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Pervaporation of Alcohol-Aromatic Hydrocarbon Mixtures Through Poly(ethylene-co-vinyl acetate) Membranes

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Poly (ethylene-co-vinyl acetate) films were prepared for the selective separation of aromatic hydrocarbons from alcohol-hydrocarbon mixtures. Dicumyl peroxide and benzoyl peroxide were used as crosslinking agents. Neat poly(ethylene-co-vinyl acetate) membranes were also prepared. Crosslinked membranes showed hydrocarbon selectivity from alcohol-hydrocarbon mixtures, while unmodified membranes did not show any hydrocarbon selectivity. Both selectivity and permeation rate were found to increase with increase in feed composition. Dicumyl peroxide crosslinked membranes showed a higher selectivity than benzoyl peroxide crosslinked membranes. Pervaporation through membranes with different loadings of dicumyl peroxide was also followed. It was observed that selectivity was independent of the thickness of the membrane. The effect of the molecular size of permeating species on permeation flux and selectivity was also investigated. The effect of free volume on pervaporation properties was investigated by positron annihilation lifetime spectroscopy (PALS).

Keywords: Pervaporation, poly(ethylene-co-vinyl acetate), aromatic hydrocarbon, selectivity

1 Introduction

The use of polymeric membranes for separation applications has steadily increased over the past few decades because of their unique advantages like low cost, easy maintenance, the continuous character of the process, simplicity and flexibility of control compared to other conventional methods. Pervaporation, a process which separates liquids by selective permeation through a membrane, has the potential for tremendous savings in energy if improvements over current membrane materials can be realized (1). In pervaporation, the liquid mixture (feed stream) is in contact with one side of a selectively permeable membrane and the components that penetrate through the membrane are removed as vapor from the opposite side of the membrane. Basically, this follows a solution-diffusion mechanism (2) i.e., flux is a function of solubility and diffusivity. The driving force for the transport is a concentration difference across the membrane due to the pressure difference. The overall transport consists of sorption of liquids at

the liquid-membrane interface, diffusion through the membrane and desorption at the downstream side.

As a result of the extensive research continuing in this field, pervaporation could find many practical applications including separation of azeotropes (3), close boiling liquids (4,5), organic liquid mixtures (6–9), removal of water from organic solvents (10) and for the removal or recovery of trace organic substance (11). Many interesting studies have been reported on the separation of binary liquid mixtures by this technique (12–16). Kusumocahyo et al. (17) prepared poly acrylic acid membranes with cyclodextrins (CD) and these membranes were used for the separation of xylene isomers. They found that fluxes were increased when the amount of cyclodextrins was increased. Gozzelino and Malucelli (18) studied the pervaporation of methanol-methyl-t-butyl ether mixtures through poly (ethylene-co-vinyl acetate) membranes and found that membranes showed a higher permeability of methanol with all membrane compositions. Huang et al. (19) studied the performance of plasticizer/polysulfone membranes with water-ethanol mixture and found that selectivity of water to ethanol was increased by an optimum amount of plasticizers. Lamer et al. (20) used a silicon membrane to extract aroma compounds from dilute aqueous solutions. The pervaporation performance of fluorine containing polyimide membranes for the separation of aliphatic/aromatic

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hydrocarbon mixtures was studied by Hong Ye et al. (21). They observed aromatic hydrocarbon selectivity. Kuznetsov et al. (22) carried out a detailed study about the pervaporation selectivity of cellulose hydrate membranes as a function of pressure and sorption properties and concluded that as the residual under membrane pressure increased the permeability was decreased. Polydimethylsiloxane based membranes were used by Xiangli et al. (23) for the separation of ethanol-water mixtures. Tian and Jiang (24) utilized propene/1-octane copolymer membranes effectively for waste water treatment.

Mixtures of alcohol and aromatic hydrocarbons are widely encountered in pharmaceutical and many other chemical industries. Extracting alcohol with water and subsequent distillation of alcohol-water mixtures conventionally separates these mixtures. This two-step process increases the operating cost and energy consumption and therefore, a single step process, like pervaporation, is more desirable for the separation of alcohol-aromatic hydrocarbon mixtures. The selection of a suitable polymer membrane for pervaporation is also very important for practical applications. Poly(ethylene-co-vinyl acetate) (EVA) is a random copolymer of ethylene and vinyl acetate, whose wide range of physical properties, which depend on the composition of the copolymer, allows it to be used in many fields. The polymer is extensively used in many engineering and industrial applications because of its toughness, chemical resistance and excellent processability. The properties of this copolymer make it a suitable material for applications in the field of membrane process. The present work deals with the selective separation of alcohol-hydrocarbon mixtures of different compositions through poly(ethylene-co-vinyl acetate) membranes. The effects of feed composition, crosslinking agents, film thickness and the molecular size of permeate on the separation process have been examined.

2 Experimental

2.1 Materials

Poly(ethylene-co-vinyl acetate) EVA (Pilene, 1802) used was supplied by Polyolefin Industries Limited, Chennai, India. The basic characteristics of copolymer are given in the Table 1. The crosslinking agents used were dicumyl peroxide (DCP) and benzoyl peroxide (BP). The solvents methanol, ethanol, benzene and toluene were double distilled before use.

2.2 Membrane Preparation

Membranes of EVA were fabricated by using two crosslinking agents, namely DCP and BP. Unmodified EVA (neat) membranes were also prepared. The unmodified membranes are represented as D₀. EVA granules were sheeted out on a two roll mixing mill with a friction ratio 1:1.4.

Table 1. Details of the materials used

Material	Properties	Source
Poly(ethylene-co-vinyl acetate) Pilene 1802	Melt flow index (kg/600s)	2 × 10 ⁻³
	Density(kg/m ³)	0.937 × 10 ³
	Vicat softening point(°C)	59.000
	Vinyl acetate(%)	18.000
	Intrinsic viscosity (m ³ /kg)	0.017
		PIL Chennai India

The sheeted out stock was pressed on a hydraulic press at 170°C and under a load of 24.5 × 10³ N. The modified membranes were prepared using BP and DCP. The mixing was done on a two roll mixing mill as done previously. The cure behavior was studied by a Geotfert rheometer. The samples were then cured up to their optimum cure times. DCP modified membranes were cured at 170°C and under a load of 24.5 × 10³ N (represented as D). BP modified membrane was cured at 120°C and under a load of 24.5 × 10³ N (represented as B₁). Membranes with different loading of DCP were also prepared. DCP modified membranes are designated as D₁, D₂, D₄, D₆ and D₈ according to the DCP content where the subscript numbers represents the grams of DCP used per 100 grams of the polymer. Similarly, BP modified membrane is represented as B₁, according to BP content.

2.3 Membrane Swelling Experiments

Membrane strips were immersed in various toluene-ethanol mixtures for 24 h at 30°C temperature. After reaching equilibrium, the membranes were taken out from the mixtures, their surfaces wiped with a tissue paper and then they were weighed immediately. The swelling ratio is calculated by the equation:

$$S = (W_s - W_d)/W_d \quad (1)$$

where, W_d and W_s, are the weight of dry and swollen membranes, respectively.

2.4 Pervaporation Experiments

The pervaporation experiments were performed using the apparatus shown in Figure 1. Membranes, which were immersed and swollen in the respective feed mixtures at room temperature, were placed in the pervaporation cell. The effective surface area of the membrane was 19.4 × 10⁻⁴ m². The feed was circulated through the pervaporation cells. Low pressure is kept at the downstream side by a vacuum pump. A pressure of 3.5–4 mm of Hg was applied. The permeate was collected in cold traps cooled by

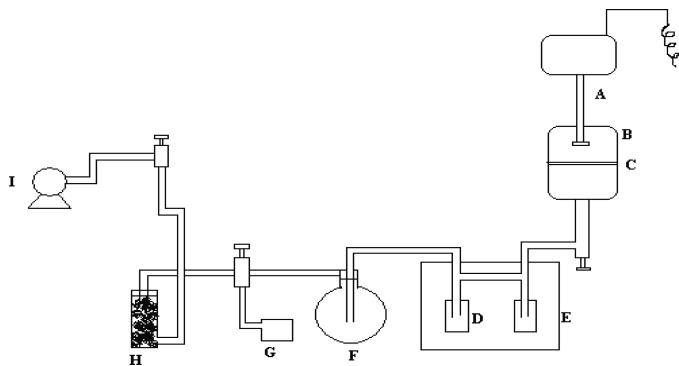


Fig. 1. Pervaporation apparatus: (A) stirrer, (B) permeation cell, (C) membrane, (D) collection traps, (E) dewar flask, (F) RB flask, (G) pressure guage, (H) moisture trap, (I) vacuum pump.

a dry ice–acetone mixture. Composition of the collected permeate was determined by gas chromatography. The experiments were carried out at 30°C, and were repeated at least three times. The reproducibility of the results was very good.

The pervaporation properties are characterized by the flux J and the separation factor α_{ij} . The permeation flux is the amount of the component permeated in unit time and per unit cross-section area of the membrane. The flux is expressed in $\text{kg}/\text{m}^2\text{h}$. The pervaporation separation factor α_{ij} is determined by:

$$\alpha_{ij} = (Y_i/Y_j)/(X_i/X_j) \quad (2)$$

where, Y_i and Y_j , represent the weight fractions of hydrocarbon and alcohol in permeate and X_i and X_j those in the feed.

2.5 X-ray Diffraction Studies

The polymer morphology was observed by X-ray diffraction. X-ray diffraction patterns of the samples were recorded with an X-ray diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation from a Philips X-ray generator. The samples of the same thickness and area were exposed. The operating voltage and the current of the tube were kept at 55 kV and 190 mA, respectively, throughout the course of investigation. The X-ray diffraction patterns for pure and modified EVA membranes are shown in Figure 2. The crystalline nature of unmodified membranes was evident from the X-ray patterns. When membranes were modified, crystallinity was reduced. The pure EVA membrane exhibits a sharp intense peak. On the other hand crosslinked membrane showed a peak with lower intensity. This reveals that the uncrosslinked EVA membrane exhibits more crystalline domains than those of crosslinked membranes.

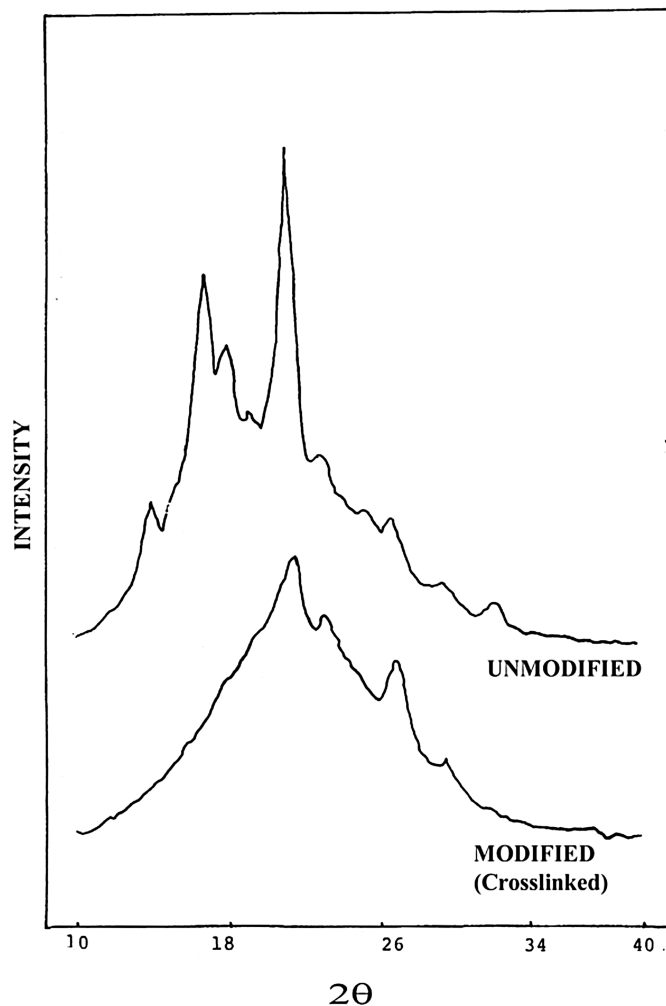


Fig. 2. X-ray diffraction patterns of (a) neat (b) modified membranes.

2.6 Positron Annihilation Lifetime Spectroscopic Analysis

Positron annihilation lifetime spectra (PALS) is used to examine the free volume present in unmodified and crosslinked EVA samples. The Positron Lifetime Spectrometer consists of a fast-fast coincidence system with BaF_2 scintillators coupled to photo multiplier tubes of type XP2020/Q with quartz window as detectors. The detectors were shaped to conical to achieve better time resolution. $\text{A}17\text{mCi}^{22}\text{Na}$ positron source, deposited on a pure Kapton foil of 0.0127 mm thickness was placed between two identical pieces of the sample under investigation. This sample-source sandwich was positioned between the two detectors of PALS to acquire lifetime spectrum. The spectrometer measures 180 ps as the resolution function with ^{60}Co source.

However, for a better count rate, the spectrometer was operated at 220 ps time resolution (25). All lifetime measurements were performed at room temperature and two to three positron lifetime spectra with more than a million

counts under each spectrum were recorded. In PALS analysis, two parameters, namely o-Ps lifetime (τ_3) and o-Ps intensity I_3 are measured. The o-Ps lifetime τ_3 measures the size of the free volume holes (V_f) and I_3 is a relative measure of the number of free volume sites in the polymer matrix.

The free volume cavity radius (R) is related to the o-Ps pick-off lifetime (τ_3) by a simple relation. The underlying assumption in the formulation of this relation is that o-Ps atom in a free volume cell can be approximated to a particle in a potential well of radius R_0 . The potential is infinite if $r > R_0$ and constant for $r \leq R_0$. Further, it is assumed that there is an electron layer in the region $R < r < R_0$, with $R_0 = R + \delta R$, where δR represents the thickness of the electron layer or the probability of overlap of the P_s wave function and electron wave function. The expression connecting the free volume radius R (in nm) and the o-Ps pick-off lifetime τ_3 (in ns) according to Nakanishi et al. (26) is:

$$\left(\frac{1}{\tau_3}\right) = 2 \left(1 - \left(\frac{R}{R_0}\right) + \left(\frac{1}{2\pi}\right) \sin\left(\frac{2\pi R}{R_0}\right)\right) \quad (3)$$

Here, the value of $\delta R = 0.1656$ nm was determined by fitting experimental τ_3 values to data from molecular materials with well-known hole size like zeolites (27). Using this value of R , the free volume size (V_f) is calculated as $V_f = (4/3)\pi R^3$. Then the relative fractional free volume is evaluated as the product of free volume (V_f) and o-Ps intensity, I_3 (%).

3 Results and Discussion

3.1 Swelling Characteristics

The plots of swelling ratio vs. feed composition for unmodified, DCP and BP modified membranes are given in Figure 3. It shows that the swelling ratio increases with an increase in the concentration of toluene in the feed. This clearly shows the preferential affinity of the membranes towards toluene. The swelling ratio is highest for BP modified membranes and the least for unmodified membranes. Since the degree of crosslinking and swelling ratio are inversely related (28), the differences in the swelling behavior of DCP and BP modified membranes can be attributed to the different degrees of crosslinking. Hence, swelling ratio values indicate that the membranes modified by DCP have the highest degree of crosslinking. The low swelling behavior of unmodified membranes can be attributed to crystallinity of the polymer. The long range order which exists in the pure EVA, generates a more compact structure and hence, a lower swelling ratio. The crystalline nature of pure EVA was identified with X-ray diffraction (Figure 2).

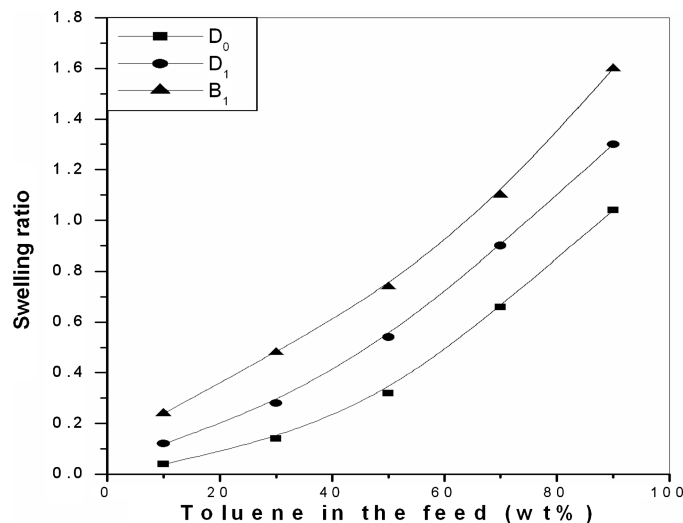


Fig. 3. Dependence of swelling ratio on the amount of toluene in the mixtures of toluene-alcohol for EVA membranes.

3.2 Positron Annihilation Lifetime Spectroscopic (PALS) Analysis

An understanding of the free volume of polymers is crucial for determining their permeability and ionic conductivity. At the present time, PALS analysis is carried out for the experimental quantification of free volume (29–32). It has been found that the estimated hole size significantly relates to the free volume property of polymer materials. Ito et al. (31) examined the relationship between the oxygen permeability and the free volume for ethylene-vinyl alcohol copolymer as the ethylene content varies, which significantly followed the free volume theory. The results obtained by them suggest that the molecular mechanism of gas permeation could be considered on the basis of the local motion of the polymer segments and the free volume size. Nagel et al. (32) correlated the free volume and transport properties of highly selective polymer membranes. Free volume values obtained for various EVA samples are placed in Table 2.

From the table, it is inferred that the uncrosslinked sample (D_0) exhibits a lower relative fractional free volume

Table 2. PALS measurements data of EVA samples

Sample	o- P_s lifetime, $\tau_3 \pm 0.01$ ns	o- P_s intensity $I_3 \pm 0.1\%$	Relative fractional free volume (%) F_v
D ₀	2.35	15.9	3.78
D ₁	2.33	20.48	4.78
D ₂	2.37	15.08	3.63
D ₄	2.34	14.53	3.42
D ₆	2.34	13.04	3.06
D ₈	2.35	12.6	2.2
B ₁	2.33	25.06	5.85

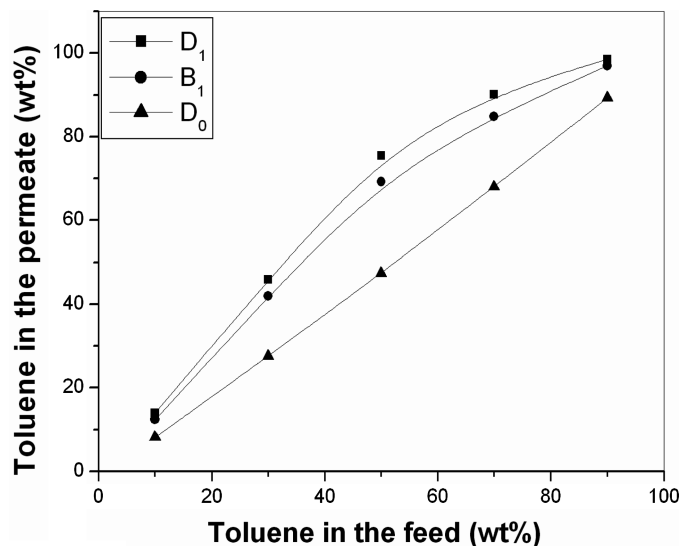


Fig. 4. Pervaporation characteristics of EVA membranes.

(F_v) % compared to B_1 and D_1 samples. The low value is due to the presence of crystalline regions in the matrix. When BP or DCP was introduced, the crystallinity was reduced due to the presence of random C-C crosslinks. Even when the number of crosslinks increase, the free volume decreases. Therefore, at the same loading of DCP/BP, maximum crosslinks were generated by DCP and hence, DCP cured samples exhibit lower F_v % values. Among the various DCP crosslinked samples, F_v % decreases from D_1 to D_8 . As the amount of DCP increases, the number of crosslinks per unit volume increases and hence the free volume decreases.

3.3 Pervaporation Characteristics of EVA Membranes

The toluene concentration in the permeate for various toluene-alcohol mixtures through unmodified, DCP and BP modified membranes is presented in Figure 4, respectively. The operating temperature is 30°C. Since this study was focused on the selective separation of organic mixtures, EVA was selected because of its affinity with hydrocarbons. EVA is highly swollen in aromatic hydrocarbons.

Since solubility parameter (δ) of EVA and toluene are close to each other (δ of EVA and toluene are 18.8 and 18.2 (MPa)^{1/2}, respectively) we expected that EVA will preferentially permeate hydrocarbons from alcohol-toluene mixture than alcohol and hence, will be more selective towards hydrocarbons. Experiments have shown, however, that unmodified membranes showed a selectivity less than unity for all concentrations. These membranes do not show any hydrocarbon selectivity.

The absence of hydrocarbon selectivity for the unmodified membrane is probably due to the long-range order of EVA, which generates a more compact structure and hence, a lower porosity. Even though the sorption of hydrocar-

bon molecule is higher, the diffusion of bigger hydrocarbon molecule is lower than alcohol molecule through the closely packed polymer chains. The available free volume of the matrix is very low due to the presence of crystallites, which generates a more tortuous path for the penetrants and subsequently, the rate of solvent ingression decreases. Long range order is responsible for the non selectivity of unmodified membranes.

Membranes modified with DCP and BP were more selective towards hydrocarbons than alcohol molecules. They showed a higher separation factor. The modification of membranes by the inclusion of BP or DCP reduces the crystallinity as a result of cross linking. This is clearly manifested in Figure 2. When membranes are modified, the free volume of the membrane increases and hence, solvent molecules can be better accommodated in the flexible networks. The above results are complemented by PALS measurements of fractional free volume percentage (Table 2). For the modified membranes, hydrocarbon selectivity is highest for DCP modified membrane. This is due to the presence of more crosslinks in DCP modified membrane and this significantly increases the selectivity of these membranes.

3.4 Influence of Feed Composition

According to solution-diffusion mechanism, permselective properties of pervaporation membranes are determined by solubility and diffusivity of the permeating components in the membrane. Since both sorption and diffusion phenomena are dependent on the composition of liquid mixture, the permeation properties are strongly influenced by the feed composition.

The effect of feed composition on the permeation rate and separation factors were investigated for different mixtures. Figure 5 represents the effect of feed composition on the permeation fluxes. Low fluxes are obtained when the toluene concentration in the feed is less for all three membranes and the fluxes increase strongly when the hydrocarbon content in the feed increases. With the increase in hydrocarbon content, free volume of the membrane increases due to plasticization and this leads to higher flux. Figure 6 gives the effect of feed composition on selectivity. The selectivity also increases with the increase in toluene concentration in the feed. As the concentration of toluene in the feed increases, the solubility of toluene in the membrane increases owing to closer solubility parameter values. The diffusivity also increases along with solubility and hence they exhibit a high selectivity.

The total flux J can be divided into the component flux of toluene (J_{toluene}) and that of ethanol (J_{ethanol}) by using the permeate composition data.

$$J_{\text{toluene}} = J \times Y_{\text{toluene}} \quad (4)$$

$$J_{\text{ethanol}} = J \times Y_{\text{ethanol}} \quad (5)$$

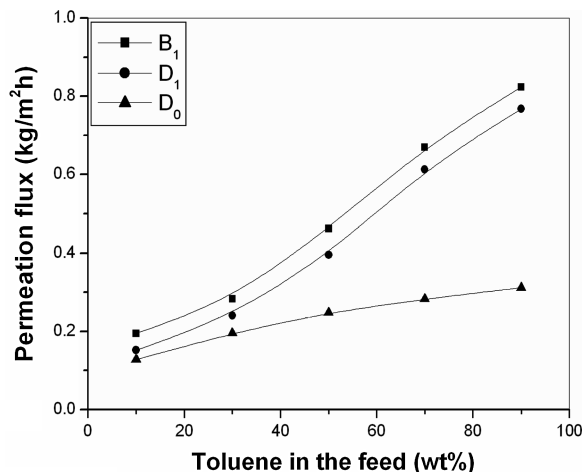


Fig. 5. Effect of feed composition on permeation fluxes.

where Y_{toluene} and Y_{ethanol} are the concentration of toluene and ethanol in the permeate respectively. The component fluxes of toluene/ethanol mixtures were calculated from the above equations and are shown in Figure 7 as a function of feed composition for D₁ membrane.

With the increase in feed composition, toluene flux increases and ethanol flux decreases. The increase in selectivity with increase in feed composition is due to the increase of toluene flux compared to ethanol flux. The high selectivity of DCP modified membranes can also be explained on the basis of the high percentage of toluene flux compared to other systems. The percentage of component fluxes is given in Table 3.

The high percentage of toluene flux and low percentage of ethanol flux contribute significantly towards the high selectivity of DCP modified membranes. The percentage of toluene flux is the least for the unmodified membrane.

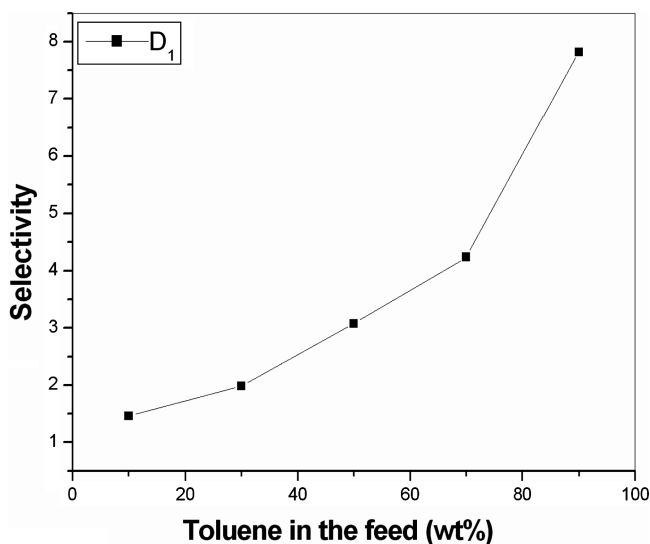


Fig. 6. Effect of feed composition on selectivity

Table 3. Component Flux (Percentage) (70/30 composition)

Systems	Toluene Flux	Ethanol Flux
D ₁	60.4	6.56
B ₁	52	9.2
D ₀	36	23.04

Thus, selectivity towards aromatic hydrocarbon decreases in the order DCP > BP > unmodified EVA membrane.

3.5 Effect of Crosslinks on Pervaporation

The effect of the number of moles of DCP in the membrane on the pervaporation performance of 50 weight percent of toluene-alcohol mixture is given in Figure 8. With an increasing number of moles of DCP in the membrane, toluene concentration in the permeate and the permeation rate decreases. Consequently, a minimum amount of DCP should be included for better performance.

The low permeation rate and absence of toluene selectivity for the unmodified EVA is due to the crystalline nature, which generates a tortuous path for solvent molecules and hence lower porosity. The porosity and selectivity are increased upon the addition of moderate amounts of DCP because these molecules introduce some disorder by forming random C-C networks. For crosslinked samples, the permeation rate and selectivity varies in the order D₁ > D₂ > D₄ > D₆ > D₈. Among the various DCP crosslinked samples, the fractional free volume % ($F_v\%$) decreases from D₁ to D₈. As the amount of DCP increases, the number of crosslinks per unit volume increases and hence, the free volume decreases. This prevents the sorption of solvent molecules.

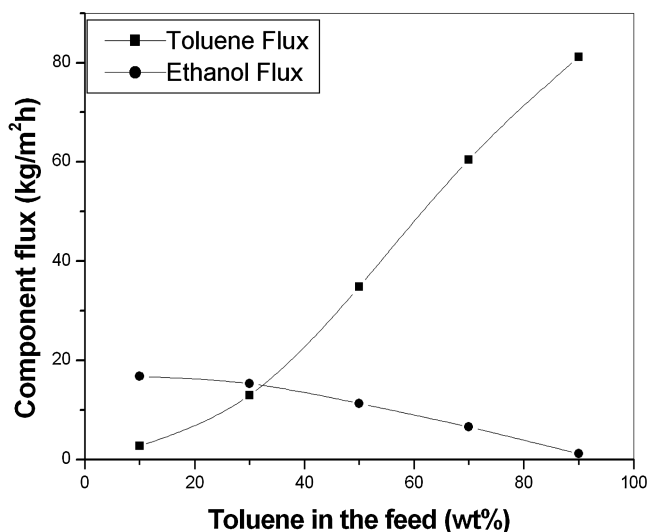


Fig. 7. Effect of feed composition on component fluxes.

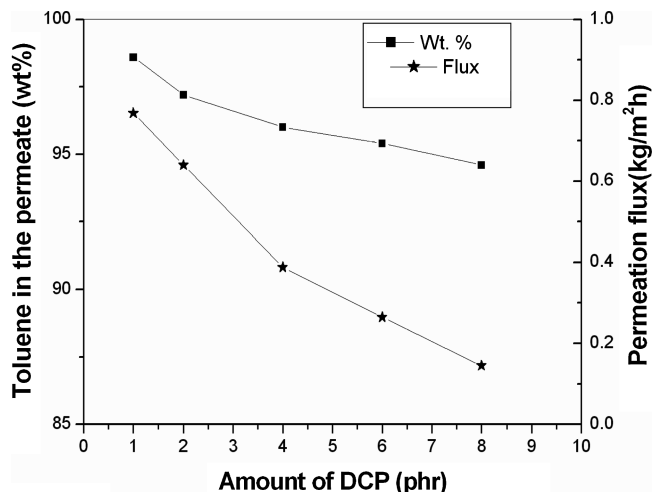


Fig. 8. Effect of crosslinking on the pervaporation characteristics of EVA membranes.

3.6 Effect of Film Thickness

Pervaporation of 50-weight percentage of alcohol-toluene mixture was carried out through different BP modified membranes with different film thickness. The weight percentage of toluene in the permeate and permeation fluxes are given in Figure 9. It is found that the separation efficiency of the membranes is independent of the thickness of the membrane. However, the permeation flux decreases with increasing thickness of the membrane.

3.7 Pervaporation of Benzene-ethanol Mixtures

The influence of the molecular weight of the predominantly permeating species on separation process was investigated by carrying out the pervaporation of benzene-ethanol mixtures through BP modified membranes. The membrane used is B₁. The trend of the dependence of flux and selectivity on the feed composition is almost the same as that for toluene-ethanol mixtures. With an increase in benzene concentration in the feed, the permeation flux and selectivity increases. It is found that for the same feed composition, the separation factor and fluxes are much higher for benzene-ethanol mixtures. This is in quantitative agreement with our expectation that low molecular weight species diffuse more easily through a compatible medium. Figure 10 represents the weight percentage of benzene in the permeate and permeation fluxes for different mixtures through BP modified membranes.

3.8 Pervaporation of Methanol-Toluene Mixtures

The pervaporation results for the methanol-toluene mixtures are given in Figure 11. The membrane used is B₁. Here again the trend of the dependence of the flux and selectivity on the feed composition is the same as that for

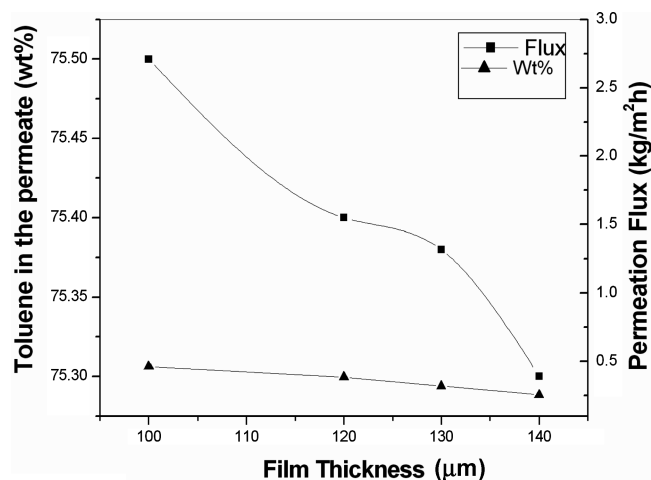


Fig. 9. Dependence of film thickness on pervaporation.

ethanol-toluene mixtures. With increasing toluene concentration in the feed, the flux and selectivity increases.

From the comparison of pervaporation properties of methanol-toluene vs. an ethanol-toluene mixture, it can be seen that in the case of ethanol-toluene, the selectivity is higher than that in the case of methanol-toluene mixtures for the same feed composition. But the pervaporation fluxes are higher for the methanol-toluene mixtures. This is due to the different degree of interaction. Methanol shows a stronger affinity towards EVA than ethanol, since methanol is more polar. EVA is also polar in nature and hence, there may be dipole-dipole interaction. This results in the reduction of selectivity of EVA membranes towards methanol-toluene mixtures. In addition the smaller methanol molecules can penetrate more easily than ethanol molecules. The molar volume of methanol is about two third of that of ethanol, which implies that methanol, the smaller molecule will permeate faster through a membrane

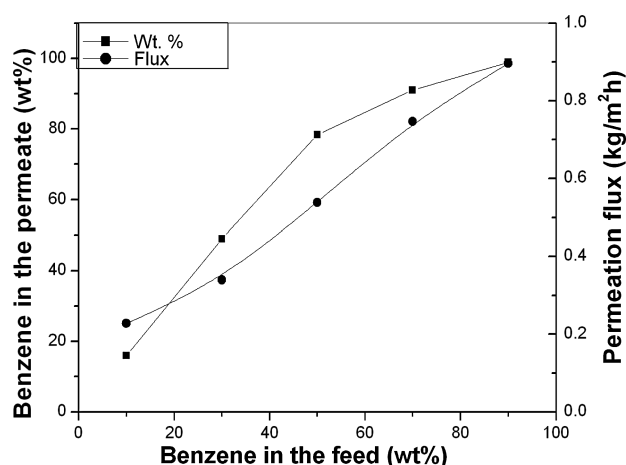


Fig. 10. Pervaporation characteristics of benzene-alcohol mixtures through B₁ membranes.

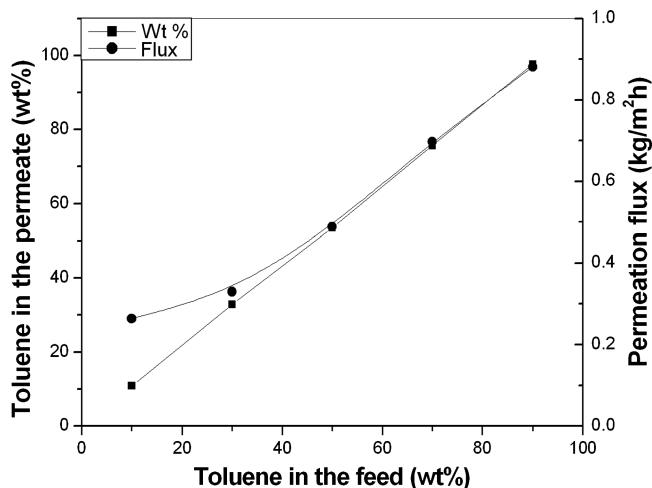


Fig. 11. Pervaporation characteristics of toluene-methanol mixtures through B₁ membranes.

than alcohol. Thus, stronger interaction of methanol towards EVA membranes reduces its hydrocarbon selectivity but increases its permeation fluxes.

4 Conclusions

Aromatic hydrocarbon selective membranes were prepared from poly(ethylene-co-vinyl acetate). DCP and BP were used for crosslinking. Virgin EVA membranes were also prepared. Their pervaporation properties were investigated using toluene-ethanol mixtures. DCP and BP modified membranes showed hydrocarbon perm selectivity. DCP showed a higher selectivity than BP modified membranes for all concentrations. However, the unmodified membranes did not show any hydrocarbon selectivity. Different membranes with different loading of DCP were also prepared. It was observed that as the amount of DCP increased, the selectivity and permeation flux decreased. Thus maximum flux and separation factor was observed for membranes with a minimum amount of DCP.

It was also observed that the membrane performance was strongly influenced by the feed mixture composition. For all the mixtures, both flux and weight percentage of hydrocarbon in the permeate increased with increasing hydrocarbon content in the feed. In the case of toluene-methanol mixtures, the fluxes are higher than toluene-ethanol mixtures, but the separation factor is higher for toluene-ethanol mixtures. This is due to stronger affinity of methanol to EVA membranes. Benzene-alcohol mixtures showed higher flux and separation factor than toluene-alcohol mixtures. The difference in the molecular size between benzene and toluene favors the permeability of the smaller molecules. The separation factor of the membranes appears to be in-

dependent of their thickness while the flux decreases with increase in membrane thickness.

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