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PVA membrane filled β-cyclodextrin for separation of isomeric xylenes by pervaporation

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Abstract

Polyvinyl alcohol (PVA) membrane filled β-cyclodextrin (β-CD) was prepared by casting an aqueous solution of PVA and β-CD oligomer. The membrane was crosslinked with glutaraldehyde for one hour. The weight content of β-CD in the membrane was 33%. The membrane was used for separation of *p*-xylene/*m*-xylene mixture by pervaporation. Based on the experiments of sorption equilibrium, the solubility and the diffusion coefficient of the permeates in the membrane was obtained. Compared with PVA membrane, the solubilities of pure *p*-xylene and *m*-xylene in PVA membrane filled β-CD increased from 0.92, 0.78 to 10.4, 2.6 g (xylene)/100 g (dried membrane), respectively, and the solubility selectivity S_p/S_m increased from 1.18 to 4.0. Also, the diffusion coefficients of *p*-xylene and *m*-xylene decreased from 8.45×10^{-12}, 8.23×10^{-12} to 6.83×10^{-12}, 7.23×10^{-12} m^2/s, respectively, and diffusion selectivity decreased from 1.03 to 0.94. These effects of β-CD can be interpreted in terms of the inclusion strength in the cavity. The pervaporation performance of the PVA membrane filled β-CD was investigated. A separation factor of 2.96 and a permeation rate of 95 g/m^2 h through the β-CD filled PVA membrane for a 10 wt.% feed *p*-xylene concentration were obtained at 25°C. The results indicated that PVA membrane filled β-CD effectively improved the pervaporation performance, especially on the separation factor.

Keywords: Polyvinyl alcohol; β-Cyclodextrin; Solubility; Diffusion coefficient; Pervaporation

1. Introduction

Mass transport in a membrane may be classified into two types: mediated transport and nonmediated transport processes. The mediated transport needs a third component (carrier) to mediate the transport. The carrier provides an additional mechanism of transport through membrane and in general accelerates the transport of specific solutes across the membrane phase.

The separation of isomeric xylenes continues to be an active research area because the present commercial processes in use are both complex and energy intensive. Pervaporation can be applied successfully to separation of mixtures, which are difficult to separate by conventional separation methods, such as azeotropic and isomeric mixtures. So it might be an alternative process for the separation of isomeric xylenes. Since early 1980, considerable research has been conducted in an attempt to find selective pervaporation membranes for this use [1–3]. McCandless and Downs tested 12 polymers as pervaporation membranes for separation of the C_8 aromatics at different temperatures [4]. The results showed that for all films separation factors for *p*- to *m*-xylene were below 1.69. Recently, Wytcherley and McCandless separated *m*- and *p*-xylene mixtures by the pervaporation technique in the presence of CBr_4 as a selective feed complexing agent [5]. The results showed that separation factors for *p*- to *m*-xylene varied from about 1.2–0.05 depending upon the experimental temperature, *p*-xylene concentration and the amount of CBr_4 present. However, the performance of these membrane remains to be further improved.

β-Cyclodextrin (β-CD) is cyclic oligosaccharide consisting of seven glucose units, and the cyclic oligosaccharide has a hydrophobic cavity of several angstroms diameter. It can form inclusion complexes with many organic compounds that are called guest molecules. So it appeared to be a good candidate as a carrier of mediated transport membrane that can be used for separation of aromatic isomers or azeotropes [6–9]. Lee paid his attention on cyclodextrin, and studied performance of hydroxypropylmethyl cellulose membranes with α- and β-CD as a mediator for transport [10]. The results showed that the addition of α-CD obtained separation

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factor 1.5 for *p*-/*m*-xylene, but permeation rates were extremely small. However, no experimental data were reported, in which the membrane with β-CD was used for separation of *p*-/*m*-xylene mixtures. Recently, Sreenivsan investigated polyvinyl alcohol (PVA) hydrogel by blending β-CD for the release of a water-soluble component [11].

In this paper, the PVA membrane filled β-CD was prepared. The sorption equilibrium of *p*-/*m*-xylene solution in the membranes were measured, and the diffusion coefficients and the equilibrium sorption amount of the permeate in the membranes were calculated. Pervaporation experiments for separation of *p*-/*m*-xylene mixtures were carried out. The results indicated that PVA membrane filled β-CD effectively improved the pervaporation performance, especially on the separation factor.

2. Experimental

2.1. Materials

β-CD oligomer was supplied from Katayama Chemical Co., and its average degree of polymerization was around 3. Polyvinyl alcohol was purchased from The Shanghai Chemical Reagent Supply Station, (the degree of saponification is more than 99%, and the average degree of polymerization is 1700), and it was used as the holding matrix of β-CD oligomer. Glutaraldehyde was used as a crosslinking reagent for PVA, sulfuric acid as a catalyst and sodium sulfate as a swelling reagent. All materials were of reagent grade. Commercially supplied *p*-xylene and *m*-xylene were used for pervaporation experiment without further purification. The polyacrylonitrile (PAN) ultrafiltration membrane used as a support material was supplied by The Water Treatment Technology Center, Hangzhou.

2.2. Membrane preparation

The preparation procedure of the membrane was based on literature [10]. A definite amount of the mixture of PVA and β-CD oligomer (8 wt.% in total) was dissolved in hot water at 100°C. After several hours of stirring, the crystalline region of PVA was dissolved and a transparent solution was obtained. A known amount of the solution was cast onto a glass plate or the PAN ultrafiltration membrane to form a membrane. Water was evaporated in a desiccator at 40°C for a day. The dried membrane was subsequently removed from the glass plate and crosslinked by a solution of 0.01% glutaraldehyde, 10% Na_2SO_4 and 0.1N H_2SO_4 for 1 h at room temperature. A transparent, homogeneous or composite membrane was obtained. The thickness of the membranes were 30±2 μm. The membrane in which the ratio of β-CD oligomer to PVA was more than 50% was easily broken and could not be used for pervaporation experiments. The PVA homogeneous or composite membrane was prepared by a similar method.

2.3. Pervaporation experiment

The schematic diagram of pervaporation apparatus was reported previously [12]. The membrane was positioned in the stainless-steel permeation cell. The temperature of the cell was thermostatically controlled. Vacuum at downstream side was maintained at about 133 Pa by a vacuum pump. The permeate collected in the glass trap was condensed with liquid nitrogen. The permeation rate was calculated from the weight change of the trap. The composition of the permeate was analyzed by gas chromatograph equipped with a thermal conductivity detector.

2.4. Sorption experiments

About 1.0 g of membrane strips were dried under vacuum (around 133 Pa) at 100°C to constant weight. The thickness of the membrane strips was measured on a micrometer with an accuracy of $\pm 10^{-4}$ cm, A dried membrane strip and a *p*-/*m*-xylene solution of known composition were placed into a 50 ml glass centrifuge tube, which was completely filled and copped. Twenty such tubes were inserted into a holder, placed in a constant-temperature bath (25°C±0.5°C), and rotated end-over-end at 2 rpm. After several periods of time, a tube was taken from the constant-temperature bath, and the membrane strip was quickly removed. The composition of solution in glass centrifuge tube was measured by gas chromatograph. The sorption amount of *p*-xylene (or *m*-xylene) in the membranes was calculated using the following equation [13]:

$$A_\tau = \frac{V}{W}(C_0 - C_\tau) \tag{1}$$

where V is the volume of *p*-/*m*-xylene solution in glass centrifuge (ml), W the weight of dried membrane strip (g), C_0 the initial concentration of *p*-xylene (or *m*-xylene) in solution (g/ml), C_τ the concentration of *p*-xylene (or *m*-xylene) in solution at a given time τ (g/ml) and A_τ is the sorption amount of *p*-xylene (or *m*-xylene) per unit mass dried membrane at a given time τ (g (xylene)/g (dried membrane)).

For the sorption of pure *p*-xylene (or pure *m*-xylene) in the membranes, the dried membrane strips and pure *p*-xylene (or pure *m*-xylene) were placed into a 50 ml glass centrifuge tube, which was placed into a constant-temperature bath (25°C±0.5°C). After several periods of time, the membrane strip was removed, and the surface was quickly wiped off with tissue paper. The weight of wet membrane strip was determined on a semi-micro balance with an accuracy of ±0.1 mg. This was continued until no further weight increase was observed. The sorption amount of pure *p*-xylene (or pure *m*-xylene) in the membranes was calculated from the difference between the weight of wet membrane and the weight of the dried membrane.

3. Results and discussion

3.1. Diffusion coefficient and solubility

For Fickian diffusion, diffusion coefficient D can be calculated from following standard equation [14]:

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

where A_τ and A_∞ are the equilibrium sorption amounts of the *p*-xylene (or *m*-xylene) per unit mass dried membrane (g (xylene)/g (dried membrane)) at time (s) τ and ∞, respectively, and l is the thickness of the dried membrane (m). At short times ($A_\tau/A_\infty \leq 0.4$), this equation reduces to

$$\frac{A_\tau}{A_\infty} = 4\left(\frac{D\tau}{\pi l^2}\right)^{1/2} \quad (3)$$

which can be rearranged to following form

$$D = \frac{\pi}{16}\left(\frac{A_\tau/A_\infty}{\sqrt{\tau}/l}\right)^2 \quad (4)$$

Due to the plot of A_τ/A_∞ against equal to the initial slope of a sorption curve ($\tan\theta$), that is

$$D = \frac{\pi}{16}(\tan\theta)^2 \quad (5)$$

The sorption of pure *p*-xylene, pure *m*-xylene and *p*-/*m*-xylene solutions in the membranes at 25°C are shown in Figs. 1–4. The curves shown in Fig. 2 (or Fig. 4) are relationship of sorption amount with sorption time (L is a constant). It is known that both *p*- and *m*-xylenes will form an inclusion complex with β-CD (*p*- or *m*-xylene+β-CD↔inclusion complex). For the PVA/β-CD membrane, there are two kinds of sorption, one is the sorption of xylene in PVA and β-CD, and other is the sorption of inclusion complex in PVA and β-CD. These lead to the two curves shown in Fig. 2 (or Fig. 4) cross in the middle. From these sorption curves, the diffusion coefficient for pure *p*-xylene, pure *m*-xylene and *p*-/*m*-xylene solutions in the membranes at 25°C were obtained and shown in Fig. 5. From Fig. 5, we could find that the diffusion coefficient of the *p*-xylene was somewhat larger than that of the *m*-xylene for the PVA membrane, and the diffusion coefficient of the *p*-xylene was somewhat smaller than that of the *m*-xylene for the PVA/ β-CD membrane. This indicates that the diffusion selectivity (D_p/D_m) were decreased by the addition of β-CD. In addition, the dependence of the diffusion coefficient on the composition

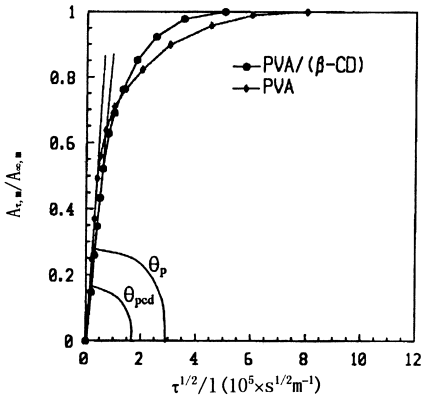

Fig. 2. Pure *m*-xylene diffusion at 25°C.

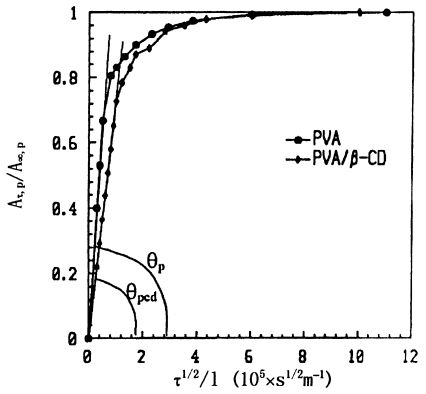

Fig. 3. *p*-Xylene diffusion for 50 wt.% *p*-/*m*-xylene solution at 25°C.

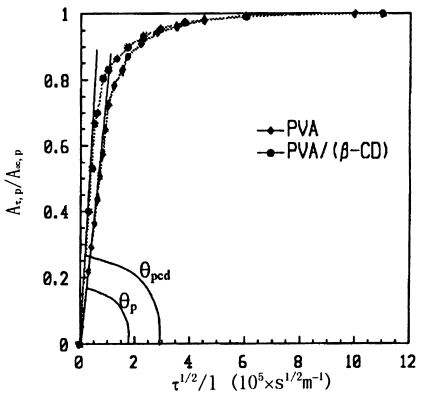

Fig. 1. Pure *p*-xylene diffusion at 25°C.

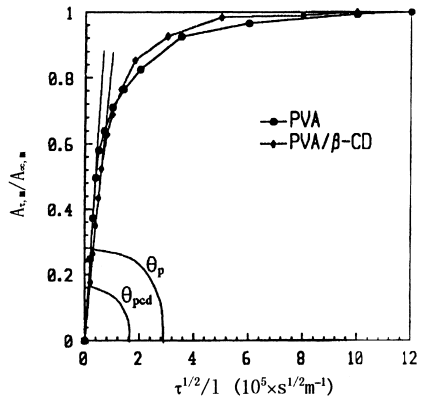

Fig. 4. *m*-Xylene diffusion for 50 wt% *p*-/*m*-xylene solution at 25°C.

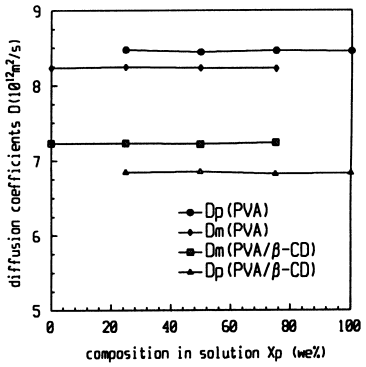

Fig. 5. *p*-Xylene and *m*-xylene diffusion coefficiants at 25°C.

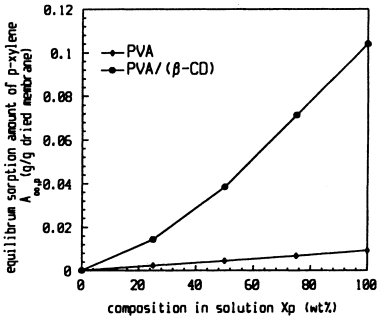

Fig. 6. Sorption of *p*-xylene at 25°C.

of *p*-/*m*-xylene solution was very small for both membrane. This indicates that the effect of the concentration of the *p*-xylene (*m*-xylene) in the membranes on the diffusion coefficients was very small.

The solubility of the *p*-xylene (or *m*-xylene) in the membranes is expressed as a relative weight increase at the equilibrium sorption. That is, A_∞ (g (xylene)/g (dried membrane)).

The solubility of the *p*-xylene and *m*-xylene are shown in Figs. 6 and 7 as a function of the composition of *p*-xylene in solution. Figs. 6 and 7 indicated that the solubility of *p*-xylene (*m*-xylene) increased with an increase in the composition *p*-xylene (*m*-xylene) in *p*-/*m*-xylene solution. In addition, the solubility of *p*-xylene and *m*-xylene were increased by the addition of β-CD.

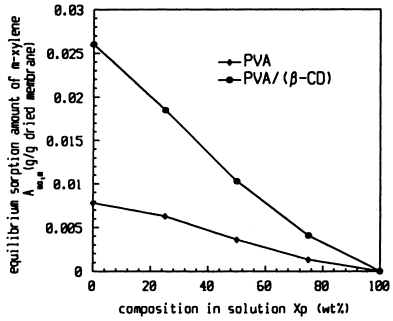

Fig. 7. Sorption of *m*-xylene at 25°C.

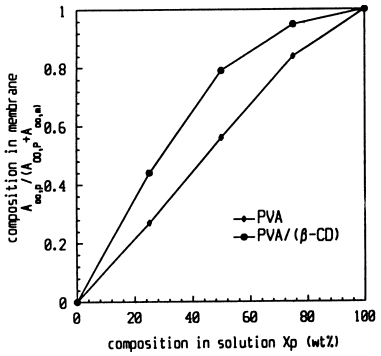

Fig. 8. The separation diagram for the sorption equilibrium at 25°C.

The separation diagram of the sorption equilibrium is shown in Fig. 8. The *p*-xylene selectivity of the PVA/β-CD membrane was much larger than that of the PVA membrane, especially at lower *p*-xylene composition in solution.

The effect of β-CD on the solubility and the diffusion coefficient of the component in the membrane can be explained in term of the inclusion in the cavity of β-CD. It is known that both *p*-xylene and *m*-xylene can form an inclusion complex with β-CD, and the inclusion between *p*-xylene and β-CD is stronger than that between *p*-xylene and PVA, the inclusion between *m*-xylene and β-CD is stronger than that between *m*-xylene and PVA. On the other hand, the inclusion between *p*-xylene and β-CD is stronger than that of both *m*-xylene with β-CD. The stronger inclusion should increase the sorption ability of the component in the membrane, and decrease the mobility of the component in the membrane. Thus, the inclusion effect should increase the solubility of *p*-xylene, the solubility of *m*-xylene, and the solubility selectivity, $A_{\infty,p}/A_{\infty,m}$, in the membrane, decrease the diffusion coefficient of *p*-xylene, the diffusion coefficient of *m*-xylene, and the diffusion selectivity D_p/D_m in the membrane.

3.2. Pervaporation characterization

Fig. 9 shows the separation diagram of the pervaporation. The separation selectivity of *p*-xylene of the PVA/β-CD membrane was much larger than that of the PVA membrane, especially at lower *p*-xylene composition.

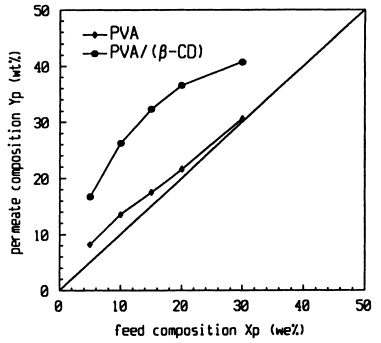

Fig. 9. The separation diagram for pervaporation at 25°C.

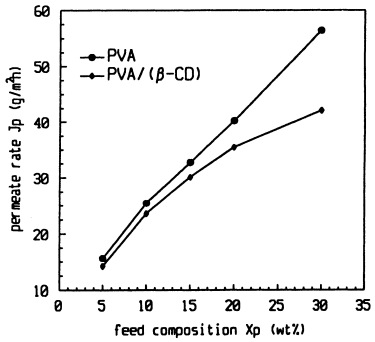

Fig. 10. *p*-Xylene permeation rate at 25°C.

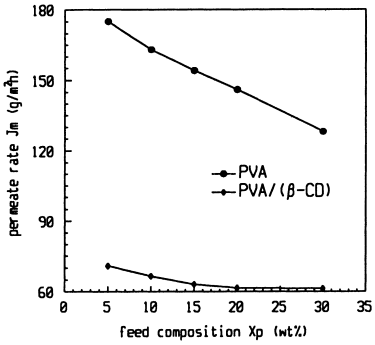

Fig. 11. *m*-Xylene permeation rate at 25°C.

The effects of β-CD on the permeation rate are shown in Figs. 10–12. The *p*-xylene permeation rate was slightly decreased, whereas the *m*-xylene permeation rate and the total permeation rate were greatly decreased by the addition of β-CD. In addition, the permeation rate of *p*-xylene increases, the permeation rate of *m*-xylene decreases with an increase in the composition of *p*-xylene in the feed for both membranes. However, the total permeation rate of the PVA membrane somewhat decreases the total permeation rate of the PVA/β-CD membrane and increases with an increase in the composition of *p*-xylene in the feed. These results were opposite to the effect of β-CD on the diffusion coefficient, and consistent with the effect of β-CD on the solubility. This indicates that the effect of β-CD on the solubility was more important than on the diffusion coefficient for the change in the pervaporation performance.

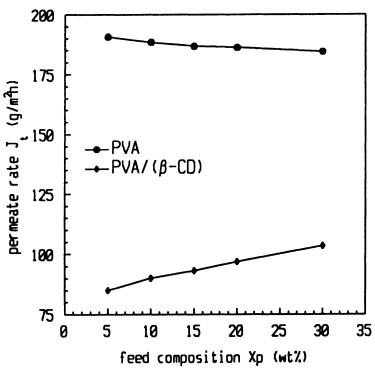

Fig. 12. Total permeation rate at 25°C.

4. Conclusions

From the experimental results of the solubilities of pure *p*-xylene and pure *m*-xylene, and the pervaporation of *p*-/*m*-xylene mixtures in the PVA membrane filled β-CD, the following conclusions can be made.

Compared with PVA membrane, the solubilities of pure *p*-xylene and pure *m*-xylene in PVA membrane filled β-CD increased from 0.92, 0.78 to 10.4, 2.6 g (xylene)/100 g (dried membrane) at 25°C, respectively, and the solubility selectivity S_p/S_m increased from 1.18 to 4.0. Also, the diffusion coefficients of *p*-xylene and *m*-xylene decreased from 8.45×10^{-12} and 8.23×10^{-12} to 6.83×10^{-12} and 7.23×10^{-12} m^2/s at 25°C, respectively.

Compared with PVA membrane, the separation factor of the PVA/β-CD membrane for *p*-xylene, considerable enhanced from 1.35 to 2.96, and the permeation rate decreased from 190 to 95 g/m^2 h for a 10 wt.% feed *p*-xylene concentration at 25°C.

The effect of β-CD on the solubilities of *p*-xylene and *m*-xylene was more important than on the diffusion coefficients of *p*-xylene and *m*-xylene for improvement in the pervaporation performance of the membrane.

The effects of β-CD on the solubility, the diffusion coefficient, and pervaporation have been interpreted by the inclusion phenomenon in the cavity. However, much further investigation is required to clarify this inclusion phenomenon.

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