Separation of Phenol–Water Mixture by Membrane Pervaporation Using Polyimide Membranes

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ABSTRACT: Separation of components of aqueous waste streams containing organic pollutants is not only industrially very important but also is a challenging process. In this study, separation of a phenol–water mixture was carried out by using a membrane pervaporation technique with indigenously developed polyimide membranes. The membranes were found to permeate water selectively. The total flux as well as that of the individual components were measured. The effect of lithium chloride modification of polyimide film on total flux was investigated. The total flux obtained with 2% lithium chloride modification was about 3.6 times higher than that obtained with virgin membrane. The effects of different parameters such as feed composition and temperature on flux, and separation factor were determined. With modified membrane, a separation factor as high as 18.0 was obtained for water at 27°C and with 8.0 wt % phenol solution. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 822–829, 2002

Key words: pervaporation; polyimide membrane; wastewater treatment; phenol–water mixture; separation factor; selectivity

INTRODUCTION

The separation of liquid mixtures (aqueous–organic and organic–organic) by using polymeric membranes is widely used in industry because it offers several advantages over the conventional processes. Major advantages of the membrane separation processes include: high product recovery, low-energy consumption, and easy process design. Pervaporation, which is one of the membrane-separation processes, has been used for alcohol dehydration, organic solvent separation from dilute aqueous solution, and recovery of useful aroma compounds.[1–4] The present work was concerned with the separation of an aqueous–organic mixture by membrane pervaporation.

Aqueous waste streams from different industries such as chemical, petrochemical, polymer, dyes, electronic, pesticide, and so forth contain some toxic organic pollutants. Aqueous waste streams containing phenols are discharged by some of these industries because phenol is used as a raw material for the synthesis of phenolic resin, bisphenol-A, caprolactum, alkyl phenols, and other chemicals. A large quantity of wastewater containing phenol is generated during production of these chemicals and its effective disposal is highly desired. A very effective disposal option may involve separation of the components of the mixture by a suitable technique. The present work was undertaken to separate phenol–water mixtures by membrane pervaporation. Because the separation characteristics of pervaporation in terms of flux and separation factors are both

theoretically and experimentally better than those of other membrane processes, such as reverse osmosis,[5,6] the pervaporation separation technique was chosen in this study.

Depending on the membrane material used, the separation of an aqueous–organic binary mixture by pervaporation may be directed at the selective removal of water or at the selective removal of organic compound from the feed. The removal of organic compound from wastewater by pervaporation, in general, requires elastomeric polymers, whereas other amorphous polymers preferentially permeate water. In the former case, among the most widely used membrane materials are polydimethylsiloxane (PDMS), cellulose acetate, crosslinked polyvinyl alcohol (PVA), copolymers of styrene and styrene derivatives, and polyether block amides (PEBA).[7–13] For preferential water permeation some widely used polymers are polyethylene, polypropylene, polyethylene terepthalate (PET), and polyimides.[14–16] The present work was concerned with the separation of an aqueous phenol solution by a water-selective pervaporation process using a polyimide membrane.

Several investigators have studied the separation of phenol–water mixtures by membrane pervaporation.[6,7,10,17–19] Pervaporation of a 5 wt % aqueous phenol solution with PEBA membranes has been reported to yield a permeate containing 80 wt % phenol.[6,7] Rhim et al.[10] studied pervaporative separation of a water–phenol mixture using PVA-crosslinked membranes with low molecular weight poly(acrylic acid). The membrane has been reported to permeate water selectively with a separation factor of 3580. Polyurethane membranes have also been used successfully in separating phenol from dilute aqueous streams.[17–19] The phenol-selective polyurethane membrane prepared by the polyaddition of 1,6-diisocyanatohexane and polytetramethylene glycol has been reported to give a permeate solution containing 65 wt % phenol from a feed solution containing only 7 wt % phenol.[17] The present work was undertaken to develop a water-selective pervaporation process for the separation of aqueous phenol solutions with phenol concentrations from 2.0 to 8.0 wt % by using a polyimide membrane developed in our laboratory.

EXPERIMENTAL

Materials

Phenol, 4-amino antipyrine, ammonium chloride, liquor ammonia, *N,N*-dimethyl formamide (DMF),

and potassium ferricyanide used in this study were obtained from E-Merck (India) Ltd. (Mumbai, India) and were of GR grade. Aqueous phenol solutions were made by dissolving different amounts of phenol in distilled water. The polyimide film was prepared from 4,4′-oxydianiline (ODA) [Fluka Chemie, Buchs, Switzerland] and benzophenone tetracarboxylic dianhydride (BTDA; Gulf Oil Corp., TX) in DMF medium.

Membrane Preparation

Polyimide film was prepared from poly(amic acid) by film casting. The required poly(amic acid) was synthesized in the laboratory at low temperature by the following procedure.[20] At first, 1.2700 g of ODA was dissolved in 10 mL of DMF in a three-necked round-bottom flask fitted with a guard tube, nitrogen inlet, thermometer, and a stirrer. The flask was kept on an oil bath maintained at about 0–10°C. Then in three to four installments 2.0422 g of BTDA was added to the flask. Finally, 14.3 mL of DMF was added to the flask to get a 12% (w/v) poly(amic acid) solution. The reaction mass was slowly stirred for 3 h. The reaction resulted in a clear, viscous solution of poly(amic acid), which was stored in a refrigerator before use.

Film Casting

Before film casting, 12 mg of lithium chloride (LiCl) was dissolved in 5 g of poly(amic acid) solution. LiCl was used as the pore-forming agent because it is highly soluble in DMF, so that it can be uniformly mixed with the poly(amic acid) solution. It is also highly soluble in water and, therefore, very easy to remove from the cast membrane by dipping into water, thereby leaving pores on the membrane. A 30-μm-thick film was cast from the prepared solution on a glass plate. The film was then dried by first heating at 40°C for 1 h and then at 50°C for 1 h in vacuum. Next the film was imidized (cyclodehydrated) by subsequent heating in an oven at elevated temperatures according to the time schedule shown in Figure 1. As a general method, others have followed a heating cycle of 1 h at 100°C, followed by 1 h at 200°C, followed by 1 h at 300°C.[21] In another report, heating at 230 to 250°C for 10 min was mentioned for obtaining >99% imidization.[22] The heating schedule used in this investigation may not be rigidly followed to obtain a membrane with desirable separation characteristics. The last part of
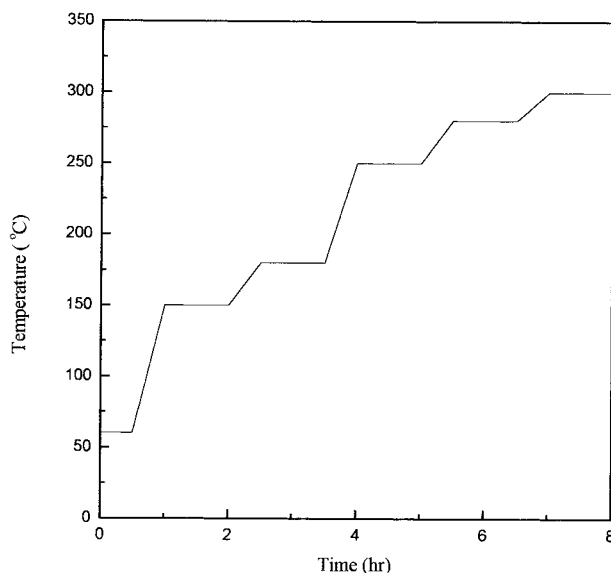
Figure 1 Heating schedule for curing of polyimide films.

the heating cycle, however, is very important for complete imidization and obtaining a membrane of sufficient strength to withstand the vacuum applied during the pervaporation study.

Characterization of Poly(amic acid) and the Film

The inherent viscosity of the synthesized poly-(amic acid) was measured at 30°C using a Ubbelhode suspended level viscometer. The polyimide film was characterized by density measurement, IR spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM) of the film surface and torn edge. IR spectra were recorded on a Shimadzu 270 spectrophotometer (Shimadzu, Japan). The X-ray diffraction pattern was recorded with a Phillips PW 1729 X-ray generator (Phillips, The Netherlands) using a Co target (λ = 1.79Å) at a scanning speed of 3°/min, and data were recorded every 0.02° ($=2\theta$) for the angular range of 10−40° ($=2\theta$). SEM was carried out for the films by using a JEOL JSM 5800 instrument (JEOL, Peabody, MA).

Lithium Chloride Leaching from the Film

Lithium chloride, which was used for modification during film casting, was removed from the film surface and film matrix by immersing the films in boiling water for 1 h.

Estimation of Phenol

The phenol in both the feed solution and the permeate was estimated by the colorimetric method.

For this, standard solutions of 4-amino antipyrine, ammonium chloride, and potassium ferricyanide were prepared. First, 1, 2, 3, 4, and 5 mL of standard phenol solution containing 0.01 mg phenol/mL of solution were introduced, respectively, into five test tubes. Then 5, 4, 3, 2, and 1 mL of distilled water were added to the test tubes. In another test tube, only 6 mL of distilled water was added. Then 2 mL of ammonium chloride solution and 0.7–1.0 mL of concentrated ammonia solution were added to each tube to make the pH around 10. Then 2 mL of 4-amino antipyrine and finally 2 mL of potassium ferricyanide solutions were added and the solutions were mixed thoroughly. A red color of increasing brightness was developed with increasing concentration of phenol. The absorbance of the colored solutions was measured by UV–vis spectrophotometer at a wavelength of 510 μm with respect to the blank (containing no phenol solution) and a calibration curve was prepared.

Experimental Setup

The experimental setup consisted of a pervaporation cell, a thermostat, a condenser-*cum*-collector, cryostat, manometer, and vacuum pump, as shown in Figure 2. The pervaporation cell consisted of a flanged feed chamber, a sintered stainless-steel plate for supporting the membrane, and a flanged permeate chamber. The feed chamber of the cell was provided with a stirrer and a thermometer pocket for measuring the temperature of the feed mixture. Hot water was circulated through the jacket of this chamber from a thermostat to maintain the temperature of the feed mixture at a desired value. The bottom of the permeate chamber was connected to a condenser-*cum*-collector, which was kept dipped in a cryostat. Although the permeate chamber shown in Figure 2 was also jacketed, refrigerated liquid was not circulated through this jacket in the present study. A vacuum pump was connected to the collector along with a manometer for measuring the downstream pressure.

Experimental Procedure

The membranes used in this study were conditioned before use in the pervaporation experiments. Each membrane was kept immersed in a phenol–water mixture of specified composition at room temperature for 24 h. During this period, the membrane material reached equilibrium with
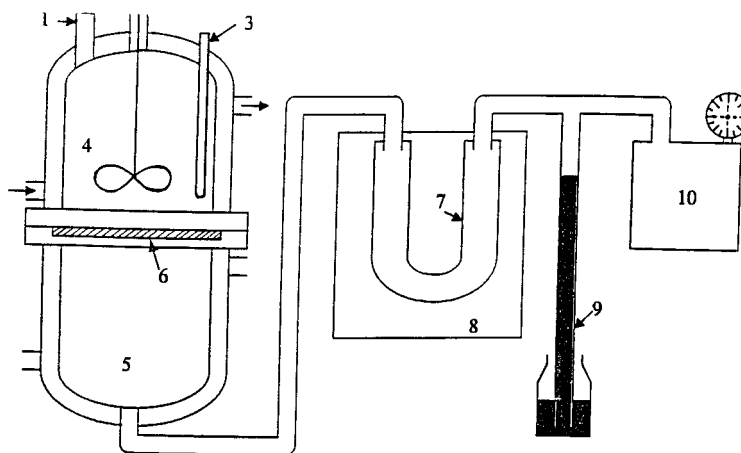
1: Feed inlet; 2: Stirrer; 3: Thermometer pocket; 4: Feed chamber; 5: Permeate chamber; 6: Sintered SS disk; 7: Condenser-cum-collector; 8. Cryostat; 9: Manometer; 10: Vacuum pump

Figure 2   Sketch of the experimental setup.

the liquid mixture. The membrane was then wiped dry and used in the experiments.

For most of the experiments, two specimens of the membrane were tested with almost identical results. Moreover, most of the experiments were repeated to check the reproducibility, which was >98%. The standard deviations of the results were in the range of 0.01 to 2.2×10^{-5}.

In a typical experiment, about 100 mL of the feed mixture of known composition was introduced into the feed chamber. After the feed was heated to the desired temperature, the condenser was connected to the permeate chamber and vacuum was applied to maintain the pressure in the permeate chamber at around 260 mmHg. After a certain time, the condensate collected in the condenser-*cum*-collector was weighed and analyzed for its composition. The experiment was repeated thrice under each condition and it was confirmed that the flux and the concentration of phenol and water in the permeate liquid were constant. The flux was calculated from the following equation:

$$Q = W/(At)$$

where Q is the flux in kg m^{-2} h^{-1}, W is the weight of permeate collected in kg, A is the effective membrane area in m^2, and t is the measuring time in h. The separation factor (α_{water}) is expressed as

$$\alpha_{\text{water}} = (Y_w/Y_p)/(X_w/X_p)$$

where Y and X are the weight percentage concentrations of components in permeate and feed, respectively. Subscripts w and p represent water and phenol, respectively.

RESULTS AND DISCUSSION

Characterization of Films

Inherent Viscosity

The inherent viscosity of the synthesized poly-(amic acid) was 1.2 dL/g, which was sufficient to obtain good quality polyimide film after thermal cyclodehydration.

Density Measurement

The density of the lithium chloride–modified film (1.44 g/cm^3) was slightly higher than that of the control film (1.39 g/cm^3). This increase in density resulted from the presence of some residual lithium chloride in the film matrix. Niyogi et al.[23] also observed similar behavior for lithium chloride–modified film.

IR Spectroscopy

IR spectra of the control and lithium chloride–modified polyimide films were identical. Typical absorption bands associated with the imide groups (at ~ 1720 and 1772 cm^{-1}) were observed. Other absorption bands characteristic of aromatic
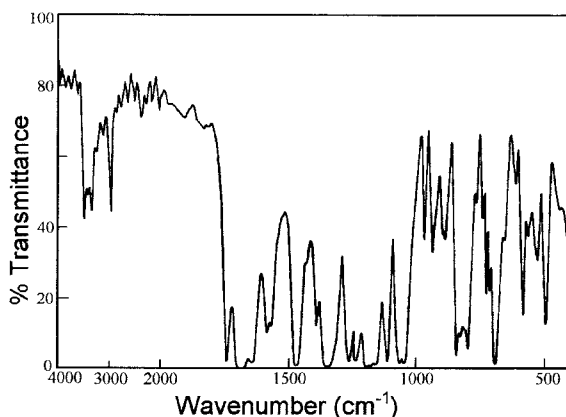
Figure 3 IR spectrum of 2% lithium chloride–modified polyimide film.

rings (1515 and 1600 cm^{-1}), C—N (1373 cm^{-1}), and C=O groups of BTDA–ODA-based films at 1671 cm^{-1} were also observed. A representative IR spectrum of lithium chloride–modified BTDA–ODA film is shown in Figure 3. This IR spectrum does not show any chemical bond formation between lithium chloride and the polyimide film, concerning which a similar observation was also made by Varma et al.[24] for metal halide–modified polyimide films.

X-ray Diffraction (XRD) Study

The X-ray diffraction pattern shows an amorphous nature for all the films.

Scanning Electron Microscopy (SEM)

The morphology of the control and lithium chloride–leached polyimide film was studied on the film surface as well as on the torn edge. The SEM micrographs [Fig. 4(a)–(d)] of lithium chloride–modified film indicate some surface grooves/pits on the air side of the film resulting from the loss of LiCl by leaching with water, and the torn-edge surface [Fig. 4(d)] indicates the presence of voids. Such pores and voids are absent in the control film [Fig. 4(a)].

Pervaporation experiments were carried out with aqueous phenol solutions of varying phenol concentrations and the total flux as well as the fluxes of individual components were determined. Effects of different parameters, such as feed phenol concentration and temperature on fluxes, and separation factor for water, were studied.

Effect of LiCl on Membrane Permeability

To determine the effect of lithium chloride modification on membrane permeability, two different polyimide membranes were made, one of which was modified with 2% LiCl and the other a virgin polyimide (i.e., without LiCl). Experiments were conducted with these two different membranes and the total flux as well as the separation factor for water were determined. It can be seen from Table I that the total flux with LiCl-modified membrane is about 3.6 times higher than that of virgin membrane, although there is a decrease in separation factor by one unit resulting from LiCl modification. The higher flux with modified film is attributed to the incorporation of pores on the membrane by leaching out of lithium chloride in water. Scanning electron micrographs of both the virgin and the modified membranes clearly indicate the presence of pores and voids in the latter [Fig. 4(b)–(d)]. Because the modified membrane gave higher flux (with nominal decrease in separation factor), all other experiments were carried out with this membrane for ease of experimentation.

Effect of Downstream Pressure

The effect of permeate side pressure on membrane permeability was studied with virgin membrane at 40°C and with 5 wt % phenol solution. The downstream pressure was varied from 100 to 260 mmHg. The total flux as well as the separation factor for water were found to remain unchanged in the pressure range studied. All other experiments were carried out with a downstream pressure of 260 mmHg.

Effect of Feed Composition

Experiments were carried out with different aqueous phenol solutions having phenol concentrations in the range of 2 to 8 wt % and the total flux was noted. It can be seen from Figure 5 that the total flux increases with increasing phenol concentration in the feed solution in the range studied. The increase in flux is attributed to the increasing plasticizing effect of phenol at increasingly higher concentrations. It can also be seen from Figure 5 that the total flux increases with temperature. It is quite expected that the increase in temperature increases the diffusivities of individual components through the polymer membrane, thereby increasing the total flux.

Effect of Feed Composition on Flux of Phenol

Figure 6 shows the effect of feed phenol concentration on flux of phenol. A similar trend was observed as that with total flux. It is also evident
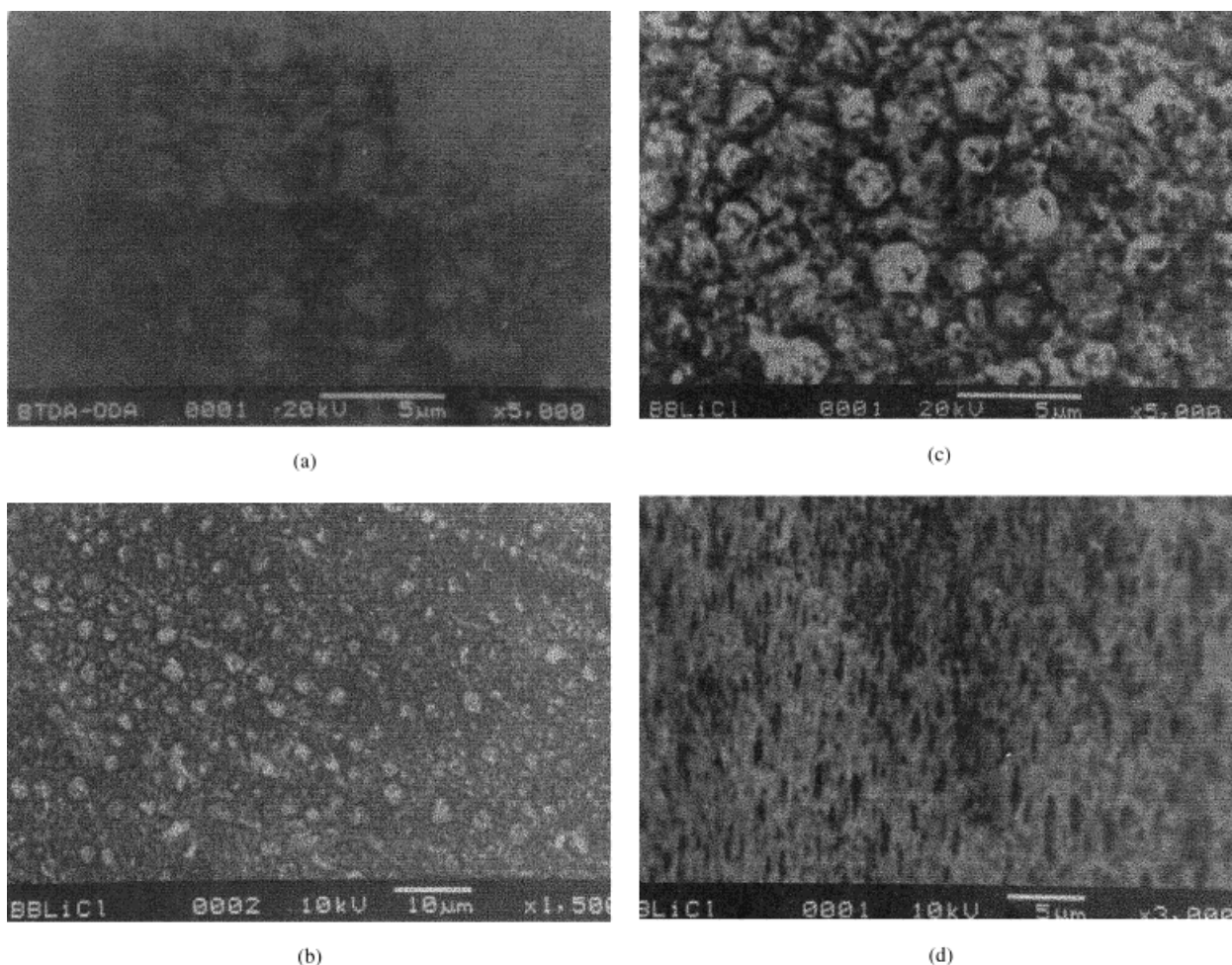
Figure 4 SEM micrographs (at indicated magnifications) of (a) control film surface (×5000); (b) lithium chloride–modified film surface (×1500); (c) lithium chloride–modified film surface (×5000); and (d) teared surface of lithium chloride modified film (×3000).

from Figure 6 that the phenol flux increases with temperature, as expected.

Effect of Temperature on Total Flux

The effect of temperature on total flux was studied in the temperature range of 27 to 50°C with different feed phenol concentrations. Figure 7 shows, in Arrhenius coordinates, the temperature dependency of total flux for 2.0, 4.0, and 6.0 wt % aqueous phenol solutions, respectively. It can be seen that the experimental data are described rather adequately by linear dependencies. From the slopes of the straight lines, overall activation energies were calculated to be 12.80, 11.75, and

Table I   Performance Comparison of Polyimide (PI) Membranes[a]

Membrane Used	Total Flux $(kg\ m^{-2}\ h^{-1})$	Phenol Flux $(kg\ m^{-2}\ h^{-1})$	Separation Factor (α_{water})
Virgin PI	0.054	2.59×10^{-4}	8.64
PI with 2% LiCl	0.1932	10.52×10^{-4}	7.61

[a] Conditions: temperature, 40°C; phenol concentration in feed solution, 4.0 wt %; permeate side pressure, 260 mmHg.
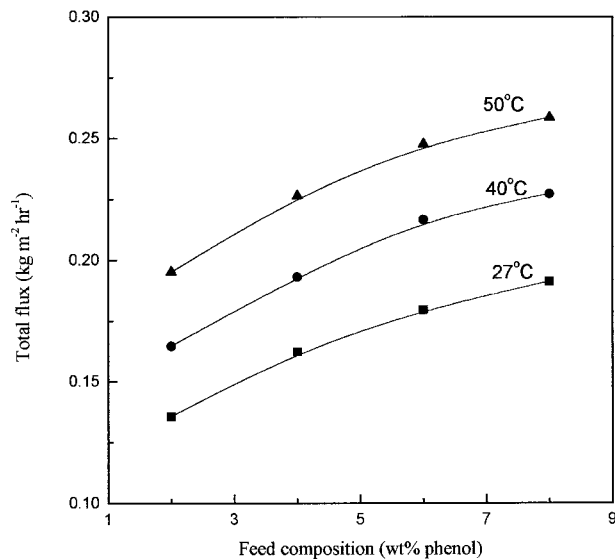
Figure 5 Effect of feed composition on total flux.

Figure 7 Effect of temperature on total flux.

11.43 kJ/mol with 2.0, 4.0, and 6.0 wt % phenol solutions, respectively. Apparent activation energies for phenol permeation were also determined in the same way and were found to be 16.43, 22.9, and 27.4 kJ/mol for 2.0, 4.0, and 6.0 wt % phenol solution, respectively. Similar activation energy values are reported in the literature for pervaporation processes.[25]

Effect of Feed Composition on Separation Factor

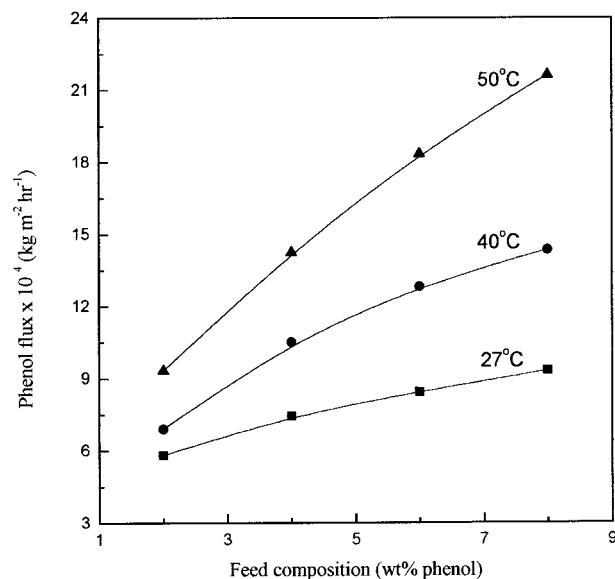The effects of feed composition as well as temperature on separation factor for water were ascer-

tained by determining the phenol concentration in the permeate. The separation factor was found to increase with increase in phenol concentration in the feed solution, as shown in Figure 8. At higher phenol concentrations, therefore, the membrane becomes more selective toward water. The separation factor, however, was found to decrease with increase in temperature, as indicated in Figure 8. This can be explained by the increase in agitational energy or motions of the polymer
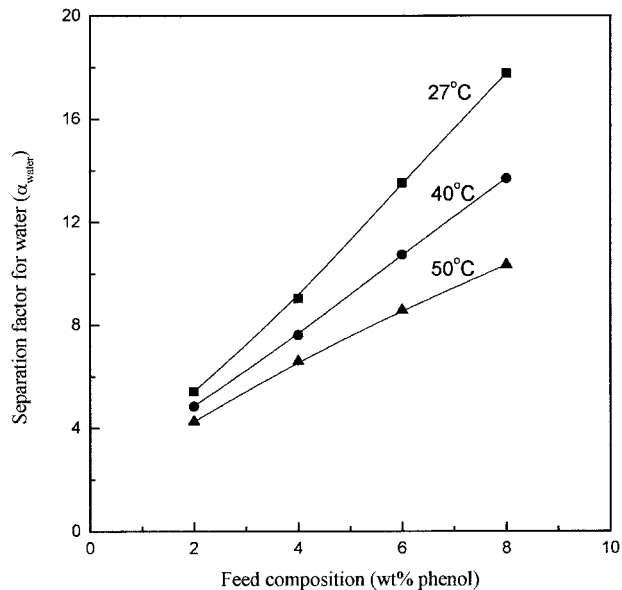

Figure 6 Effect of feed composition on flux of phenol.

Figure 8 Effect of feed composition on separation factor for water.

chains at higher temperatures. According to Eyring's hole theory of diffusion, the formation of holes in the polymer requires enough energy to break down a number of secondary valence bonds. At low temperatures there are more smaller holes than larger holes in the amorphous regions. These holes allow more water than phenol to go through, in that the size of the water molecule is smaller than that of the phenol molecule. At higher temperatures, larger holes are produced as a result of the higher agitational energy of the polymer chains. More phenol molecules can thus diffuse through the larger holes and thus the separation factor (α_{water}) decreases at higher temperatures.

CONCLUSIONS

The separation of a phenol–water mixture was carried out by membrane pervaporation using polyimide membranes. These membranes were found to permeate water more selectively than phenol and a separation factor of 18 was obtained for water at 27°C taking 8.0 wt % phenol solution as the feed. The total flux was found to increase with temperature and an apparent activation energy of 12 kJ/mol was obtained. The separation factor for water was found to decrease with temperature, which could be explained by Eyring's hole theory of diffusion.

As the membranes used in this study selectively permeate water, the following concept could be used in wastewater treatment applications. Industrial wastewater containing the phenol compound could be concentrated up to 80–90 wt % phenol by an organic-selective process, and then these concentrated phenol solutions could be handled by a water-selective process similar to that of the present study. The pure water could be produced at the down compartment of this stage and circulated for reuse.

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