

Pervaporation Behavior of PVA Membrane Containing β -Cyclodextrin for Separating Xylene Isomeric Mixtures

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To evaluate molecular recognition function of β -cyclodextrin to xylene isomers, β -CD polymer of branching chain extension (β -CD-EGDE) was synthesized by crosslinking β -CD with ethylene glycol diglycidyl ether (EGDE). The pervaporation blend membranes of β -CD-EGDE/PVA were prepared by casting an aqueous solution of PVA and β -CD polymer mixture, and the membranes were used for separation of *p*-/*m*- and *p*-/*o*-xylene mixtures. It was observed that the pristine PVA membrane almost had no selectivity for xylene isomer mixtures. The PVA membrane incorporating β -CD polymer had molecular recognition function, which selectively facilitated the transport of the xylene isomers. To ascertain pervaporation behavior, the sorption and desorption processes of the membrane in xylenes were investigated. The sorption result showed that the complex formation constant between β -CDs and xylenes played a key role in swelling behavior. There was a significant difference between diffusion coefficients D and D^0 , calculated from the sorption and desorption measurements, respectively, indicating that the diffusivity selectivity in desorption stage may have remarkable effect on the total selectivity during pervaporation process. © 2012 American Institute of Chemical Engineers *AIChE J.*, 59: 604–612, 2013

Keywords: β -cyclodextrin, poly(vinyl alcohol), pervaporation, xylene isomers, diffusion coefficient

Introduction

As one of the most important raw materials, xylenes have been widely used in chemical industry. However, xylenes often exist as isomeric mixture and should be separated and purified before application. Conventional techniques for separating xylene isomers, such as distillation, low-temperature crystallization and adsorption, are energy-intensive.

Pervaporation selectivity generally depends on the interaction between membrane and separation component, and it can be applied successfully to separate mixtures such as azeotropic and isomeric mixtures, hence, it may be an alternative process for the separation of isomeric xylenes. Since 1980s, considerable researches have focused on finding selective pervaporation membranes for the separation of xylene isomers.^{1–5} It is found that membrane containing selective carriers is a potential method. Cyclodextrins (CDs) are cyclic oligosaccharides consisting of D-glucopyranose units bonded through α -1,4-linkages. The hydrophobic cavities of CDs allow them to form inclusion complexes with many organic compounds. Therefore, it appears to be a good candidate as a carrier of mediated transport membrane used for separation of xylene isomers.^{6–9} Several works have been

done to immobilize CDs in polymer membranes. Lee⁶ immobilized α - and β -CDs in hydroxypropylmethylcellulose membranes, respectively, and evaluated the membranes performance for the separation of isomeric xylenes. The results showed that the addition of α -CD obtained separation factor 1.5 for *p*-/*m*-xylene, but permeation rates were very small. Recently, Kusumocahyo et al.⁸ introduced CDs into the poly(acrylic acid) (PAA) pervaporation membranes by blending for the pervaporative separation of *p*-/*o*-xylene mixture. The incorporation of CDs resulted in membranes with molecular recognition function, which selectively facilitated the transport of the xylene isomers. However, the ionic charges of the polyelectrolyte-PAA served as a barrier to block the permeation of xylene molecules, which resulted in extremely small permeation rates. Consequently, the performance of these membranes remains to be further improved.

Some research reported that immobilization of CDs in PVA membrane showed good selectivity for butanol isomer mixture^{10,11} and benzene-cyclohexane mixture.¹² PVA/CD membrane prepared by casting an aqueous solution of PVA and β -CD oligomer crosslinked with glutaraldehyde showed a separation factor of 2.96 for *p*-/*m*-xylene.⁷ The result indicated that the pervaporation performance was improved by filling β -CD oligomer into PVA membrane.

However, CDs were unstable in the blend membrane and likely to dissolve out during the pervaporation operation. Fortunately, some literatures^{13–15} reported that the CD

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polymer of branching chain extension not only reserved the structure of the cavity of CD, but also would be more stable and durable for its stereo network structure.

The typical model accounting for the transport mechanism of pervaporation process is the solution-diffusion model. It shows that the transport mechanism of pervaporation includes three successive stages: (a) solubilization of permeates from the feed solution to the membrane surface (i.e., sorption), (b) diffusion of permeates in the membrane, and finally (c) desorption of permeates from the down-stream of membrane interface to the strip solution (i.e., evaporation). Generally, it has been thought that the first and the second stages are the decisive steps to the transport of permeate through the membrane, and the third step does not have considerable influence on the transport of permeates under common pervaporation operation conditions. The pervaporation selectivity is determined by the solubility and diffusivity differences (i.e., solubility and diffusivity selectivities) of permeates in the membrane. Several studies have used solution-diffusion model for predicting permeation performance of CD-containing membranes.^{16–18}

In this work, PVA blended membranes with β -CD polymer were used to separate xylene isomers based on the molecular recognition function of β -CD. The influence of diffusivities in sorption as well as desorption process on the total diffusivity selectivity of the membrane was ascertained by comparing the diffusion coefficients D and D^0 calculated from sorption and desorption experiments, respectively. Based on diffusivity selectivity, the preferential permeation of xylene isomers through the β -CD-EGDE/PVA membrane also was evaluated.

Experimental

Materials

Ethylene glycol diglycidyl ether (EGDE) is purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). PVA (degree of polymerization is 1700), which is used as the holding matrix of the CD polymer, and beta-cyclodextrin (β -CD), ethanol, *para*-, *meta*- and *ortho*-xylene are obtained from Sino-pharm Chemical Reagent Co., Ltd. (Shanghai, China). The xylene isomers are of chemical grade, the other chemicals are all of analytical grade and all the chemicals are used without further purification. Dialysis bag (MWCO 3500) is purchased from Shanghai Shisheng cell Biotechnology Co., Ltd. (Shanghai, China). The polyacrylonitrile (PAN) ultrafiltration membrane, used as a support layer, is supplied by the Water Treatment Technology Center (Hangzhou, China).

Preparation of membranes

β -CD is dissolved in 1 mol.L⁻¹ NaOH hot aqueous solution at 40°C with stirring for about 15 min. The crosslinker EGDE (the amount of EGDE to β -CD was 36.9, 46.7 and 53.9 wt %, respectively) is added to the mixture with continuous stirring at 80°C. After 30 min, the solution is dialyzed using dialysis bag, and then the concentrated solution is precipitated by ethanol and filtered to get the polymer of β -CD-EGDE.

A definite amount of the mixture of β -CD polymer and PVA (4 wt % in total, the amount of β -CD polymer to PVA was 38.5 wt %) is dissolved in hot water at 90°C for 2 h, and a transparent solution is obtained. The solution is cast onto a glass plate or a PAN ultrafiltration membrane using a casting knife. The membranes are allowed to dry at room temperature for 48 h, and then peeled off. The membranes,

which are cast on the glass plate, are used for characterization, adsorption and desorption measurements. The composite membranes cast on the PAN UF membrane are used for pervaporation measurements.

Membrane characterization

FTIR spectra of β -CD, PVA and the blend membrane are obtained by a Thermo Nicolet IR 200 FTIR spectrometer. SEM (FEI SIRION 100) is used to study the morphology of membrane.

Sorption and desorption measurements

After being kept in desiccator to desorb any moisture sorbed from the air, the preweighed membranes are immersed in xylene solvents in a closed bottle at room temperature over 48 h for an equilibrium swelling. The membranes are weighed periodically until the mass being constant. The membrane sample is taken out and wiped off the surface solution carefully with tissue paper, and weighed in a tightly closed bottle. The relative amount of absorbed liquid in the membranes is expressed as the degree of swelling (S), which is calculated by following equation

$$S = \frac{m_t - m_0}{m_0} \quad (1)$$

where m_0 (g) is the weight of dry membrane, and m_t (g) is the weight of swollen membrane at time t (min). The S , which reaches an equilibrium state, is defined as S_{eq} .

The membranes at swollen equilibrium are taken out from xylene, and exposed to the atmosphere, weighed at a definite time interval until the weight of membrane samples does not change any more. The desorption rate of membranes d , can be calculated by the following equation¹⁹

$$d = \frac{Q_d}{Q_0} \times 100\% \quad (2)$$

where Q_0 (g) is the equilibrium adsorption amount uptake of dry membrane (i.e., $Q_0 = S_{eq} \times m_0$), and Q_d (g) is the amount of liquid removed from the swollen membrane at time t .

Pervaporation measurements

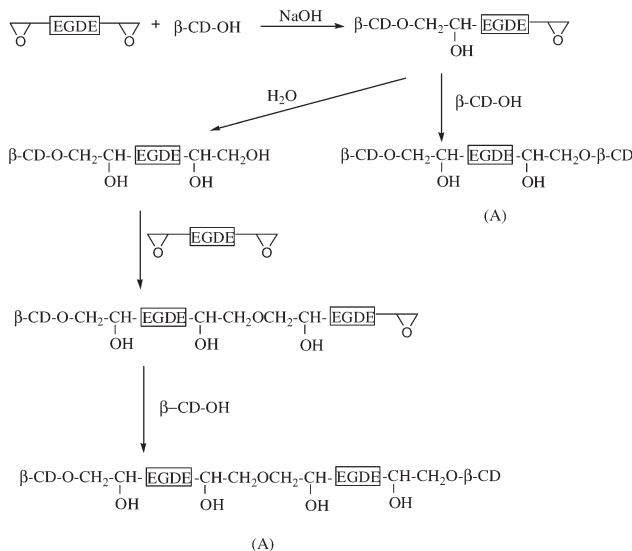
Pervaporation separation experiments were carried out by a laboratory-made apparatus as reported previously.²⁰ The membrane is positioned in the stainless-steel cell with an effective membrane area of 15.9 cm². The temperature of feed is thermostatically controlled. Vacuum at downstream side is maintained at about 135 Pa by a vacuum pump. The permeated vapor is collected in the glass trap cooled with liquid nitrogen. The permeation flux is calculated from the weight change of the trap under a certain time. The composition of the permeated mixture is analyzed using a gas chromatography.

The permeation flux (J), and the separation factor (α) for all membranes are calculated according to the following equations

$$J = \frac{\Delta G}{A \times \Delta t} \quad (3)$$

$$\alpha_{ij} = \frac{Y_i/Y_j}{X_i/X_j} \quad (4)$$

where ΔG is the weight of the permeated mixture during the operation time Δt ; A is the effective membrane area; Y is the



Note: (A) is β -CD-EGDE.

Scheme 1. Crosslinking reaction between EGDE and β -CD. Note: (A) is β -CD-EGDE.

concentration of xylene in the permeate, and X is the concentration of xylene in the feed (i and j represent different kinds of isomers).

Results and Discussion

β -CD polymer preparation

β -CD could leak from membrane during pervaporation process because of its small size, and then β -CD polymer can be immobilized in membrane very stably. β -CD can react with the crosslinking reagents which have epoxide rings, as reported in the literature,²¹ so the crosslinking reaction between β -CDs and EGDE can be expressed as Scheme 1. The cyclodextrin rims are lined with primary hydroxyls on one side and secondary hydroxyl groups on the other side of the cavity.²² In this way a β -CD molecule can connect with several molecules of the crosslinking reagents EGDE, and the EGDE molecules can react with other β -CDs as

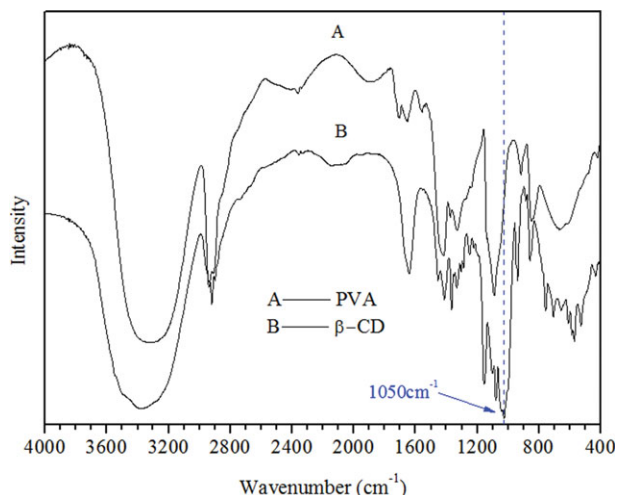


Figure 1. FTIR spectra of β -CD and PVA.

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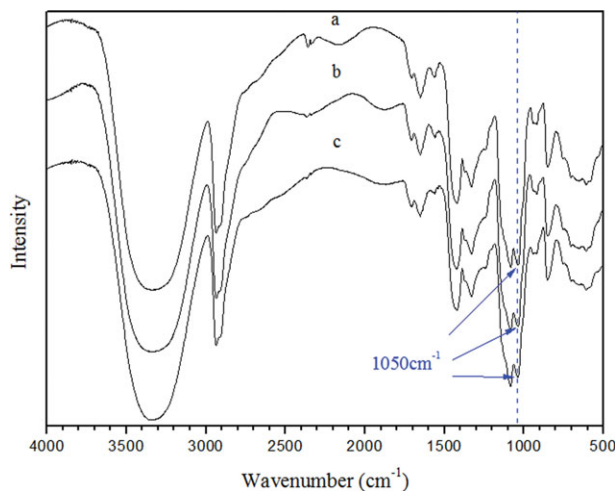


Figure 2. FTIR spectra of β -CD-EGDE/PVA blend membranes with different EGDE contents (a) $W_{EGDE} = 36.9\%$, (b) $W_{EGDE} = 46.7\%$, and (c) $W_{EGDE} = 53.9\%$.

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well. Then β -CD-EGDE branching chain extension polymer can be obtained.

Membrane characterization

FTIR spectra of pure β -CD and PVA are displayed in Figure 1. The spectra of PVA and β -CD show common absorption stretching vibration bands at some wave numbers: (1) 3,400–3,300 cm^{-1} are attributed to the stretch vibration of $-\text{OH}$; and (2) 3,000–2,850 cm^{-1} are associated with the antisymmetric stretch vibration of CH_2 or $\text{C}-\text{H}$; (3) 1,450 cm^{-1} is due to the bend vibration of CH_2 and CH_3 . The characteristic peaks around 1,050 cm^{-1} are related to the stretch vibration of $\text{C}-\text{O}-\text{C}$ in the cavity of β -CD. Peaks at 3,330 and 1,090 cm^{-1} are the features of secondary hydroxyl of PVA and they are quite intense.

Figure 2 shows the FTIR spectra of blend membranes filled with β -CD polymers prepared with different EGDE contents. Compared with Figure 1, all the blend membranes have the similar FTIR features and properties. The intense peak at 3,400–3,300 cm^{-1} related to hydroxyl group reflects the membranes are hydrophilic. The peaks at 1,090 cm^{-1} and 1,600–1,720 cm^{-1} indicate the existence of PVA. The peak at 2,900 cm^{-1} associated with $-\text{CH}_2$ is much stronger than that of β -CD and similar to PVA. It reflects that PVA is the main component in the membranes. Apparent peaks detected at a wave number of about 1,050 cm^{-1} in the spectra indicate that the structure of β -CD cavity exists in all the blend membranes.

Figure 3 illustrates the SEM images of the cross section of the PAN substrate membrane and the blend membrane. Two layers can be clearly observed in the blend membrane. The bottom layer is PAN UF membrane and the upper is the separation layer of the membrane, and the top layer is about 3 μm .

Sorption, desorption and diffusion of xylene isomers in the membranes sorption of xylene isomers

Figure 4 shows the swelling performance of the pristine PVA membrane in *p*-xylene (PX), *m*-xylene (MX) and *o*-xylene (OX), respectively. As seen, the values of S_{eq} in three kinds of xylene solvents are almost the same for the pristine PVA membrane. Therefore, it can be concluded that the interactions between PVA membrane and the three

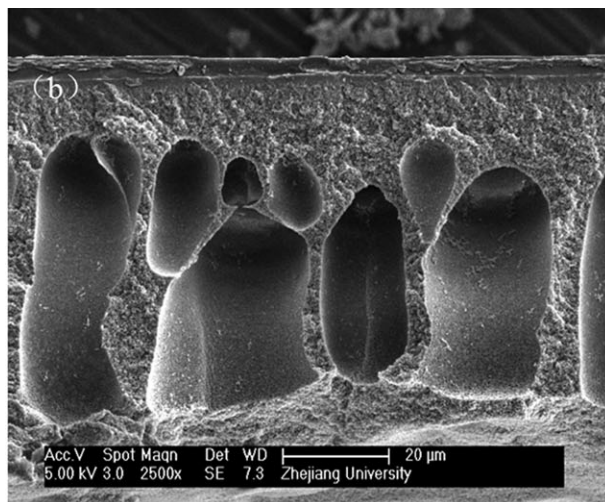
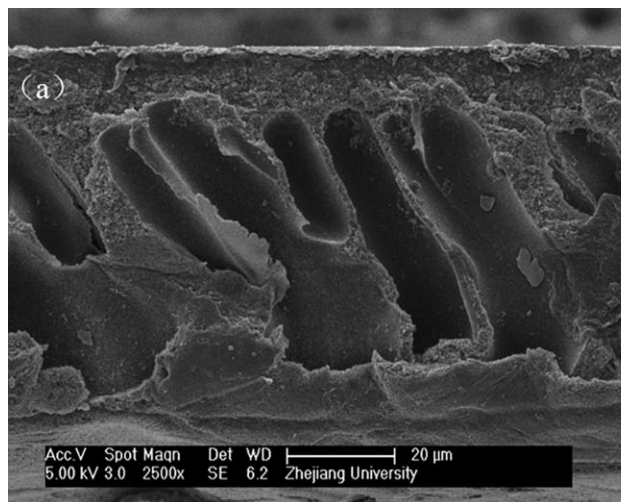


Figure 3. SEM images of the cross section of substrate and blend membranes (a) PAN substrate membrane, and (b) blend membrane.

xylene isomers are similar and the pristine PVA membrane almost has no effect in separation of xylene isomers.

Figure 5 depicts the swelling behavior of the β -CD-EGDE/PVA blend membranes with different EGDE contents in the xylene isomers. The swelling behaviors of the blend membranes are almost the same despite some differences of the values of S_{eq} . It is found that the order of S_{eq} of blend membranes in different xylene isomers is $S_{eq(OX)} > S_{eq(PX)} > S_{eq(MX)}$. To explain this result, it is important to understand the inclusion phenomena between CD and xylenes. CD can include guest molecules into their cavities to form host-guest complexes. The inclusion strength between CD and the guest molecular depends on the size of the cavity of CD, and also on the size, shape and the nature of the guest molecular. The inclusion strength is generally expressed by a stability constant (or complex formation constant) K , which is defined as the ratio of the forward rate constant k_1 and the backward rate constant k_{-1} ($K = k_1/k_{-1}$).⁸ Table 1 depicts the stability constants of β -CD with xylene isomers cited from reference.²³ Interestingly, the order of K is $K_o > K_p > K_m$, which is consistent with the order of S_{eq} . It means that,

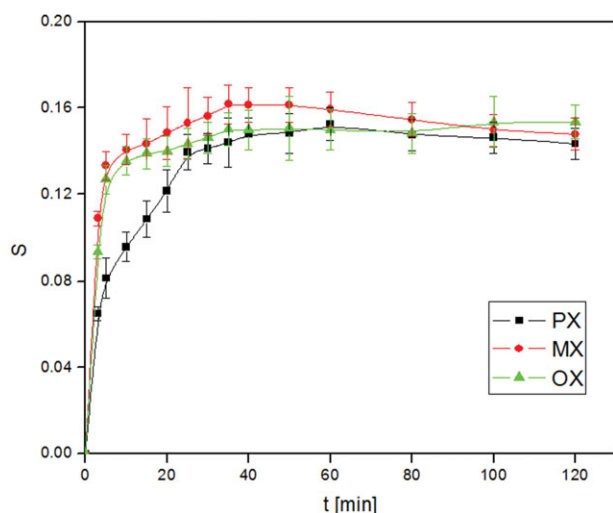


Figure 4. Swelling performance of pristine PVA membrane in xylene isomers.

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for the blend membranes, the stronger the inclusion strength between CDs and xylene isomers is (i.e., larger value of K), the more amount of xylenes is absorbed by the membranes. The complex formation constant plays an important role in the swelling behavior of the blend membranes.

Figure 5 also indicates that the values of S_{eq} of the membranes filled with polymers prepared with EGDE contents of 46.7 and 53.9% are lower than that of 36.9%. It can be illustrated by the reaction shown in Scheme 1. As shown, the cross-linking reaction between EGDE molecules is more prone to occur with the increasing content of EGDE, and it leads to less β -CDs for every EGDE molecular to link with, thus the amount of β -CDs per weight of β -CD polymer falls. Thereby, the S_{eq} of the membrane filled with polymers prepared with EGDE content of 36.9% is larger than that of 46.7 and 53.9%.

Desorption of xylene isomers

Figure 6 shows the desorption curves of xylene isomers in the pristine PVA membrane and the β -CD-EGDE/PVA blend membrane with W_{EGDE} of 36.9% at room temperature. According to Figure 6, xylene isomers can release out from the blend membrane nearly after 10 min, so it means that β -CDs in the membranes wouldn't form firm inclusion complexes with xylene isomers to prevent desorption of xylenes from membrane in the downstream, and also can facilitate transport of xylenes. Both kinds of membranes can reach the desorption rate of 100%, which means that xylenes in the membranes can be desorbed completely and there is no weight loss in the membranes (if the membranes have lost some weight, d will exceed 100%). The desorption curves of xylene isomers in blend membranes filled with β -CD polymers prepared with EGDE contents of 46.7 and 53.9% are similar to that of 36.9%, and show maximum desorption rate of 100% as well (data are not shown). The result implies that β -CDs in the blend membranes are stable and will not leach out during the swelling process.

Diffusion of xylene isomers through membranes

Transport mechanism. To gain insight into the transport mechanism, the sorption data were analyzed using the empirical Eq. 7^{24–26}

$$\frac{M_t}{M_\infty} = k t^n \quad (7)$$

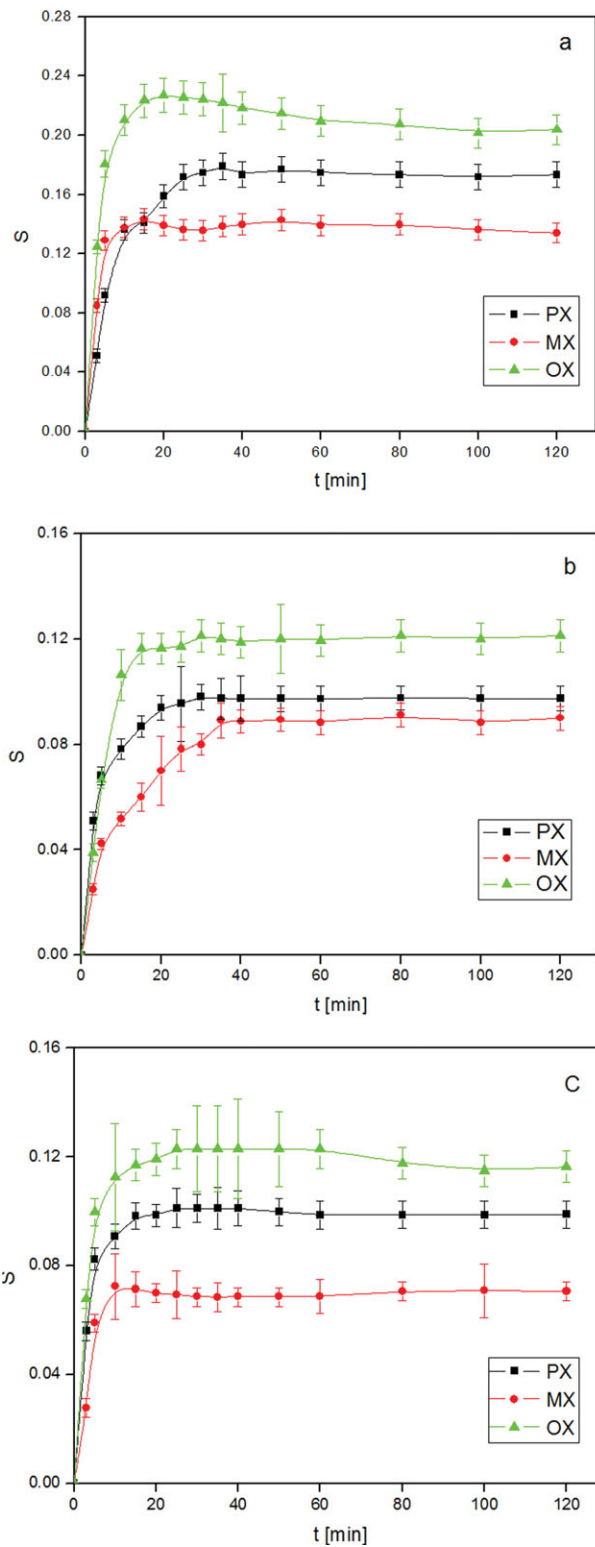


Figure 5. Swelling performance of β -CD-EGDE/PVA blend membranes with different EGDE content (a) $W_{EGDE} = 36.9\%$, (b) $W_{EGDE} = 46.7\%$, and (c) $W_{EGDE} = 53.9\%$, in xylene isomers.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where, M_t and M_∞ are the mass of solvent sorbed per weight of the membrane at time t and at equilibrium, respectively. The k parameter is a constant which depends on the structural

Table 1. Stability Constants for Complexes of β -CD and Xylenes at 25°C ²³

Type of CD	Stability constants K ($\text{L}\cdot\text{mol}^{-1}$)		
	<i>o</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene
β -CD	300 ± 10	240 ± 10	160 ± 10

characteristic of the membrane and on the interaction between solvent and membrane. The exponent n is used to indicate the type of diffusion. A value of $n = 0.50$ implies Fickian diffusion, a value of $n = 1.00$ implies Case II transport, and for values of n greater than 1.0 Supercase II transport is observed. Values of n of $0.50 < n < 1.00$ are indicative of anomalous transport behavior. Eq. 7 is useful for preliminary analysis of sorption data, although it may only be used up to 80% of the final weight of solvent sorbed. The least-squares estimations of n and k obtained are presented in Table 2.

In the majority of cases, the values of n range from 0.35 to 0.66 which indicate that the transport mechanism of xylenes through membranes deviates slightly from the Fickian mode. For the Fickian diffusion, the diffusion rate of permeates is much less than the relaxation rate of the polymer chains.²⁷

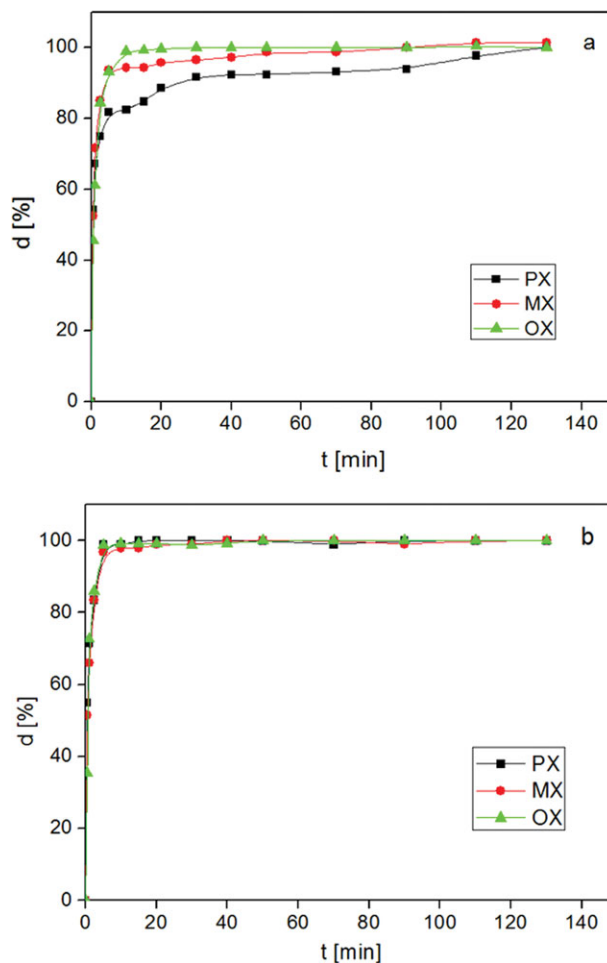


Figure 6. Desorption curves of xylene isomers from two membranes (a) pristine PVA membrane, and (b) blend membrane filled by β -CD-EGDE with W_{EGDE} of 36.9%.

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Table 2. Sorption Results of Membrane-Solvent Systems

solvent	W _{EGDE} (wt%)	n±0.05	k(×10 ² ±0.05 g/g min ⁿ)
<i>p</i> -Xylene	0 ^a	0.40	3.09
	36.9 ^b	0.42	1.28
	46.7 ^c	0.39	3.74
	53.9 ^d	0.40	3.88
<i>m</i> -Xylene	0 ^a	0.35	5.58
	36.9 ^b	0.40	4.28
	46.7 ^c	0.50	1.85
	53.9 ^d	0.66	1.88
<i>o</i> -Xylene	0 ^a	0.36	4.68
	36.9 ^b	0.45	3.67
	46.7 ^c	0.57	1.50
	53.9 ^d	0.50	3.76

^aThe pristine PVA membrane.

^{b,c,d}Blend membranes filled with β-CD polymers prepared by different EGDE content (W_{EGDE} = 36.9, 46.7 and 53.9 wt %), respectively.

Determination of diffusion coefficient from sorption experiments

For Fickian diffusion, diffusion coefficient D can be calculated from the following expression^{28,29}

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{D(2n+1)^2 \pi^2 t}{l^2}\right) \quad (8)$$

According to literatures,^{7,30} at short time ($M_t/M_\infty \leq 0.4$), the equation can be simplified to the following form

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{Dt}{l^2}} \quad (9)$$

where M_t and M_∞ are the amounts of solvent sorbed per weight of dried membrane [g (xylene)/g (dried membrane)] at time t and at equilibrium, respectively, and l is the thickness of the dried membrane (m).

$t_{1/2}$ is defined as the corresponding time t when M_t reaches the half amount of M_∞ . The value of $t_{1/2}$ can be obtained from the plot of $\frac{M_t}{M_\infty}$ vs. t . Then D can be calculated by the following Eq. 10, and it can be used for the explanation of the pervaporation performances. The calculated D values are listed in Table 3

$$D = \frac{0.049}{t_{1/2}/l^2} \quad (10)$$

Determination of diffusion coefficient from desorption experiments

To further investigate the diffusion behavior of solvent in the prepared membrane, diffusivities of xylene isomers at zero concentration in membranes were determined by desorption experiments. If diffusion of a gas or liquid in membranes is Fickian, desorption data can be analyzed for long duration by Eq. 11, a generally used desorption theory³¹

$$\frac{d \ln\left(\frac{G_\infty - G_t}{G_\infty}\right)}{2dt} = -\frac{\pi^2 D^0}{l^2} \quad (11)$$

where D^0 is the diffusivity at zero concentration, G_t and G_∞ are the amounts of liquid removed from the membrane at time t and at equilibrium, respectively. The G_t and G_∞ are related to the mass of the sample at different time by the following equations

$$G_t = W_0 - W_t \quad (12)$$

$$G_\infty = W_0 - W_\infty \quad (13)$$

where W_0 , W_t and W_∞ are the mass of membrane sample at time zero, time t and at equilibrium, respectively. W_∞ is equal to the mass of dry membrane. G_t and G_∞ are equal to Q_d and Q_0 , respectively. Eq. 11 can then be rewritten as

$$\frac{d \ln\left(\frac{W_t - W_\infty}{W_0 - W_\infty}\right)}{dt} = -\frac{\pi^2 D^0}{l^2} \quad (14)$$

Equation 14 was used to calculate the diffusivity D^0 in the desorption experiments.

At room temperature, according to the weight change of the swelled membrane with time, and D^0 is calculated by Eq. 14. The diffusivity D^0 in desorption experiments can be regarded as an effective diffusion coefficient for the membrane system. Table 3 lists the diffusion coefficient D and diffusivities at zero concentration D^0 , calculated from sorption and desorption measurement, respectively.

According to Table 3, for the pristine PVA membrane, the order of D of the three xylene isomers is $D_p < D_m = D_o$, which coincides with the kinetic diameter order of xylene isomers, PX (0.585 nm) = MX = OX (0.685 nm).^{32,33} It is probably means that the transport of xylenes in pristine PVA membrane is just Fickian diffusion. When β-CD polymers are introduced into the membranes, the values of D increase in general. It is because, for the polymers possessing, the cavity structure of CD served as fixed carriers will facilitate the transport of xylenes.^{8,34,35} In the case of *o*-xylene, the stability constant of β-CD with *o*-xylene is much stronger than those of the other two isomers (see Table 1). It is suggested that the strong inclusion strength between β-CD and *o*-xylene decrease the effective diffusivity of *o*-xylene in the membrane. On the other hand, *m*-xylene, which is weakly included into the cavity of β-CD, had a higher diffusivity in the membrane. As a result, *m*-xylene preferentially diffuses in the sorption process. The S_{eq} of *o*-xylene is bigger than that of *p*-xylene, so the sorption amount of *o*-xylene is more than that of *p*-xylene. This may increase the diffusivity of *o*-xylene. However, the PVA matrix absorbed *m*- and *o*-xylene in preference to *p*-xylene. So the suggested order of D in the blend membranes will be $D_m > D_o > D_p$ in the sorption

Table 3. Diffusion Coefficient D and Diffusivities at Zero Concentration D^0 , Calculated from the Sorption and Desorption Measurement

solvent	W _{EGDE} (wt%)	D (10 ⁻¹² m ² /s)	D^0 (10 ⁻¹² m ² /s)	D^0/D
<i>p</i> -Xylene	0 ^a	0.075	0.886	11.81
	36.9 ^b	0.149	3.902	26.18
	46.7 ^c	0.159	3.274	20.59
	53.9 ^d	0.389	6.972	17.92
<i>m</i> -Xylene	0 ^a	0.140	1.598	11.41
	36.9 ^b	0.212	3.833	18.08
	46.7 ^c	0.071	0.726	10.22
	53.9 ^d	0.691	3.073	4.45
<i>o</i> -Xylene	0 ^a	0.140	3.367	24.05
	36.9 ^b	0.192	3.887	20.24
	46.7 ^c	0.088	1.510	17.16
	53.9 ^d	0.463	3.749	8.10

^aThe pristine PVA membrane.

^{b,c,d}Blend membranes filled with β-CD polymers prepared with different EGDE contents (W_{EGDE} = 36.9, 46.7 and 53.9 wt %), respectively.

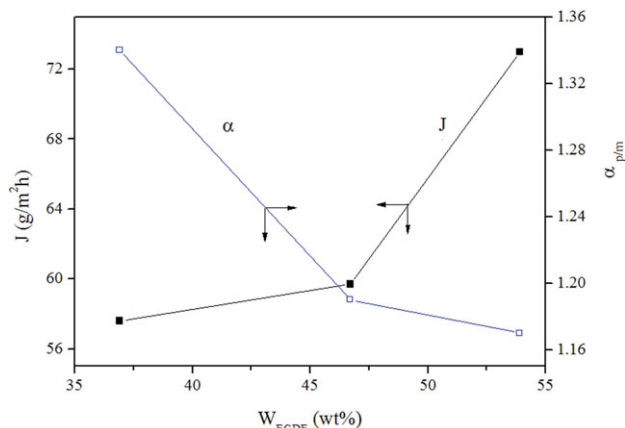


Figure 7. Variation of separation factor and flux of β -CD-EGDE/PVA blend membranes with different EGDE contents for *p*-/*m*-xylene mixture (10 wt % *p*-xylene, 30°C).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

measurement. In comparison to the data in Table 3, the prediction is accurate for the β -CD-EGDE/PVA blend membranes with W_{EGDE} of 36.9% and 53.9% but 46.7%. For D_m and D_o of this membrane are much smaller than those of 36.9% and 53.9%, the discrepancy may be caused by the error of sorption measurements.

According to Table 3, the D^0 values of xylenes for all the membranes are much higher than the corresponding D values. This coincides with the fact that desorption of permeates from the membrane interface of downstream does not have considerable influence on the transport of permeates. However, the remarkable difference between D^0/D for different permeates in the given membrane system implies that desorption stage may have effect on the selectivity of the membranes.

For the three kinds of blend membranes, the order of D^0 for xylene isomers is $D_p^0 > D_o^0 > D_m^0$, which is in opposition to the order of D in the sorption process, $D_m > D_o > D_p$. It implies that there is diffusion selectivity in the desorption process. At the same time, the values of D^0/D for all the blend membranes are in the same order, $D^0/D_{(PX)} > D^0/D_{(OX)} > D^0/D_{(MX)}$. It is suggested that in desorption process, the diffusion of *p*-xylene increase a lot. As a result, *p*-xylene preferentially desorbs from the downstream of the membranes. It may be due to the lower boiling point of *p*-xylene than those of the other two isomers (PX b.p.:138.35°C, MX b.p.:139.10°C, OX b.p.:144.41°C). Consequently, *p*-xylene may be the preferential permeated component through the membranes during pervaporation. By comparing D and D^0 , it is found that the solubility and diffusivity selectivities will determine the pervaporation characteristics of the membrane collectively.

Pervaporation performance of β -CD-EGDE/PVA membranes *p*-/*m*-xylene mixture

The pervaporation performance of the PVA composite membrane was investigated in *p*-/*m*-xylene mixture, and a separation factor of 0.98 and a permeation rate of 12.4 $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ through the membrane for a mixture with 10 wt % *p*-xylene in feed were obtained at 30°C. It meant that the PVA composite membrane had no separation effect for *p*-/*m*-

xylene mixture. The pervaporation performance of the blend membranes is shown in Figure 7.

According to Figure 7, it shows that the selectivity of the blend membranes containing β -CD polymer are much better than that of PVA membranes, which agrees well with the difference between the sorption equilibrium in the two kinds of membranes. The permeation flux increases, whereas the separation factor decreases gradually with the increase of W_{EGDE} . It is due to the fact that the amount of β -CD per weight of β -CD polymer decreases with the increase of W_{EGDE} , whereas β -CD unit in the membrane falls, therefore, the blend membranes with W_{EGDE} of 36.9% have a higher separation factor for *p*-/*m*-xylene mixture than others.

The solution-diffusion model can be applied to explain the pervaporation behavior of these membranes. The swelling degrees S_p and S_m at equilibrium decreased from 0.172, 0.138 to 0.10 and 0.068 (see Figure 5), and the diffusion coefficients D_p and D_m increased from 0.149×10^{-12} , $0.212 \times 10^{-12} \text{ m}^2\cdot\text{s}^{-1}$ to 0.389×10^{-12} and $0.691 \times 10^{-12} \text{ m}^2\cdot\text{s}^{-1}$ with W_{EGDE} increased from 36.9% to 53.9%, respectively (see Table 3). It is clear that the increment percent of D is much larger than the decrement percent of S , thus the flux will increase according to the formula $P = S \times D$. The separation factor decrease gradually with the increase of W_{EGDE} . This phenomenon coincides with the trade-off relationship between separation factor and the flux.

***p*-/*o*-xylene mixture**

The pervaporation performance of the PVA composite membrane was also investigated in *p*-/*o*-xylene mixture, and a separation factor of 1.02 and a permeation rate of 74.2 $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ through the membrane for a mixture with 10 wt % *p*-xylene in feed were obtained at 30°C. It meant that the PVA composite membrane also had no separation effect for *p*-/*o*-xylene mixture.

Figure 8 depicts pervaporation performance of blend membranes for separating *p*-/*o*-xylene mixture. As seen, the permeation flux increases and the separation factor decreases gradually with the increase of W_{EGDE} . The membrane filled with β -CD polymers prepared with W_{EGDE} of 36.9% has the highest separation factor for *p*-/*o*-xylene mixture than others.

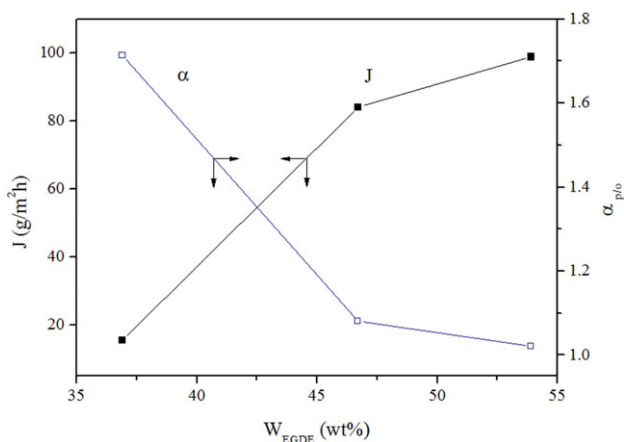


Figure 8. Variation of separation factor and flux of β -CD-EGDE/PVA blend membranes with different EGDE contents *p*-/*o*-xylene mixture (10 wt % *p*-xylene, 30°C).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Using the same method elaboration for Figure 7, the pervaporation performance of the blend membranes in the *p*-/*o*-xylene mixture can also be explained successfully. According to the explanation, it is drawn that the effect of the diffusivity selectivity is more important than the solubility selectivity in the pervaporation performance for xylenes. *p*-Xylene is the preferential component permeated through the membrane during pervaporation, which coincides with the prediction from the sorption and desorption measurements. It indicates that the diffusivity selectivity of permeate in the desorption stage also has effect on the pervaporation selectivity of the membrane as well as the sorption process.

Although all separation factors were not very high for xylene isomers, the pervaporation performance revealed that the selectivity could be improved by filling β -CD into polymer membrane, and β -CD is provided with the molecular recognition function for xylene isomers. However, the selectivity is not enough for application, the improvement of effective selectivity of β -CD are necessary, so the orientation and increase of β -CD in membrane are alternative methods in the future.

Conclusions

β -CD-EGDE/PVA blend membranes were prepared and pervaporation performances of xylene isomers were investigated. The FTIR spectra showed that the blend membranes had the structure of β -CD cavity. The result of the swelling measurement of blend membranes in xylene isomers showed that the complex formation constant between β -CDs and xylene isomers and the kinetic diameter of xylenes were the two main factors in swelling. The desorption measurement showed that β -CD polymers in the blend membranes would not leach out from the membrane in the process. The difference between diffusion coefficients D and D^0 indicated that the diffusivity selectivity in desorption stage could have remarkable effect on the total selectivity of the membrane.

The pervaporation performances of blend membranes were better than that of pristine PVA membrane. The permeation flux increased and the separation factor decreased gradually in the blend membranes with the increase of W_{EGDE} both for *p*-/*m*-xylene and *p*-/*o*-xylene mixtures. The blend membrane with 36.9% W_{EGDE} gave the highest pervaporation performance than the pristine PVA and other blend membranes.

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Notation

A = effective membrane area, m^2
 D = desorption rate of the swollen membrane, %
 D = diffusion coefficient, $m^2 \cdot s^{-1}$
 D^0 = diffusion coefficient at zero concentration, $m^2 \cdot s^{-1}$
 D_p, D_m = diffusion coefficients of *p*-, *m*- and *o*-xylene, respectively and D_o ($m^2 \cdot s^{-1}$)
 G_t = amount of liquid removed from the membrane at time t in desorption experiment, g
 G_∞ = amount of liquid removed from the membrane at equilibrium in desorption experiment, g
 ΔG = permeation weight during the operation time Δt , g
 J = permeation flux of the composite membrane, $g \cdot m^{-2} \cdot h^{-1}$
 k = a constant
 K = complex formation constant of β -CD and xylenes, $L \cdot mol^{-1}$
 K_o, K_p = Complexes formation constants of β -CD with *o*-xylene, and K_m *p*-xylene and *m*-xylene at 25°C ($L \cdot mol^{-1}$)

l = thickness of the dried membrane, m
 m_0 = weight of dried membrane, g
 m_t = weight of swollen membrane at time t , g
 M_t = sorption amounts of *p*-, *m*- or *o*-xylene per unit mass of dried membrane at time t , g (xylene)/g (dried membrane)
 M_∞ = equilibrium sorption amounts of *p*-, *m*- or *o*-xylene per unit mass of dried membrane at time ∞ , g (xylene)/g (dried membrane)
 N = exponent
 Q_0 = maximum adsorption amount uptake of dried membrane, g
 Q_d = desorbed amount of xylene of swollen membrane at the given time interval, t (g)
 S = swelling degree of membrane, that is, solubility
 S_{eq} = degree of swelling at equilibrium
 S_p, S_m and S_o = swelling degrees of membrane for *p*-, *m*- and *o*-xylene, respectively
 t = time, min
 Δt = operation time, min
 $t_{1/2}$ = corresponding time t when M_t reaches the half amount of M_∞
 W_{EGDE} = EGDE content in the blend membrane containing EGDE, wt %
 W_0 = membrane sample weight at $t = 0$ in desorption experiments, g
 W_t = membrane sample weight at time t in desorption experiments, g
 W_∞ = membrane sample weight at equilibrium in desorption experiments, g
 X_i = concentration of *i*-xylene in *i*-/*j*-binary xylene isomers mixture in feed
 Y_i = concentration of *i*-xylene in *i*-/*j*-binary xylene isomers mixture in permeate

Greek letters

α = separation factor of the composite membrane
 α_{ij} = separation factor of the composite membrane for *i*-xylene to *j*-xylene in *i*-/*j*-xylene isomers mixture

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