

Separation of Phenol from Aqueous Solution by Membrane Pervaporation Using Modified Polyurethaneurea Membranes

Barun Sinha,¹ Ujjal K. Ghosh,¹ Narayan C. Pradhan,¹ Basudam Adhikari²

¹Department of Chemical Engineering, Indian Institute of Technology, Kharagpur-721 302, India

²Materials Science Centre, Indian Institute of Technology, Kharagpur-721 302, India

Received 27 February 2005; accepted 20 October 2005

DOI 10.1002/app.23566

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Hydroxy-terminated polybutadiene-based porous and nonporous polyurethaneurea membranes were prepared and used to study the phenol separation efficiency from dilute aqueous solution. The porosity was developed by incorporation of lithium chloride in polymer matrix with subsequent leaching of the same in hot water. The porous membrane showed higher phenol flux over that of nonporous membrane. Permeate containing about 97 wt % phenol was obtained from feed containing 7 wt % phenol, when pervaporation was carried out with porous polyurethaneurea membrane at 75°C. The activation energies for diffusion,

permeation, and pervaporation were calculated from Arrhenius plots. From the activation energy values, it was observed that the pervaporation process became easier with increased phenol concentration in the feed and porosity of the membrane used. The membrane boundary resistance was observed to decrease with increase in temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1857–1865, 2006

Key words: pervaporation; polyurethaneurea; aqueous phenol; porous membrane; separation factor; flux

INTRODUCTION

Phenol is one of the major polluting by-products in petrochemical, coal liquefaction, and paper pulp industries. The separation of phenol from aqueous waste streams is, therefore, very important and challenging for the sake of industrial safety and environmental protection. Membrane technology has attracted attention for removal of phenols and other low volatile organics from industrial wastewater.^{1–4} Many researchers have used polymeric membranes for the separation of phenol from aqueous solution by pervaporation.^{5–8} Membranes with higher phenol affinity (permselectivity), such as polyether-*block*-polyamides (PEBA),⁵ polyurethane,⁶ and poly(dimethylsiloxane) (PDMS),⁹ have been used in pervaporative separations. Hoshi et al.⁶ and Jonquiere et al.^{10,11} prepared pervaporation membranes from hydroxyterminated polyether-based polyurethanes and found the pervaporation performances to be guided by the flexible (soft) segments of polyurethanes. Lai et al.¹² and Schauer et al.¹³ prepared polybutadiene-based polyurethanes and studied organic/organic as well as organic/aqueous separations. Many researchers reported the effect of soft segment length,¹⁴ influence of

polar atoms borne by hard segments,¹⁵ crosslink ratio as well as chemical and physical crosslinking⁸ on pervaporation performance. In an earlier communication,¹⁶ we reported the introduction of polybutadiene-based polyurethane and polyurethaneurea membranes for the first time for the separation of phenol from dilute aqueous solution and showed the potentials of these types of membranes for delivering high phenol selectivity. The effect of variation in hard segment fraction and crosslink density on phenol selectivity and flux were reported in details. But in spite of high selectivity of phenol, the flux obtained in permeate seemed to be lower when compared with other commercial membranes. We have investigated further to increase the flux by incorporating porosity to those membranes by treatment with lithium chloride and subsequently leaching out the same in hot water.

In this communication, we present a detailed study on pervaporation performances of porous polyurethaneurea membranes for separation of phenol from aqueous solutions. The synthesized porous polyurethaneurea membranes were characterized by FTIR spectroscopy and scanning electron microscopy (SEM). Effects of various operating parameters such as feed phenol concentration, feed temperature on separation performance of the membranes were studied. The experimental results were analyzed by using resistance-in-series model.

Correspondence to: N. C. Pradhan (ncp@che.iitkgp.ernet.in).

EXPERIMENTAL

Materials

Hydroxyterminated polybutadiene (HTPB, functionality = 2.4, hydroxyl value = 43.2 mg of KOH g⁻¹) with a number average molecular weight of 2580 was received from Vikram Sarabhai Space Centre (VSSC), India, and was used as received. 2,4-Toluylene diisocyanate (TDI), obtained from Fluka AG (Germany), was used without further purification. 4,4'-Diaminodiphenylsulfone (DADPS, Germany) was first dehydrated overnight under vacuum and then it was sublimed. The catalyst dibutyltindilaurate (DBTDL) and lithium chloride, both of Fluka AG (Germany), were used as received. Tetrahydrofuran (THF) (Merck, India) was purified before use. For purification of THF (Merck, India), solid sodium was added first as drying agent and then refluxed for 24 h.

Synthesis of polyurethaneurea membranes

Prepolyurethane (PPUD) was prepared by the reaction of HTPB and TDI in THF with NCO : OH mole ratio of 2 : 1 at 30°C and in presence of 0.05 wt % DBTDL as catalyst. After 45 min of reaction between HTPB and TDI, 100 mol % diamine (DADPS) solution in THF (with respect to M_n of HTPB) was added slowly to the reaction mixture containing prepolyurethane with constant stirring. The reaction was continued for further 15 min. The excess solvent and entrapped bubbles were removed from the viscous solution by evacuation. The polyurethaneurea film was cast on clean Teflon[®] plate. The cast films of polyurethaneurea (PUUSD100) were left overnight at room temperature for moisture curing followed by thermal curing at 80°C for 3 h. For preparation of porous polyurethaneurea membranes (PUUSD100L1 and PUUSD100L2), 1 and 2 wt % LiCl, respectively, (with respect to reactant weight) were mixed in the reaction mixture prior to casting of the film. The moisture-cured films were treated with hot water to leach out LiCl from the polymer matrices.

Characterization of membranes by FTIR/ATR spectroscopy and scanning electron microscopy

Porous polyurethaneurea membranes were characterized in ATR mode of a Thermo Nicolet 2500 FTIR/ATR analyzer with 32 scans performed each time.

Scanning electron microscopy of porous membranes (PUUSD100L1 and PUUSD100L2) (after leaching of LiCl in hot water) surfaces was carried out in JEOL 2500 scanning electron microscope both before and after phenol permeation.

Experimental set-up

Pervaporation of phenol–water mixture was carried out in a pervaporation cell. It is assembled from two

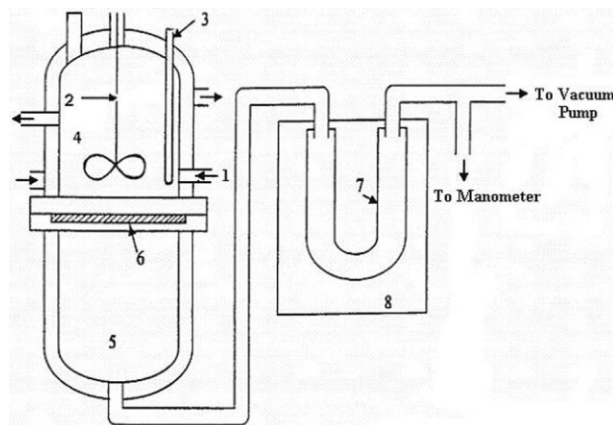


Figure 1 Sketch of the experimental set-up (1: Feed inlet; 2: Stirrer; 3: Thermometer pocket; 4: Feed chamber; 5: Permeate chamber; 6: Sintered SS disk; 7: Condenser-cum-collector; 8: Cryogenic bath).

cylindrical half-cells made of stainless steel fastened together by nuts and bolts. The membrane was supported on a sintered stainless steel plate placed in between two cells. The feed liquid was circulated using a peristaltic pump. The feed temperature was maintained by circulating hot water through the cell jacket. For all measurements, the downstream pressure was maintained at 5 mmHg by applying vacuum. The permeate vapor was collected in a glass condenser suspended inside a cryogenic bath kept at -15°C . The schematic of the experimental set-up is shown in Figure 1.

Analysis of permeate

The permeate collected in glass condenser was analyzed for phenol content by volumetric redox titration. Standard $\text{BrO}_3^-/\text{Br}^-$ solution was added to acidified diluted permeate and the excess bromine was estimated by iodometric back titration. The flux (J) of permeation was calculated from the following expression:

$$J = Q / (A \times t) \text{ gm}^{-2} \text{ h}^{-1} \quad (1)$$

where, Q (g) is the weight of permeate (either phenol or water or whole permeate) obtained after time t (h) and A is the effective membrane area in m^2 .

Boundary resistance parameter

The separation factor for permeation (α_p) of phenol can be expressed as

$$\alpha_p = \frac{C_{i2} C_{j1}}{C_{i1} C_{j2}} \quad (2)$$

where C_{i1} and C_{i2} are the concentrations of phenol in feed and permeate and C_{j1} and C_{j2} are the concentrations of water in feed and permeate, respectively. The partition coefficient (K_{i1}) is defined as

$$K_{i1} = \frac{C_{i3}}{C_{i1}} \quad (3)$$

where C_{i3} is the concentration of phenol inside the membrane. It was estimated by vaporization and condensation of absorbed phenol from a swollen piece of membrane. This was done by heating the swollen membrane at 70°C in a sealed glass vessel and collecting the vapors in a cold trap connected to vacuum.

The permeability constant of phenol (P_i) was measured following the equation

$$P_i = D_i K_{i1} \quad (4)$$

where D_i is the diffusion coefficient of phenol.

The boundary resistance (k_L^{-1}) at the feed-membrane interface can be calculated according to resistance-in-series model using the formula

$$1/k_{ov} = 1/k_L + l/P_i \quad (5)$$

where, k_{ov} is overall mass transfer coefficient and l is the membrane thickness. The overall mass transfer coefficient (k_{ov}) was calculated from the following expression for flux:

$$J_i = k_{ov} C_{i1} \quad (6)$$

RESULTS AND DISCUSSION

The HTPB-based polyurethaneurea membranes were prepared and modified with LiCl. The modification

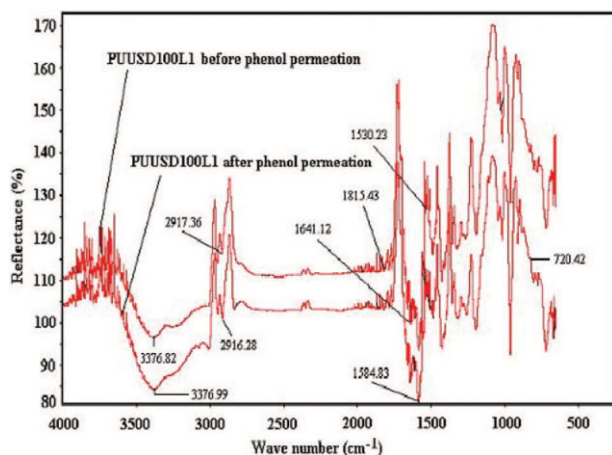
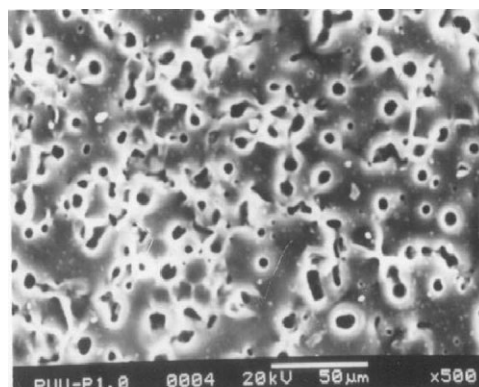
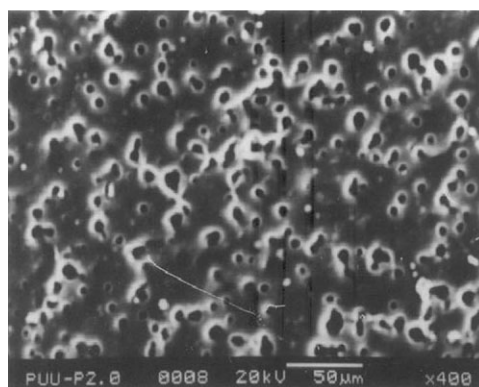


Figure 2 FTIR-ATR spectroscopy of PUUSD100L1 membrane before and after phenol permeation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



(a)



(b)

Figure 3 Scanning electron micrographs of LiCl-modified PUUSD100 membranes: (a) PUUSD100L1 and (b) PUUSD100L2.

was done to develop porosity in the membranes. The prepared membranes were characterized by FTIR-ATR and SEM techniques. FTIR-ATR spectroscopy of the polymer surface of PUUSD100L1 membrane was taken before and after phenol permeation as shown in Figure 2. ATR peaks that appeared at 3376 cm^{-1} stands for N-H stretching frequency band of urethane and urea. Peak at 2917 cm^{-1} stands for C-H stretching of polybutadiene segment. The peaks at wave number of around 1641 cm^{-1} is indicative of C=O stretching. Other peaks found at 662, 721, and 917 cm^{-1} are for spectra that arose out of C=C stretching modes. As can be seen from Figure 2, there was no shift of the bands, particularly those for N-H and C=O stretchings due to exposure of the membrane to phenol solution. This clearly indicates that the synthesized polyurethaneurea membrane is very stable in phenol solution.

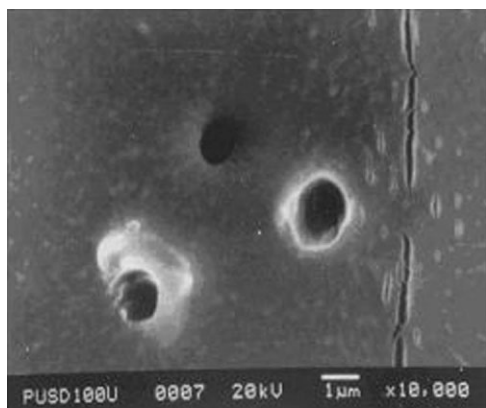
SEMs of polyurethaneurea membranes modified with 1% LiCl and 2% LiCl, respectively, are shown in Figure 3. In each case, existence of definite porous structures was noticed. The SEMs were analyzed for the pores using Image Pro Plus 5.1 software. The

TABLE I
Properties of LiCl-Modified Polyurethaneurea Membranes

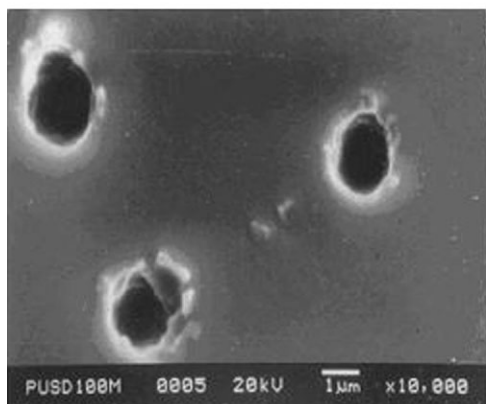
Membrane	LiCl (wt %)	Porosity	Average pore diameter (μm)	
			Before phenol permeation	After phenol permeation
PUUSD100L1	1.0	0.17	3.0	3.4
PUUSD100L2	2.0	0.20	3.8	4.1

porosity and average pore diameters were calculated as reported in Table I. The SEMs of PUUSD100L1 was taken before and after phenol permeation as shown in Figure 4. As can be seen, the pore dimension became larger after phenol permeation (Table I).

As mentioned in the membrane preparation section, LiCl was mixed in the reaction mixture prior to casting of the film and the moisture-cured films were treated with hot water to leach out LiCl from the polymer matrices. During permeation, LiCl remained in the



(a)



(b)

Figure 4 Scanning electron micrographs of PUUSD100L1 membranes (a) before phenol permeation and (b) after phenol permeation.

TABLE II
Comparison of Phenol Flux for Porous and Nonporous Membranes

Phenol conc. in feed (%)	Temperature ($^{\circ}\text{C}$)	Phenol flux with PUUSD100 ($\text{g m}^{-2} \text{h}^{-1}$)	Phenol flux with PUUSD100L1 ($\text{g m}^{-2} \text{h}^{-1}$)
3	30	2.24	2.81
	45	4.49	6.02
	60	7.65	11.89
5	30	4.56	6.88
	45	7.66	13.81
	60	14.10	24.10
7	30	5.47	12.85
	45	10.18	22.41
	60	17.30	33.95

membrane (not leached out before) gets dissolved in the permeating water, thereby increasing the porosity of the membrane. LiCl washed away from the pore surfaces may be responsible for increase in size of the pores after phenol permeation.

Pervaporation experiments were performed with both nonporous (PUUSD100) and porous (PUUSD100L1) membranes at various temperatures and feed solutions containing 3, 5, and 7 wt % phenol, respectively. Before pervaporation experiments, the membranes were immersed in the phenol–water solution of same composition as that of the feed mixture at room temperature for 24 h. During this time, the membrane material came to equilibrium with the solution. As can be seen from Table II, the LiCl modification of polyurethaneurea membrane increases the phenol flux substantially and about a twofold increase in phenol flux was obtained at 60°C with 7 wt % phenol solution as feed. Experiments were also carried out with 2% LiCl-modified polyurethaneurea (PUUSD100L2) membrane and the results obtained are reported in Table III. It is evident from this table that with 2% LiCl modified membrane the total flux as well as phenol flux increase over that of 1% LiCl-modified membrane. The separation factor of phenol, however, decreases with increase in porosity of the membrane.

Study of the diffusion parameters

Pervaporation process consists of three steps, sorption, diffusion, and permeation. Sorption and permeation are very fast processes compared to diffusion, and hence diffusion is the controlling factor in pervaporation process. It is, therefore, necessary to measure the diffusion coefficient to explain the pervaporation process.

Experiments were carried out to measure the various diffusion parameters with 1% LiCl modified PUUSD100 membrane and with varying phenol feed

TABLE III
Pervaporation through Modified PUUSD100 Membranes

Phenol in feed (wt %)	Phenol conc. in permeate (wt %) with		Total flux (g m ⁻² h ⁻¹) with		Phenol Flux (g m ⁻² h ⁻¹) with		Separation Factor (α _p) obtained with	
	A	B	A	B	A	B	A	B
3	78.58	63.44	28.35	28.92	22.28	18.35	118.7	56.0
5	91.68	80.94	40.08	43.61	36.74	35.30	209.0	80.7
7	97.12	91.22	46.06	51.21	44.73	46.72	446.8	138.2

Conditions: temperature, 75°C; A: 1% LiCl-modified PUUSD100 membrane; B: 2% LiCl-modified PUUSD100 membrane.

concentrations at different temperatures. The value of average diffusion coefficient (D_m) was calculated from the slope of a plot of relative weight gain $(M_t/M_\alpha) \times l$ against $t^{1/2}$ following the sorption equation:¹⁷

$$\frac{M_t}{M_\alpha} = 4 \left[\frac{Dt}{\pi l^2} \right]^{1/2} \quad (7)$$

where, M_t and M_α are fractional weight gains of sample at time t and at equilibrium, respectively, and l is the initial sample thickness. The measured value, D_m , was edge-corrected following the known method¹³ to get the near actual diffusion coefficient (D_a). A fresh polymer sample was immersed in solution containing 3% phenol (by weight) in a stoppered conical flask kept at the specified temperatures in an oven. The sample was taken out from the flask from time to time to measure the weight and returned to the system within 30–40 s to avoid incorporation of errors due to solvent evaporation. The same experiment was repeated for 5 and 7% phenol (by weight) solutions. Figure 5 shows

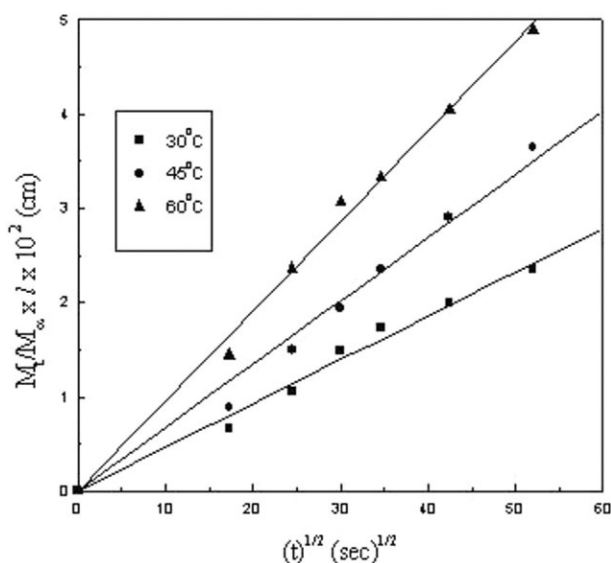


Figure 5 Variation of $(M_t/M_\alpha) \times l$ for PUUSD100L1 membrane with square root of time at different temperatures in 5 wt % phenol solution.

a plot of $(M_t/M_\alpha) \times l$ versus $t^{1/2}$ for 5 wt % phenol solution. Similar plots were obtained with 3 and 7 wt % phenol solutions. The diffusion coefficient was calculated from the slopes of those plots and is reported in Table IV.

Effect of feed phenol concentration

As can be seen from Table IV, the diffusion coefficient increases with increase in feed phenol concentration. The increase in diffusion coefficient with increase in phenol concentration can be explained by taking into account the hydrophobic nature of the membrane. The polybutadiene group present in the membrane is responsible for the hydrophobic nature of membrane. As the polyurethaneurea membrane is hydrophobic in nature, the interaction between the membrane matrix and phenol is higher than that of water. Increase in phenol concentration of the feed solution increases this interaction between phenol and the membrane matrix. Consequently, diffusion coefficient increases as the feed phenol concentration increases.

The permeability of phenol in the membrane, which is defined as the product of diffusion coefficient of phenol and partition coefficient of phenol, also increases with feed phenol concentration as both diffusion coefficient and partition coefficient increase with phenol concentration in the feed solution (Table IV).

Effect of temperature

The effect of feed temperature on diffusivity and permeability of phenol was studied in the temperature range of 30–60°C. As can be seen from Table IV, increase in feed temperature increases the diffusivity of phenol. At higher temperature, the folded chains of polyurethaneurea membrane becomes unfolded and consequently some free space is generated in the membrane matrix. The penetration of phenol becomes higher through the free space generated in the hydrophobic polyurethaneurea membrane at higher temperature. Thus, the sorptivity of the membrane increases with increase in temperature. Moreover, both the glass transition (T_g) and melting transition (T_m) of PB lie

TABLE IV
Diffusion Coefficients and Permeability of Phenol in 1% LiCl-modified PUUSD100 Membrane

Phenol in feed (wt %)	Temperature (°C)	Diffusion coefficient (cm ² s ⁻¹)		Permeability, <i>P</i> (10 ⁷ cm ² s ⁻¹)
		<i>D_m</i> (10 ⁷)	<i>D_a</i> (10 ⁷)	
3	30	1.72	1.24	33.72
	45	4.47	2.83	78.19
	60	14.89	9.08	254.46
5	30	4.22	3.21	87.72
	45	8.87	6.26	172.91
	60	17.87	12.28	344.0
7	30	7.9	5.52	150.7
	45	18.65	10.83	298.91
	60	22.67	13.93	389.93

well below room temperature (T_{gr} -86°C; T_{mr} -20°C). Therefore, at the operating temperature, the segmental mobility of PB would be expectedly higher, increasing the free volume, favoring diffusion and sorption. The permeability of phenol, therefore, increases with feed temperature as both the diffusion coefficient and sorptivity increase with temperature.

Activation energy for diffusion

The effect of temperature on diffusion coefficient can be described by the Arrhenius equation:

$$D = A_D \exp(-E_D/RT) \quad (8)$$

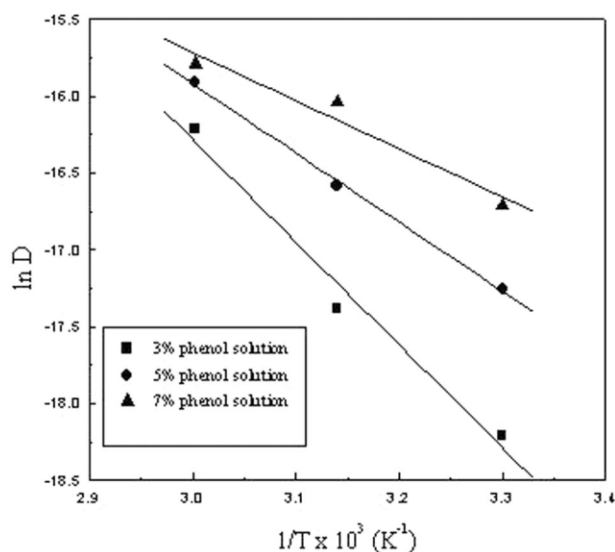


Figure 6 Arrhenius plots for diffusion coefficient of phenol in 1% LiCl-modified PUUSD100 membrane at different feed concentrations.

where E_D is the activation energy for diffusion. The activation energy for diffusion can be measured by plotting $\ln D$ against $1/T$ as shown in Figure 6.

Similarly the effect of temperature on permeability can be described by van't Hoff-Arrhenius equation:

$$P = A_p \exp(-E_p/RT) \quad (9)$$

where E_p is the activation energy for permeation. The activation energy for permeation can be measured by plotting $\ln P$ against $1/T$ as shown in Figure 7.

The values of activation energies for diffusion and permeation are given in Table V. It is clear from this table that with increase in phenol feed concentration, activation energy for diffusion as well as that for per-

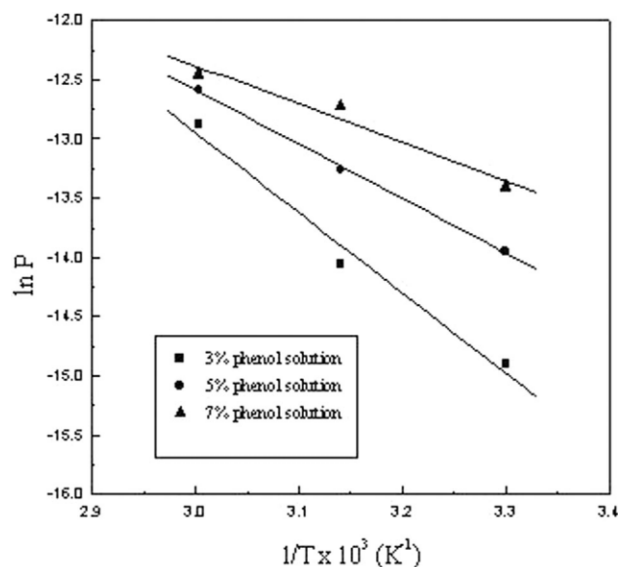


Figure 7 van't Hoff-Arrhenius plots for permeation of phenol in 1% LiCl-modified PUUSD100 membrane at different feed concentrations.

TABLE V
Activation Energy for Diffusion and Permeation of Phenol through 1% LiCl-modified PUUSD100 Membrane

Phenol in feed (wt %)	Activation energy of diffusion (E_D) (kJ mol ⁻¹)	Activation energy of permeation (E_P) (kJ mol ⁻¹)	Enthalpy of diffusion ($\Delta H = E_P - E_D$) (kJ mol ⁻¹)
3	55.53	56.24	0.71
5	37.46	38.16	0.69
7	26.15	26.84	0.69

meation of phenol decreases. This is due to phenol permselectivity of hydrophobic HTPB membrane. As activation energy denotes the difficulty of diffusion, we can say that with increase in phenol concentration, it becomes easier for phenol to diffuse, which is expected.

Enthalpy of diffusion, which can be calculated by subtracting activation energy of diffusion from activation energy of permeation, is also tabulated in Table V. As can be seen from this table, the change in enthalpy of diffusion is almost negligible with change in feed phenol concentration.

Penetrant transport mechanism

In liquid penetration experiment, where a penetrant front advancing into the polymer is observed, a simple descriptive way to quantify the penetration rate is by using the relationship:^{18–20}

$$M_t/M_\alpha = kt^n \quad (10)$$

where k is a constant, called rate constant of penetration, which depends on the structure of the polymer and its interaction with solvent. The magnitude of the Fickian index, n , denotes the transport mode. For the Fickian mode of transport, the rate of polymer chain relaxation is higher compared to the diffusion of the

penetrant, and the corresponding value appears very close to 0.5. From the plot of $\ln(M_t/M_\alpha)$ against $\ln t$ for various temperatures at different phenol feed concentrations, the rate constant of penetration and Fickian index obtained are presented in Table VI. It can be inferred from Table VI that with low feed phenol concentration and at low temperature, transport follows non-Fickian mechanism, whereas for high feed phenol concentration, the transport mechanism becomes closer to Fickian mode because of higher polymer chain relaxation (increased swelling).

Study of pervaporation parameters

Effect of phenol concentration

The results of the pervaporation experiments show that the total flux as well as the phenol flux increases with increase in feed phenol concentration at a constant temperature. The phenol flux increases from 8.32 to 33.95 g m⁻² h⁻¹ by increasing phenol feed concentration from 1 to 7% at 60°C for 1% LiCl modified membrane. It increases from 7.35 to 34.54 g m⁻² h⁻¹ by increasing phenol feed concentration from 1 to 7% at 60°C for 2% LiCl-modified membrane. These results are shown in Figure 8.

TABLE VI
Penetration Parameters in 1% LiCl-Modified PUUSD100 Membrane

Phenol in feed (wt %)	Temperature (°C)	Rate constant of penetration, k (10 ² min ⁻ⁿ)	Fickian index (n)
3	30	1.73	0.62
	45	1.97	0.62
	60	3.92	0.56
5	30	3.69	0.57
	45	4.63	0.56
	60	6.27	0.54
7	30	3.78	0.57
	45	4.41	0.55
	60	5.33	0.54

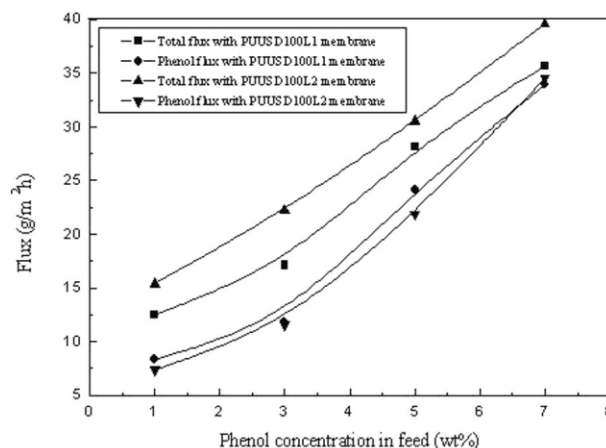


Figure 8 Effect of phenol concentration in feed on various fluxes at 60°C with modified polyurethaneurea membranes.

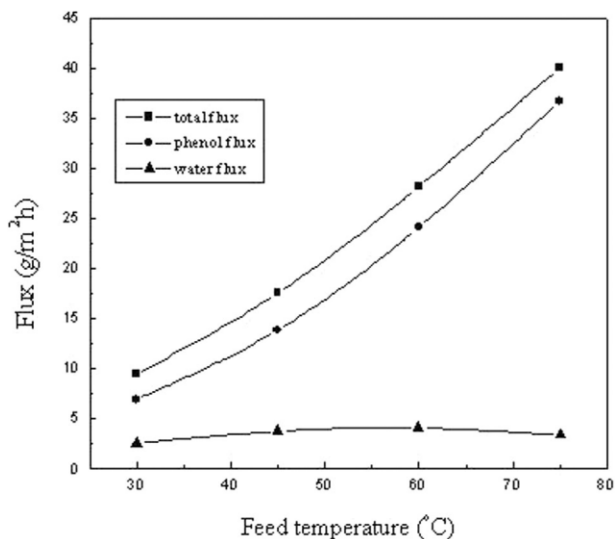


Figure 9 Effect of feed temperature on flux using PUUSD100L1 membrane with 5% phenol solution as feed.

The increase in phenol flux with increase in phenol feed concentration can be explained by the increase in diffusion coefficient with increasing phenol concentration as discussed earlier.

Effect of temperature

The results of pervaporation experiments show that the total and the phenol fluxes increase with increase in temperature at constant feed phenol concentration. The variation of flux with temperature is shown in Figure 9 for 1% LiCl-modified membrane. The feed temperature is the driving force for faster permeation through membrane. Temperature not only increases

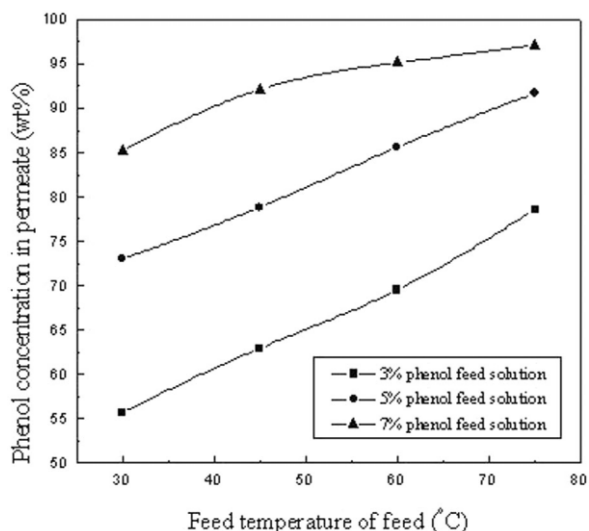


Figure 10 Effect of feed temperature on phenol concentration in permeate using PUUSD100L1 membrane.

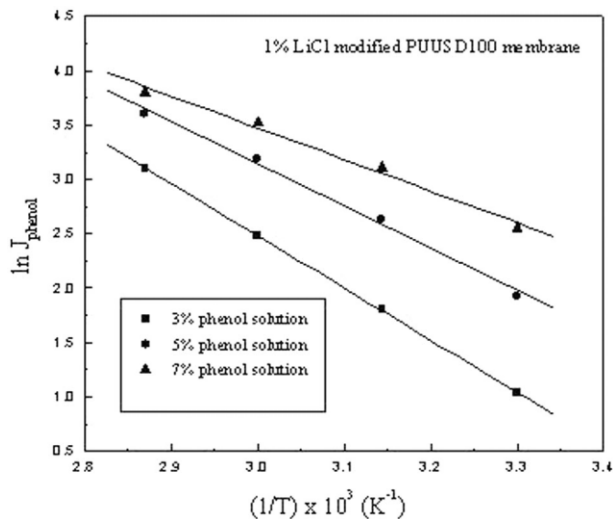


Figure 11 Arrhenius plots for phenol flux at different feed concentrations.

diffusion coefficient, but it also makes the pervaporation process faster.

Figure 10 shows the effect of feed temperature on phenol concentration in permeate at various feed phenol concentrations. It is evident from this figure that the phenol concentrations in permeate increase with feed phenol concentration as well as the temperature.

Activation energy for pervaporation

The temperature dependence of pervaporation can be expressed by Arrhenius equation:

$$J_i = J_{i0} \exp(-E_{Perv}/RT) \tag{11}$$

where E_{Perv} is the activation energy for pervaporation. The value of activation energy for pervaporation can be evaluated by plotting $\ln J_i$ against $1/T$. The plot of $\ln J_{phenol}$ versus $1/T$ for 1% LiCl-modified PUUSD100 membrane is shown in Figure 11. A similar plot was made for 2% LiCl-modified PUUSD100 membrane. The values of activation energy of pervaporation obtained from these plots are tabulated in Table VII. We can see that the activation energy decreases with the increase in phenol feed concentration. This indicates

TABLE VII
Activation Energy for Pervaporation

Phenol in solution (wt %)	Activation energy ($E_{Perv.}$) (kJ mol ⁻¹)	
	1% LiCl-modified PUUSD100	2% LiCl-modified PUUSD100
3	39.90	30.57
5	32.42	28.96
7	24.22	22.83

TABLE VIII
Boundary Layer Resistance of 3% Phenol Conc. Feed in 1% LiCl-Modified PUUSD100 Membrane

Temperature of feed (°C)	Membrane resistance, $l/P \times 10^{-3}$ (h m ⁻¹)	Overall resistance, $1/k_{ov} \times 10^{-3}$ (h m ⁻¹)	Boundary layer resistance, $1/k_L \times 10^{-3}$ (h m ⁻¹)
30	3.29	9.61	5.03
	4.12	10.18	
	4.53	11.41	
45	1.42	5.45	3.22
	1.77	5.86	
	1.95	6.32	
60	0.43	3.26	2.08
	0.54	3.48	
	0.60	3.71	

the ease of pervaporation with increasing phenol concentration. Another important observation is the decrease in activation energy with increase in the amount of LiCl, the pore-forming agent. This indicates that pervaporation becomes easier with increase in porosity.

Resistance-in-series model

The concentration polarization effect is taken into account in the resistance-in-series model. Resistance-in-series model predicts two resistances acting in series, the membrane resistance and the fluid-membrane boundary layer resistance. The boundary layer resistance ($1/k_L$) was evaluated from the plot of overall resistance ($1/k_{ov}$) against membrane resistance (l/P_i) as given in Table VIII. The intercept values from the plots are the boundary layer resistance ($1/k_L$). Since in all cases, an intercept was obtained, the existence of boundary layer and its resistance was proved. From Table VIII, we can see that the boundary layer resistance value decreases with increase in temperature.

CONCLUSIONS

Porous and nonporous polybutadiene-based polyurethaneurea membranes show high phenol selectivity in pervaporation process. A separation factor as high as 447 was obtained for phenol when the separation was carried out at 75°C with 7% phenol solution and 1% LiCl-modified polyurethaneurea membrane. Porous membrane produces higher flux over that of nonporous one, hence the former is better suitable for the treatment of industrial wastewater containing phenol. The low membrane boundary resistance in case of porous membrane signifies that it facilitates phenol permeation. The activation energy for phenol permeation through porous membrane was found to decrease with increase in feed phenol concentration. The

boundary layer resistance for the pervaporation process was calculated according to the resistance-in-series model and it was found to decrease with temperature.

References

1. Uramoto, H.; Kawabata, N.; Teramoto, M. *J Membr Sci* 1991, 62, 219.
2. Roy, S. K.; Sawant, S. B.; Joshi, J. B.; Pangarkar, V. G. *Sep Sci Technol* 1997, 32, 2669.
3. Pereira, C. C.; Habert, A. C.; Nobrega, R.; Borges, C. P. *J Membr Sci* 1998, 138, 227.
4. Lipnizki, F.; Hausmanns, S.; Ten, P. K.; Field, R. W.; Laufenberg, G. *Chem Eng J* 1999, 73, 113.
5. Boddeker, K. W.; Bengstone, G.; Bode, E. *J Membr Sci* 1990, 53, 143.
6. Hoshi, M.; Kogura, M.; Satioh, T.; Nakagawa, T. *J Appl Polym Sci* 1997, 65, 469.
7. Lee, L. T.; Ho, W. S.; Liu, K. J. U.S. Pat. 3,956,112 (1976).
8. Ohst, H.; Hildebrand, K.; Dhein, R. In *Proceedings of the 5th International Conference on Pervaporation Process in the Chemical Industry*; Bakish, R., Ed.; Bakish Material: Englewood, NJ, 1991; p 7.
9. Han, S.; Ferreira, F. C.; Livingston, A. *J Membr Sci* 2001, 188, 219.
10. Jonquiere, A.; Roizard, D.; Cuny, J.; Vicherat, A.; Lochon, P. *J Appl Polym Sci* 1995, 56, 1567.
11. Jonquiere, A.; Roizard, D.; Lochon, P. *J Membr Sci* 1996, 118, 73.
12. Lai, J.-Y.; Tseng, C.-W.; Huang, S.-L. *J Polym Res* 1994, 1, 361.
13. Schauer, J.; Bartz, D.; Marousek, V. *Angew Makromol Chem* 1999, 268, 41.
14. Schuker, R. C. U.S. Pat. 4,921,611 (1990).
15. Ho, W. S. W.; Sartori, G.; Thaler, W. A.; Ballinger, B. H.; Dairymple, D. C.; Mastondron, R. P. U.S. Pat. 5,028,685 (1991).
16. Gupta, T.; Pradhan, N. C.; Adhikari, B. *J Membr Sci* 2003, 217, 43.
17. Crank, J. *The Mathematics of Diffusion*; Clarendon: Oxford, 1956; p 248.
18. Shanthamurthy, U.; Aminabhavi, T. M.; Cassidy, P. E. *J Membr Sci* 1990, 50, 225.
19. Frason, N. M.; Peppas, N. A. *J Appl Polym Sci* 1983, 28, 1299.
20. Chiou, J. S.; Paul, D. R. *Polym Eng Sci* 1986, 26, 1228.