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PERMEATION OF XYLENE ISOMERS THROUGH SUPPORTED LIQUID MEMBRANES CONTAINING CYCLODEXTRINS

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ABSTRACT

The permeation of *p*- and *m*-xylenes through supported liquid membranes (SLM) containing cyclodextrins (CDs) was investigated in this study. Three CDs were used in the experiments, α-CD, β-CD, and hydroxypropyl-β-CD (HP-β-CD). The mass transfer mechanisms with and without facilitating carriers (CDs) were studied individually by applying the solution–diffusion model. The facilitated mass transfer mechanism was elucidated as partitioning of xylenes from the organic phase into an aqueous phase, formation of an inclusion complex with CDs, diffusion of the complex, and extraction into the receiving phase. The formation constants in aqueous solutions for CDs and *p*-xylene were 1.6–2.4 times higher than that of CDs and *m*-xylene. The diffusivity coefficient of the xylene–CD complex (D_m) and the

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equilibrium extraction constant (K_{ex}) associated with each CD were determined. Meanwhile, K_{ex}, the parameter used to describe the ability of CD to extract xylene and to form a complex, of *p*-xylene and CDs was almost twice as much as that for *m*-xylene and CDs. Thus, the addition of CD into the membrane phase for xylene separation yields a two-fold benefit in favor of *p*-xylene: an increase in selectivity and an enhancement of the mass transfer flux.

Key Words: Cyclodextrins; Facilitated transport; Separation; Supported liquid membranes; Xylene isomers

INTRODUCTION

Effective and efficient separation of organic compounds has been an important subject for the petrochemical industry for decades. The separation of isomers, such as *p*-xylene and *m*-xylene, is difficult to achieve using conventional distillation methods due to their close boiling points and similar volatility. They are separated and purified on an industrial scale using adsorption–desorption methods on molecular sieves or through crystallization methods. Recently, many membrane techniques have been proposed to separate xylene isomers, including the pervaporation method (1–4), evapomeation (4), and liquid membranes. Liquid membranes were first employed by Italian researchers in 1980 to separate *o*-/*m*-xylenes, and *o*-/*p*-xylenes (5). The separation factors obtained were 0.97–2.02 (*o*-/*m*-xylene) and 0.9–1.57 (*o*-/*p*-xylene). Andreaus et al. (6) used methyl-α-cyclodextrin (M-α-CD) as a facilitating carrier into an o/w/o liquid membrane system. Cyclodextrins are water-soluble oligosaccharides with hydrophobic cavities, which allow CDs to form host–guest complexes with *para*-isomers rather than *ortho*- and *meta*-counterparts (7). They found that the addition of a surfactant, required to maintain a stable emulsion, had an adverse effect on the solubility and partitioning of *o*- and *p*-xylenes in aqueous solutions. This study investigated a supported liquid membrane (SLM) process containing CD as a method for the separation of xylenes. In this way, the addition of a surfactant is eliminated and the selectivity is still achieved using CD. The objective of this study was to study the mass transport mechanism (including various equilibrium constants, partition coefficients, and diffusivity coefficients) of both simple permeation and facilitated transfer of xylenes in a CD-containing SLM system. The effects of different CD configurations on xylene permeation were also investigated.

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THEORY

Xylene transport through a CD-containing SLM system may be considered a solution–diffusion process and consists of multiple steps, described as follows:

(1) Xylenes diffuse into an aqueous membrane phase from the organic phase.
(2) Xylene molecules and CDs form inclusion complexes in the aqueous membrane phase, as appropriate and reach an equilibrium state. The remaining xylenes and CDs retain a free form.
(3) The complex, along with the free xylene, diffuses through the SLM from the source–membrane phase interface into the membrane–receiving phase interface.
(4) The complex dissociates into free CD and xylene at the membrane–receiving phase interface.
(5) The xylene is then extracted into the receiving phase.

In order to analyze the mass transport model, several assumptions were made in this study:

I. The source phase and the receiving phase were mixed well without significant concentration gradients.
II. The external transport resistance can be neglected.
III. The solubility of CD in the organic phase is negligible.
IV. CD and xylene form a 1:1 inclusion complex.
V. A fast extraction equilibrium exists for xylenes at the organic–aqueous interface and at the aqueous–organic phase interface.
VI. Both simple permeation of xylenes and their facilitated transport with CD progress independently.
VII. The diffusion of the free xylene and the xylene–CD complex through the SLM is the rate-limiting step.
VIII. The diffusivity coefficients of the free xylene and the CD–xylene complex remain constant throughout the permeation process.

The first two assumptions were made possible by sufficient stirring in both phases. Assumption III is to be verified in this study. Assumption IV has been proven (6,8). The last four assumptions serve as the basis for the deriving the mathematical equations as follows. The concentration profile for the transport of xylene through SLM is shown in Fig. 1, assuming that simple xylene permeation and its facilitated transport with CD progress independently.

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Facilitated Transport

Applying Fick's law with the last two assumptions above, the facilitated flux of xylene through a CD-contained SLM at steady state is:

$$J_f = \frac{D_m}{\delta}([X{\cdot}CD_{(aq)}]_{ms} - [X{\cdot}CD_{(aq)}]_{mr}) \quad (1)$$

where J_f is the mass flux of facilitated transport, D_m the effective diffusion coefficient of the xylene–CD complex through SLM, δ the membrane thickness, $[X{\cdot}CD_{(aq)}]_{ms}$ the concentration of the xylene–CD complex at the source–membrane phase interface, and $[X{\cdot}CD_{(aq)}]_{mr}$ is the concentration of the complex at the membrane–receiving phase interface. At the initial stage of the mass transfer, with no xylene in the receiving phase, the value of $[X{\cdot}CD_{(aq)}]_{mr}$ is zero and Eq. (1) can be simplified as an initial flux ($J_{0,f}$) as shown in Eq. (2):

$$J_{0,f} = \frac{D_m}{\delta}[X{\cdot}CD_{(aq)}]_{ms} \quad (2)$$

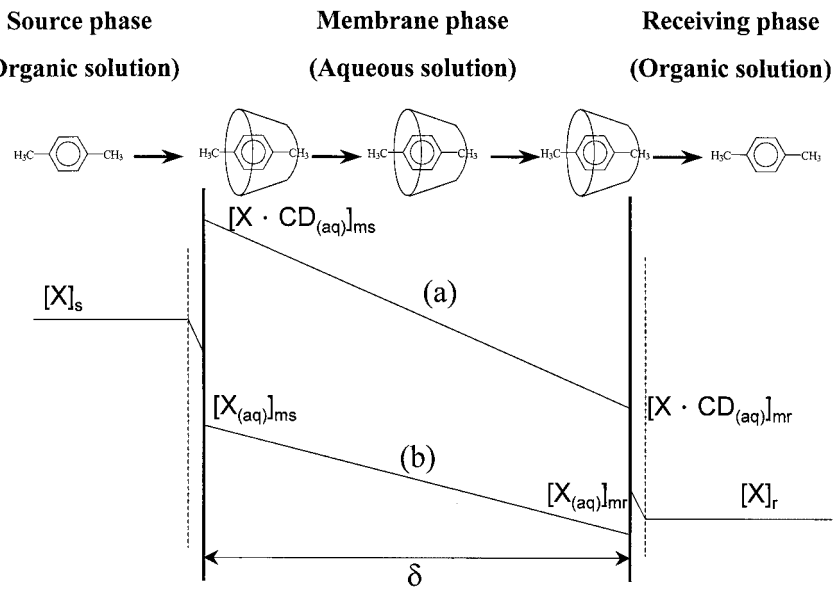

Figure 1. Concentration profile of xylene through SLM of (a) facilitated transport, and (b) simple permeation.

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In this study, a flux was considered initial if the mass transport (in mol/m^2) vs. time (in seconds) shows a linear relationship through the origin, and is so during the first 30 min of operation.

In order to determine $[X{\cdot}CD_{(aq)}]_{ms}$ in Eq. (2), one needs to start with the solution–diffusion model, as shown above. When xylene diffuses from the organic phase into the aqueous membrane phase (either containing CD or without CD), it possesses a partition equilibrium between the organic and the aqueous phases:

$$X \leftrightarrow X_{(aq)} \quad K_p = \frac{[X_{(aq)}]}{[X]} \tag{3}$$

where X and $X_{(aq)}$ represent xylene in the organic and aqueous phases, and K_p is the partition coefficient. Xylene in the aqueous phase forms a complex with CD according to the following equation:

$$CD_{(aq)} + X_{(aq)} \leftrightarrow X{\cdot}CD_{(aq)} \quad K_a = \frac{[X{\cdot}CD_{(aq)}]}{[X_{(aq)}][CD_{(aq)}]} \tag{4}$$

where K_a is the complex formation constant in the aqueous phase. One can obtain Eq. (5) by combining Eqs. (3) and (4):

$$X + CD_{(aq)} \leftrightarrow X{\cdot}CD_{(aq)} \quad K_{ex} = \frac{[X{\cdot}CD_{(aq)}]}{[X][CD_{(aq)}]} \tag{5}$$

where $K_{ex} = K_a K_p$. Meanwhile, taking mass balance on CD yields:

$$[CD_{(aq)}]_t = [CD_{(aq)}] + [X{\cdot}CD_{(aq)}] \tag{6}$$

where $[CD_{(aq)}]_t$ is the initial CD concentration in the aqueous phase, and $[CD_{(aq)}]$ and $[X{\cdot}CD_{(aq)}]$ are the concentrations of free CD and xylene–CD complex in the aqueous solution, respectively. Combining Eqs. (5) and (6) gives:

$$[X{\cdot}CD_{(aq)}]_0 = \frac{K_{ex}[X]_0[CD_{(aq)}]_t}{1 + [X]_0 K_{ex}} \tag{7}$$

Substituting Eq. (2) with Eq. (7) yields:

$$J_{0,f} = \frac{D_m}{\delta} \frac{K_{ex}[CD_{(aq)}]_t[X]_0}{(1 + [X]_0 K_{ex})} \tag{8}$$

Eq. (8) may be rewritten as Eq. (9):

$$\frac{1}{J_{0,f}} = \frac{\delta}{D_m K_{ex}[CD_{(aq)}]_t[X]_0} + \frac{\delta}{D_m[CD_{(aq)}]_t} \tag{9}$$

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According to Eq. (9), one can obtain a straight line by plotting $1/J_{0,f}$ vs. $1/[X]_0$ with the following:

$$\text{intercept} = \frac{\delta}{D_m[CD_{(aq)}]_t} \tag{10}$$

$$\text{slope} = \frac{\delta}{D_m K_{ex}[CD_{(aq)}]_t} \tag{11}$$

As long as D_m (the apparent diffusion coefficient of the xylene–CD complex in the aqueous phase) is determined from Eq. (10), it will be used to calculate K_{ex} according to Eq. (11).

Complex Formation Constant

To measure the complex formation constant (K_a), the extraction experiments proposed previously (6) were employed. The solubility of xylenes in CD solutions was measured after the pure xylene solvent had reached equilibrium with the aqueous solution and the amount of xylene in the aqueous solution was determined. The xylene solubility in CD solutions (S) is equal to the amount of xylene dissolved in water as free molecules and that as complexes with CD. Thus,

$$S = [X{\cdot}CD_{(aq)}] + [X_{(aq)}] \tag{12}$$

Combining Eqs. (4), (6), and (12) yields:

$$S = [X_{(aq)}] + \frac{[CD_{(aq)}]_t K_a[X_{(aq)}]}{1 + K_a[X_{(aq)}]} \tag{13}$$

One will expect to obtain a straight line by plotting S vs. $[CD_{(aq)}]_t$ with the following:

$$\text{intercept} = [X_{(aq)}],$$

and

$$\text{slope} = \frac{K_a[X_{(aq)}]}{1 + K_a[X_{(aq)}]}$$

In this way, the concentration of free xylene in CD solutions ($[X_{(aq)}]$) and the complex formation constant of xylene and CD in aqueous phase (K_a) can be determined.

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Simple Permeation

Under the circumstances where xylenes transport through SLM containing no carriers, the mass transfer is due to diffusion because of the concentration gradient of xylenes in the aqueous phase between the feed–membrane interface and the membrane–receiving solution interface. The mass flux equation similar to Eq. (1) may be applied:

$$J_s = \frac{D}{\delta}([X_{(aq)}]_{ms} - [X_{(aq)}]_{mr}) \tag{14}$$

where J_s is the mass flux of simple permeation without CD, D is the effective diffusion coefficient of xylenes in a pure water solution within the membrane, δ is the membrane thickness, $[X_{(aq)}]_{ms}$ is the concentration of xylene in the aqueous phase at the source–membrane phase interface, and $[X_{(aq)}]_{mr}$ is the concentration of xylene in the aqueous phase at the membrane–receiving phase interface. Assume that the rate-limiting step is, again, the diffusion step within the membrane phase. At the initial period, the concentration of xylene in the membrane–receiving solution interface is zero. The initial flux, then, becomes:

$$J_{0,s} = \frac{D}{\delta}[X_{(aq)}]_{ms} \tag{15}$$

The value of D may be calculated once $[X_{(aq)}]_{ms}$ is determined from Eq. (13) and $J_{0,s}$ is measured experimentally.

EXPERIMENTAL

Reagents and Membrane Preparation

Para- and *meta*-xylenes (99%) were purchased from Acros Organics (Geel, Belgium) without further purification. Alpha-cyclodextrin (α-CD, 98+%) and beta-cyclodextrin (β-CD, 99%) were obtained from Acros Organics, and hydroxypropyl-β-cyclodextrin (HP-β-CD) was from Aldrich Chemical Co. (Milwaukee, WI). The properties of the CDs are shown in Table 1. Deionized water, produced on a Millipore water purifier (models RiOs-5 and Millipore-Q Gradient, Millipore Corp., Bedford, MA) was used to prepare CD solutions. Under circumstances in which CD was not completely soluble in water, urea (Acros Organics, Geel, Belgium) was added into the solution to help the CD dissolve and sodium hydroxide (Shimakyu's Pure Chemicals, Osaka, Japan) was added to adjust the pH of the resulting CD solution at 7.0. Toluene (also from Acros Organics) was used as the receiving phase.

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Table 1. Properties of Cyclodextrins Used in This Study (7)

Cyclodextrin	No. Glucose Residue	Molecular Weight	Water Solubility (g/100 mL)	Cavity Dimensions (Å)	
				Internal Diameter	Depth
α-CD	6	972	14.5	4.5 (4.7–5.2[c])	6.7
β-CD	7	1135	1.85	7.0 (6.0–6.4[c])	7.0
HP-β-CD[a]	7	~1380[a]	—[b]	—	—

[a] Molar substitution = 0.6, from Aldrich product information.
[b] Not available.
[c] From reference (14).

The hydrophilic microporous support was a polycarbonate membrane from Nuclepore® (Whatman Inc., Newton, MA) with a pore size of 0.05 μm and a membrane thickness of 6 μm. It was a track-etched type and the tortuosity was approximately unity. The membrane support was immersed for 15 min in 10 mL of 0–0.03 *M* CD solutions inside a beaker. The beaker was then placed in a vacuum at 25°C for 20 min to exclude air, if any, remaining in the aqueous phase entrapped within the pores of the polymer membrane. The membrane was then removed from the vacuum oven and the excess water on the membrane surface was wiped away.

Supported Liquid Membranes Operation

A membrane, treated as described above, was clamped between two cylindrical vessels for SLM experiments. Figure 2 shows the experimental set-up for SLM testing. Water at 25°C was circulated into the jacket of the vessel using a peristaltic pump (Cole–Parmer Instrument Co., Vernon Hills, IL). One hundred milliliters of source phase and 100 mL of receiving solution were placed into the vessels. Both the source and receiving solutions were agitated constantly at 300 rpm using magnetic stirrers (Model MS-1, Shin Kwang Machinery Industry Co. Ltd., Taiwan). At predetermined time intervals, the volume of both the source and receiving solutions were recorded and a 0.25 mL sample aliquot was taken from the receiving solution for gas chromatography (GC) analysis. The simple permeation rate of xylene through the SLM without CD (i.e., only pure water in the membrane phase) was measured first and the facilitated transfer rate as a result of CD facilitation was corrected after subtracting the 'blank'.

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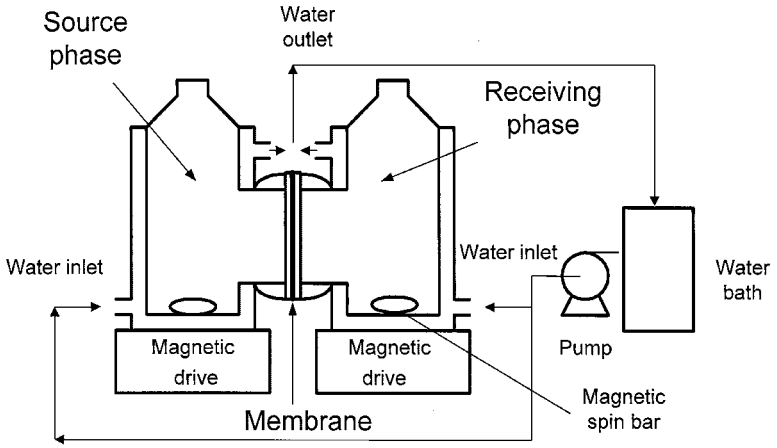

Figure 2. Permeation cell set-up for SLM operation.

Determination of Complex Formation Constants

Twenty-five milliliters of pure xylene solvent was equilibrated with 25 mL of CD solution of varying concentrations in an Erlenmeyer flask. The flask was placed in a shaking machine rocking at 100 strokes/min at 25°C for 3 hr. After equilibrium was reached, the content was poured into a separatory funnel and allowed to settle for 2 hr. The organic and aqueous phases were separated and their volumes measured. The xylene content in the aqueous phase was extracted using solid phase extraction (SFE). The aqueous phase was filtered into a SFE disk (ENVI-18 DSK, Supelco, Supelco Park, Bellefonte, PA), 3 mL of methanol (HPLC grade, Acros Organics, Geel, Belgium) was used to elute the absorbed xylene, and the composition of the methanol solution was determined by a gas chromatograph.

Chromatographic Procedure

An aliquot of 0.02 μL of organic sample was injected into a gas chromatograph (HP 4890, Hewlett-Packard Co., Palo Alto, CA) with a flame-ionization detector. High purity nitrogen (99.999%) at a linear velocity of 28 cm/sec swept the analytes through a stainless steel capillary column (Bentone® 34/DNDP SCOP, 15 m × 0.051 cm I.D, Supelco, Supelco Park, Bellefonte, PA) for analysis. The temperature of the oven was maintained at 75°C, and that of injector and detector was 220°C.

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A series of standard solutions containing *p*-xylene and *m*-xylene were prepared at various concentrations. An aliquot of 0.02 μL of each standard was injected into the gas chromatograph. The calibration curve was obtained by plotting peak area vs. mass of xylene (μg) and by forming a regression line through the origin using the least squares method. The equation for the calibration line was $Y = 3.367 \times 10^6 X$ for *p*-xylene, and $Y = 3.692 \times 10^6 X$ for *m*-xylene, with coefficients of determination (R^2) of 0.987 and 0.990, respectively.

Solubility of Cyclodextrins in Organic Solvents

The CDs exhibit optical characteristics and are used to determine the solubility of CDs in organic solvents. Twenty-five milliliters of ca. 0.01 *M* aqueous CD solutions were mixed with three organic solvents (*m*-xylene, *p*-xylene, and toluene) separately. The content was shaken for 3 hr at 25°C and settled in a separatory funnel for 2 hr. The aqueous solution was removed and its optical rotation was measured using a digital polarimeter (DIP 1000, Jasco Corp., Tokyo, Japan). The light source was a sodium lamp, 589 nm in wavelength. The sample cell was 100 mm long and the time span was 5 sec. Each sample was measured five times and the average was used to report the results.

RESULTS AND DISCUSSION

Solubility of Cyclodextrins in Organic Solvents

In order to verify that CDs are not soluble in organic solvents and that Eq. (6) holds true, optical rotation of CD solutions were measured before and after equilibrating with organic solvents. The results shown in Table 2 indicate that the solubility of CD in *p*-xylene, *m*-xylene, and toluene are negligible.

Xylene Solubility in Cyclodextrins Solutions

The extraction procedure outlined in "Determination of Complex Formation Constants" was carried out in order to plot line charts according to Eq. (13). A typical graph is shown in Fig. 3, showing the solubility of *p*-xylene and *m*-xylene in α-CD solutions at 0–0.03 *M* concentration. Increasing the CD concentration in the aqueous solution enhanced the solubility of the xylenes due to the formation of an inclusion complex with CD. The least squares method was used to fit the regression lines and the solubility of xylenes in pure water ($[X_{(aq)}]$)

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Table 2. Comparison of Optical Rotation (in Degrees) Results Before and After Extraction with Organic Solvents

Solvent/CD	α-CD	HP-β-CD
Control	1.29[a]	1.86
p-Xylene	1.25	1.83
m-Xylene	1.28	1.84
Toluene	1.29	1.94

[a] Theoretical value = 1.30, calculated using specific rotation (α_D^{25}) of α-CD of 150.5 (7).

and the complex formation constants (K_a) were calculated. The results indicate that the solubility of *p*-xylene and *m*-xylene was 0.322 and 0.214 g/L, respectively. The 95% confidence interval for the solubility of xylenes can be determined using statistical methods. The interval was 0.199–0.445 g/L for *p*-xylene and 0.184–0.244 g/L for *m*-xylene. These numbers agree well with the literature values. It has been reported that the solubility of *p*-xylene and *m*-xylene are both 0.214 g/L and 0.160 g/L, respectively (8). Andreaus et al. (6) found that the solubility of *p*-xylene is 0.232 g/L.

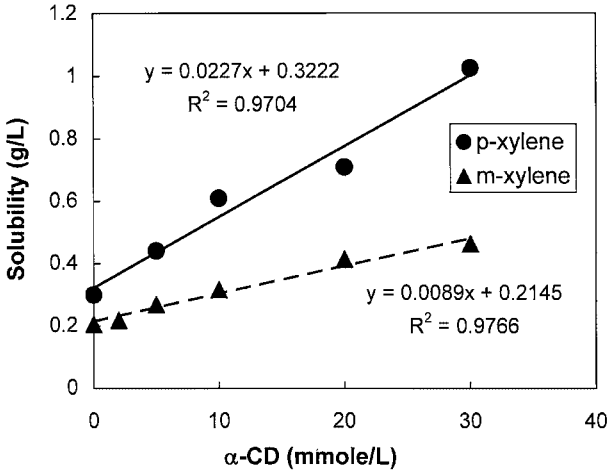

Figure 3. Xylene solubility in α-CD solutions.

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To test if the complex formation is independent and no competition occurred between xylenes and CD when the two components co-exist, mixed solutions of two xylenes (20/80, 50/50, 80/20 v/v) were prepared and allowed to contact with CD solutions until equilibrium was reached. The solubility of xylene was measured and compared with the calculated value. The calculated value was performed using the following procedure. When *p*- and *m*-xylenes are both present in the organic phase and reach equilibrium with the CD solution, the complex formation reactions are:

$$CD_{(aq)} + pX_{(aq)} \leftrightarrow pX{\cdot}CD_{(aq)} \quad K_{a,pX} = \frac{[pX{\cdot}CD_{(aq)}]}{[pX_{(aq)}][CD_{(aq)}]} \tag{16}$$

$$CD_{(aq)} + mX_{(aq)} \leftrightarrow mX{\cdot}CD_{(aq)} \quad K_{a,mX} = \frac{[mX{\cdot}CD_{(aq)}]}{[mX_{(aq)}][CD_{(aq)}]} \tag{17}$$

and the mass balance for CD is:

$$[CD_{(aq)}] = [CD_{(aq)}]_t - [pX{\cdot}CD_{(aq)}] - [mX{\cdot}CD_{(aq)}] \tag{18}$$

Combining Eqs. (16–18) yields:

$$[CD_{(aq)}] = \frac{[CD_{(aq)}]}{1 + K_{a,pX}[pX_{(aq)}] + K_{a,mX}[mX_{(aq)}]} \tag{19}$$

where $K_{a,pX}$, $K_{a,mX}$ are the complex formation constants for *p*- and *m*-xylene, respectively, as determined in "Complex Formation Constants" and $[pX_{(aq)}]$ and $[mX_{(aq)}]$ are the solubilities of free xylenes in the pure water solution. The value for $[CD_{(aq)}]$ can be determined from Eq. (19) and the complex concentration (taking *p*-xylene for example, $[pX{\cdot}CD_{(aq)}]$) is established from Eq. (16). The solubility of the pure solvent (S_{pX} for *p*-xylene) can be calculated as the sum of $[pX_{(aq)}]$ and $[pX{\cdot}CD_{(aq)}]$. The solubility of pure xylene in CD solution (say, S_{pX}) times the xylene mole fraction (of *p*-xylene, for example) was used as the calculated value. Shown in Fig. 4 is the xylene solubility in the aqueous phase at various xylene compositions in contact with 0.01 *M* α-CD solution. The experimental values were very close to the calculated values, and this indicates that the complex formation phenomena between xylenes and CD are independent.

Complex Formation Constants

From the slope of Fig. 3, one can calculate the complex formation constants (K_a) associated with various CDs using Eq. (13). Summarized in Table 3 are the results of complex formation constants in comparison with those from previous works. It is noted that the values for K_a of xylenes and α- and β-CD in this study

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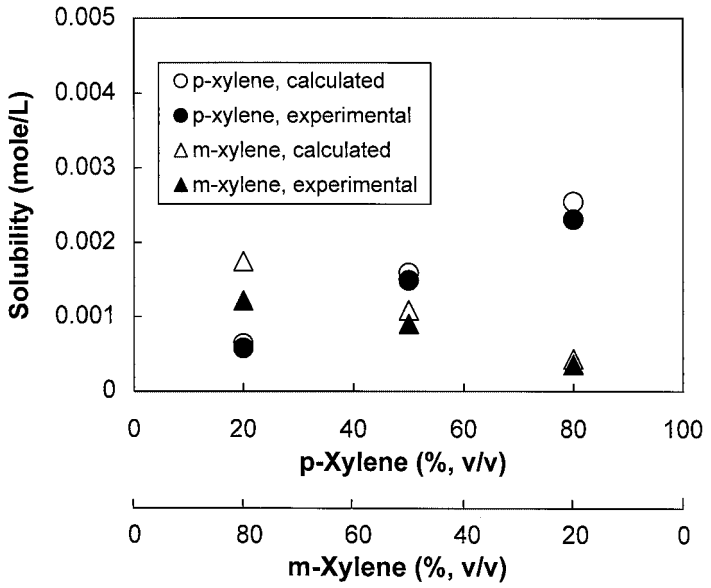

Figure 4. Xylene solubility at various xylene compositions using 0.01 *M* α-CD.

Table 3. Complex Formation Constants (K_a, in L/mol) of Xylenes and Cyclodextrins in Aqueous Solutions (25°C)

			References	
Cyclodextrin	Xylene	This Work	(9)	(10)
α-Cyclodextrin	*p*-Xylene	72	56 ± 20	72 ± 7
	m-Xylene	42	32 ± 2	40 ± 1
β-Cyclodextrin	*p*-Xylene	233	230 ± 5	240 ± 10
	m-Xylene	127	120 ± 50	160 ± 10
HP-β-Cyclodextrin	*p*-Xylene	308	—[a]	—
	m-Xylene	131	—	—

[a] Not available.

are consistent with the results reported in other studies (8,10). *para*-Xylene has higher formation constants with all three CDs than *m*-xylene, showing that CDs preferentially form inclusion complex with *p*-xylene. It is noted that HP-β-CD tends to form more complexes with xylenes, with a complex formation constant

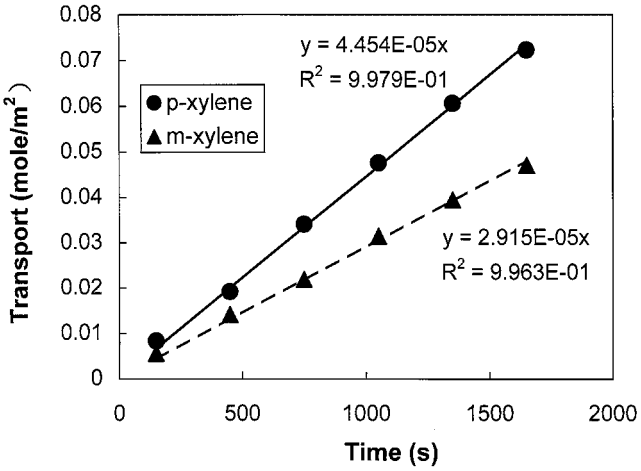

Figure 5. Simple permeation of xylenes through SLM without CD (source phase: pure xylene solvent).

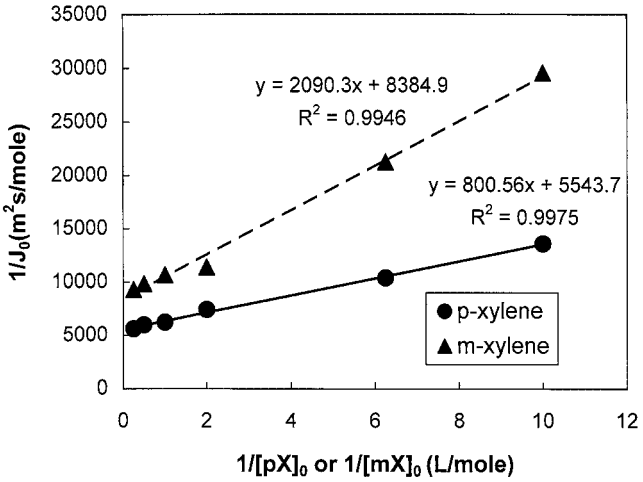

Figure 6. Xylene flux of facilitated transport through SLM containing 0.01 *M* β-CD (source phase: xylene in toluene).

significantly higher than its unsubstituted β-CD counterpart. This may be because the additional hydrophobic interactions between the cavity of the substituted-CD and the xylenes lead to an increase in complex formation constants and the increased solubility of xylenes in water. Andreaus et al. (6) employed methyl-α-

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CD to study the complex formation constants with *p*- and *o*-xylenes and stated that the additional hydrophobic interactions between the methyl groups of the M-α-CD and the xylene lead to an increase in K_a. Kusumoto (11) also found that the complex constant of di-*O*-methyl-β-CD is seven times higher than unsubstituted β-CD. For the same reason, the hydroxypropyl derivative of β-CD has more hydrophobic groups, favoring complex formation with xylenes, and possesses higher K_a.

Simple Diffusion of Xylenes Through Supported Liquid Membranes

A preliminary study indicates that the mass transfer rate of free xylenes through SLM without CD is substantial and may not be neglected. Therefore, the permeation experiments of xylene through SLM were carried out first without CDs. The initial flux in Eq. (15) was used to evaluate *D*, the apparent diffusivity of xylene molecules in pure water. When the source solution consisted of pure xylene solvent, the value of $[X_{(aq)}]_{ms}$ can be estimated as the value of $[X_{(aq)}]$ determined in previous section. Figure 5 shows the transport of *p*- and *m*-xylene through SLM without CD. The fact that the regression line in Fig. 5 is linear and passes through the origin indicates that the flux at this stage may be treated as initial flux. Substituting Eq. (15) with the data of the initial flux, xylene solubility in pure water, and membrane thickness, the diffusivity coefficient of free xylene in aqueous solutions can be obtained. The results indicate that the effective diffusivity coefficient of free *p*- and *m*-xylenes in an aqueous solution is close to one another, in a range of $8.85-8.91\times10^{-11}\text{m}^2/\text{s}$.

Facilitated Transport of Xylenes with Cyclodextrins

Now the situation in which xylene diffuses through SLM containing CD is considered. The initial flux of xylenes through SLM containing CD was carried out using the procedure shown in "Supported Liquid Membranes Operation". Figure 6 shows the plot of $1/J_{0,f}$ vs. $1/[X]_0$ of *p*- and *m*-xylenes using β-CD, indicating excellent linearity with R^2 of 0.9946 and 0.9975, respectively. This demonstrates that the equation in Eq. (8) describes the mechanism of facilitated transport in the xylene–CD system adequately. The values for the complex diffusivity (D_m) and overall equilibrium constant (K_{ex}) were determined according to Eqs. (9)–(11). Table 4 summarizes the results for D_m and K_{ex} using various CDs.

The diffusivity of the host–guest complex between CD and aromatic compounds has not been reported so far. In fact, the information on complex

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Table 4. Summary of D_m and K_{ex} of Xylenes and Cyclodextrins[a]

	D_m ($\times 10^{-11}$ m^2/s)		K_{ex} (L/mol)	
Cyclodextrin	*p*-Xylene	*m*-Xylene	*p*-Xylene	*m*-Xylene
α-CD	10.64	6.78	5.244	3.538
β-CD	10.82	7.16	6.924	4.011
HP-β-CD	11.81	7.66	8.726	4.296

[a] 0.01 *M* of CD at 25°C.

diffusivity in SLM processes is very limited. Wang and Hu (12) found that the diffusivity of phenol–trioctylamine salt complex, $[(TOA)_2H_2SO_4{\cdot}PhOH]$, is $4.2-6.2\times10^{-10}$ m^2/sec in membrane phase of kerosene with 0.025–0.2 *M* trioctylamine salt as carrier. Lee et al. (13) established the diffusivity of silver–D2EHPA (di-2-ethylhexyl phosphoric acid) complex to be 9.187×10^{-8} m^2/sec in kerosene solution containing 2–10 mmol/dm^3 carrier and surfactant. This work provides a reliable alternative method for the determination of diffusivity in inclusion complexes.

CONCLUSION

The simple permeation of xylenes and the facilitated transport of xylene–CD complexes can be described adequately using a solution–diffusion model. The results indicate that these two mechanisms proceed simultaneously and independently. The hydrophobic cavity of the CD molecule forms inclusion complexes with *p*-xylene rather than with *m*-xylene. The formation constants in aqueous solutions for CDs and *p*-xylene are 1.6–2.4 times higher than those for CDs and *m*-xylene. Among the CDs tested, HP-β-CD has the highest complex binding constants, followed by β-CD, and α-CD has the lowest. The addition of CD to the aqueous membrane phase not only increases the xylene solubility in an aqueous solution, but also enhances the mobility and diffusivity of the inclusion complex.

SYMBOLS

$[CD_{(aq)}]$ concentration of uncomplexed cyclodextrin in aqueous phase (mol/L)
$[CD_{(aq)}]_t$ concentration of cyclodextrin in aqueous phase as prepared (mol/L)

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D	effective diffusivity coefficient of xylene in pure water with SLM (m^2/sec)
D_m	effective diffusivity coefficient of CD–xylene complex in aqueous CD solution within SLM (m^2/sec)
J	flux of xylene through SLM (mol/m^2 sec)
J_0	initial flux of xylene through SLM (mol/m^2 sec)
K_a	complex formation constant of xylene and CD in the aqueous phase (L/mol)
K_p	partition coefficient of xylene between the organic and aqueous phases (−)
K_{ex}	product of K_a and K_p
S	solubility of xylene in a CD solution (mol/L)
[X]	xylene concentration in the organic phase (mol/L)
$[X_{(aq)}]$	concentration of free xylene in the aqueous phase, also xylene solubility in pure water (mol/L)
$[m\,X_{(aq)}]$	concentration of free *m*-xylene in the pure water solution (mol/L)
$[p\,X_{(aq)}]$	concentration of free *p*-xylene in the pure water solution (mol/L)
$[X{\cdot}CD_{(aq)}]$	concentration of xylene–CD complex in the aqueous phase (mol/L)
δ	membrane thickness (m)

Subscripts

0	at initial stage
(aq)	in aqueous phase
f	as a result of facilitated transport using CD
s	as a result of simple permeation without CD
ms	in aqueous membrane phase at membrane–source interface
mr	in aqueous membrane phase at membrane–receiving interface
pX	for *p*-xylene
mX	for *m*-xylene

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