



ORIGINAL ARTICLE

Separation of isopropyl alcohol–toluene mixtures by pervaporation using poly(vinyl alcohol) membrane



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Abstract The application of pervaporation for the removal of volatile organic compound has been fascinating for the last few years. This is due to the increasing level of petrochemical solvents in the environment. In this work performance of poly(vinyl alcohol) membrane was studied for the separation of isopropyl alcohol–toluene mixtures by pervaporation. Alcohol-aromatic mixtures are difficult to separate using conventional methods and pervaporation has been a promising technology in this case. Pervaporation properties of poly(vinyl alcohol) membrane for isopropyl alcohol–toluene mixtures were studied for feeds in composition of 10–40 wt. % toluene at different temperatures (i.e., 35–50 °C) and different pressures (i.e., 4–16 psi). For understanding membrane morphology Fourier transform infrared spectroscopy and scanning electron microscopic studies were performed. Membrane performance was studied by calculating flux, selectivity and pervaporation separation index. The maximum toluene content of 78% in the permeate was obtained at optimum conditions, i.e., 12 psi applied pressure, 40 °C temperature and 10 wt. % toluene in feed solution. The flux increased with increasing amount of toluene in the feed, but selectivity decreased reasonably.

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1. Introduction

Pervaporation separation is a widely accepted membrane technology for the dehydration of organic liquids in various indus-

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trial processes (Park et al., 1994). Membrane separation processes are considered as cost effective and energy saving methods as compared to conventional processes such as distillation or adsorption to carry out separation of desired components from mixtures (Baker, 2004; Chovau et al., 2010; Porter, 1990; Qiao et al., 2005). Reverse osmosis (Chong et al., 2008; Porter, 1990), nanofiltration (Toh et al., 2008), ultrafiltration (Kwon et al., 2008; Porter, 1990; Shah et al., 2007), gas permeation (Chung et al., 2007; Ockwig and Nenoff, 2007) and pervaporation (Chapman et al., 2008; Shao and Huang, 2007) are considered as promising techniques in commercial applications due to their ease of operation, eco-friendliness and energy saving aspects. Separation of mixtures using

pervaporation can be divided into: (1) dehydration of aqueous-organic mixtures, (2) removal of trace volatile organic compounds from aqueous solution and (3) separation of organic–organic mixtures (Panek and Konieczny, 2007).

The success of pervaporation dehydration process depends on the following: (1) nature of membrane, (2) its structure, (3) physical state, (4) diffusion properties of feed components, and (5) membrane selectivity (Sairam et al., 2006). The transport mechanism of pervaporation takes place in three steps: (1) selective dissolution of liquid feed penetrates molecules into the upstream feed, (2) diffusion through the membrane and (3) desorption of permeate in vapor form at downstream surface (Lee and Hong, 1997; Sampranpiboon et al., 2000).

The first membrane material which was used for the pervaporation of water–ethanol mixture was poly (vinyl alcohol) (PVA). It was developed by Gesellschaft fur Trenntechnik of Germany in 1982 (Xiao et al., 2006). PVA membranes are popular in pervaporation dehydration process. For the separation of toluene various types of membranes, viz., poly dimethyl siloxane (PDMS) (Chovau et al., 2010), polyurethane and PDMS (Lue et al., 2010), poly(vinyl alcohol) – poly(acrylic acid) blend membrane crosslinked with varied doses of glutaraldehyde (Singha et al., 2009), mixed matrix membranes of chitosan (Patil and Aminabhavi, 2008), polyether block amide were used (Panek and Konieczny, 2008).

PVA is a highly hydrophilic polymer, and could be irreversibly adsorbed on some hydrophobic polymer surfaces (Wu et al., 2005). PVA is a non-toxic, water soluble, bio-compatible and biodegradable synthetic polymer and has better fiber-forming and highly hydrophilic properties (Jia et al., 2007). A common drawback in using PDMS membrane is the low selectivity, which is because of the large polymer free-volume pore size that exhibits limited capability to differentiate permeant diffusion rates and the plasticization/swelling effect which gives a further decrease in separation efficiency (Plate and Yampolskii, 1994; Lue et al., 2010).

Toluene is used as an octane booster in gasoline fuels used in internal combustion engines, as a coolant due to its good heat transfer capabilities in sodium cold traps used in nuclear reactor system loop and in the process of removing the cocaine from coca leaves. Toluene is used as coolant due to its good heat transfer capabilities in nuclear reactor system. It is soluble in isopropyl alcohol in all ratios. Toluene-isopropyl alcohol mixture forms an azeotropic solution at a composition of 42 wt. % toluene. Thus, its separation by simple distillation results in high energy costs. Hence we have attempted its separation by pervaporation.

From the literature survey it was observed that most of the work has been carried out on the separation of toluene–methanol and toluene–ethanol (Chovau et al., 2010; Lue et al., 2010; Panek and Konieczny, 2008; Park et al., 1994; Patil and Aminabhavi, 2008; Singha et al., 2009). To the best of our knowledge information about the use of plain PVA membrane for the separation of isopropyl alcohol–toluene mixtures is feeble.

In the present work, an attempt has been made to study the separation of isopropyl alcohol–toluene mixtures using a plain PVA membrane. Various parameters studied are flux, separation selectivity, pervaporation separation index and weight percent of toluene in permeate. Pervaporation experiments have been performed at 35, 40, 45 and 50 °C for different feed concentrations (10–40 wt. % toluene in feed).

2. Experimental

2.1. Materials

The main chemicals used are isopropyl alcohol (IPA) and toluene (purchased from Finar Chemicals, Ahmedabad, India). The chemicals used were of analytical grade (AR). Distilled water of pH 5.9 ± 0.2 , conductivity $1.0 \mu\text{S}/\text{cm}$ (Millipore, Elix, Bangalore, India) is used throughout the experiments.

2.2. Membrane

Poly(vinyl alcohol) membrane was purchased from Permionics Membranes, Vadodara, India. The membrane was used as such without further treatment. The membrane can withstand the temperature up to 80 °C, pH of 2–11 and pressure up to 60 psi.

2.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the PVA membrane were recorded on a Perkin Elmer spectrum GX range. The spectra were of 20 scans per second at a resolution of 0.15 cm^{-1} in the wavelength region of $4000\text{--}400 \text{ cm}^{-1}$ with a MIRTGS detector.

2.4. Scanning electron microscopy (SEM)

SEM studies of PVA membrane were recorded on Scanning Electron Microscope XL 30 ESEM with EDX. The studies were done by magnifying the image 1000 times.

2.5. Pervaporation experiments

The experiments were carried out using Perma®-pilot scale membrane system (Permionics Membranes, Vadodara, India) as shown in Fig. 1, which is a continuously feeding type. The pervaporation experiments were performed by employing two stainless steel pervaporation cells. The feed mixture enters the cell through the inlet opening from one side and leaves the cell through opposite side, which allows relatively higher fluid velocity parallel to the membrane surface. The effective membrane surface area is 27.34 cm^2 and the feed tank has a feed solution capacity of approximately 4000 cm^3 . First the membrane was allowed to equilibrate for about half an hour in the feed compartment at the corresponding feed concentration before performing the experiment. The experiments were carried out at 35, 40, 45 and 50 °C. Temperature of the feed mixture was maintained by a constant temp bath (Julabo Labortechnik GmbH, Germany, type: EH) through which hot water is circulated in the jacket to maintain the feed temperature. The partially vaporized form of feed solution is pumped by circulation pump (Syp Engineering Company, Mumbai, India) through upper side of the membrane which was held on a porous support between the two half cells. This is circulated over the face of the membrane with the retentate being recycled into the feed tank. After attaining the steady state, permeate vapors were collected in a trap immersed in cold water on the downstream side at fixed time intervals of 1 h. The vacuum on the downstream side of the apparatus was maintained at 0.19 psi using a vacuum pump (ILMVAC GMBH, Germany, type: LVS310Zp).

From the pervaporation data, performance of the membrane is determined in terms of total flux (J_V), separation selec-

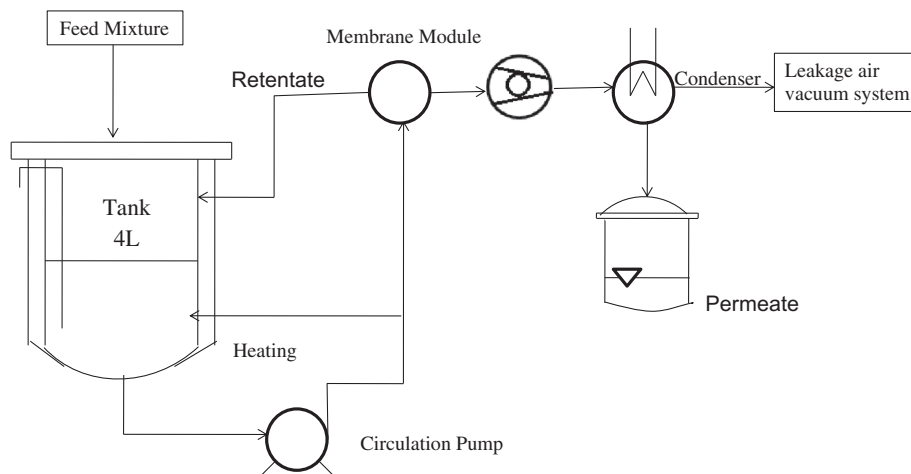


Figure 1 Schematic representation of pervaporation experimental setup.

tivity (α) and pervaporation separation index (PSI) and these were calculated, using the following equations (Panek and Konieczny, 2007):

$$J_V = \frac{V_r}{S_m t} \quad (1)$$

$$\alpha = \frac{Y_a/Y_b}{X_a/X_b} \quad (2)$$

$$PSI = J_V(\alpha - 1) \quad (3)$$

where V_r is the amount of permeate (kg), S_m is the effective membrane surface area (m^2), t is the permeation time (h), a is the amount of toluene and b is the amount of IPA, X is

the concentration of the component a or b in the feed and Y is the concentration of the component a or b in permeate.

2.6. Analysis

The samples collected were analyzed for the amount of toluene present in the sample using titration method. The sample was titrated against KOH using phenolphthalein as indicator.

3. Result and discussion

3.1. FTIR analysis

In FTIR spectrum of the PVA membrane (Fig. 2) the wide stretch located around the $3600\text{--}3200\text{ cm}^{-1}$ is for the

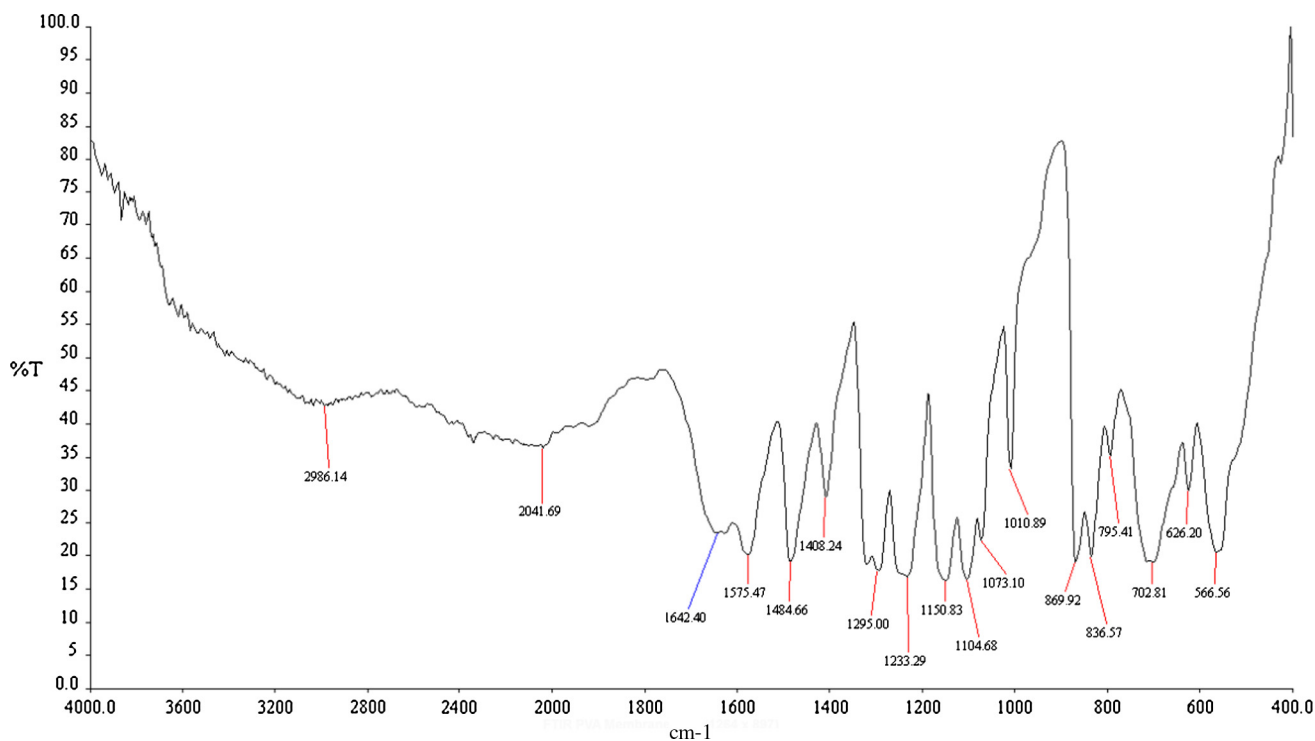


Figure 2 FTIR spectra of PVA membrane.



Figure 3 SEM image of PVA membrane.

intermolecular hydrogen bonding and the O–H stretch vibrations. The absorption for asymmetrical stretching vibrations occurs in the range of $3000\text{--}2850\text{ cm}^{-1}$, the peak at 1408.24 cm^{-1} may also be accounted for alkanes group leading to C–H scissoring and bending. Absorption in the region of $1260\text{--}1000\text{ cm}^{-1}$ is produced by C–O stretching vibration.

3.2. SEM analysis

Fig. 3 shows the micrograph of the PVA membrane, which is composed of fibrous structure. Better fibrous structure improves the performance of the membrane (Jia et al., 2007).

3.3. Effect of feed composition

The pervaporation of IPA-toluene solutions has been studied using plain PVA membrane at various feed concentrations. Fig. 4 shows the effect of toluene concentration in feed on total flux and selectivity of toluene at temperatures 35, 40, 45 and 50 °C, respectively. The results presented in Fig. 4 show that the permeate flux increases with increase of toluene concentration in feed. At higher concentrations of toluene in feed more toluene molecules come in contact with the selective layer of membrane resulting in an increase in the permeate concentration of toluene. The variation of feed concentration on selectivity of toluene is also shown in Fig. 4 and Table 1. From Fig. 4 it can be seen that as the concentration of toluene in the feed increases the selectivity decreases. This may be due to polymer free volume or various minor components present

Table 1 Pervaporation data for isopropanol/toluene mixtures using PVA membrane at 40 °C and pressure = 12 psi.

Toluene in feed (wt. %)	Toluene in permeate (wt. %)	Selectivity	PSI
10	78.16	8.35	16.01
20	75.27	7.10	14.16
30	73.86	6.59	13.38
40	71.02	5.72	12.13

in the membrane (Lue et al., 2010). Similar behavior was observed in the literature for ethanol and methanol systems (Chovau et al., 2010; Lue et al., 2010; Patil and Aminabhavi, 2008).

From the total permeation flux individual fluxes of IPA and toluene were calculated and composition obtained at various concentrations. The nature of permeate fluxes for individual components as a function of varying toluene concentration present in the feed was shown in Fig. 5. The experiments were carried out at different toluene concentrations between 10–40 wt. %, temperatures in the range of 35, 40, 45 and 50 °C, respectively, and at various pressures in the range of 4–16 psi. Best results were obtained at 12 psi which was maintained constant throughout the experiment.

The variation of IPA and toluene in permeate with concentration of toluene in feed is shown in Fig. 6. All the results were obtained by varying toluene concentration in between 10 and 40 wt. %, keeping temperature in the range of 35–50 °C and varying pressure in the range of 4–16 psi. The best results were obtained at 12 psi which was kept constant throughout the experiments. A Maximum of 80% toluene was observed in permeate at 10 wt. % toluene beyond which the value decreases.

3.4. Effect of temperature

Pervaporation experiments performed at different temperatures (35–50 °C) and feed compositions (10–40 wt. % toluene) are shown in Fig. 4. The maximum values for total flux and selectivity of the membrane obtained at 10 wt. % toluene at 40 °C are $2.18\text{ kg/m}^2\text{ h}$ and 8.35, respectively. As expected with increase in temperature both total and partial flux increase. At a higher temperature flux increases due to increased rate of diffusion. Due to increase in thermal motion of the polymer chains at higher temperatures increase in rate of diffusion is observed (Singha et al., 2009).

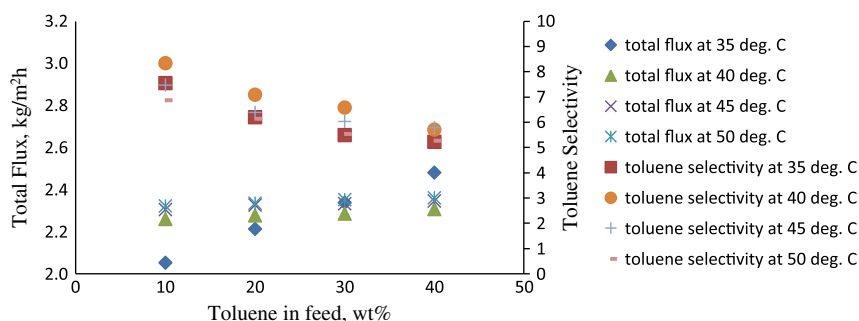


Figure 4 Effect of toluene feed concentration on total flux and toluene selectivity [Temperature: 35–50 °C and Pressure: 12 psi].

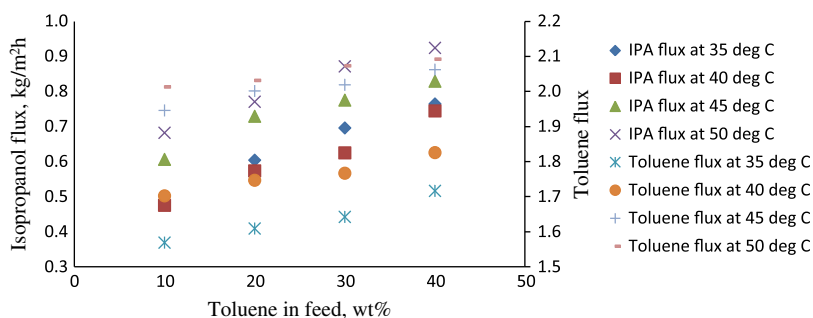


Figure 5 Effect of toluene feed concentration on IPA flux and toluene flux [Temperature: 35–50 °C and Pressure = 12 psi].

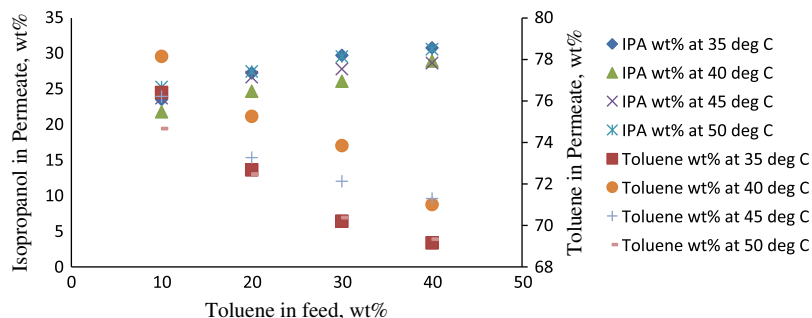


Figure 6 Effect of toluene feed concentration on IPA wt. % and toluene wt. % in permeate [Temperature: 35–50 °C and Pressure = 12 psi].

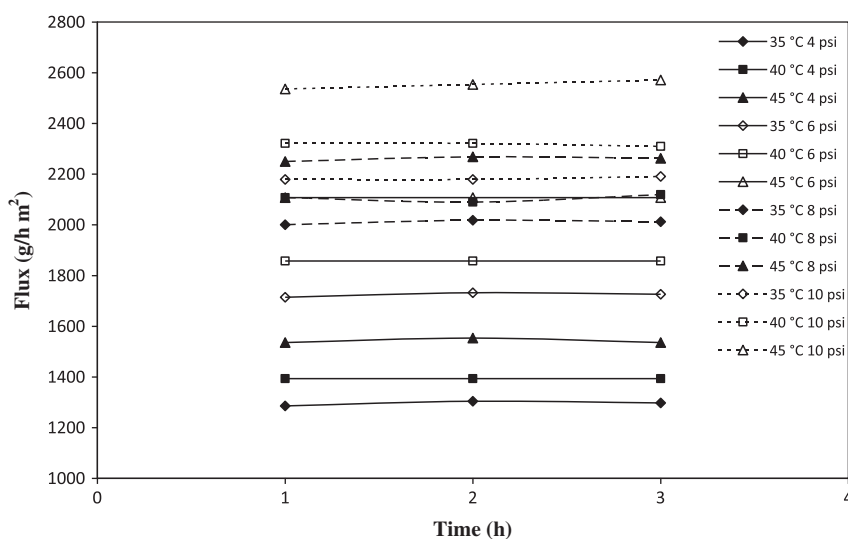


Figure 7 Effect of pressure variation and temperature on flux with respect to time.

3.5. Effect of pressure

The effect of pressure variation and temperature on flux with respect to time is shown in Fig. 7.

4. Conclusions

Separation of IPA-toluene mixtures by a plain PVA membrane has been reported. The membrane was employed at different

temperatures (35–50 °C), different toluene feed concentrations (10–40 wt. %) and different pressures (4–16 psi) for the separation but the best results were obtained at a pressure of 12 psi. The highest selectivity of 8.35 and maximum toluene content of 80% in permeate were obtained at optimum conditions (12 psi, 40 °C and 10 wt. % toluene in feed). From this study it may be concluded that as the wt. % of toluene in the mixture increases it leads to increases in the flux and decreases in the selectivity.

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