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Application of *O*-phenylacetyl β-CD as a carrier for selective transport of lead(II) across polymer inclusion membranes

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ABSTRACT

The *o*-phenylacetyl β-CD derivative **1** was obtained by substitution of β-CD and characterized by spectroscopic methods. Competitive transport of equimolar mixtures of Pb(II), Cd(II), Cu(II), and Na(I) ions from aqueous nitrate feed phase across polymer inclusion membranes (PIMs) using *O*-phenylacetyl β-CD **1** derivative as an ion carrier has been investigated. The influence of the phenylacetyl groups attached to β-CD rings on the selectivity and efficiency of metal ions transport across PIMs containing cellulose triacetate (CTA) as the support was studied. The efficiency of a membrane for the selective transport of Pb(II) ions has been investigated, and several parameters affecting metal transport have been evaluated, such as the carrier concentration, the plasticizer content, and the acidity of the aqueous phase. We found that facilitated transport of metal ions across the above PIMs proceeds via a carrier-mediated mechanism and is dependent on pH-driving force. PIMs including **1** selectively transported Pb(II) ions at concentration of ion carrier in membrane equal to 0.6 M and have shown the preferential selectivity order: Pb(II) >> Cd(II) > Cu(II) > Na(I). The repeated transport experiments of PIM indicated the long-term integrity of PIM.

Keywords: Polymer inclusion membrane; Competitive transport; *O*-phenylacetyl β-CD derivative; Metal ions

1. Introduction

Heavy metals are toxic pollutants released into the surface and ground water as a result of certain industrial activities, such as mining and agricultural. The rapid pace of industrialization has led to severe problems of water pollution. Awareness encouragement of pollutant toxicity has forced industries and municipal authorities to treat wastewater before discharging it to natural water bodies [1].

Lead is one of the industrial pollutants; possibly entering the ecosystem through soil, air, and water. According to the WHO, the maximum permissible limit (MPL) of lead in drinking water is 0.1 mg/L [2]. Hence, the appropriate treatment of industrial wastewater which releases lead into the aquatic and terrestrial systems is very important.

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Polymer inclusion membranes (PIMs), i.e. the immobilized plasticizer membranes concept has been known for 40 years and has been proposed as a possible alternative to the conventional solvent extraction. PIMs are usually composed of a carrier, a base polymer (CTA) and plasticizer [3,4]. The ion carrier is essentially the ion exchanger responsible for binding to the metal species. For the macrocycle carriers such as crown ethers, calixarenes, and modified cyclodextrins (CDs), the transport across PIMs relies on the concentration gradient of method ions–carrier complexes or ion-pair formed within plasticizer membranes [5–8].

CDs belong to macrocyclic compounds, and they are cyclic oligomers composed of six, seven, or eight anhydrous glucopyranosyl units (known as α-, β-, and γ-CDs, respectively) connected by α-l,4-linkages [9,10]. The ring structure provides a relatively hydrophobic central cavity and a hydrophilic outer surface [11]. The most notable feature of CDs is their ability to form inclusion compounds with a very wide range of solid, liquid, and gaseous compounds by molecular complexation [12]. When CDs are substituted, they become less soluble and more stable and therefore, the CD derivatives can be used to remove or isolate many organic and inorganic substances [9,10].

It should be noted out that CD polymers are promising drug carriers for controlled drug release [13–15], and they are also used in the study of enzymatic processes [16–18]. The CD polymers can bind metal ions; the transport of metal ions is promising for the removal of toxic metal ions from wastewaters [15,19]. The β-CD polymer may be used as an optical receptor to detect of organic compounds. This molecularly imprinted β-CD polymer was prepared from β-CD, using toluene diisocyanate as a cross-linking agent; in this procedure, *N*-phenyl-1-naphthylamine served as a template. The molecularly imprinted polymer was fluorometrically characterized using a fiber optic cable attached to a flow-cell [13].

Membranes containing CD units are employed in a number of metal ions separations. Liquid membranes with CDs have received recently a considerable attention due to their high selectivity resulting from the presence of CDs in membranes as carriers. In the search for new ion carriers, the β-CD polymers were investigated [10].

The 6-*O*-benzylated β-CD samples were deposited on the silica surface without coupling reagent and were used as an electrolyte–insulator–semiconductor (EIS) heterostructure for the detection of cations in aqueous solutions. The sensitivity of EIS devices has been examined for Ca(II), Cu(II) and K(I), as well as for Cd(II) and Pb(II) ions. Membranes with incorporated benzylated β-CDs showed a Nernstian response toward Pb(II) with good selectivity. The sensitivity toward Cd(II) ions was weak, whereas in the case of Pb(II) ion it was strong; this latter observation results from the fact that benzylated CD molecules retain the ionic recognizing properties of the native CDs. It was found that α-CD/PS membrane shows a good affinity toward Cd(II) ions and β-CD for Pb(II) ions. The Cd(II) ions surrounded by their hydration shells are preferentially fixed at α-CD cavities and Pb (II) ions at β-CD cavities. The β-CD/PS membrane shows good sensitivity toward Pb(II) ion, and this fact being due to the complementarity of the β-CD cavity and hydrated radius of Pb(II). The Nernstian response of β-CD/PS gel membrane is not interfered by K(I), Ca(II), and Cd(II) ions. It should be pointed out that both membranes α-CD/PS and β-CD/PS have a long (above three months) lifetime and can be regenerated by washing with acidulated (pH 5) water [21]. Similar results were obtained when CD molecules were incorporated into plasticized poly(vinyl chloride) (PVC) membranes [22,23].

The β-CD polymers cross-linked by 2-(1-docosenyl)-succinic anhydride, i.e. by derivative of succinic anhydride containing long (C_{21}) lipophilic chain have been obtained [20]; it was found that at the room temperature the β-CD dimer and at 100˚C, the β-CD polymers were formed. For β-CD dimer and polymer, the selectivity order was Pb(II) >> Cu(II), Zn(II); the selectivity coefficients for Pb(II) over Cu(II) and Zn(II) were very high, especially for β-CD dimer.

In the present study, the prepared *O*-phenylacetyl β-CD derivative **1** was used as the ion carrier. It was applied to ion carrier in plasticized membranes for competitive transport of Pb(II), Cd(II), Cu(II), and Na (I) from aqueous solutions. Moreover, the molecular weight of *O*-phenylacetyl β-CD derivative was measured using MALDI-TOF spectra, and the ^{1}H NMR, and FTIR spectroscopy results of above species were discussed.

2. Materials and methods

2.1. Reagents

β-Cyclodextrin (purum, ⩾99.8, HPLC), purchased from Fluka was dried. Pyridine (purum, 99.0%, POCh Gliwice, Poland) was purified by boiling over KOH for 3 h and next distilled under dry argon. Phenylacetyl chloride (99.8%), *N,N′*-dimethylaminopyridine (purum, ⩾99.0%) (DMAP), dichloromethane, *o*-nitrophenyl pentyl ether (ONPPE), and cellulose triacetate (CTA) were purchased from Fluka and used without further purification. Inorganic compounds, i.e. $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $NaNO_3$, and HCl were obtained as reagents of analytical grades from POCh (Gliwice, Poland).

2.2. Methods

^{1}H NMR spectra were recorded in d_6-DMSO on Bruker 600 MHz spectrometer at room temperature, with TMS standard. MALDI-TOF MS experiments were performed on MALDI-TOF MS—Reflex IV (Bruker Saxonia) spectrometer using 2,5-dihydroxybenzoic acid (DHB) as a matrix. Samples were dissolved in $CHCl_3$/MeOH, 1:1 v/v (10 mg/mL) and mixed with the solution of DHB matrix (200 mg/mL) in MeOH and NaI solution in water (10 mg/mL), in a 5:50:2 v/v ratio. The resulted solution (1 µL) was placed on the analysis steel plate. To obtain the spectrum, 200 laser shots were averaged. FT-IR spectra were recorded on Nicolet NEXUS spectrophotometer.

2.3. Synthesis of *O*-phenylacetyl β-CD **1**

Dried β-CD (1.135 g, 1 mmol) was dissolved in dry pyridine (20–30 ml) and magnetically stirred for about 1 h. The obtained solution was cooled to 0˚C and was treated with *N,N´*-dimethylaminopyridine (DMAP) (0.366 g, 3 mmol) and stirred to complete dissolution. The flask was then equipped with a reflux condenser with a $CaCl_2$ trap, and phenylacetyl chloride (2.781 ml, 21 mmol) was injected into it. The reaction mixture was kept at constant temperature equal to 60˚C, with stirring, for 48 h. The resulting product **1** (Fig. 1) after purification was characterized with MALDI-TOF MS and ^{1}H NMR spectroscopy. ^{1}H NMR: (DMSO-d_6) 8.52 (*p*-phenyl, d, 21 H); *p*-phenyl 8.89 (*m*-phenyl, d, 42 H); 4.69 (CD–H_1, s, 7 H); 4.47–3.20 (CD–H_2, H_3, H_4, H_5, H_{6a}, H_{6b}, CH_2-benzyl, m, 70 H).

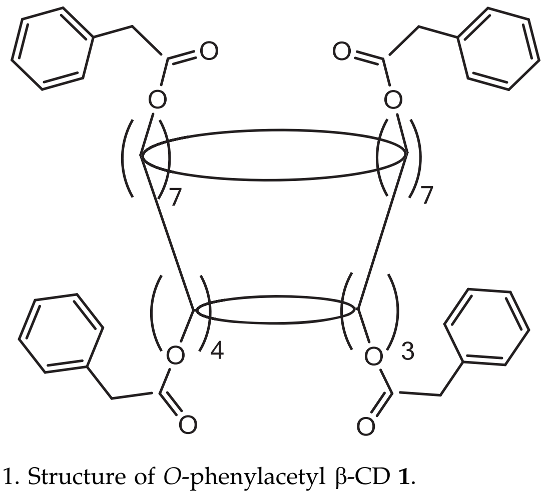

Fig. 1. Structure of *O*-phenylacetyl β-CD **1**.

2.4. Preparation of polymer inclusion membranes

The solution of CTA was prepared by dissolving an appropriate amount of CTA in 15 cm^3 of chloroform. A separate chloroform solutions containing known amounts of ONPPE and β-CD derivative **1** were prepared. These solutions were mixed (total volume 25 cm^3) and ultrasonicated for 15 min to form the casting solution of PIM. Finally, this casting solution was spread on a 9.0 cm diameter flat-bottom glass plate which was kept on a leveled surface. The Petri dish was covered with a glass plate in such a way that the aeration was possible, and any cross-contamination was prevented. Chloroform was allowed to evaporate slowly over a period of 12 h. After evaporation of chloroform, PIM was peeled off from the Petri dish. The weight of PIM was found to be identical (±1%), as expected, with the total weight of CTA, ONPPE, and β-CD derivative **1** used for PIM casting.

The thickness of the PIM samples was measured using a digital micrometer (Mitutoy) with an accuracy of 0.0001 mm. The thickness of membrane was measured 10 times for each case and shown as average value of these measurements with the standard deviation below 1%. The thickness of membrane before and after the transport was the same. The prepared membranes had average thickness equal to 25 µm.

Each experimental point (i.e. the membrane formation by immobilization, thickness measurement and calculation of transport parameters) was repeated four times. Experimental reproducibility was high with standard deviation below 1% measured values.

2.5. Membrane transport experiments

Transport experiments were carried out in a permeation module cell described in earlier study [24]. The membrane permeation experiments were carried out using a two-compartment membrane cell provided with a circular window (diameter of 3.8 cm) where the membrane was placed. The feed and the stripping solutions (50 mL each) were placed in each compartment of the cell on both sides of the membrane. The experiments were initiated when stirring was started with a stirring rate of 900 rpm. Samples were taken from the feed and strip compartment at a regular time intervals and analyzed by atomic absorption spectroscopy method (AAS Spectrometer, Solaar 939, Unicam).

The kinetics of the transport across PIMs was described as a first-order reaction in metal-ion concentration:

$$\ln\left(\frac{c}{c_i}\right) = -kt \tag{1}$$

where c is the metal ion concentration at a given time in the feed phase (M), c_i is the initial concentration of metal ion in the feed phase (M), k is the rate constant (s^{-1}), and t is the time of transport (s).

To calculate k values, the plots of $\ln(c/c_i)$ vs. time were prepared. The relationship of $\ln(c/c_i)$ vs. time was linear, as it was confirmed by high values of determination coefficients (r^2), i.e. $\leqslant 0.98$. The determined standards deviation of rate constant was $\leqslant 1\%$. The permeability coefficient (P) was calculated as follows:

$$P = (V/A) \times k \tag{2}$$

where V is the volume of the aqueous feed phase, and A is the area of the effective membrane. The initial flux (J_i) was determined to equal:

$$J_i = P \times c_i \tag{3}$$

To describe the extraction efficiency ($\%E_m$) of metal ion transport from feed phase to the membrane phase was calculated as:

$$\%E_m = (c_i - c)/c_i \times 100\% \tag{4}$$

The selectivity coefficient S was defined as the ratio of initial fluxes for $M1$ and $M2$ metal ions, respectively.

$$S = J_{i,M1}/J_{i,M2} \tag{5}$$

The reported values correspond to the average of three replicates with the standard deviation within 2%.

3. Results and discussion

3.1. Characterization of phenylacetyl cyclodextrin derivative **1**

In the FT-IR spectrum of the product obtained in the reaction of β-CD with phenylacetic acid chloride, the bands characteristic for C=O groups of phenylacetyl substituents as well as ester groups were observed ($\gamma_{C=O}$ 1,736 cm^{-1} and $\gamma_{C–O–C}$ 1,252 cm^{-1}, respectively). Although the FT-IR spectrum does not allow to determine the number of hydroxyl groups substitution, the very low intensity of a band at the 2,928 cm^{-1} suggests a high degree of CD substitution. The band at the 1,494 cm^{-1} is probably due to the phenyl stretching vibration. Nevertheless, some very weak bands appear above 3,400 cm^{-1}. They should be assigned to O–H stretching vibrations of water molecules involved in different hydrogen bonding schemes.

^{1}H NMR analysis of the product obtained in the above reaction indicates that 15 substituted CD derivatives were formed (see Section 2). However, MALDI-ToF MS spectrum of this product showed in the mass range of m/z 1,500–3,700 the presence of the series of the signals. The mass spacing between the respective signals are equal to 118 Da, which corresponds to the molar mass of the phenylacetyl substituent. The observed peaks were ascribed to the Na^+ of CDs, substituted by adducts 4–18 phenylacetyl groups. The most intensive peaks in the spectrum corresponded to the sodium cation adducts with β-CDs substituted by 12 and 13 phenylacetyl groups. This result is compatible with NMR data. The presented MS analysis shows clearly that the obtained product is the mixture of β-CDs substituted by 4–18 phenylacetyl groups, and the average degree of substitution determined using NMR spectroscopy is equal to 15. The FT-IR spectrum (4,000–500 cm^{-1}; KBr) of β-CD substituted by phenylacetyl groups is presented in Fig. 2.

3.2. Transport of metal ions across PIM with phenylacetyl cyclodextrin derivative **1**

In the previous studies [20,24], the synthesis of β-CD polymers was described, which shows the hydrophobic properties due to the attached hydrocarbon group in the linker of polymers. The blank experiments, for the metal ions transport when the ion carrier was absent, show no significant flux across PIM.

In this study, we applied kinetic model of metal ion transport through a liquid membrane proposed by Danesi [25]. This is a simplified model relating to a stationary state where $J_{\text{feed}} = J_{\text{membrane}} = J_{\text{strip}}$. It is assumed that the chemical reaction at the interface of the aqueous solution/membrane is rapid, the concentration gradient of the metal in the diffusion boundary layer is linear as well as the reaction of decomplexation at the receiving phase/membrane *occur quickly*. The profile of the metal concentration in both aqueous phase and membrane solution in Pb(II) transport across PIM was studied in this section. The change of the metal molar ratio of Pb(II) in feed and strip solutions on time transport was shown in Fig. 3. It indicates that the transport percentage of Pb(II) occurs at quasi stationary state where J obtained for

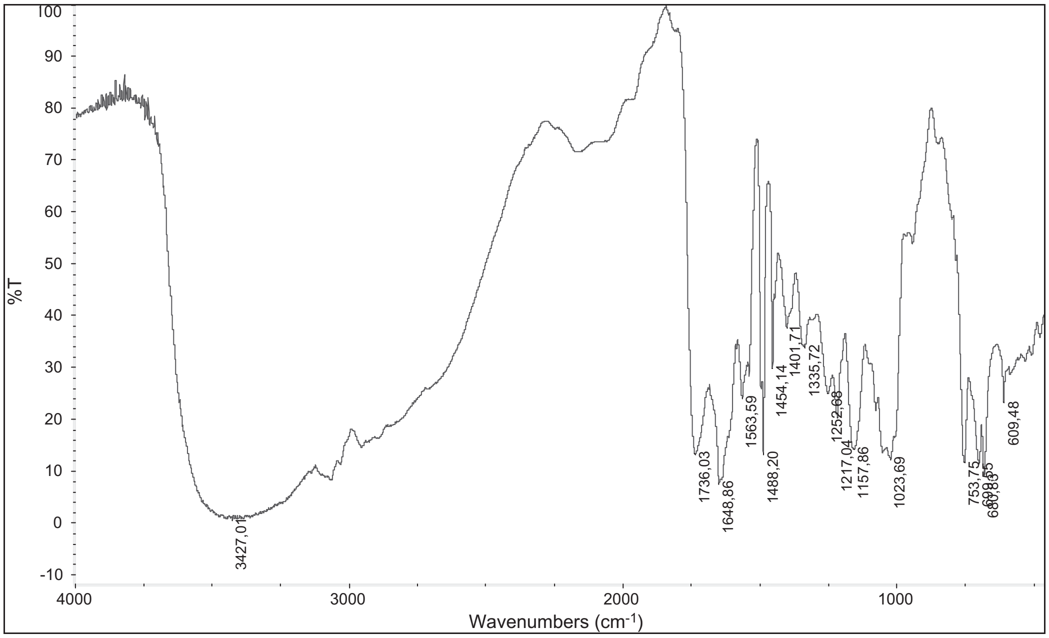

Fig. 2. FT-IR spectrum (4,000–500 cm^{-1}; KBr) of β-CD substituted by phenylacetyl groups.

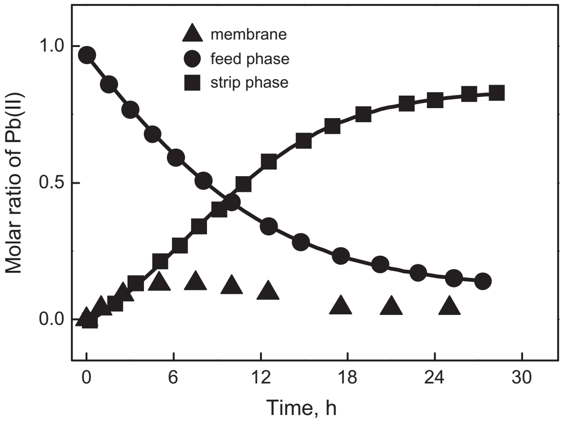

Fig. 3. The lead(II) profile concentration in feed, strip and membrane phase in transport across PIM with 0.5 M *O*-phenylacetyl β-CD **1**; 2.0 cm^{3}ONPPE/1.0 g CTA.

feed/membrane and membrane/strip phase were equaled 4.26 and 4.21 μmol/m^{2}s, respectively.

Moreover, two different values of the fluxes for Pb (II) ions were determined: one measured from the decrease in the metal concentration in the feed solution and the other determined from the increase in the metal ion concentration in the stripping solution. The flux values for Pb(II) transport from feed and stripping phase were equal 3.1 and 3.0, respectively. The lack of differences, below 1% value, in the values of J_{feed} and J_{strip} indicates that retention of the metal ion within the membrane phase does not occur.

3.2.1. *Influence of ion carrier concentration*

The most important factor influencing the transport of metal ions through liquid membranes is the nature of the ion carrier, especially its hydrophilic–lipophilic properties; the maximum concentration of carrier plays also an important role in saturation of membranes.

The effect of ion carrier concentration on the competitive transport of metal ions was investigated under following experimental conditions: feed phase: 1.010^{-3} M of Cd(II), Pb(II), Cu(II), and Na(I) solution at pH 5.0; stripping phase: 0.1 M HNO_3. Membrane composition was: 2.0 cm^3 plasticizer (ONPPE) per 1.0 g CTA, and different ion carrier concentration in the range 0.1–1.0 M based on the volume plasticizer.

The pH 5.0 value was chosen as a value for establishing a high pH gradient between both aqueous phases (driving force of the metal cation transport) while preventing lead hydroxide formation occurring at higher basic pH.

The results shown in Fig. 4 indicate that transport of Pb(II) increases with increasing β-CD concentration up to 0.6 M. For this β-CD concentration, the Pb(II) maximal flux values were equal to 4.03 μmol/m^2 s. The process selectivity is defined by a sequence of metal ions transport fluxes, which decrease in the following order: Pb(II) > Cd(II) > Cu(II) > Na(I). The Cd (II) ions were transported at a lower rate, and the maximum J_i value for 1.0 M of CD in the membrane was 1.35 mol/m^2 s.

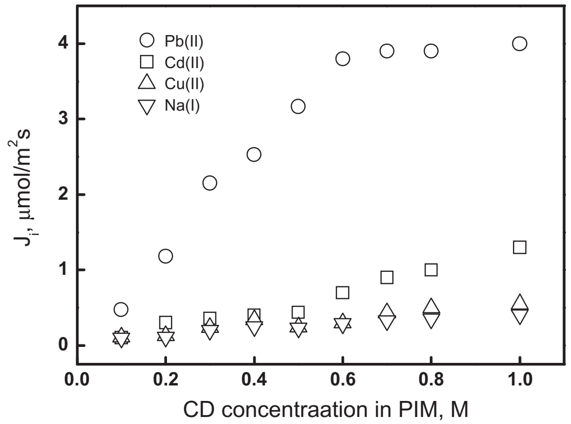

Fig. 4. Relationship of initial metal fluxes vs. carrier concentration in membranes. Feed phase: 1.0×10^{-3} M of Cd(II), Pb(II), Cu(II) and Na(I) solution at pH 5.0; stripping phase: 0.1 M HNO_3. PIM: 4.0 ml ONPPE/1.0 g CTA.

Mechanism of ion metal transport with β-CD relays upon interaction of hydrophobic β-CD ring with simultaneous neutralization of electric charge by nitrate anions. Analogous mechanism is observed for the transport of metal ions with crown ethers or calixarenes. Total transport flux of nitrate anions was twice higher than flux of metal cations for membrane with 0.6 M *O*-phenylacetyl β-CD **1** and was equal to 9.4 mol/m^2 s. This confirms the facilitated transport of metal ions with β-CD carrier.

In the present study, the low constant of transport for Cu(II) and Na(I) was observed. Results obtained revealed significant change in the Cd(II) permeability only at higher ion carrier concentrations, i.e. 0.6 M; it also appears that Na(I) transport is modestly depressed in the competitive transport system. This behavior may be explained by increased ability of β-CD to complex cations with large ionic radii. Increase in Cd(II) complex formation results also in the increase in its concentration gradient within the membrane during the membrane saturation.

Li and Purdy [26] have underlined the importance of the geometrical factor for determining the stability of the inclusion complexes with CDs. Differences in radii between hydrated ions and internal cavities of CDs probably account for the behavior of the present systems. The Cd(II) ion (0.97 Å) is preferentially lodged in α-CD cavities (5.7 Å) and Pb(II) (1.2 Å) in β-CD ones (7.8 Å).

In the aim to obtain the center coordination in CD carrier, the IR spectra of membranes after transport were measured. The IR spectra of PIMs after transport process of metal ions show the decreased intensity of bands characteristic for C=O groups of phenylacetyl substituents in $\gamma_{C=O}$ 1,736 cm^{-1} and region of γ_{OH} band in the 3,350–3,480 cm^{-1} as compared to the membrane before the transport experiment. This result confirms the association of CD with metal ions, and the subsequent complexing of metal ions with cavity and substituents of the CD molecule.

To study the type of transport mechanism involved, the membrane thickness (l) was modified by varying the CTA content. The transport of Pb(II) ions across PIMs of a different thickness, but with an identical β-CD derivative **1** concentration in the membrane equal to 0.6 mol/dm^3, has been also investigated. The prepared membranes had thicknesses of 25, 30, 39, and 55 μm. A decrease in flux (J) with increase in membrane thickness was observed, indicating a Fickian-type mechanism. Considering that l equals the length of the transport path in Fick's first law of diffusion, i.e. in a well-stirred membrane system, the aqueous boundary layer thickness is much lower than l, and taking into account initial fluxes ($C \approx C_0$), the apparent diffusion coefficient of the Pb(II)-containing species in the membrane phase was estimated from relation of $J = DC/l$; the calculated value of 1.82×10^{-9} m^2 s^{-1} was similar to the values observed for some PIM systems using a macrocyclic carrier (10^{-9} m^2 s^{-1}) [20].

3.2.2. Effect of plasticizer content

In an early investigation, Sugiura [27] observed that the lanthanide ion flux through a CTA membrane increased to an optimum value and then dropped as the plasticizer concentration increased from 0 to 4 cm^3 per 1 g CTA. Although a plausible explanation for this observation was not given, it is consistent with similar observations in recent studies by Fontas et al. [28] and De Gyves et al. [29].

In the present study, the dependence of a plasticizer content on the Pb(II) permeation through PIM incorporating β-CD derivative **1**, we investigated. The Fig. 5 shows the effect of the plasticizer content on Pb (II) flux across PIM with the CD. When the plasticizer content increased up to about 3.25 cm^3 ONPPE/1 g CTA, the flux increased sharply. A further increase in the plasticizer content above 3.5 cm^3 ONPPE/1 g CTA resulted in a decrease in the flux, probably due to higher membrane viscosity, with depression of the diffusivity of the ion carrier complex in the membrane. The optimum composition of the membrane and the highest plasticized matrix occur when PIM contains 41% plasticizer, 12% CTA and 47% carrier. This observation is in accordance with results of our previous study [30], showing the permeability of Cr(VI) as a function of the plasticizer (ONPPE) concentration.

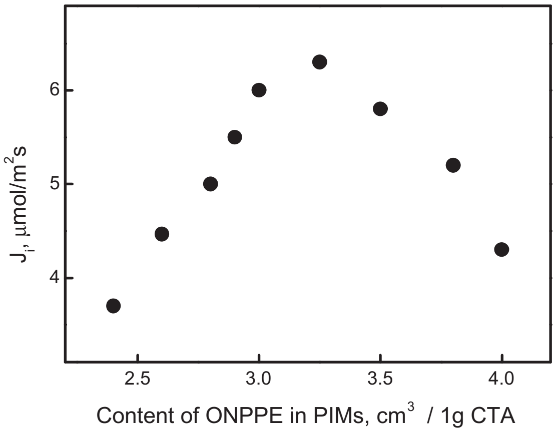

Fig. 5. Relationship of initial Pb(II) fluxes vs. plasticizer concentration in membranes. Feed phase: 1.0×10^{-3} M of Cd(II), Pb(II), Cu(II) and Na(I) solution at pH 5.0; stripping phase: 0.1 M HNO_3. PIM: different volume of ONPPE/ 1.0 g CTA, 0.6 M carrier.

3.3.3. Effect of pH of the feed phase

In Table 1, the variation of the metal fluxes is plotted versus aqueous pH of the feed phase for the competitive transport of Pb(II), Cd(II), Cu(II), and Na (I) from aqueous solutions containing 5×10^{-4} M of each metal ion. Membrane phases contained 0.6 M phenylacetyl cyclodextrin derivative 1 based on plasticizer volume. It was observed that Pb(II) transport in the presence of Cd(II), Cu(II), and Na(I), increases as the pH is increasing; whereas in the case of other metal ions, the transport is slow at all pH values and remains almost constant.

Dung and Ludwig [31] have also shown that extraction selectivity of divalent Pb(II), Hg(II), Cd(II), Zn(II), and Co(II) cations from weakly acidic media into toluene is governed by the relationship between ion and cavity radius. The *t*-Butylcalix [4] arenecrown-6 derivatives preferably extract cations with larger ion radii, i.e. Hg(II) and Pb(II). Ulewicz et al. [7] investigated competitive transport of Zn(II), Cd(II), and Pb (II) ions through PIMs containing imidazole azocrown ethers as ion carriers. It was found that the type of the group attached to the macrocyclic molecule influences the selectivity and transport efficiency of transition and heavy metals through PIMs. For the above azocrown ethers, the values of selectivity coefficients for Pb(II)/Cd(II) are lower than **1** [32].

In the present study, the overall PIM transport process leads to highly selective removal of toxic metals from the feed phase. Separation factor Pb(II)/Cd (II) was found to be 50.83. These large separation factors among divalent heavy metal cations are higher than those reported by Aguilar et al. for the separation of lead from cadmium in a PIM transport system with Kelex 100 as a carrier [32], as well as those reported by Kozlowska et al. [33] and Ulewicz et al. [7]. Although these [7,32,33] papers deal with the separation of some transition metal ions, they do not report the selective separation of Pb(II). To our knowledge, the present study is the first report of successful

Table 1
The initial fluxes, selectivity orders, and selectivity coefficients Pb(II), Cd(II), Cu(II), and Na(I) transport across PIMs with phenylacetyl cyclodextrin derivative. The feed phase: 50 cm^3 of model aqueous solution, the stripping phase: 50 cm^3 of 1.0 M HNO_3 solution, PIM: 3.25 cm^3 ONPPE/1.0 g CTA at different carrier concentrations

pH of source phase	Metal ions	Initial fluxes, J_i, mole/m^{2}s	Selectivity orders and selectivity coefficients
3	Pb(II)	4.20	Pb(II) > Cd(II) > Cu(II) > Na(I) 38.2 42 84
	Cd(II)	0.11	
	Cu(II)	0.1	
	Na(I)	0.05	
4	Pb(II)	6.1	Pb(II) > Cd(II) > Cu(II) > Na(I) 50.8 55.5 101.7
	Cd(II)	0.12	
	Cu(II)	0.11	
	Na(I)	0.06	
5	Pb(II)	7.90	Pb(II) > Cd(II) > Cu(II) > Na(I) 49.37 41.57 87.77
	Cd(II)	0.16	
	Cu(II)	0.19	
	Na(I)	0.09	
6	Pb(II)	8.11	Pb(II) > Cd(II) > Cu(II) > Na(I) 11.9 33.8 57.9
	Cd(II)	0.68	
	Cu(II)	0.24	
	Na(I)	0.14	

separation with a PIM system of Pb(II) from a feed phase solutions containing a mixture of Zn(II), Pb(II), and Cd(II) ions.

However, the extraction of metal ions by CD derivatives used in this study, however, depends not only on the size fit, but also on the ion–dipole interaction between the acyl groups and the cations, steric effect of the cavity, space-regulating effect [34]. The initial flux values at various pH values of source phase probably indicates a "fixed-side" mechanism in transport across PIM with **1** as carrier.

3.2.4. Stability of membranes

The stability of PIM with CD derivative **1** is its very important factor. In repeated Pb(II) transport, both the aqueous phases were renewed every day, while the PIM remained the same as in the first run. Generally, the stability of PIM depends on the retention of concentration of immobilized carrier in plasticized matrix and on the stability of inclusion pores in support during the operations. Fig. 6 shows the stability of PIM during continuous operation of membrane cell for 30 days. The results indicate that the porous support material is stable during the 30 days operation. In observed experiments, we observed that the slight decrease in the initial fluxes can be explained by the distribution of carrier between the PIM and the aqueous solution. This observation results probably from the slow dissolution of the organic plasticizer in aqueous phases.

3.2.5. Recovery of lead(II) and other metal ions from waste waters

The recovery of metal ions from the industrial solutions is necessary. The study uses effluent from the smelter of zinc and lead from the factory treatment (pretreatment) containing metal ions; the concentration of metal ions in the initial solution at pH 2.0 was as follows: Cu(II)—52 mg dm^{-3}, Pb(II)—12 mg dm^{-3}, Cd (II)—2.0 mg dm^{-3}, and Na(I)—100 mg dm^{-3}. This solution contained also sodium nitrate at concentration of 4.0 g dm^{-3}. Extraction efficiency values for Cu(II), Pb (II), Cd(II), and Na(I) from the aqueous feed phase, determined in PIM transport with 0.60 M CD **1** into 0.1 M nitric acid as the stripping phase are shown in Fig. 7.

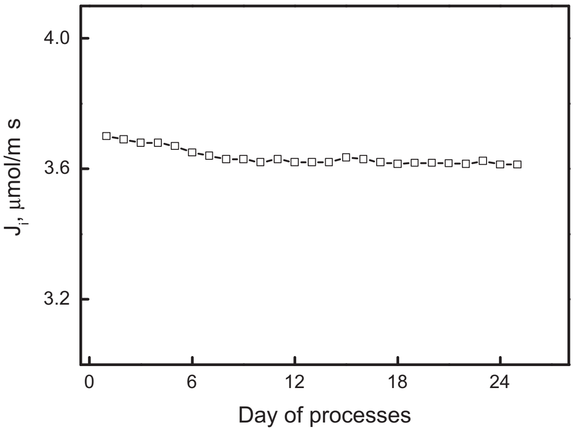

Fig. 6. Relationship of initial lead(II) fluxes vs. time of transport processes. PIMs: 0.60 M carrier, 1.3 cm^3 plasticizer/1.0 g CTA.

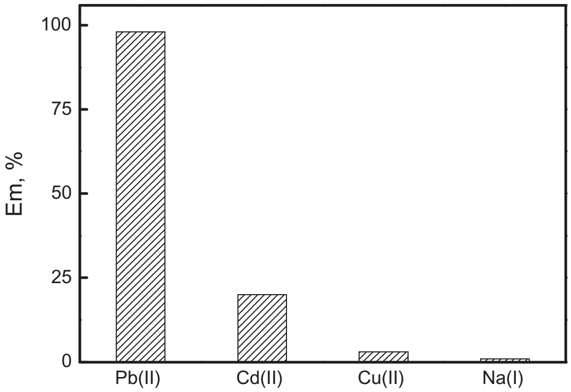

Fig. 7. Extraction efficiency obtained for Pb(II), Cd(II), Cu (II) and Na(I) after 48 h of transport across PIM with cyclodextrin **1** at different concentrations. The feed phase: 50 cm^3 of aqueous wastewater, the stripping phase: 50 cm^3 of 0.1 M HNO_3 solution, PIM: 3.0 cm^3 ONPOE/1.0 g CTA and 0.6 M carrier.

After 48 h of the competitive transport of metal ions across PIM, the concentration of Cu(II), Pb(II), Cd (II), and Na(I) in the aqueous source phase was reduced to 50.44, 0.24, 1.6, and 99 mg dm^{-3}, respectively. Facilitated transport through PIMs containing CD derivative **1** was found to be an effective method for separation and recovery of Pb(II) from industrial waste waters since the E_m was 98 %. The extraction efficiency for Cd(II), Cu(II), and Na(I) was low and equal to 20, 3, and 1%, respectively.

4. Conclusion

It was established that PIMs including phenylacetyl cyclodextrin derivative **1** selectively transfer Pb (II) over Cd(II), Cu(II), and Na(I) ions at concentration of ion carrier in membrane equal to 0.6 M. With the use of phenylacetyl cyclodextrin derivative as an ion carrier, the competitive transport of metal ions shows the preferential selectivity order: Pb(II) >> Cd (II) > Cu(II) > Na(I). The influence of the amount of plasticizer on the ion transport through PIMs is also presented. The initial fluxes of lead ions significantly decrease by changing the plasticizer ONPPE up to 1.3 mg per 1.0 g CTA. In the test of the long-term stability of PIM, the flux of Pb(II) decreased only slightly during 30 days. One should point out that the most important value of above PIMs is their durability.

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