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Preparation and characterization of α-cyclodextrin-containing membranes—application to the selective extraction of xylene isomers

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Abstract

Polymer membranes containing α-cyclodextrin (α-CD) were prepared by the casting method using cross-linking reaction with hexamethylenediisocyanate. The film synthesis conducted with and without dibutyltin dilaurate as catalyst, resulted in two series of materials in which α-CD host entities were chemically linked to polyvinyl alcohol and physically entrapped, respectively. The obtained membranes were successfully applied to the separation of *o*-/*p*- and *o*-/*m*-xylene isomer mixtures by pertraction from water. *p*- and *m*-xylenes were found to be the faster permeants compared to the *o*-isomer. The separation factor of *p*-xylene over *o*-xylene varied from 7.75 to 0.35 depending on the membrane α-CD content and the feed concentration ratio. Permeation rate and separation selectivity data were discussed in terms of molecular recognition by α-CD and of coupling transport effect. Both kinds of materials showed similar behaviour in their permeation performances indicating that inclusion interaction was not changed by the chemical grafting on PVA chains.

Keywords: α-Cyclodextrin-containing membrane; Facilitated transport; Xylene isomers

1. Introduction

Many efforts to improve the efficiency and the selectivity of membrane processes have been investigated, leading to the attractive development of membranes based on molecular recognition properties. These membranes present affinity and selectivity properties owing to designed recognition sites able to form host-guest complexes by supramolecular interactions. Cyclodextrins (CDs), water-soluble oligosaccharides consisting of 6, 7 and 8 glucose units for α-, β- and γ-CD, are among the most widely used host molecules in separation science [1,2]. Indeed, CDs possess a hydrophobic cavity having the remarkable ability to form inclusion complexes with a wide variety of organic compounds. The selectivity originates from the different binding constants to CD depending on the size and shape of guest molecules. This fitting effect has been successfully exploited for separation of positional isomers and enantiomers in such techniques as HPLC and capillary electrophoresis (see for instance Refs. [1–3]).

The need for large scale separation using continuous processes has motivated the development of membrane based separation techniques. Supported liquid membranes have been developed for this purpose [4–7] but their application was limited by their instability due to the leaching out of the internal phase in the surrounding phase. Immobilization through entrapment and covalent binding to the membrane matrix has been developed to overcome this problem. It appears from literature that CD-containing membranes have been mainly based on the immobilization onto hydrophilic polymers acting as a barrier for hydrophobic compounds and thereby limiting their non selective diffusion [8–13]. Polyvinyl alcohol (PVA) seems to be one of the most efficient polymer matrixes for CD-containing membranes owing to its ability to form free-standing films and its hydrophilic character due to the presence of hydroxyl groups. In these membrane materials CDs have been either trapped in PVA [10,11] or covalently linked to the chain [9,12]. The ability of membranes to discriminate between isomers has been investigated through the permeation of model molecules including xylenes. For example β-CD trapped in PVA was found to be selective to *p*-xylene over

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o-xylene with a separation factor of 1.4 (50% *p*-isomer feed concentration) [11]. On the other hand, PVA/CD membrane prepared by casting an aqueous mixture of PVA and a β-CD oligomer crosslinked with glutaraldehyde, showed a separation factor for *p*-/*m*-xylenes of 2.96 (10% *p*-isomer feed concentration) [12].

Pervaporation and vapour permeation were the separation processes used in those studies. Recently we have developed a new pertraction process based on a continuous liquid–liquid extraction mediated by CD-containing membrane contactors [14,15]. Organics having a high affinity for the CD cavity were extracted from a feed solution and transferred through the membrane to a stripping solution. The membranes were prepared from PVA and CDs using epichlorohydrin and hexamethylene diisocyanate (HMDI) cross-linking agents. The pertraction process was successfully applied to the selective extraction of C-60 fullerene using γ-CD as the recognition site [15]. Another application was the extraction of organics (toluene) from an aqueous phase using membranes with various CD content (0–50 wt%) and cavity size (α-CD, β-CD, γ-CD) [14]. Permeation rate was found to be enhanced by increasing the CD content up to 38 wt% and better membrane efficiency was obtained for β-CD based membranes. Using a similar pertraction technique, Krieg et al. described the separation of the racemic pharmaceutical chlorthalidone in water:methanol (85:15) by a ceramic membrane impregnated with a β-CD/epichlorohydrin polymer [16]. Interestingly, they obtained a separation factor of 1.24 in spite of the instability of the membrane.

As the liquid–liquid extraction mediated by CD immobilized in membrane appears as a promising separation technique, our aim is to evaluate performance of this process for isomer discrimination using PVA/CD membranes. In the present work, geometrical xylene isomers were chosen as model molecules since numerous data can be found in the literature. A preliminary study [17] showed that selectivity for this separation was much higher using α-CD based membranes than β-CD ones, in accordance with a recent study on pervaporation of mixed xylenes through CD-containing polyacrylic acid membranes [13]. We report here on the preparation and characterization of α-CD-containing membrane materials based on PVA. The modification of molecular recognition properties with the chemical nature of substituent and the degree of CD derivatization is a well-documented phenomenon for separation using chromatographic stationary phases [1,2]. In order to get a clear insight into the effect of the covalent linkage between α-CD and PVA on the selectivity of membranes, two kinds of materials were fabricated: membranes containing α-CD chemically grafted to the PVA chain and underivatized α-CD physically trapped into the polymer matrix. Extraction experiments were carried out for *o*-/*p*- and *o*-/*m*-xylene isomer mixtures of varying composition. Water was used as an intermediate phase to allow the transfer to take place under favorable conditions [4,14]. In this study, we focus on the nature of α-CD immobilization (grafted or trapped) and its content within the membrane in relation with the membrane performances. Flux rate and separation selectivity data will be discussed in terms of molecular recognition by α-CD. Furthermore, an approach based on a solution–diffusion mechanism for the modelling of the mass transport of xylene isomers within the membrane will be proposed.

2. Experimental

2.1. Materials

PVA (degree of polymerisation of about 1600, degree of hydrolysis 97.5–99.5 mol%), HMDI, dibutyltin dilaurate, and *m*-xylene (99%) were purchased from Fluka. Ethyl alcohol (analytical grade), starch paste (1%), and sulfuric acid were obtained from Carlo Erba. Dimethyl sulfoxide (DMSO) and DMSO D_6 (>99.8%) were purchased from SDS (France). Iodine (0.05 mol/L) and sodium thiosulfate (0.1 mol/L) were obtained from Riedel-de Haën. *o*-Xylene (97%) and *p*-xylene (99%) were obtained from Aldrich. All the aqueous solutions were prepared using 18 MΩ cm MilliQ water.

2.2. Membrane preparation

2.2.1. General procedure

Membranes were prepared from solutions in DMSO containing a dry solid content (PVA and α-CD) of 8 wt% according to a work previously reported [14]. The desired amount of α-CD to PVA was varied from 0 to ca. 50 wt%. HMDI was the cross-linking agent and the employed weight fraction to PVA and CD was 15 wt%. The compositions of the different starting reaction mixtures are listed in Table 1. The obtained solutions were then cast on a glass plate using a casting knife with a gap of 250 μm and dried at 60 °C for 3 h as previously described [14]. The film was removed from the glass plate by immersion into warm water and washed in water several times. Thickness of the resulting dried membranes was determined to be 17 ± 1 μm. The absence of defects (crack, pin hole) was checked under gas pressure (2 bar).

2.2.2. PVA membrane containing no α-CD

PVA was dissolved in DMSO (9 g) at 80 °C. HMDI in DMSO (1g) was then added to the PVA solution after cooling it at room temperature. The mixture was thoroughly stirred for less than 1 min and rapidly cast on a glass plate.

2.2.3. PVA membranes containing entrapped α-CD

The desired α-CD/PVA ratio (Table 1) was dissolved in DMSO (9 g). HMDI in DMSO (1 g) was then added and the mixture immediately cast on a glass plate after a vigorous stirring during a short time (1 min).

Table 1
Composition of the starting reaction mixtures and α-CD content of the resulting membranes

Composition of the starting mixtures				Membrane α-CD content (wt%)	
$m_{\alpha\text{-CD}}$ (g)	m_{PVA} (g)	V_{HMDI} (mL)	$m_{catalyst}$ (mg)	Th.	Exp.
0	0.80	0.115	1.8	0	0
0.05	0.75	0.115	1.8	5.4	5.0
0.10	0.70	0.115	3.5	10.8	9.9
0.20	0.60	0.115	7.1	21.6	20.7
0.28	0.52	0.115	9.9	30.1	29.3
0.34	0.46	0.115	12.2	36.0	35.6
0.40	0.40	0.115	14.2	44.9	44.9
0.12	0.68	0.115	–	13.0	11.8
0.20	0.60	0.115	–	21.7	18.7
0.32	0.48	0.115	–	34.8	27.1
0.40	0.40	0.115	–	43.5	34.1
0.56	0.24	0.115	–	60.9	50.5

2.2.4. PVA membranes containing grafted α-CD [18]

HMDI was added to a given amount of α-CD dissolved in 3 g of DMSO (Table 1). Dibutyltin dilaurate in a 5.5% molar ratio to α-CD was used as catalyst. The mixture was stirred at 65 °C for 1 h under nitrogen. After cooling the reaction mixture at room temperature, it was added to a solution containing the corresponding PVA amount (Table 1) dissolved in DMSO (7 g). The temperature was again raised to 65 °C and the reaction mixture stirred for 2 h under nitrogen. The obtained solution was then cast on a glass plate.

2.3. α-CD titration

α-CD immobilized in the obtained membranes was titrated by adapting a procedure mentioned in literature [19]. CD moieties were hydrolyzed in H_2SO_4 to form glucose-residue derivatives followed by iodine oxidation according to a α-H-substitution reaction. I_2 that did not react with glucose was quantified using $Na_2S_2O_3$.

The work-up was as following: 0.1g of dried membrane was refluxed in 50 mL of 1 M H_2SO_4 at 100 °C overnight. The resulting solution was adjusted to 100 mL. A 20 mL assay was then neutralized with 1 M NaOH up to pH 7. A mixture of 2 mL of 0.05 M aqueous I_2 and 3 mL of 0.1 M NaOH was added to the solution. The solution was allowed to stand in a dark place for at least 20 min. The oxidation time (20 min or longer) had no significant influence [19]. The solution was neutralized by adding 5 mL of 1 M H_2SO_4. Then the I_2 excess was titrated using 0.1 M $Na_2S_2O_3$ in presence of 1% starch solution until the solution became completely transparent. The same titration was repeated at least three times and the result was taken as the mean value of the three determinations (confidence interval within 0.05 mL). The α-CD amount immobilized in membranes reported in Table 1 was calculated from the difference between added I_2 $\left(C_{I_2}V^0_{I_2}\right)$ and titrated I_2 $(C_{I_2}V_{Na_2S_2O_3})$ according to the following equation

$$m_{CD} = \frac{5C_{I_2}\left(V^0_{I_2} - V_{Na_2S_2O_3}\right)}{6}\frac{972}{0.964} \quad (1)$$

where the factor 5 arises because the measurement was performed on a 20 mL assay which represents 1/5 of the total volume (100 mL), the factor 6 stands for the number of glucose units in α-CD and 972 the molar mass of α-CD. Indeed, α-CD was not completely hydrolyzed in water, whereas the oxidation of the glucose by I_2 was complete. The systematic error incurred was determined from titration of a known amount of α-CD powder. In that case, theoretical and obtained values were compared and gave a relative error of 3.6%. The determination of CD moieties in membranes was then systematically corrected by the factor 0.964 (Eq. (1)). In literature, the relative error was reported to be about 10% [19].

2.4. Membrane characterization

The dibutyltin dilaurate catalysis of the reaction between HMDI and the hydroxyl groups of α-CD was studied through two series of experiments corresponding to the membrane preparation with and without catalyst. In the first series, 1g of α-CD in 30 mL DMSO was allowed to react at 65 °C with HMDI (15 wt% to α-CD) and dibutyltin dilaurate (5.5% molar ratio to α-CD) for 1 h under nitrogen. In the second series, 1 g of α-CD in 30 mL DMSO was reacted only with HMDI (15 wt%) for 1 h at room temperature. In both cases, the solutions were afterwards precipitated in acetone to remove unreacted HMDI and the obtained solid was washed three times with ether to eliminate possible inclusion complexes formed between α-CD and HMDI. The solids were dried on P_2O_5 and characterized by ^{1}H NMR using a Brucker Avance 300 MHz and by FTIR using a Nicolet 710 FTIR Spectrometer. X-ray measurements were carried out using a Pan Analytical X'pert Pro.

2.5. Swelling experiments

After complete drying in an oven at 80 °C overnight, membrane samples were soaked in water solution at room temperature. At different times, each sample was taken out, wiped with filter paper and weighted until a constant mass was observed. The degree of swelling (DS) was determined from Eq. (2)

$$\mathrm{DS} = \frac{m_s}{m_d} \times 100 \tag{2}$$

where m_s is the mass of the membrane swollen in water and m_d (g) the mass of the dried membrane.

2.6. Permeation measurements

Liquid/liquid extraction was carried out at 23 °C using a Teflon™ cell in which the feeding and the stripping phases (100 mL) were separated by the membrane. Each solution was continuously circulated by two peristaltic pumps. The active membrane surface area (A) was 13.85 cm^2. The membrane was supported by a stainless grid coated with Teflon™ obtained from Millipore. It was equilibrated for 24 h between two aqueous phases before introducing xylenes in the feed. The xylene concentration extracted in the receiving phase (water) was determined using a HPLC apparatus (Beckman System Gold pump equipped with an autosampler). Xylene isomers were analyzed through a Waters Spherisorb S5 ODS2 column using an ethanol: water (55:45 wt:wt) mobile phase. Detection was achieved using a KONTRON 430 spectrophotometer operating at 267 nm. After each experiment, remaining xylenes were removed from membrane by circulating ethanol in the device overnight. Using this procedure, membranes exhibited good stability with time and good reproducibility as repeated permeation tests gave same flux and selectivity performances.

The mole amount of each isomer transferred in the stripping phase per surface area was plotted against time as shown in Fig. 1 for a permeation experiment of an *o*-/*p*-xylene mixture (50/50) using a membrane containing 20.7 wt% of grafted α-CD. The shape of the permeation curves shows three stages. A time-lag was at first observed, characteristic of the time required for the first xylene molecules to cross the membrane. Then, the flux (J_i) reaches a quasi steady state involving the transport of each species through the membrane. This value was calculated from the slope at this stage according to Eq. (3)

$$J_i = \frac{1}{A}\frac{\mathrm{d}Q_i}{\mathrm{d}t} \tag{3}$$

where A is the active surface area of the membrane (13.85 cm^2) and Q_i the mole number of xylene isomer transported across the membrane. Finally, the curves reach a plateau when xylene concentration is equal in both feeding and receiving phases. An additional experiment showed that the transport can be restored with the same value of permeation flux by regenerating the receiving phase.

The selectivity of a membrane to isomer i with respect to isomer j was then determined by the separation factor $\alpha_{(i/j)}$, calculated following Eq. (4)

$$\alpha_{(i/j)} = \frac{J_i}{J_j} \times \frac{F_j}{F_i} \tag{4}$$

where J is the respective slope of the permeation curve and F the respective mole fraction in the feed phase of each isomer.

3. Results and discussion

3.1. Preparation of membranes

Immobilization of CD in membranes based on a PVA matrix can be achieved either using a coupling agent [10,14,15] or by γ-ray irradiation [20]. The coupling agent (glutaraldehyde, epichlorohydrin and diisocyanate derivatives) is supposed to establish covalent linkages via an

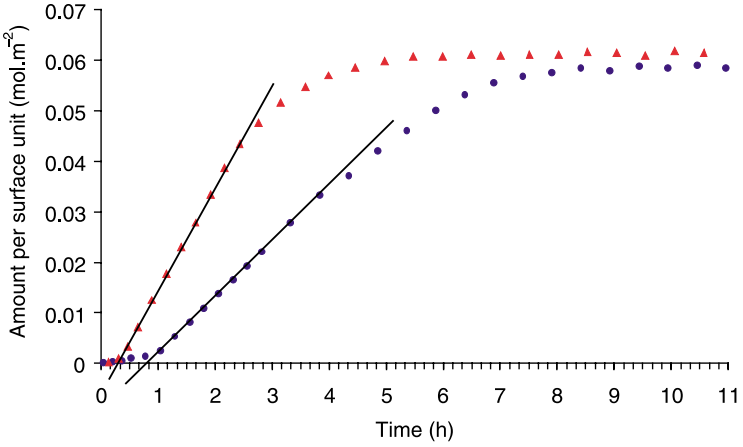

Fig. 1. Permeation curves of an *o*-/*p*-xylene mixture (50/50) obtained with a membrane containing 21 wt% of grafted α-CD: (●) *o*-xylene; (▲) *p*-xylene.

addition reaction between its reactive functions and the hydroxyl groups located on PVA chain and on the rim of CD cavity. Indeed, the isocyanate function hardly reacts with the hydroxyl groups of CD so that the requirement for CD derivatization using HMDI are temperatures of reaction higher than 60 °C [21–23] and use of a catalyst [18]. We prepared two series of CD-containing membranes from PVA and α-CD using HMDI: The first series was prepared at room temperature in absence of the catalyst. The reaction mixture gelled very rapidly so that the film had to be cast immediately after mixing with HMDI. The second series of membranes was prepared in presence of dibutyltin dilaurate according to the procedure described by Sreenivasan for the preparation of PVA-β-CD copolymer membranes [18]. In that case, the solution took a longer time (about 1 h) before gelling. It should be noted that PVA alone reacted very rapidly with HMDI in both cases.

At this point we assumed that the gelation rate was indicative of the reaction of α-CD hydroxyl groups with HMDI. Our findings thus seemed to demonstrate that α-CD moieties were only physically trapped in the cross-linked PVA network when no catalyst was added to the reaction mixture, whereas they were chemically linked to the PVA network in the second series of membrane materials. To verify this assumption, the reactivity of α-CD with HMDI under the conditions used to prepare both series of membranes was monitored by ^{1}H NMR. No modification of the α-CD resonances was observed for the solid obtained in the absence of catalyst (Fig. 2, product A), indicating that no reaction occurred between HMDI and α-CD. On the other hand, a broadening of the α-CD peaks featuring the substitution of hydroxyl groups as well as the presence of a signal characteristic of a hexamethylene chain between 1 and 1.5 ppm can be seen in the ^{1}H NMR spectrum of the solid obtained in the presence of catalyst (Fig. 2, product B).

Furthermore, FTIR spectra of α-CD and products A and B were compared in Fig. 3. α-CD and product A exhibit similar bands, whereas product B presents different new vibrations. Two bands were assigned to the carbonyl (C=O, stretch) (hydrogen bonded) and to the NH δ-bands of the urethane function at 1707 and 1551 cm^{-1}, respectively [24]. The N–H stretching band located around 3300 cm^{-1} could not be observed because of the overlapping with the O–H band of α-CD hydroxyl groups.

These data confirmed those obtained by ^{1}H NMR demonstrating that α-CD reacted with HMDI only in presence of catalyst under our conditions. It follows that two series of membrane materials were fabricated depending on the operating conditions of synthesis: α-CDs physically trapped in the matrix (t-CD) and α-CDs covalently grafted to the PVA polymer chain (g-CD).

3.2. Membrane characterization

3.2.1. α-CD titration

α-CD content (wt%) was determined by chemical titration of glucose released after acidic hydrolysis of membrane materials. The obtained results are plotted in Fig. 4 against the α-CD mass fraction in the starting reaction mixture. CD immobilization was found to be quantitative for g-CD membranes. The loss of CD moieties (10–20% of the total content) observed for t-CD membranes likely came from the successive washings performed during the work-up. As outlined below, for swelling experiments, the higher the CD content, the larger was the membrane swelling of t-CD membranes. Consequently, more α-CD molecules were

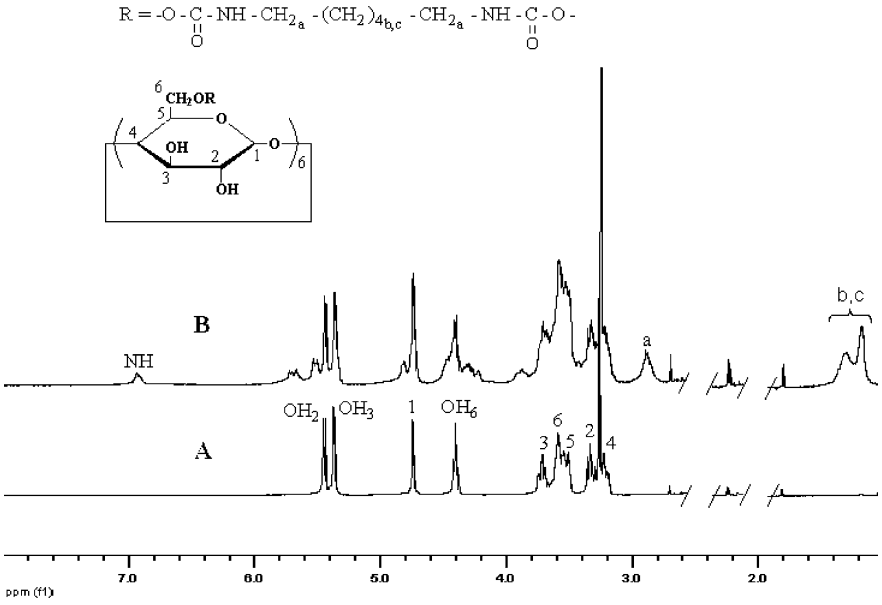

Fig. 2. ^{1}H NMR spectra in DMSO-D_6 of the solids isolated after reaction between α-CD and HMDI: (A) without catalyst; (B) with dibutyltin dilaurate as catalyst.

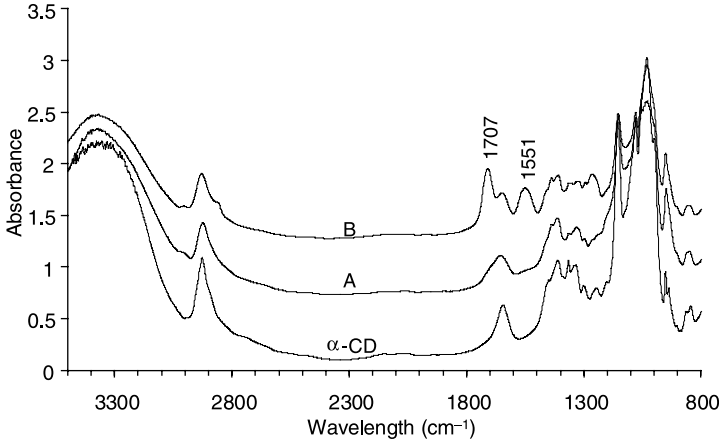

Fig. 3. FTIR spectra of α-CD, products A and B.

only loosely trapped in the PVA matrix for high CD contents and could easily escape from the membrane material during the washing step. This phenomenon might account for the larger discrepancy from the quantitative immobilization (solid line in Fig. 4) which was observed for CD contents higher than 30 wt%.

3.2.2. Swelling experiments

Effect of the membrane CD content on DS was investigated in water and ethanol. As shown in Fig. 5, the swelling of both g-CD and t-CD materials is high in water and low in ethanol, indicating the hydrogel behaviour of the obtained membranes. DS appears to be independent of the CD content for g-CD contrary to the case of t-CD for which DS increased with an increasing CD content. Increasing the content of α-CD in the t-CD materials should give rise to loose domains containing clusters of CDs surrounded by highly cross-linked domains. On the contrary, a more homogeneous cross-linked structure should stem from the linkage of α-CD moieties to the PVA chain in g-CD membranes.

3.3. Permeation results

Extraction experiments of mixed *o*-/*p*- and *o*-/*m*-xylenes were carried out using a control PVA membrane to determine the intrinsic performances in permeability and selectivity of the polymer matrix. These results were compared to those obtained with both series of prepared membranes to examine the role played by α-CD and its microenvironment. The second point considered was the influence of the feed *o*-/*p*-ratio on selectivity. In all these experiments, the xylene concentration in the feed phase was kept at the saturation concentration (ca. 1.68 mmol/L). Water was used as solvent for the feed and receiving phases.

3.3.1. Influence of α-CD content on the membrane permeability

The membrane permeability to a given component is the first performance factor to be determined. As mentioned in the experimental part, permeation across the membranes can be characterized both by the time-lag corresponding to the xylene apparent diffusion through the membranes and

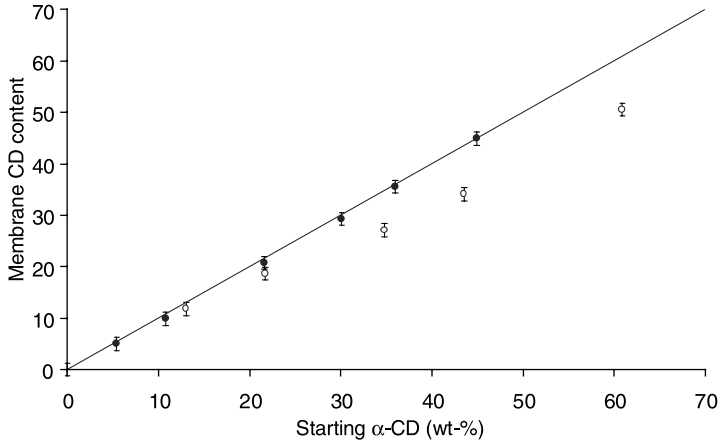

Fig. 4. α-CD content in g-CD membranes (●) and t-CD membranes (○) as a function of the α-CD mass fraction in the starting reaction mixture. The solid line represents a quantitative immobilization of α-CD moieties.

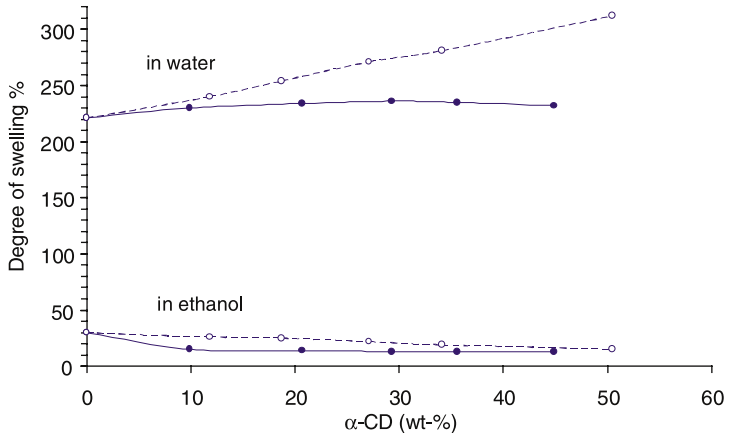

Fig. 5. Effect of the membrane CD content on the degree of swelling by water and ethanol for g-CD membrane (●) and t-CD membrane (○).

the slope in the quasi steady state. These two parameters exhibited strong variations depending on the membrane α-CD content.

The time-lag was found to be very similar (30–35 min) whatever the permeating xylene isomer in the case of the plain PVA membrane. Meanwhile, increasing the α-CD content induced discrimination between the time-lag values observed for the different isomers. At 21 wt% α-CD content, the time-lag for *p*-xylene decreased to 15 min while it increased to 45 min for *o*-xylene (Table 2).

Beyond 21 wt% α-CD content, the time-lag values decreased for both the isomers while its ratio remained constant (ca. 3). A similar behaviour was observed for the couple *o*-/*m*-xylene, *m*-isomer being the first to cross the α-CD containing membranes. For each couple of isomers the faster permeating isomer was the one having the higher stability constant (22, 42, 72 M^{-1} for *o*-, *m*- and *p*-xylene, respectively [6,25]). These data suggested a facilitated transport across the membrane by formation of a host-guest inclusion compound for the more interacting isomer. It should be noted that the transfer of the less interacting isomer (*o*-xylene) was first strongly slowed down (α-CD $\leq$ 21 wt%) and then increased for higher CD contents. This phenomenon will be discussed later (Section 3.3.2).

The flux of each isomer (J_i) was determined by the slope of the corresponding permeation curve in the steady state. The variation of flux as a function of the membrane α-CD content is represented in Fig. 6 for equimolar *o*-/*p*-xylene mixture. A percolation-like threshold can be observed corresponding to α-CD incorporation value of ca. 18 and 10 wt% for *o*- and *p*-xylene. A similar behaviour was observed for *o*-/*m*-mixture with a percolation threshold of ca. 15 and 10 wt% for *o*- and *m*-xylene. Below these threshold values, no clear discrimination between the different isomers was found and the transfer was almost identical to that of PVA membrane. Increasing the membrane α-CD content resulted in an increase in the xylene flux with a maximum for ca. 36 wt%. Again this result can be explained by the facilitated transport of xylenes by accommodation into the α-CD cavities. To cross the membrane according to this mechanism, xylene molecules must jump from one α-CD to another one. As a consequence, a minimum distance between two host sites is required to allow the facilitated transport. This assumption accounts for the low and constant permeation rate observed below 10 wt% of incorporated α-CD since the distance between the host sites should be too large to allow this mechanism to take place for the faster isomer (*m*- and *p*-xylene). In the case of *o*-xylene, the threshold value depended on the nature of the competing isomer. The more pronounced difference in complex stability constant for the *o*-/*p*-xylene mixture induced a larger threshold value than for the *o*-/*m*-xylene mixture. As outlined before, *o*-xylene has the lower binding interaction with α-CD. In the case of mixed isomers, the apparent hopping distance should be dependent on the affinity of the other guests because of the competition for accommodation into the α-CD host cavities.

For membranes having α-CD content higher than ca. 36 wt%, the permeation rate was found to drastically

Table 2
Time-lag determined from the permeation curves for an equimolar mixture of *o*- and *p*-xylene as a function of the membrane α-CD content

α-CD Content (wt%)	0	5.0	9.9	20.7	35.6	44.9
Time-lag for *o*-xylene (min)	30	31	38	49	26	24
Time lag for *p*-xylene (min)	35	33	25	15	9	8
Ratio *o*-/*p*-	0.9	0.9	1.5	3.3	2.9	3.0

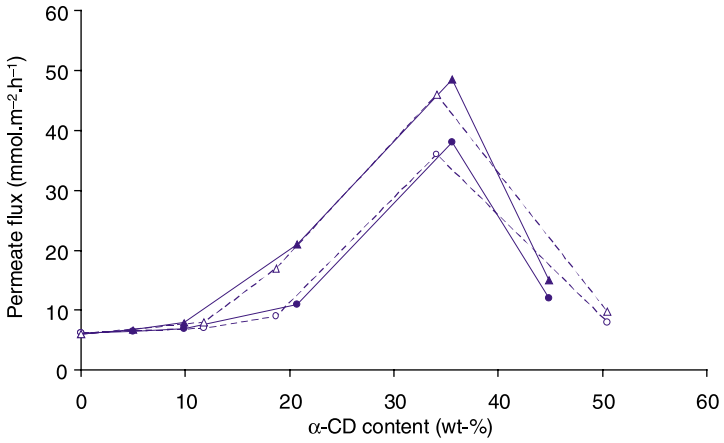

Fig. 6. Effect of α-CD content on the permeation rates of *o*-/*p*-xylene mixture (50/50) for g-CD membrane (—) and t-CD membrane (- - -): (●, ○) *o*-xylene; (▲, △) *p*-xylene.

decrease whatever the isomer component. Two possibilities could be invoked to explain the observed flux drop. The first one is the formation of inclusion compounds involving two α-CD cavities or more due to the high local concentration of recognition sites in the membrane (estimated to be ca. 0.12 mol/L for the swollen membrane containing 36 wt% α-CD). This speculation is supported by the fact that the formation of the 2:1 (α-CD:xylene) inclusion compound in solution was reported for a α-CD concentration range of 0.01–0.02 mol/L [25]. Such entities involving two or more hosts decrease the number of recognition sites available for the transfer. Moreover, they are much more stable than the corresponding inclusion compounds with lower host:guest ratio so that the third step of facilitated transport mechanism (complex dissociation at the stripping phase) might be dramatically hindered. Another possibility concerns the formation of small α-CD aggregates as H-bonded networks unavailable for accommodating xylene molecules [26]. However, no crystallized α-CD domains were observed by X-ray diffraction for membranes at high α-CD content, contrary to the case previously reported for β-CD/PVA membranes cross-linked with epichlorohydrin containing more than 38 wt% β-CD [14]. Therefore, the formation of inclusion compounds involving several CD cavities seems to be the more reasonable explanation to account for the observed permeability drop.

Finally, no marked difference in time-lag values, nor in permeation behaviour between g-CD and t-CD membranes was found. So it can be, therefore, concluded that covalent grafting of α-CD moieties on the PVA chain did not modify their molecular recognition towards the xylene isomers.

3.3.2. Influence of α-CD content on membrane selectivity

Fig. 7 presents the membrane selectivity $\alpha_{(p/o)}$ and $\alpha_{(m/o)}$ (Eq. (4)) for binary *o*-/*p*- and *o*-/*m*-xylene mixtures of equimolar composition versus the α-CD content in g-CD membranes. PVA films showed no specific interaction for the different xylene isomers. Increasing the α-CD content within membrane gave rise to a selective extraction, *o*-xylene being the slower isomer to cross the membrane in each case as mentioned above for the time-lag. The isomer discrimination reached a maximum value for a α-CD content of about 21 wt%. The highest selectivity observed was 1.9 for *p*-xylene over *o*-xylene and 1.75 for *m*-xylene over *o*-xylene. Again this result demonstrated the facilitated transport through molecular recognition by the CD cavities. Surprisingly, the membrane selectivity was found to be lower for CD contents higher than 21 wt%. This result can be correlated to the variation of time lags presented in Table 2. Beyond a α-CD content of 21 wt%, the time-lag values of competing isomers varied in a constant ratio meaning that the ratio of their effective diffusion coefficients is roughly constant. We assumed that a coupling transport effect might occur between the two isomers because of the high host concentration within membrane. This assumption is further supported by the parallel evolution of the isomer fluxes (*o*-/*p*-xylene mixture) between 21 and 36 wt% of CD as seen in Fig. 6.

3.3.3. Influence of the feed composition on membrane performances

The selectivity obtained for the membrane containing 21 wt% of α-CD was found to be strongly dependent on the *p*-xylene mole fraction in the feed. As shown in Fig. 8, a separation factor $\alpha_{(p/o)}$ as high as 8 is observed for a *p*-xylene feed mole fraction of 10%. This value is the highest ever reported for the discrimination of xylene isomers using CD-containing membranes. The selectivity decreased from about 8–0.35 when the *p*-xylene ratio increased from 10 to 90 mol%. This result indicates that the *p*-isomer was preferentially extracted for *p*-xylene ratios lower than 70 mol%, whereas the selectivity was inversed for higher contents. In the later case, the stripping phase was richer in *o*-xylene than the feed.

A similar behaviour was observed to a lesser extent for the membrane containing 36 wt% of α-CD. A separation

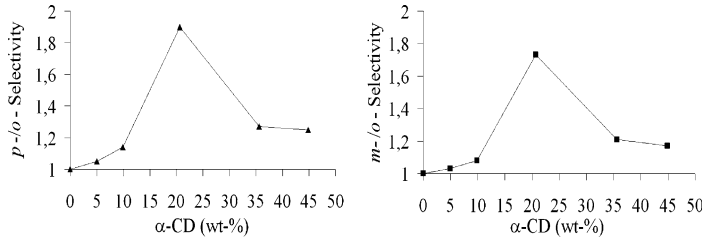

Fig. 7. Effect of α-CD content on the selectivity performance of g-CD membranes for: (▲) *p*-/*o*-; (■) *m*-/*o*-xylene isomer mixture (50/50).

factor of 3 was found for the *p*-xylene feed mole fraction of 10%, whereas the membrane showed almost no selectivity for *p*-xylene feed mole fractions higher than 50%.

Fig. 9 presents the fluxes (J_i) and (J_p+J_o) as a function of the feed composition for both membranes. The following remarks are worthy noting: (1) The total flux (J_p+J_o) does not vary much in the middle range of mole fraction (between 20 and 80% *p*-xylene mole fraction) for the 21 wt% membrane (Fig. 9(a)) and remains constant in the overall 10–90% range for the 36 wt% membrane (Fig. 9(b)); (2) on the other hand the individual isomer fluxes (J_i) display quite different evolutions regarding the CD membrane content; (3) the higher fluxes are observed for the higher separation factor in the case of the more efficient membrane (Fig. 9(a)). This last result is rather unexpected, since permeability generally evolves in the opposite way of selectivity.

Calculation of the ratio of individual fluxes J_o/J_p (Table 3) showed that it is nearly constant in the middle range of *p*-xylene mole fraction for the 21 wt% membrane. If we take the ratio, J_o/J_p, to be strictly constant and equal to 0.53 (the value appropriate for the middle range of *p*-xylene mole fraction), then the predicted selectivity established from Eq. (4)

$$\alpha_{(o/p)} = \alpha^{-1}_{(p/o)} = \frac{J_o}{J_p} \times \frac{F_p}{F_o} \approx 0.53 \times \left(\frac{F_p}{1-F_p}\right) \quad (5)$$

would be strictly proportional to the feed mole fraction ratio, F_p/F_o. A glance at Fig. 10 shows that this simplifying approximation works well between 20 and 80% *p*-xylene mole fraction. In Section 3.4 below we present one possible explanation for this behaviour using a simple solution–diffusion transport model.

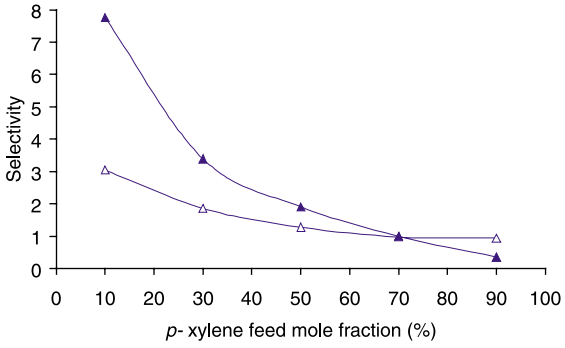

Fig. 8. Effect of the feed isomer composition on *p*-/*o*-extraction selectivity for the g-CD 21 wt% (▲) and g-CD 36 wt% (△) membranes.

From the data presented in Table 3, it appears that the oversimplified Eq. (5) cannot apply to the 36 wt% membrane since the calculated ratio depends on the *p*-xylene mole fraction in the feed isomer mixture. This result reflects the marked difference of permeation behaviour between the two membranes. The predominance of a coupled isomer transport for the latter as above assumed is further confirmed by the much lower selectivity and the more than twice higher total flux compared to the 21 wt% membrane. Actually the absence of selectivity observed in the mole fraction range, where *p*-xylene is the majority isomer (Fig. 8), corroborates a coupling transport effect of *o*-xylene by the faster permeant (*m*- and *p*-xylene).

The comparison of our findings with the reported selectivity for separation of xylene isomers using CD-containing membranes was not straightforward, as the materials were fabricated from various polymeric matrixes and applied to different separation processes [8,11–13]. However, the dependence of the separation factor with the feed composition appears to be a general trend in literature data. For instance, preferential extraction of *p*-xylene from a mixture containing 90% *o*-xylene using evapomeation on PVA membrane containing 40 wt% trapped β-CD was reported with a selectivity factor $\alpha_{(p/o)}$ of 3.93 [11]. In the same way, a PVA membrane containing 33 wt% trapped β-CD exhibited a maximum selectivity at 10% *p*-xylene for pervaporation of *m*-/*p*-isomer binary mixtures ($\alpha_{(m/p)}$ of 2.96) [12]. For both cases, the selectivity decreased as the *p*-xylene feed mole fraction increased.

Meanwhile it should be noted that in literature (except in Ref. [12]) the faster isomer was generally the one having the lesser affinity with the CD immobilized in the membrane. It thus appears that in our pertraction studies, contrary to other membrane separation processes, stronger inclusion interaction between α-CD and xylene isomers leads to faster transport.

3.4. Permeation mechanism

The mathematical description of the isomer selectivity was performed using the following model. We assume that inclusion phenomenon in α-CD was the key interaction of the molecular recognition of xylene isomers. The proposed mechanism of extraction based on a solution–diffusion

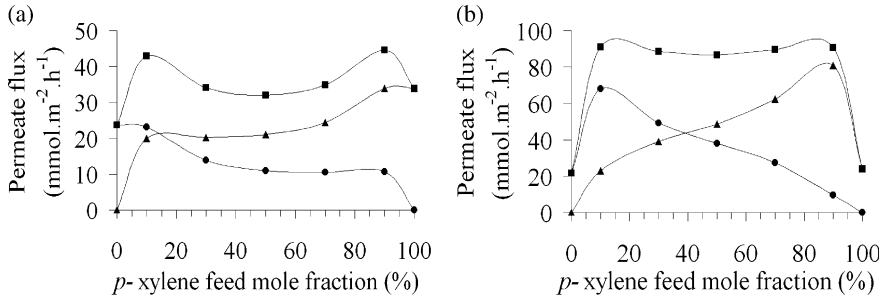

Fig. 9. Effect of the feed isomer composition on the permeation rate for the g-CD 21 wt% (a) and g-CD 36 wt% (b) membranes: *o*-xylene (●); *p*-xylene (▲); total (■).

mechanism consists of three different stages: (a) sorption at the feeding side of membrane by complex formation between xylene molecules and α-CD, (b) xylene diffusion from a recognition site to another across the membrane, and (c) complex dissociation at the stripping side. We also assume that there is no coupled transport across the membrane. This was supposed to be true for the membrane containing 21 wt% of α-CD in the middle range of *p*-xylene feed mole fraction as demonstrated above.

The concentration gradient between the two aqueous phases is the driving force for the mass transport (Eq. (6))

$$J_i = \frac{D_i}{e}\left(C_{im}^{f} - C_{im}^{s}\right) \tag{6}$$

where D_i is the effective diffusivity, e the membrane thickness, C_{im}^{f} and C_{im}^{s} the membrane concentration of the isomer i at the feed and strip interfaces, respectively. From stage (a) C_{im}^{f} and C_{im}^{s} are related to the solution concentration through the solubility parameter S_i

$$C_{im}^{f} = S_i \times C_i^{f} \text{ and } C_{im}^{s} = S_i \times C_i^{s} \tag{7}$$

therefore

$$J_i \frac{D_i S_i}{e}\left(C_i^{f} - C_i^{s}\right) \cong \frac{D_i S_i}{e} C_i^{f} \tag{8}$$

considering that C_i^{s} can be neglected compared to C_i^{f} in the steady state part of the permeation curve. The data plotted in Fig. 9(a) and Table 3 show that the isomer fluxes are nearly independent of the isomer concentration in the feed at least in the middle range of mole fraction. One possible explanation for this behaviour is that the isomer concentration nearly reaches a saturation value in the membrane (at the feed interface), C_{im}^{0}, that is independent of isomer mole fraction. The solubility parameter can then be written as

$$S_i = \frac{C_{im}^{0}}{C_i^{f}} \tag{9}$$

Combining Eqs. (8), (9) with (4) gives

$$\alpha_{(i/j)} = \frac{D_i C_{im}^{0}}{D_j C_{jm}^{0}} \times \frac{F_j}{F_i} = K_{(i/j)} \times \frac{F_j}{F_i} \tag{10}$$

with $K_{(i/j)} = J_i/J_j$ independent of isomer mole fraction and equal to $\left(D_i C_{im}^{0}\right)/\left(D_j C_{jm}^{0}\right) = K_{(j/i)}^{-1}$.

By taking $K_{(o/p)} = K_{(p/o)}^{-1} = 0.53$ as the optimum fitted choice for this parameter, the predicted selectivity for this model is as shown in Fig. 10. We observe that the selectivity trends as a function of the feed composition are in good agreement with the experimental data for the *o*-/*p*-separation using the membrane containing 21 wt% α-CD. The discrepancies observed for the borderline compositions (i.e. *p*-xylene mole fraction less than 20% and greater the 80%) could result from the non-validity of the assumptions used to arrive at Eq. (10), i.e. under these borderline conditions coupled transport effects may be present and partitioning saturation at the feed interface may no longer hold. We have undertaken more detailed investigations, including sorption experiments, to test our model assumptions and the results of this study will be given elsewhere.

4. Conclusion

PVA membranes containing α-CD recognition sites for the discrimination of xylene isomers were fabricated using two routes. Physical trapping gave rise to materials with an

Table 3
Ratio of individual isomer fluxes J_o/J_p as a function of the *p*-xylene feed mole fraction for the g-CD 21 wt% and g-CD 36 wt% α-CD containing membranes

	p-Xylene feed mole fraction				
	10%	30%	50%	70%	90%
J_o/J_p (21 wt% α-CD)	1.16	0.69	0.53	0.43	0.32
J_o/J_p (36 wt% α-CD)	2.96	1.26	0.78	0.44	0.12

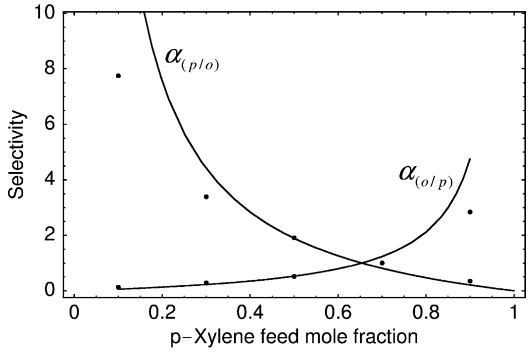

Fig. 10. Modelling of the *p*-/*o*-extraction selectivity for the g-CD 21 wt% membrane as a function of the feed isomer composition. (●) Experimental points; (—) predicted selectivity.

incorporation rate of 80 and 90% from the starting CD, whereas covalent attachment was quantitative. The prepared membranes were used as contactors in water/water pertraction tests for the separation of binary mixtures of xylene isomers. They showed a high discrimination of *p*- and *m*-xylene over *o*-xylene. Flux and selectivity depended on the α-CD membrane content with a threshold concentration indicating facilitated xylene transport through molecular recognition. The nature of the CD immobilisation did not modify the freedom with which CD cavities could accommodate xylene molecules. Materials in which CD were grafted to the polymer matrix should be preferred for reason of lasting stability. Pertraction using CD immobilized membranes appears to be quite effective. More studies with other isomer mixtures, including chiral systems, are needed to validate this approach.

The dependence of the selectivity with the feed composition suggested that the limiting step of the transport comes mainly from the solubility stage at the membrane interface. A mathematical model based on a solution–diffusion mechanism assuming saturation of recognition sites at the feed interface was presented to explain the selectivity change with the feed concentration. The good agreement with experimental results corroborates our hypothesis that the separation mechanism of xylene isomers using α-CD-containing PVA membranes is governed by the sorption step.

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