree of crystallinity. From Fig. 6 it is also observed that for the same feed concentration, methanol flux is much higher than toluene flux, signifying methanol selectivity of the membranes. Further, rate of increase in methanol flux with increasing feed concentration is much higher than toluene flux. It is also observed from this figure that up to 10 wt% feed concentration of methanol in feed, the toluene partial flux

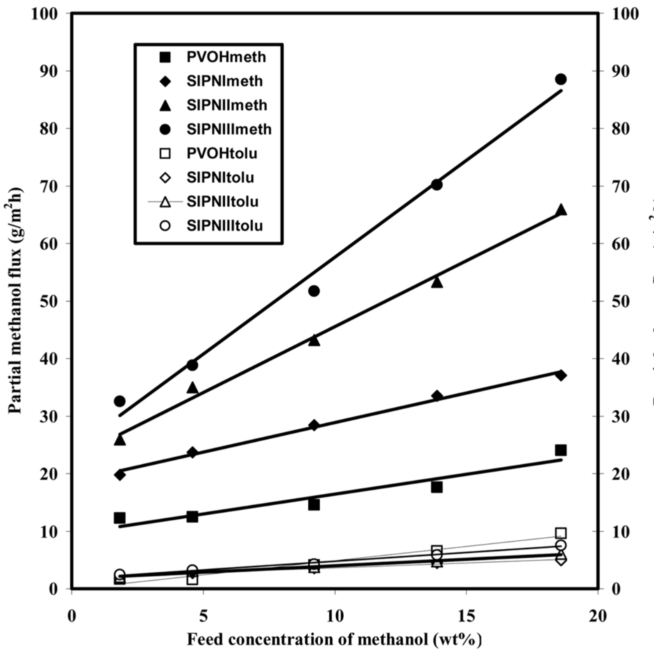


FIG. 5. Variation of partial flux of methanol and toluene with feed concentration of methanol at 30°C ■ PVOHmeth; ■ SIPNImeth; ▲ SIPNIImeth; ● SIPNIIImeth; □ PVOHtolu; ◆ SIPNImethtolu; △ SIPNIItolu; ○ SIPNIIItolu.

Downloaded At: 08:37 25 January 2011

Downloaded At: 08:37 25 January 2011

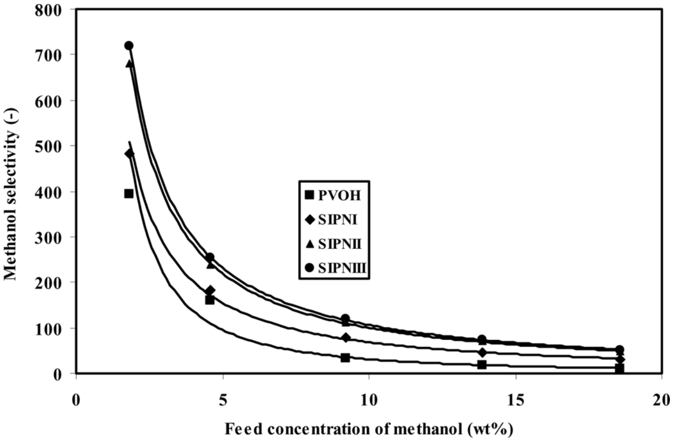


FIG. 6. Variation of methanol selectivity with feed concentration of methanol at 30°C ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII.

is very low and the difference in the extent of toluene flux among the membranes are marginal. Above this (~10 wt% methanol in feed) feed concentration, the methanol selective membranes become plasticized with the increase in toluene flux in the same order. The permeability of both methanol and toluene were calculated from the slope of the linear plot (regression coefficient >0.9) of the feed concentrations against the corresponding partial flux (16) and these permeability values are given in Table 2.

In Fig. 6 methanol selectivity of all the membranes are plotted against feed concentration of methanol. From this figure it is observed that the membranes show the same trend of selectivity as flux i.e., for the same feed concentration it increases from SIPNI to SIPNIII. It is observed that for all the four membranes selectivity decreases drastically with increase in feed concentration following a power type trend lines. At very low concentration of methanol in feed the SIPN membranes show very high methanol selectivity. As the methanol concentration in feed increases, selectivity decreases and above 10 wt% methanol in feed the selectivity values for all the membranes go below 100. Chemical modification of PVOH by incorporating hydrophilic water soluble polyHEMA in its matrix increases methanol selectivity from PVOH to SIPNIII as this hydrophilic polyHEMA absorbs more of the methanol than toluene.

TABLE 2
Methanol and toluene permeability (cm^3 cm/cm^2 h) of the membranes

Name of the membrane	$P_{methanol}$	$P_{toluene}$
PVOH	0.34	0.25
SIPNI	0.52	0.08
SIPNII	1.14	0.11
SIPNIII	1.68	0.15

At methanol feed concentration above 10 wt%, these membranes become plasticized with an increase in both methanol and toluene permeation and hence decrease in methanol selectivity.

Effect of Feed Concentration on Permeation Separation Index (PSI) and Enrichment Factor

Figure 7 shows variation of PSI for methanol with its feed concentration at 30°C. In general, flux and selectivity bears an opposite relationship with respect to feed concentration as also seen for the SIPN membranes. Permeation separation index or PSI relates both the permeation flux and selectivity of the desired component in one equation (Eq. (3)) and hence the optimum performance of a membrane can be evaluated in terms of its PSI. PSI was found to be maximum at the lowest feed concentration, i.e. around 1.8 wt% methanol signifying optimum flux and selectivity at lower feed concentration of methanol. PSI was found to decrease exponentially with increase in feed concentration. For the same feed concentration PSI was also found to decrease from SIPNIII to SIPNI. The enrichment factor for all the membranes are shown in Fig. 8 which showed a similar trend. The enrichment factor was also found to decrease exponentially from SIPNIII to SIPNI membrane.

Effect of Temperature on Flux and Selectivity

With the increase in temperature, both the methanol and toluene flux increases while methanol selectivity decreases at higher temperature in the same order for all the membranes as shown for 4.38 wt% feed concentration of

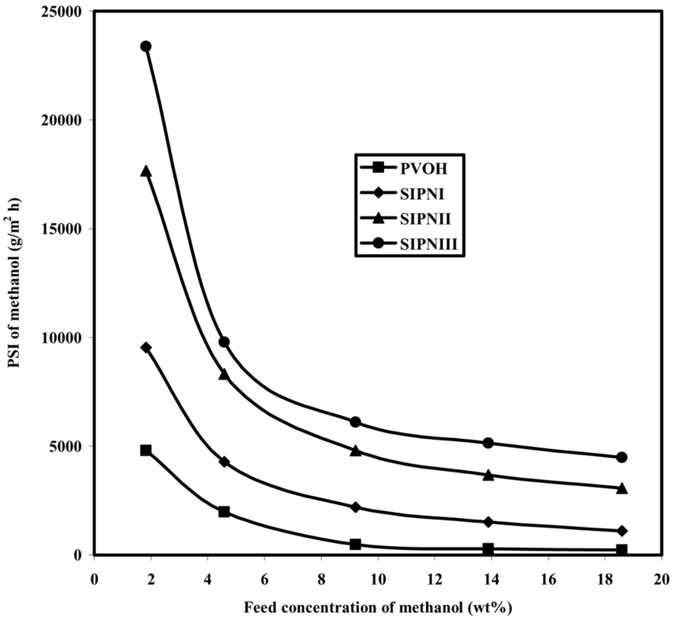


FIG. 7. Variation of PSI of methanol with its feed concentration at 30°C ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII.

Downloaded At: 08:37 25 January 2011

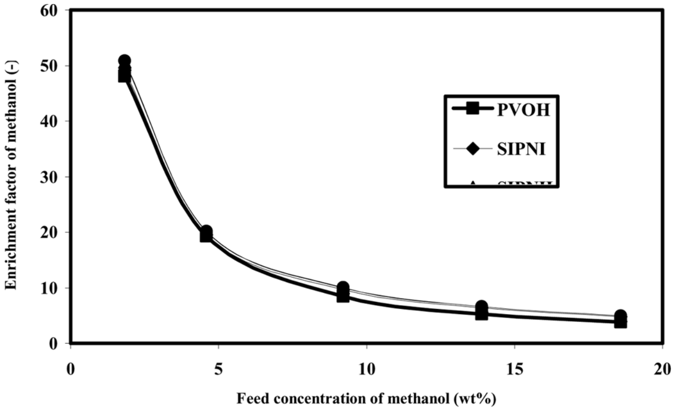


FIG. 8. Variation of enrichment factor of methanol with its feed concentration at 30°C ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII.

methanol in Figs. 9 and 10, respectively. At higher temperature flux increases due to increased rate of diffusion. The increased rate of diffusion at higher temperature is caused by increased thermal motion of the polymer chains at higher temperatures. Activation energy for permeation (E_P) of both methanol and toluene was obtained from the slope of the Arrhenius type linear plot of logarithmic of partial flux (Q) against the inverse of the absolute temperature (1/T) as shown in Fig. 11a (for methanol) and 11b (for toluene), respectively using the following Eq. (5).

$$\ln Q = \ln A - \left(\frac{E_P}{RT}\right) \tag{5}$$

Here 'A' is a pre- exponential factor and 'R' is the universal gas constant. Thus, the activation energy for the permeation of toluene and methanol for 4.38 wt% feed concentration of methanol was calculated as shown in Table 3. From this table, it is observed that the activation energy for the permeation of methanol is much lower than that of toluene. The much smaller kinetic diameter of methanol [methanol- 0.38 nm (21), toluene- 0.61 nm (22)] makes its permeation much easier through these methanol selective membranes with lower activation energy.

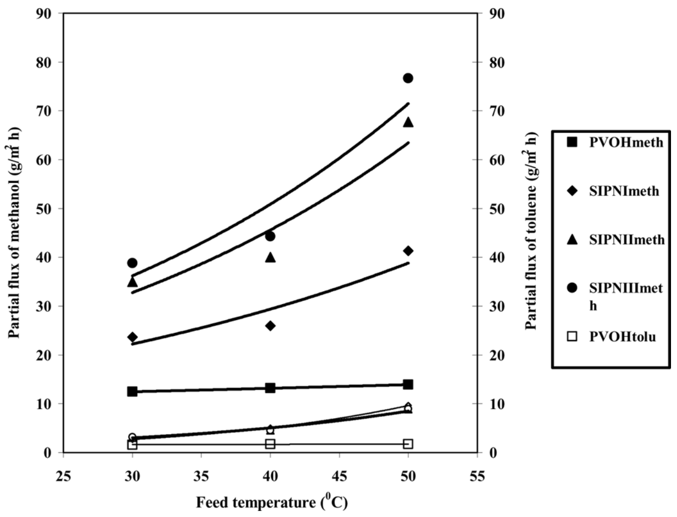


FIG. 9. Variation of partial flux with feed temperature. ■ PVOHmeth; ◆ SIPNImeth; ▲ SIPNIImeth; ● SIPNIIImeth; □ PVOHtolu; ◆ SIPNI-methtolu; △ SIPNIItolu; ○ SIPNIIItolu.

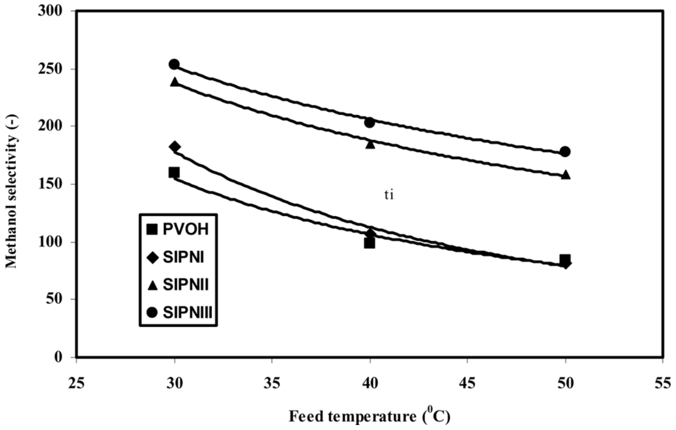


FIG. 10. Variation of methanol selectivity with feed temperature for 4.6 wt% feed concentration of methanol ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII.

Effect of Feed Concentration on Permeation Ratio

Permeation ratio quantifies the effect of one component on the permeation rate of the other component. Huang and Lin (23) 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,

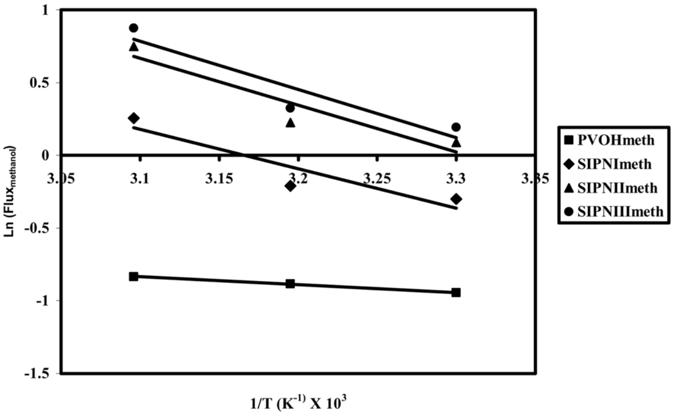
$$\theta_i = -\frac{J_{i\ \mathrm{expt\ at\ x\ conc.}}}{J^0_{i\ \mathrm{expt\ at\ x\ conc.}}} \tag{6}$$

$$J^0_{i\ (\mathrm{at\ x\ conc.})} = J^0_{(\mathrm{pure}\quad i)} \times x_i \tag{7}$$

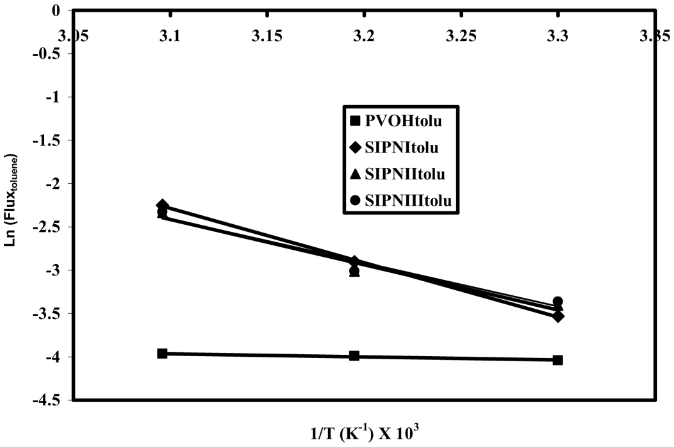
TABLE 3
Activation energy for permeation (E_p) of methanol and toluene for 4.6 wt% feed concentration of methanol

Name of the membrane	$E_{pmethanol}$ (kj/mol K)	$E_{ptoluene}$ (kj/mol K)
PVOH	3.07	4.50
SIPNI	2.25	5.21
SIPNII	2.70	4.35
SIPNIII	2.75	4.20

Downloaded At: 08:37 25 January 2011

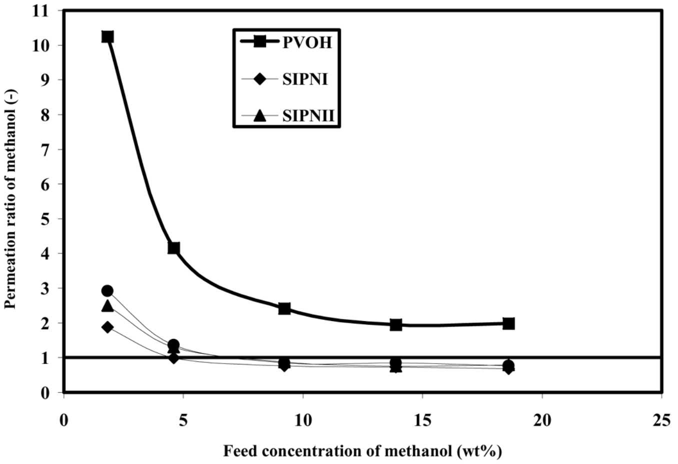


(a)

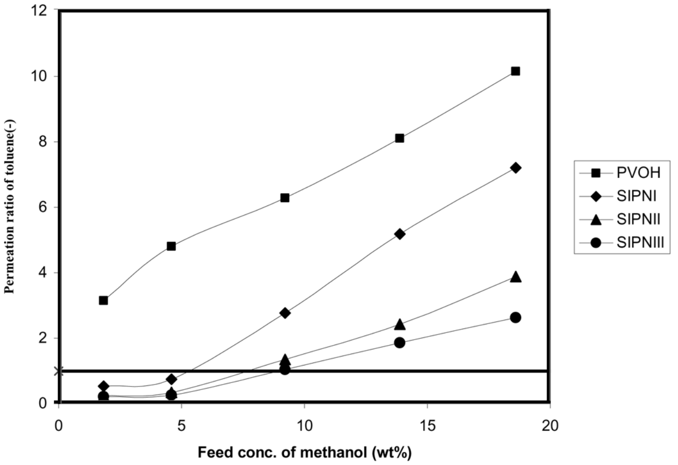


(b)

FIG. 11. (a) Arhenius Plot for partial flux of methanol. ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII; (b) Arhenius Plot for partial flux of toluene. ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII.



(a)



(b)

FIG. 12. (a) Variation of Permeation ratio of methanol with its feed concentration at 30°C ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII; (b) Variation of Permeation ratio of toluene with its feed concentration at 30°C ■ PVOH; ◆ SIPNI; ▲ SIPNII; ● SIPNIII.

Where 'i' denote component 'i' in the binary mixture, x is the weight fraction in the feed mixture, superscript 0, denotes ideal permeation. From Fig. 12a it is observed that at very low concentration of methanol, i.e., at very high concentration of toluene (around 99 wt% or more) in the feed, the permeation ratio of methanol, is far above unity for all the membranes signifying a positive coupling effect of toluene on methanol flux. In this case, toluene-methanol interaction is more than methanol-membrane interaction. As the methanol % in feed increases, the permeation ratio of methanol decreases drastically for all the methanol selective membranes and becomes close to unity, i.e., the coupling effect of toluene on methanol flux becomes negligible because of much higher methanol-membrane interaction (through hydrogen bonding) than toluene-methanol interaction at higher feed concentration of methanol. From the figure it is also observed that for the same feed concentration, the permeation ratio decreases from PVOH to SIPNIII. The highest permeation ratio of PVOH is due to its minimum methanol selectivity. As methanol selectivity of the membranes increases from PVOH to SIPNIII, the extent of the methanol-membrane interaction increases in the same orders resulting in the above order of the permeation ratio of methanol. Figure 12b shows the variation of the permeation ratio of toluene with the feed concentration of methanol which shows a similar trend.

Comparison of Membrane Performance with Literature Data

The relative performances of different membranes used for the separation of methanol from its mixtures with toluene are given in Table 4. In this case the flux data has been normalized with thickness for better comparison. From these results it transpires that the performance of the SIPN

TABLE 4
Comparison of performance of various membranes reported for pervaporative separation of methanol–toluene mixtures

Polymer used as membrane	Methanol in the feed (wt %)	Temperature of experiment (°C)	Normalized flux (kgμm/m^2 h)	Methanol selectivity	Reference
Polyvinyl alcohol-polyacrylic acid blend	20	60	Good	148	(14)
Composite membrane of N-acetylated chitosan supported on polyetherimide	10	30	4.84	607	(24)
PPY-PTS blend	1–95	57.5	0.05–10	5–60	(13)
Cellulose	5–90	1200–25	15–67		(10)
Cellulose triacetate-polyacrylic acid blend		20–4	17–68		(10)
PPY-PF blend	1–80	–	0.05–10	10–600	(13)
Polyvinyl alcohol-acrylic acid-co-Hydroxyethylmethacrylate full IPN (PVAHII)	1.8–18.6 wt%	30	0.759–2.88	622–16	(16)
Polyvinyl alcohol-Hydroxyethylmethacrylate semiIPN (SIPNIII)	1.8–18.6 wt%	30	1.750–4.8	718.92–51.57	(Present work)

Downloaded At: 08:37 25 January 2011

membranes used for the present study show a good separation factor for methanol with reasonable flux to those reported for similar systems.

CONCLUSION

Three crosslinked SIPN membranes termed here as SIPNI, SIPNII, and SIPNIII, earlier used for dehydration of dioxane (17) were used for the separation of toluene-methanol mixtures. These membranes showed measurable flux and separation factor for methanol. The flux and selectivity of these SIPN membranes were found to be much higher than polyvinyl alcohol membrane (PVOH) crosslinked with glutaraldehyde. Among the three membranes, SIPNIII containing 75 wt% polyHEMA showed optimum performance in terms of flux and selectivity.

ACKNOWLEDGEMENTS

The first author of this manuscript is grateful to CSIR, India for providing a fellowship.

REFERENCES

1. Ray, S.K.; Sawant, S.B.; Joshi, J.B.; Pangarkar, V.G. (1997) Development of new synthetic membranes for separation of benzene-cyclohexane mixture by pervaporation-a solubility parameter approach. *Ind. Eng. Chem. Res.*, 36: 5265–5276.
2. Ray, S.; Ray, S.K. (2006) Separation of organic mixtures by Pervaporation using crosslinked rubber membranes. *J. Membr. Sci.*, 270: 132–145.
3. Ray, S.; Ray, S.K. (2006) Separation of organic mixtures by pervaporation using crosslinked and filled rubber membranes. *J. Membr. Sci.*, 285 (10): 8–119.
4. Lue, S.J.; Ou, J.S.; Kuo, C.H.; Chen, H.Y.; Yang, T.H. (2010) Pervaporative separation of azeotropic methanol/toluene mixtures in polyurethane–poly (dimethylsiloxane) (PU–PDMS) blends membranes: Correlation with sorption and diffusion behaviors in a binary solution system. *J. Membr. Sci.*, 34: 108–115.
5. Hao, J.; Tanaka, K.; Kita, H.; Okamoto, K. (1997) The pervaporation properties of sulfonyl containing polyimide membranes to aromatic/aliphatic hydrocarbon mixtures. *J. Membr. Sci.*, 132: 97–108.
6. Muralidharan, M.N.; Kumar, S.A.; Thomas, S. (2009) Pervaporation of alcohol-aromatic hydrocarbon mixtures through poly(ethylene-co-vinyl acetate) membranes. *J. Macromolecular Sci. Part A: Pure and Applied Chem.*, 46: 274–281.
7. Patil, M.B.; Aminabhavi, T.M. (2008) Pervaporation separation of toluene/alcohol mixtures using silicalite zeolite embedded chitosan mixed matrix membranes. *Sep. and Purific. Tech.*, 62: 128–136.
8. Ray, S.; Ray, S.K. (2006) Synthesis of highly Methanol Selective Membranes for Separation of Methyl tertiary butyl ether (MTBE) - Methanol Mixtures by Pervaporation. *J. Membr. Sci.*, 278: 279–289.
9. Pal, S.M.; Pangarkar, V.G. (2005) Acrylonitrile-based copolymer membranes for the separation of methanol from methanol–toluene mixture through pervaporation. *J. Appl. Polym. Sci.*, 96: 243–252.
10. Mandal, S.; Pangarkar, V.G. (2002) Separation of methanol-benzene and methanol–toluene mixtures by pervaporation: effects of thermodynamics and structural phenomenon. *J. Membr. Sci.*, 201: 175–190.
11. Bhat, A.A.; Pangarkar, V.G. (2000) Methanol-selective membranes for the pervaporative separation of methanol–toluene mixtures. *J. Membr. Sci.*, 167: 187–201.
12. Sommer, S.; Melin, T. (2005) Influence of operation parameters on the separation of mixtures by pervaporation and vapor permeation with inorganic membranes. Part 2: Purely organic systems. *Chem. Eng. Sci.*, 60: 4525–4533.
13. Zhou, M.; Persin, M.; Sarrazin, J. (1996) Methanol removal from organic mixtures by pervaporation using polypyrrole membranes. *J. Membr. Sci.*, 117: 303–309.
14. Park, H.C.; Meertens, R.M.; Mulder, M.H. (1998) Sorption of alcohol–toluene mixtures in poly (acrylic acid)–poly (vinyl alcohol)

blend membranes and its role on pervaporation. *Ind. Eng. Chem. Res.*, 37: 4408–4417.

15. Singha, N.R.; Kar, S.; Ray, S.; Ray, S.K. (2009) Separation of Isopropyl alcohol-water mixtures by Pervaporation using crosslink IPN membranes. *Chem. Eng. and Processing: Process Intensific.*, 48: 1020–1029.
16. Singha, N.R.; Kuila, S.B.; Das, P.; Ray, S.K. (2009) Separation of toluene–methanol mixtures by pervaporation using crosslink IPN membranes. *Chem. Eng. and Processing: Process Intensific*, 48: 1560–1565.
17. Singha, N.R.; Kar, S.; Ray, S.K. (2009) Synthesis of chemically modified polyvinyl alcohol membranes for dehydration of dioxane by pervaporation. *Sep. Sci. and Technol.*, 44: 422–446.
18. Sperling, L.H. (1981) Interpenetrating polymer networks In EPST 1st ed., Suppl. Vol. 1, pp. 288–306, Lehigh University; ‘‘Interpenetrating Polymer Networks’’ in EPSE 2nd ed., Vol.8, pp. 279–341, by D. Klempner, University of Detroit, and L. Berkowski, BASF Corp.
19. Gangopadhyay, R.; De, A. (2002) Conducting semi-IPN based on polyaniline and crosslinked poly (vinyl alcohol). *Synthetic Metals*, 132: 21–28.
20. Karabanova, L.V.; Lloyd, A.W.; Mikhalovsky, S.V.; Helias, M.; Phillips, G.J.; Rose, S.F.; Mikhalovska, L.; Boiteux, G.; Sergeeva, L.M.; Lutsyk, E.D.; Svyatyna, A. (2006) Polyurethane/poly(hydroxyethyl methacrylate)semi-interpenetrating polymer networks for biomedical applications. *J Mater Sci: Mater Med.*, 17: 1283–1296.
21. ten Elshof, J.E.; Abadal, C.R.; Sekuli, J.; Roy Chowdhury, S.; Blank, D.H.A. (2003) Transport mechanisms of water and organic solvents through microporous silica in the pervaporation of binary liquids. Micropor. *Mesopor. Mater.*, 65: 197–208.
22. Iliyas, A.; Eić, M.; Hassan, M.; Niaki, Z.; Vasenkov, S. (2005) Towards Observation of Single-File Diffusion Using TZLC, diffusion-fundamentals The Open-Access Journal for the Basic Principles of Diffusion Theory. *Experiment and Application*, 5: 1–3.
23. Huang, R.Y.M.; Lin, V.J.C. (1968) Separation of liquid mixtures by using polymer membranes. I. Permeation of binary organic liquid mixtures through polyethylene. *J. Appl. Polym. Sci.*, 12: 2615–2631.
24. Huang, R.Y.M.; Moon, G.Y.; Pal, R. (2000) N-acetylated chitosan membranes for the pervaporation separation of alcohol/toluene mixtures. *J. Membr. Sci.*, 176: 223–231.

Downloaded At: 08:37 25 January 2011