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Review

The use of membranes with cyclodextrin units in separation processes: Recent advances

Cezary A. Kozlowski *, Wanda Sliwa

Institute of Chemistry and Environment Protection, Jan Dlugosz University of Czestochowa, 42-201 Czestochowa, Armii Krajowej 13 Ave, Poland

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Abstract

In the review, selected membranes containing cyclodextrin (CD) units are described. The paper is divided into two parts, the first one is dealing with liquid membranes, and in the second part polymer membranes are presented.

Keywords: Cyclodextrin; Membrane; Separation; Transport

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1. Introduction

Membrane techniques are widely used for separation purposes; many methods of these processes exist (Ajhar et al., 2006; Brickwedde & Schwake, 2005; Davis, Sheppard, & Smith, 2007; Jeon & Kwak, 2007; Kozlowski, 2007; Rösler, 2005; Sisson, Shah, Bhosale, & Matile, 2006; Van der Graaf, Schroën, & Boom, 2005; Yang et al., 2006). In the paper, selected membranes containing CD units are presented; the liquid membranes, described in the first part are followed by polymer membranes, shown in the second part.

Membranes containing CD units are used in a number of separations (Lamers, 2007; Lue & Peng, 2003; Peng et al., 2006; Touil, Tingry, Palmeri, Bouchtalla, & Deratani, 2005); it should be emphasized that separations of metal ions by membranes in the aim of their removal and recovery is today a challenge in view of economy and environmental protection (Resina, Macanas, de Gyves, & Munoz, 2006; Scindia, Pandey, & Reddy, 2005; Tayeb, Fontas, Dhahbi, Tingry, & Seta; 2005). Among CD polymers (Huang et al., 2006; Maeda, Mochizuki, Watanabe, & Yashima, 2006; Tomatsu, Hashidzume, & Harada, 2006) those which may coordinate metal ions (Berto et al., 2007; Choi & Geckeler, 2007; Jiang et al., 2006) deserve a special attention.

CDs are water soluble macrocycles consisting of six, seven or eight α-D-glucose units, which are 1,4-linked; they form α-, β-, and γ-CDs, respectively. CDs have hydrophobic cavity and hydrophilic exterior. The cavity of CDs may encapsulate guest molecules *via* noncovalent bonds in aqueous solutions or in the solid phase to give inclusion complexes. CDs play an important role in analytical chemistry and in separation techniques; one should point out their usefulness in chiral recognition (Schneiderman & Stalcup, 2000; Singh, Sharma, & Banerjee, 2002; Szejtli, 1998; Szejtli, 2004).

The review presents selected works concerning the separation procedures with the use of membranes. This topic, especially separation of metal ions is an investigation area of our research group (Kozlowska, Kozłowski, & Koziol, 2007; Kozlowski 2006; Kozlowski, Kozlowska, Pellowski, & Walkowiak, 2006; Kozlowski & Walkowiak, 2002; Kozlowski & Walkowiak, 2004; Kozlowski & Walkowiak, 2005; Kozlowski & Walkowiak, 2007; Kozlowski, Walkowiak, Pellowski, & Kozioł, 2002), connected with our study of CDs, mainly in view of supramolecular systems built from their inclusion complexes (Choi, Girek, Shin,

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* Corresponding author. Tel.: +48 34 3615154; Fax: +48 34 3665322.
E-mail addresses: c.kozlowski@ajd.czest.pl (C.A. Kozlowski), w.sliwa@ajd.czest.pl (W. Sliwa).

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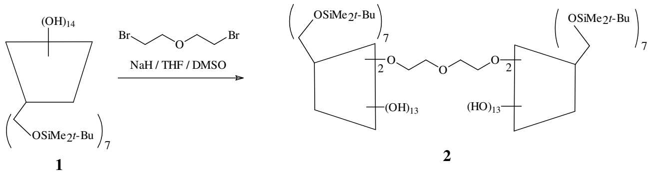
& Lim, 2002; Girek, Kozlowski, Koziol, Walkowiak, & Korus, 2005; Girek, Shin, & Lim, 2000; Girek & Sliwa, 2006; Kozlowski, Girek, Walkowiak, & Kozlowska, 2006; Sliwa, 2001; Sliwa & Bachowska, 2006; Sliwa & Dondela, 2000; Sliwa & Girek, 2003; Sliwa & Girek, 2005; Sliwa, Girek, & Koziol, 2004; Sliwa & Peszke, 2007).

2. Liquid membranes

Among applications of liquid membranes (Chiha, Samar, & Hamdaoui, 2006; Kubota & Goto, 2005), the selective transport of saccharides will be described as an example (Ikeda, Matsuhisa, & Ueno, 2002). The separation of a mixture of saccharides is difficult, since most of them are isomers that only differ in the configuration of specific hydroxyl groups. The systems for selective transport of saccharides through a liquid membrane containing artificial carriers are useful not only for separation of mixtures of saccharides but also for elucidation of saccharide transport through a biomembrane. It is noteworthy that carriers often bind saccharides *via* selective formation of hydrogen bonds.

The transport rate of the saccharide through a hydrophobic liquid membrane is slow since saccharide has a hydrophilic character. It was observed that this rate increases if the saccharide is covered up by a hydrophobic shell having functional groups able to interact with the hydroxyl groups of the saccharide inside the shell. The β-CD is insoluble in chloroform but soluble in water; such solubility would be inconvenient for a saccharide transporter. The silylated CD derivative **1**, however, is soluble in chloroform, and not in water.

For preparation of the carrier all the primary hydroxyl groups of β-CD were protected by *t*-butyldimethysilyl groups to give **1**; in this way they achieve the hydrophobic character. It was found that β-CD dimer **2** is a convenient carrier for saccharides; **2** can wrap saccharides with hydrogen bonds by the secondary hydroxyl groups, whereas the primary OH groups of CD are chemically modified to be hydrophobic. The dimer **2** was obtained from **1** by reaction with bis(2-bromoethyl)ether.



1

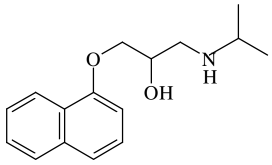
2

The transport experiments were made in the U-tube glass cell across a chloroform liquid membrane from an aqueous feed phase containing a saccharide to an aqueous receiving phase (Ikeda et al., 2002). As saccharides methyl-α-D-glucoside, methyl-α-D-galactoside, and methyl-α-D-mannoside, as well as D-ribose and D-2-deoxyribose were investigated (Ikeda, Matsuhisa, & Ueno, 2003; Ikeda et al., 2002). It was observed that their transport rates using CD dimer **2** were higher than in the case of **1**. The above results show that **2** is more effective than **1**, since **2** can wrap saccharides.

The liquid/liquid extraction with the use of selective carriers for each of enantiomers is a promising method for separation of racemic mixtures. It is known that the inherent chirality of CDs allows formation of diastereomeric complexes. Chiral separation with the use of CDs involves the interaction of one enantiomer with CD molecule, while such interaction in the case of the second enantiomer is more difficult due to its different configuration. For the resolution of racemic mixture a difference in stability of inclusion complexes of both enantiomers is necessary (Ferreira, Coelhoso, Ramalhete, & Marques, 2006).

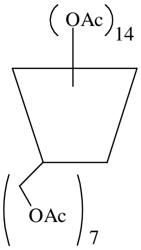
The liquid membrane extraction is a convenient process since the simultaneous extraction and receiving occur in only one equipment. In a liquid membrane system, two miscible liquid phases, often aqueous phases, are separated by an immiscible phase, *i.e.* the liquid membrane. The selective transport of a solute from one miscible phase to another across the liquid membrane may proceed when a suitable carrier is used. The bulk liquid membrane (BLM) contains only liquid phases; the supported liquid membrane (SLM) contains additionally a polymeric membrane to support the organic phase.

Resolution of racemic propranolol (**3**) was performed using liquid membranes containing peracetylated β-CD (**4**) (Ferreira et al., 2006). In this procedure two liquid membranes, bulk liquid membrane (BLM) and supported liquid membrane (SLM) were used. Since **3** is in aqueous phase, the water insoluble peracetylated CD, *i.e.* **4** served as a carrier. The enantioselective interaction occurs in the feed side membrane interface; the (*S*)-**3** preferably interacts with **4**, and is transported across the membrane.



propanolol

3



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In a BLM a large volume of organic phase is used, therefore the quantity of **4** available for transport is high, but there is a long distance for solute transport between the two aqueous phases. In SLM, however, the volume is much lower, and the distance between the two aqueous phases is small, corresponding to the membrane thickness. In this case, the transport rate of **3** is high since SLM is thin. It should be noted that due to the thin form of SLM a very small amount of carrier is required for separation. Taking the above facts into account, SLM seems to be more convenient than BLM in the resolution of racemic **3**.

The selective separation of toluene and *n*-heptane with the use of emulsion liquid membranes (ELMs) was performed (Chakraborty & Bart, 2006; Chakraborty, Ivanova-Mitseva, & Bart, 2006). Since the boiling points of toluene and *n*-heptane are very close, the conventional distillation cannot be applied for their separation.

It is known that the separation of hydrocarbons by liquid membrane is based on the selectivity, resulting from the difference in the permeation rate of a given species through the liquid membrane. In ELMs the feed is emulsified by the surfactant solution. The emulsified droplets which are surrounded by the surfactant solution are contacted with the receiving solvent to collect the more permeable solute. The use of ELMs involves the carrier-mediated transport. It should be noted that the application of carriers to oil/water/oil (o/w/o) type ELMs (Chakraborty & Bart, 2005) was not so intensively studied as in the case of more conventional w/o/w systems.

The selective separation of toluene from *n*-heptane was performed *via* ELM containing CD as a carrier in o/w/o system. For experiments α- and β-CDs, as well as hydroxypropyl-α- and β-CDs (HP-α-CD and HP-β-CD, respectively) were used.

The aqueous membrane solution was prepared by dissolving a given CD and sodium lauryl sulfate, serving as an emulsifier, in water. The hydrocarbon mixture was added to this solution and shaken; the occurring inclusion complexation of toluene molecules in CD cavities leads to the separation of two layers: the upper one, *i.e.* the organic phase, and the lower one, *i.e.* the CD solution in which toluene is extracted by formation of inclusion complexes with CD molecules.

The ability of CD to form an inclusion complex with a guest molecule requires a good matching of size of CD cavity with the guest dimensions. The high selectivity of β-CD in separation of toluene from *n*-heptane results from the better fitting of toluene into the β-CD cavity than in the case of *n*-heptane. The presence of the hydroxypropyl group in HP-α-CD and HP-β-CD lowers the inclusion selectivity as compared with that of unsubstituted α- and β-CDs. It was observed that the selectivity of separation decreases in the order: β-CD > α-CD > HP-α-CD > HP-β-CD.

It should be mentioned that the selective separation of benzene from hydrocarbon mixtures may be performed *via* liquid–liquid extraction, with the use of aqueous solutions of CD derivatives (Uemasu & Kushiyama, 2004).

The separation of isomers, *e.g. p*- and *m*-xylenes by conventional distillation is difficult due to their close boiling points and similar volatility, therefore for separation many membrane techniques were applied, among them the use of liquid membranes. The permeation of *p*- and *m*-xylenes across supported liquid membranes (SLMs) containing CDs was studied, choosing for experiments α-CD, β-CD and hydroxypropyl-β-CD (HP-β-CD) (Lue, Juang, & Hou, 2002).

Xylene transport across a CD-containing SLM system is a solution-diffusion process consisting of several steps. First the diffusion of xylenes from the organic phase into an aqueous membrane phase occurs then xylene molecules form with CDs the inclusion complexes in the aqueous membrane phase, and reach an equilibrium state. The complex diffuses through the SLM from the feed/membrane phase interface into the membrane/receiving phase interface, where it dissociates into xylene and free CD. At last xylene is extracted into the receiving phase. It was observed that the ability for complex formation with CDs was higher for *p*-xylene than for *m*-xylene. The complex binding constants decrease in the order: HP-β-CD > β-CD > α-CD.

3. Polymer membranes

The application of polymer membranes (Gardner et al., 2006; Pithan, Staudt-Bickel, Hess, & Lichtenthaler, 2002; Sodaye, Suresh, Pandey, & Goswami, 2007) in separation processes is very important, several examples of these procedures are shown below.

The selective pertraction of isomeric xylenes by polymer membranes containing α- and β-CD complexing units was also performed (Touil, Tingry, Bouchtalla, & Deratani, 2006). Pertraction is a continuous membrane – based extraction process. In this technology, the membrane contactor combines two functions, *i.e.* separation and extraction.

In the experiments a hydrogel consisting in a poly(vinyl alcohol) (PVA) matrix grafted with CD units was used. The membrane contactors were prepared by cross-linking with hexamethylene diisocyanate (HMDI).

Pertraction experiments have shown that the transfer of xylenes across the above membranes containing CDs was facilitated as compared to PVA membrane without CD units. It was found that membranes based on α-CD were more selective than those containing β-CD units. The order of the permeation flux: *p*-xylene > *m*-xylene > *o*-xylene across membrane with α-CD units is the same as that of stability constants of α-CD complexes with xylenes.

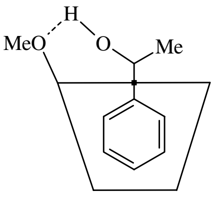
The above extraction, mediated by CD immobilized membrane proceeds *via* the solution – diffusion mechanism. Basing on this concept, the isomer is transferred from the feed phase into membrane so by specific sorption involving formation of CD inclusion complex as well as by nonspecific sorption. Then it passes across the membrane by jumping from one CD molecule to another and diffusing through the polymer matrix, and at last it is released at the receiving interface. Selectivity of the process results from the different stability constants of CD complexes with particular isomers.

Polymer membranes with CD units such as poly(acrylic acid)/α-CD (Kusumocahyo, Kanamori, Sumaru, Iwatsubo, & Shinbo, 2004) or PVA/β-CD membranes (Chen, Wu, Tan, & Zhu, 2000) were also investigated in separation of xylene isomers. It should be mentioned that the polymer membrane with CD moieties grafted on PVA may be applied to separation of fullerene mixtures (Eddaoudi, Deratani, Tingry, Sinan, & Seta, 2003).

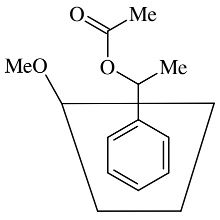
Studying resolution of racemates with the use of enzyme processes occurring in a membrane reactor, the enantioselective ester hydrolysis catalyzed by lipase was performed (Ceynowa & Koter, 2001). The reactor containing lipase which was immobilized in the polyamide membrane served for separation of (*R,S*)-1-phenylethanol and (*R,S*)-1-phenyl-1-propanol which were formed during hydrolysis of their esters (acetates and propionates).

Since organic substrates are poorly water soluble, many hydrolysis reactions must be carried out in a two-phase systems; for this purpose the use of membrane reactor with a catalyst immobilized in the membrane is suitable. The hydrolysis of two 1-phenylalcohol esters in a two-phase enzyme membrane system was investigated along with simultaneous separation of produced alcohols. The alcohols were extracted on-line in a membrane extraction module using methyl-β-CD. The enzyme membranes were prepared by chemical immobilization of lipase derived from *Pseudomonas* in a polyamide hollow-fiber membrane. The two-phase system for hydrolysis contained organic phase, *i.e.* the ester solution in *n*-heptane and the aqueous buffer solution (pH 8.0).

The interior of CD cavity is hydrophobic, therefore the nonpolar moiety of the molecule (such as phenyl or naphthyl) can penetrate inside. If the guest may additionally interact with functional groups of the modified CD, *e.g.* methyl-β-CD, the inclusion complex may form. Such behavior is observed in the case of alcohol molecule which can form hydrogen bond with the methoxyl group of modified CD, however for the ester it is impossible.



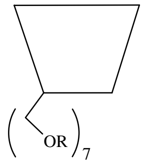
1-phenylethanol



1-phenylethyl acetate

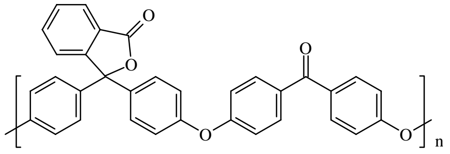
The polyetheretherketone PEEK-WC and *O*-octyloxycarbonyl-β-CD (**5**) were used to prepare polymer membranes. The β-CD derivative **5** immobilized in a membrane can form an inclusion complex with naringin, a bitter species present in grapefruits (Fontananova, Basile, Cassano, & Drioli, 2003). It is noteworthy that the removal of bitter components from fruit juices is important for their quality.

The membrane was prepared by adding **5** to a homogenous solution of PEEK-WC in DMF. The regeneration of membranes is made by their washing with an alkaline solution; in this way their reuse is possible. It should be mentioned that PEEK-WC membranes without **5** have no recognition properties towards naringin.

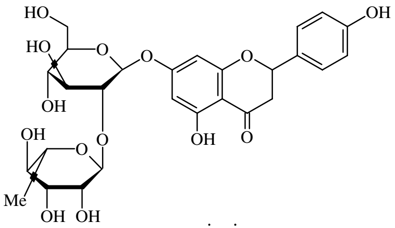


R = $C(O)OC_8H_{17}$

5



PEEK-WC



naringin

The polymer membrane consisting of thermosensitive polymer chain with pendant CD molecules was prepared. The pendant CD units have been introduced into the poly(*N*-isopropylamide), *i.e.* PNIPAM chain; the obtained copolymer was fixed onto the pore surface of a poly(ethylene) (PE) porous substrate with the use of plasma – graft polymerization (Yanagioka, Kurita, Yamaguchi, & Nakao, 2003).

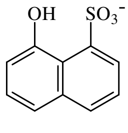
The membrane shows a high selectivity in the complexation ability of CD molecules. Complexation of guests by CD molecules depends on temperature; PNIPAM is thermosensitive and therefore may control the complexation. In the study of complexation dependence on temperature, it was observed that the binding constants of formed complexes decrease in passing from below to above the lower critical solution temperature (LCST) of polymer chains in aqueous solutions.

When the part of the guest molecule that is outside the cavity is introduced into the cavity, the binding constant of the CD changes due to the volume change of the copolymer at temperatures around the LCST. At temperatures below the LCST the copolymer swells, and steric hindrance from the polymer near the cavity is small, therefore the guest molecule can fit into the cavity. At temperatures above the LCST the copolymer shrinks, and the polymer chains agglomerate around the cavity; the resulting increase of a steric hindrance leads to a lower binding constant of CD.

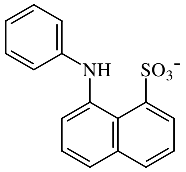
Since a moderate change in the temperature can influence the molecular recognition ability, it is possible to make a specific molecule adsorb to, and desorb from the substrate. Thus, the investigated membranes may serve either as a separation system or as a molecular sensing material.

It should be pointed out that the membrane shows a much faster response to an environmental stimulus than in the case of a normal cross-linked gel. A normal cross-linked gel needs a longer time to undergo a change in volume because of its poor water diffusivity. Moreover, the poor diffusivity results in the cross-linking, which restricts chain mobility. On the contrary, the membrane containing a linear polymer chain without any cross-linkages undergoes a faster volume change.

To investigate the complex formation mechanism, two types of guest molecules were used: 1-naphthol-8-sulfonate (NS), which can be totally included into the CD cavity, and 8-anilino-1-sulfonate (ANS) whose molecule is bigger and therefore it can be only partially included into the CD cavity.



NS



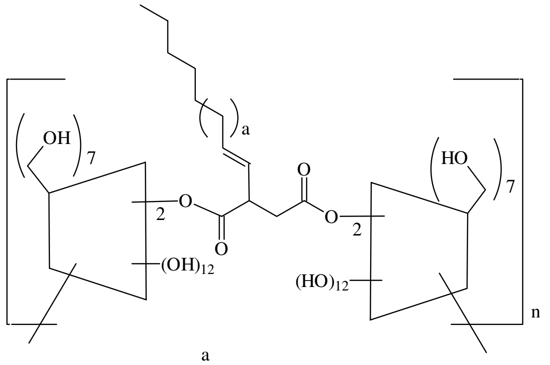
ANS

For a guest molecule which can be totally enclosed in the CD cavity (*i.e.* NS), the binding constant is the same when the copolymer chain either shrinks or swells, because there is no steric hindrance effect for molecules which are outside the cavity, since they are absent.

On the other hand, bigger guest molecules (*i.e.* ANS, whose benzene moiety protrudes from the CD cavity) can be only partially included in the CD cavity during the complex formation, and the part of the molecule situated outside the cavity is affected by the copolymer shrunken state due to the steric hindrance. These experiments show the importance of swelling of copolymer for the complexation.

The polymer inclusion membranes (PIMs) prepared by physical immobilization of β-CD polymers as ion carriers in cellulose triacetate (CTA) matrix, were used for metal ions transport. The metal ions were transported from aqueous solutions through plasticized CTA membranes into distilled water; as plasticizer *o*-nitrophenyl pentyl ether (ONPPE) was used (Kozlowski, Girek, Walkowiak, & Koziol, 2005).

The β-CD polymers **6** and **7** have been synthesized by the cross-linking of β-CD with nonenyl and dodecenyl derivatives of succinic anhydride, respectively (Choi et al., 2002; Girek et al., 2000). For experiments the polymer **6** was used, since **7** showed too low solubility in ONPPE.



	a
6	1
7	5

The transition metal ions were removed by competitive transport of Cu(II), Co(II), Ni(II) and Zn(II) through PIM containing polymer **6** (Kozlowski et al., 2005). In this process, the facilitated transport of metal ions through PIMs with β-CD polymer occurs.

For the carrier preparation the solution of β-CD in DMF was treated with solid NaH, followed by (2-nonen-1-yl)succinic anhydride or (2-dodecen-1-yl)succinic anhydride to give CD polymers **6** and **7**, respectively. The chloroform solution of β-CD polymer and ONPPE was mixed with the chloroform solution of CTA to form a casting solution of membrane, which after the evaporation of chloroform yielded PIM.

The competitive transport of Cu(II), Co(II), Ni(II) and Zn(II) ions through plasticized immobilized membranes involves formation of metal ion pairs with CD hydroxyl groups. The transport of ions may be considered as an induced fit mechanism, providing that the CD polymer in the presence of metal ion guest undergoes structural changes due to the flexibility of CD cavities.

It was established that the polymer of β-CD containing the nonenyl groups *i.e.* **6** shows the following selectivity order: Cu(II) > Co(II) > Ni(II) > Zn(II). The kinetics of metal ions transport across PIM was described, and for the determination of the efficiency of metal ion removal from the feed phase the recovery factor (RF) was calculated (Kozlowski et al., 2005).

Recently, it was reported that β-CD polymers prepared by cross-linking of β-CD with 2-(1- docosenyl)-succinic anhydride derivatives show selectivity of lead(II) over other metal ions in the transport across plasticized membranes. In the case of competitive transport of Pb(II), Cu(II), and Zn(II) ions through PIM the selectivity order was Pb(II) >> Cu(II) > Zn(II) (Kozlowski, Walkowiak, & Girek, 2008).

The considered PIMs are advantageous for their durability. Facilitated transport across PIMs containing β-CD polymers is an effective method for separation and recovery of chromium(VI), copper(II) and cadmium(II) from industrial waste waters and municipal sludge eluates. It is noteworthy that PIMs have proven to be very convenient for separation of metal ions (Kozlowski, 2007; Kozlowski & Walkowiak, 2004).

It should be noted that β-CD polymers obtained by cross-linking of CD with succinic anhydride (Girek et al., 2005) or with phthalic and 3-nitrophthalic anhydrides (Kozlowski et al., 2006) are useful in the removal of Cu(II), Zn(II) and Cd(II) ions from diluted aqueous solutions by ion flotation method.

The transport of metal ions across inherently conducting polymer (ICP) membranes containing CD dopants has been investigated (Reece, Ralph, & Wallace, 2005). It is known that ICPs combine the properties of synthetic polymers with electrical conductivity of metals (Wallace, Spinks, Kane-Maguire, & Teasdale, 2003).

After preparation, ICPs exist in a neutral, conducting state. During synthesis, anions are doped into their structure to balance the positive charges present along the conducting polymer chain. When ICP is reduced, the conducting polymer backbone becomes neutral. If the anions which were incorporated during synthesis of ICP are immobile, the cations present in the surrounding solution may be incorporated into the polymer to maintain overall charge neutrality.

The subsequent re-oxidation of the ICP by a positive potential restores the initial, positively charged state; as a result the cations are repelled from ICP. Therefore the switching of the redox state of the polymer by application of adequate potentials, enables ICPs to function as cation exchange materials.

Reduction and subsequent re-oxidation of ICPs can be accompanied by expulsion and incorporation of dopant anions to maintain charge neutrality. When large immobile dopants, *e.g.* polyelectrolytes are present, the charge neutralization occurs mainly *via* movement of cations.

In the study of polymers containing CD units which may noncovalently bind metal ions, the conducting polymer membranes consisting of polypyrrole (PPy) doped with sulfonated α-CD (*i.e.* α-CDS) or sulfonated β-CD (*i.e.* β-CDS) were prepared electrochemically by depositing PPy·α-CDS or PPy·β-CDS onto platinum sputter-coated polyvinylidene filters. It was shown that both polymers were electroactive.

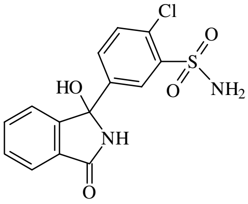
The higher permeability towards most metal ions investigated was found for PPy·β-CDS as compared to PPy·α-CDS; the permeability of PPy·α-CDS membranes decreased in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+} > Fe^{3+}$ whereas for PPy·β-CDS membranes the sequence was $Ni^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Cu^{2+} > Fe^{3+}$ (Reece et al., 2005).

The transport of metal ions involves passage of hydrated ions through pores of a polymer membrane; the diameter of pores should be equal to or larger than the diameter of the largest hydrated metal ion studied. The above considerations show that the formation of inclusion complexes of CD dopants with metal ions strongly influences the membrane permeability.

The flux values of transition metal ions across membranes consisting of PPy doped with sulfonated α- and β-CDs, *i.e.* PPy-α- and PPy-β-CDs (Reece et al., 2005), and across membrane containing polypyrrole/polyvinylphosphate conducting polymer materials (Davey, Ralph, Too, & Wallace, 1999), as well as across plasticized membrane (Kozlowski et al., 2005) are summarized in Table 1. The results show that a high transport rates and relatively good selectivity are achieved in the case of sulfonated CDs used as dopants (Krieg, Breytenbach, & Keizer, 2000).

Besides described above polymeric membranes, also ceramic membranes impregnated with polymers deserve an attention; such example will be presented. In the study of CD modified ceramic membranes (Takaba & Way, 2003), the porous tubular ceramic membrane consisting mainly of Al_2O_3 and Zr_2O_3 was impregnated with a β-CD polymer to give a chiral-selective membrane. Polymerization of CD in the presence of epichlorohydrin proceeds in the alkaline medium (Krieg et al., 2000). The mixture of β-CD with water was treated with NaOH and $NaBH_4$ and then the ceramic membrane was added, followed by epichlorohydrin.

The obtained membrane was able to separate the enantiomers of the racemic drug chlorthalidone (**8**). For this purpose, the CD impregnated ceramic membrane was placed in a cell designed to evaluate the permeation of racemic **8**. The separation mechanism is based on the preferential complexation of CD with one enantiomer. The above chiral – selective membrane combines the strength and inertness of an inorganic support with the chiral selectivity of CD.



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One should also mention here bilayer vesicles of amphiphilic CDs, since they can function as host membranes recognizing small guest molecules by hydrophobic inclusion at their surface (Falvey et al., 2005). Amphiphilic CDs are CDs modified with hydrophobic and hydrophilic substituents that can aggregate into lyotropic phases in water. The hydrophobic groups drive hydrophobic aggregation of the amphiphiles, and the hydrophilic groups guarantee sufficient water solubility. The CD vesicles consist of bilayers

Table 1
The fluxes of transition metal ions across polymer membranes (Davey et al., 1999; Reece et al., 2005) and across plasticized membrane (Kozlowski et al., 2005)

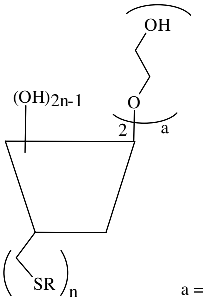
Metal ions	Flux expressed as 10^6 mol/m^2 s			
	PPy-α-CDS (Reece et al., 2005)	PPy-β-CDS (Reece et al., 2005)	PPy-α-BCS* (Davey et al., 1999)	β-CD polymer (Kozlowski et al., 2005)
Co(II)	9.3	85	7.2	4.5
Ni(II)	13	140	6.6	5.8
Cu(II)	65	15	46	2.9
Zn(II)	4.8	130	13	1.5

* BCS, bathocuproinedisulfonic acid.

of CDs in which the hydrophobic “tails” are directed inward and the hydrophilic macrocycle “head groups” are facing water; in this way aqueous interior is enclosed.

For their existence as water-soluble amphiphiles, CDs should bear hydrophobic alkyl substituents on one face of the CD molecule and hydrophilic, *e.g.* poly(ethylene glycol), sulfonate, ammonium etc. substituents on the other face. The CD vesicles have properties of liposomes and macrocyclic host molecules, they can encapsulate water-soluble molecules into the bilayer membrane, and they can bind guest molecules through inclusion in CD cavities at the surface of the vesicle. Such encapsulation of small guest molecules by CD hosts assembled in a bilayer membrane may serve as a model of recognition of substrates or ligands by receptors on the surface of cell membranes (Huskens et al., 2004; Marchi-Artzner, Brienne, Gulik-Krzywicki, Dedieu, & Lehn, 2004).

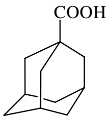
For experiments, α-, β- and γ-CDs were modified with hydrophobic *n*-dodecyl and *n*-hexadecyl substituents and with hydrophilic oligo(ethylene glycol) substituents to give amphiphilic CDs **9** and **10**, forming bilayer vesicles in aqueous solutions.



a = 1-3

	n
α-CD	5
β-CD	6
γ-CD	7

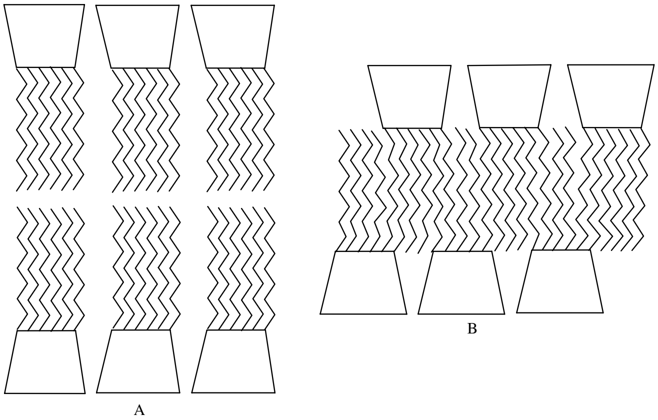
	R
9	$C_{12}H_{25}$
10	$C_{16}H_{33}$



11

The inclusion of a small guest molecule in the CD cavities at the surface of the vesicles was also studied, choosing adamantane 1-carboxylate **11** as an example. Molecular recognition of a hydrophobic anion such as **11** by CD vesicles was examined by capillary electrophoresis. It was observed that β-CD vesicles, in spite of the presence of oligo(ethylene glycol) substituents, retain their affinity for hydrophobic **11**, which decreases in the order: β-CD > γ-CD > α-CD.

In the study of the bilayer packing of CD amphiphiles it was established that for filling the “void” under the macrocycle to obtain nonleaky bilayer membrane, the alkyl chains should interdigitate or tilt; in other case the macrocycle should collapse. The extended (A) and interdigitated (B) packing of alkyl chains in CD bilayer is shown below.



It was observed that the most likely molecular packing occurs by a deep interdigitation of alkyl chains. This interdigitated mode of bilayer packing restricts the mobility of alkyl chains in the bilayer.

4. Conclusion

In the review, the use of liquid and polymer membranes in the separation processes is described. Albeit not exhaustive, presenting only selected examples, the paper highlights to some extent the membrane processes and their usefulness in industry and in analytical chemistry.

The review was written in the continuation of our laboratory work dealing with separation procedures of metal ions (Kozlowska et al., 2007; Kozlowski, 2007; Kozlowski et al., 2006). It should be pointed out that the attention paid today to use of PIMs in separation processes is growing rapidly. PIMs show durability, high efficiency and long term integrity in the transport of metal ions, numerous reports on this theme being reflection of their promising properties in selective removal and recovery of metals (de Gyves, Hernandez-Andaluz, & de san Miguel, 2006; Fontas et al., 2007; Gardner, Walker, & Lamb, 2004; Kozlowski, 2006; Kozlowski, 2007; Kozlowski & Walkowiak, 2002; Kozlowski & Walkowiak, 2004; Kozlowski & Walkowiak, 2007; Kozlowski et al., 2002; Kusumocahyo et al., 2006; Nghiema et al., 2006; Sodaye, Tripathi, Pandey, & Reddy, 2004).

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