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TRANSPORT OF LEAD ACROSS POLYMER INCLUSION MEMBRANE WITH *p-tert*-BUTYLCALIX[4]ARENE DERIVATIVE

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The facilitated transport of lead(II) across polymer inclusion membranes (PIMs), which consist of cellulose triacetate as polymeric support, *o*-nitrophenyl octyl ether as plasticizer and 25, 26, 27, 28 – Tetrakis(*N*-hydroxy-*N*-methylcarbamoylmethoxy)-*p-tert*-butylcalix[4]arene (**L**) as ion carrier was reported. PIM was characterized by using atomic force microscopy (AFM). The results show that Pb²⁺ can be separated very effectively from other heavy and transition metal cations as Zn²⁺, Cd²⁺, Co²⁺, Ni²⁺ (each at a concentration of 10⁻³ M). The rate limiting step in the transport of Pb²⁺ across PIM doped with calix[4]arene derivative may be the diffusion coefficient of the carrier cation complex across the membrane. The stability of PIM with *p-tert*-butylcalix[4]arene derivative was described using Danesi's thermodynamic model. The apparent partition constant of the carrier was experimentally estimated and compared with different carriers.

key words: polymer inclusion membrane (PIM), lead(II), p-tert-butylcalix[4]arene-hydroxamate

INTRODUCTION

The removal of heavy metal species, particularly lead and cadmium ions, from waste waters has an important environmental aspect. Among the several methods that

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can be used to remove toxic metals from aqueous solutions, liquid membranes techniques have become important for use in separation process. Recently, polymer inclusion membranes (PIMs), first introduced by Sugiura (Sugiura, 1980), have received increasing attention as an alternative to SLM. The transport of metal ions across PIMs is accomplished by a carrier, which is essentially an ion exchanger or a complexing agent. There are several commercially available compounds, but carriers newly synthesized, especially macrocyclic compounds (Nghiem et al., 2006), have also tested. Calixarenes and calixcrowns have successfully been used for metal ions separation by solvent extraction and transport through liquid membranes systems. The use of application of macrocyclic compounds as ion carriers in liquid membranes was reviewed (Ulewicz, 2008) and (Walkowiak and Kozłowski, 2009).

Several functionalized calixarenes with different donor atoms have been used for Pb(II) ions extraction. New allyl functionalized calix[4]arene-thioamide in 1,3-alternate conformation as well as di-ionizable calix[4]arene-1,2-crown-5 ligands exhibit high extraction ability toward Pb²⁺ ions (Arena et al., 2001; Tu et al., 2008). Also, the ability to bind two lead(II) ions with a single molecule of calix[4]arene tetracarboxylic acid has been reported (Otho et al., 1999). The order of extraction selectivity to metal ions was as follows: Pb(III) >> Fe(III) > Al(III) > Cu(II) > Zn(II).

Calixarenes and their derivatives are a new generation of highly selective carrier for heavy and transition ions across liquid membranes. Hui-Min et al. (Hui-Min et al., 2001) studied the selective transport of Cu²⁺, Fe³⁺, Co²⁺, Ni²⁺ and Zn²⁺ across liquid membrane with new calix[4]crowns. One of those calix crowns, 25, 27-dihydroxy-26,28-(3',6'-dioxo-2',7'-dioxooctylene)dioxy-calix[4]arene, transported Cu²⁺ cations. Efficiently. Whereas thiacalix[4]arene was found to be an effective ion carrier for the transport of Cd(II) ions (80%) across SLMs (Zaghbani et al., 2005). The transport of Pb²⁺ from an aqueous solutions across BLMs containing *p-t*-butylthiacalix[4]aren was examined (Nechifor et al., 2002).

Alpoguz et. al. (2002) studied co-transport of metal ions (Hg²⁺, Pb²⁺, Na⁺) from an aqueous solution into an aqueous receiving phase through the bulk liquid membrane containing calix[4]arene nitrile derivatives as ion carriers. The transport rates show that both nitrile derivatives are efficient and selective for Hg(II) ions with respect to Na⁺ and Pb²⁺ ions and the dinitrile derivatives was a better carrier than the tetranitrile derivative. The membrane entrance and exit rate constant depend on the solvent type and are found to be of the following order: CH₂Cl₂ > CHCl₃ > CCl₄.

Recently, competitive transport of an equimolar mixture of Zn(II), Cd(II) and Pb(II) cations from aqueous source phase across PIMs with calix[4]crown-6 derivatives, as ion carriers, were examined by Ulewicz et al. (2007). The maximum percentage of lead(II) removal increased in the following order of R groups attached to the compounds: -OH < -OCH₃ < -OCH₂COOH < OCH₂COOC₂H₅ < OCH₂CONHOCH₂C₅H₆. In this paper, we describe the selective transport of heavy and transition ions across PIM doped with *p-tert*-butylcalix[4]aren with four N-methyl



hydroxamic acid moieties. Physical and chemical properties of lipophilic, functionalized *p*-tert-butylcalix[4]arene make it a potentially useful ion-carrier.

EXPERIMENTAL

REAGENTS

Inorganic chemicals such as zinc(II), copper(II), cadmium(II), nickel(II), cobalt(II), lead(II) nitrates and nitric acid were of analytical grade and were purchased from POCh (Gliwice, Poland). Organic reagents such as cellulose triacetate (CTA), *o*-nitrophenyl octyl ether (*o*-NPOE) and dichloromethane were also of analytical grade, were purchased from Fluka and used without further purification. The 25, 26, 27, 28-Tetrakis-(*N*-hydroxy-*N*-methyl-carbamoylmethoxy)-*p*-tert-butylcalix[4]arene (**L**) (Fig. 1) was synthesized according to the procedure described in (Lesińska and Bocheńska, 2006).

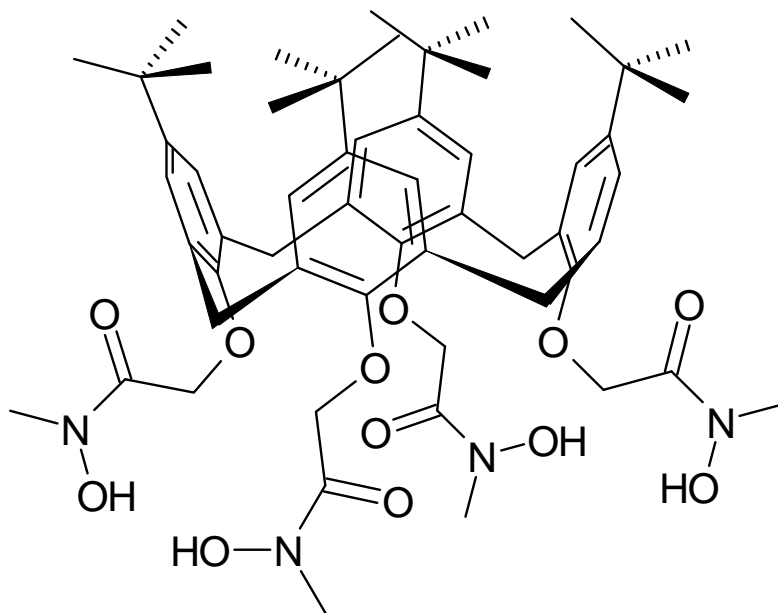


Fig. 1. Formula of studied ion-carrier L

POLYMER INCLUSION MEMBRANE PREPARATION

Membranes were prepared as previously described (Ulewicz et al., 2007). A solution of cellulose triacetate as the support, plasticizer and ion carrier L was

prepared in dichloromethane. A specified portion of this solution was poured into a membrane mould consisting of a 9.0 cm diameter glass ring placed on a glass plate with cellulose triacetate-dichloromethane glue. After slow solvent evaporation overnight, the resulting membrane was peeled off from the glass plate by immersion in cold water. The membrane was soaked for 12 hours in distilled water to achieve homogeneity. Two samples of membrane were cut from the same membrane film for duplicate transport experiments. The membrane was made of 2.6 cm³ *o*-NPOE /1g CTA, and 0.05 M carrier *L* calculated on plasticizer. The average PIM thickness was estimated to be 30 μm.

MEMBRANE CHARACTERIZATION - ATOMIC FORCE MICROSCOPY

Surface characterization of the polymer membranes was carried out using atomic force microscopy (AFM). AFM was carried out on a MultiMode with NanoScope IIIa and Quadrex controllers from Veeco Instruments. Maximal scan range *x*, *y*: 10 μm, *z*: 2.5 μm. The microscope worked as AFM in the Tapping Mode using RTESP probe (Veeco). Two samples of 1cm² from different regions of the same membrane were examined. For the analysis of surface pore characteristics, the AFM image processing program NanoScope v.5.12 was used. Using this program, two parameters, roughness (R_q) and porosity (ϵ), were calculated. Parameter R_q is the standard deviation of the *z* values within the box cursor and is calculated as:

$$R_q = \sqrt{\frac{\sum (z_i)^2}{n}} \quad (1)$$

where: z_i is the current *z* value, *n* is number of points within the box cursors.

TRANSPORT STUDIES

Transport experiments were carried out in a permeation module cell as described previously (Ulewicz et al., 2007). The membrane film (with a surface area of 4.9 cm²) was tightly clamped between two cell compartments. Both the source and receiving aqueous phases (45 cm³ each) were mechanically stirred at 600 rpm. The receiving phase was 0.5 M HNO₃. The PIM transport experiments were carried out at the temperature of 20 ± 0.2°C. Small samples (0.1 cm³ each) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine cation concentrations by atomic absorption spectroscopy (AAS Spectrometer, Solaar 939, Unicam). The source phase pH was kept constant (pH = 5.0) and monitored using a pH meter (CX-731 Elmetron, with combine pH electrode, ERH-126, Hydromet, Poland). The permeability coefficients (*P*, m/s) of metal ions across polymer membranes were described using the following equation:



$$\ln\left(\frac{c}{c_i}\right) = -\frac{A}{V} \cdot P \cdot t \quad (2)$$

where c is the metal ion concentration (M) in the source aqueous phase at some given time; c_i is the initial metal ion concentration in the source phase; t is the time of transport (s); V is volume of the aqueous source phase (m^3); and A is an effective area of membrane (m^2).

The linear dependence of $\ln(c/c_i)$ in the source phase versus time was obtained and the permeability coefficients were calculated from the slope of the straight line that fits the experimental data. The initial flux (J_i) was determined:

$$J_i = P \cdot c_i. \quad (3)$$

The diffusion coefficient D_o (cm^2/s) of the metal-complex across the organic phase can be determined in the case of absence of diffusion resistances in the aqueous layer source phase/membrane by the following equation (Danesi, 1984-85) :

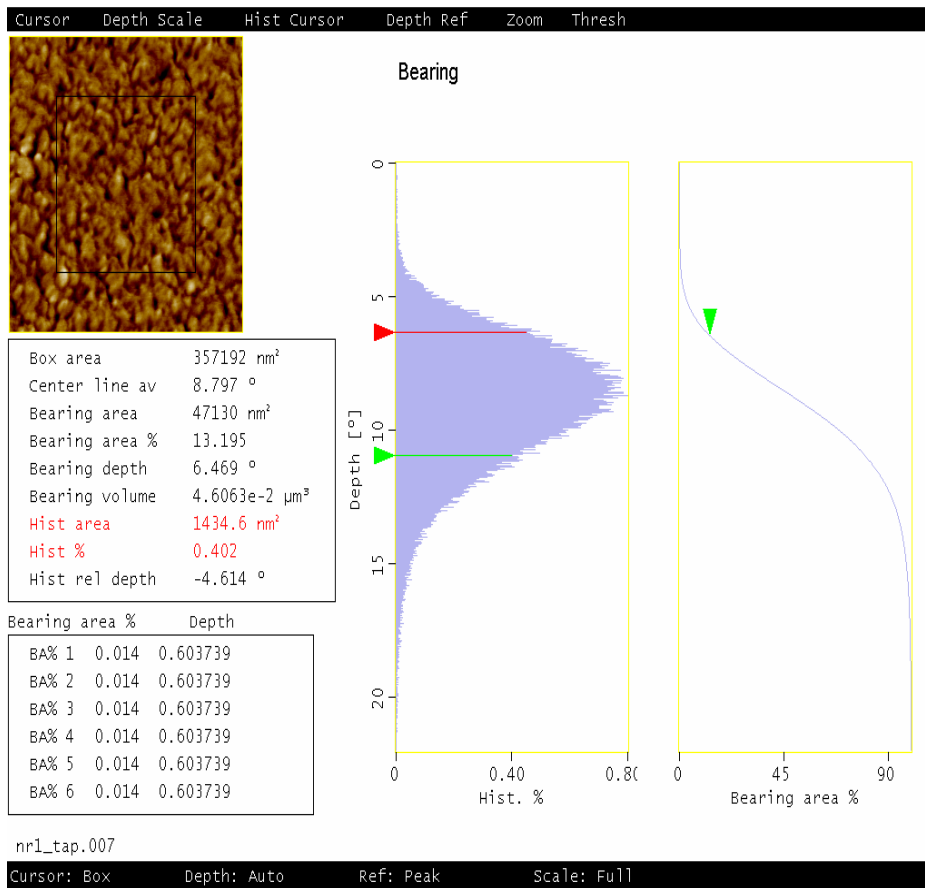
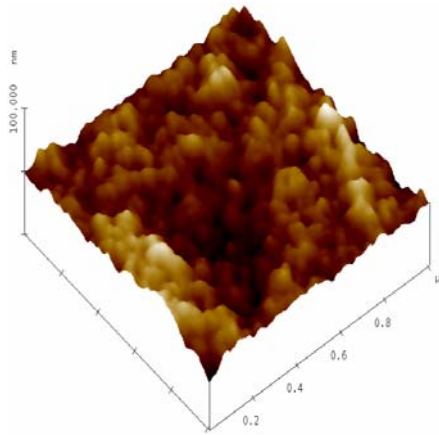
$$c = c_i - \frac{[L]_o \cdot A \cdot t}{n \cdot V \cdot \Delta_o} \quad (4)$$

where $\Delta_o = d_o/D_o$ (s/cm) is the resistance of transport by diffusion across the membrane, d_o (cm) is the thickness of the membrane, n - is the number of moles of the carrier in the complex (in our case $n = 1$); and $[L]_o$ is the initial concentration of the extractant in the organic phase (M). Plotting $[\text{Me}^{2+}]_i - [\text{Me}^{2+}]_t$ vs. time gives a slope equal to $([L]_o \cdot A)/(\Delta_o \cdot V)$ which can be used to calculate the diffusion coefficients D_o of the metal complex species in the membrane phase.

RESULTS AND DISCUSSION

The transport of metal ions across a liquid membrane depends on many factors. One of the important aspects of PIMs is the distribution of the organic carrier in the polymer matrix, which determines their transport efficiency (Arous et al., 2004). Atomic force microscopy was used to characterize morphology of prepared PIM. Figures 2 (a) and (b) show the AFM images of blank polymer membrane (supported with plasticizer) and polymer inclusion membrane containing 0.05M *p*-tert-butylcalix[4]arene derivative, respectively, in three-dimensional format of 1.0 x 1.0 μm . As can be seen from Fig 2b, the carrier *L* crystallizes inside the membrane matrix, which might be why the surface texture is relatively homogenous. One of the membrane features is well defined pores. The pores are clearly visible as small, well-defined dark areas.

a)



b)

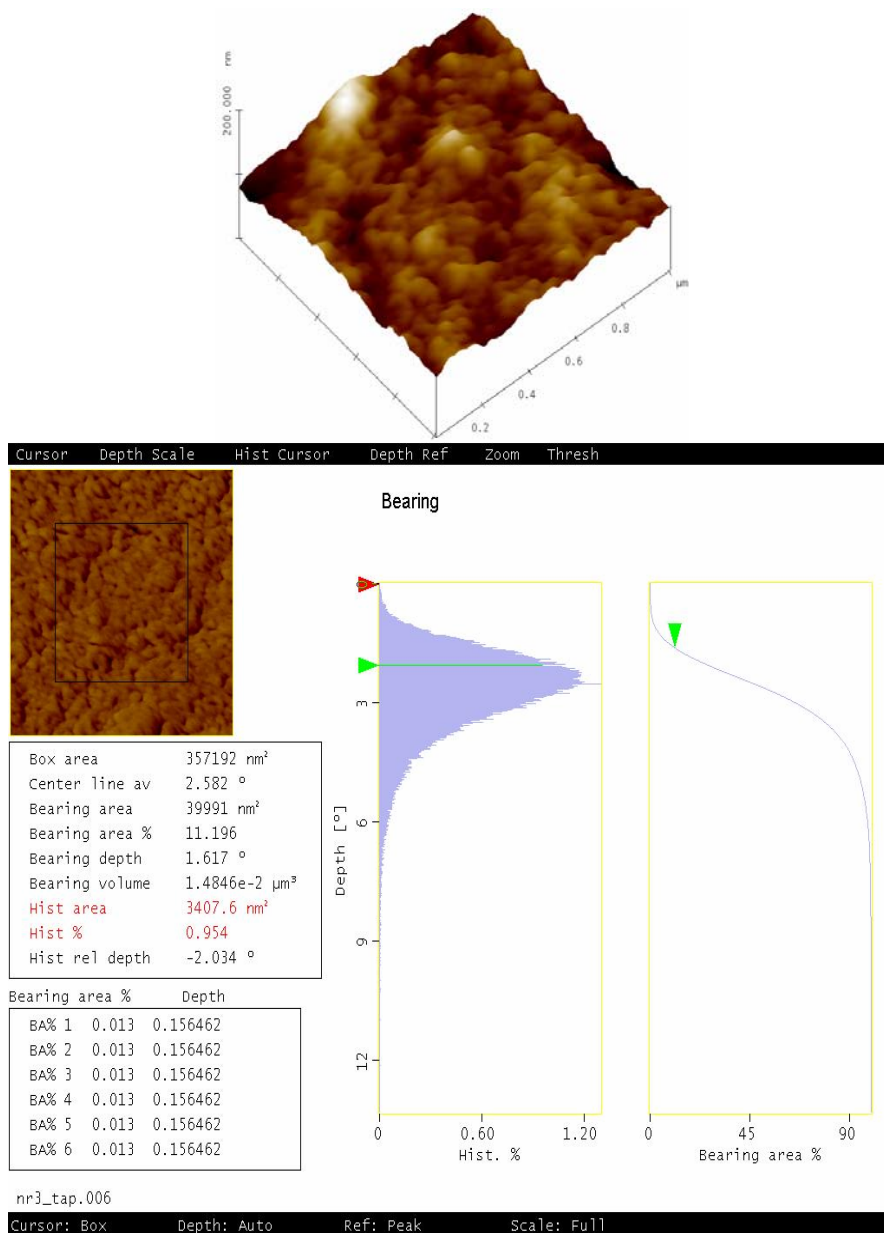


Fig. 2. 3D-view atomic force micrographs of matrix membrane - CTA-*o*NPOE (a) and polymer membrane CTA-*o*NPOE containing 0.05M carrier *L* (b)

Membranes without ion carrier containing only cellulose triacetate have a porous structure with a porosity of 50% (Arous et al. 2004). The pores of CTA membrane are

filled by the *o*-NPOE molecules, the membrane less porous. The calculated porosity (ϵ) for membrane composed only with 2.67cm^3 *o*-NPOE/1g CTA is 13.2%, whereas the porosity of this membrane with carrier is only 11.2 %. The roughness (R_q) of membrane constituted by CTA-*o*NPOE and CTA-*o*NPOE with carrier were 10.0 and 7.3 nm, respectively. The roughness of investigated PIMs with carrier is higher than that found in polymer membrane with D2EHPA ($R_q = 4.6$ nm) prepared by Salazar-Alvarez et al. (2005) and lower than in membranes prepared by Tor et al. (2009) for DEHPA (268 nm).

In earlier studies on heavy and transition metal ions separations, soft metal ions as Pb^{2+} or Ag^+ display great affinity for soft coordination centres like nitrogen or sulphur atoms. Therefore, the calix[4]aren with functional group containing nitrogen atoms was used as ion carriers for the competitive heavy and transition metal ions transport from a source aqueous phase into receiving nitric acid solutions across PIM. The study included two different solutions containing of Zn(II), Cd(II), Pb(II) (mixture 1) and Co(II), Ni(II), Pb(II) ions (mixture 2) at concentration of metal equal 0.001M each. The kinetic curves of metal ions transport are shown in Fig. 3. Only Pb(II) ions were transported. Transport efficiency for the zinc(II) ions were generally less than 3%, whereas the other metal ions (Ni^{2+} , Co^{2+} , Cd^{2+}) were not transported. The driving force of Pb^{2+} cations transport was the exchange of protons from the receiving phase with metal ions from the source phase. The initial fluxes of Pb(II) from mixtures 1 and 2 were $2.69 \cdot 10^{-7}$ and $2.88 \cdot 10^{-7}$ mol/m²·s, respectively.

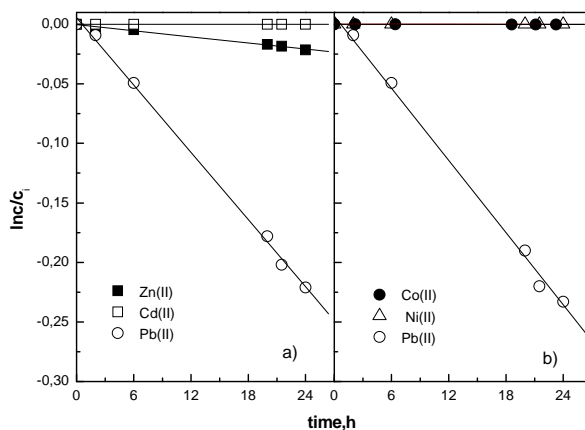


Fig. 3. Kinetics curves for metal ions transport across PIM with *p-tert*-butylcalix[4]aren derivative from different equimolar mixture of metal ions; $c_{Me} = 0.001$ M each, pH = 5.0

In Fig. 3, the correlation graphs $[\text{Pb}^{2+}]_i - [\text{Pb}^{2+}]_t$ versus time of Pb(II) transport from different mixture solutions across PIM doped with *L* is presented. The diffusion coefficient of Pb(II) was calculated for each mixture solutions, substituting $D_0 = d_0/\Delta_0$,

where d_0 is the thickness of the membrane (0.003 cm), and Δ_0 could be evaluated by plotting $[\text{Pb}^{2+}]_i - [\text{Pb}^{2+}]_t$ versus time.

The corrected (normalized) membrane diffusion coefficient $D_{o,n}$, which considers the morphological features inside the membrane (ε - porosity and τ - tortuosity), was calculated using the following equation: $D_{o,n} = D_o \cdot (\varepsilon/\tau)$ (Salazar-Alvarez et al., 2005). The membrane tortuosity was determined from the relationship developed by Wolf and Strieder (1990): $\tau = 1 - \ln \varepsilon$ and equal to 3.19 (for $\varepsilon = 0.112$). Diffusion coefficients are presented in Table 1. The values are comparable with previously reported values for different membranes are in the range 10^{-6} to 10^{-12} cm^2/s , and show that the limiting step of the process is the transfer of metal complex across the membrane barrier. The average value of the diffusion coefficient of Pb(II)-carrier species of $4.16 \cdot 10^{-9}$ cm^2/s is smaller than the value of $1.5 \cdot 10^{-7}$ cm^2/s reported for the lead complex with the D2EHPA in PIM reported by Salazar-Alvarez et al. (2005).

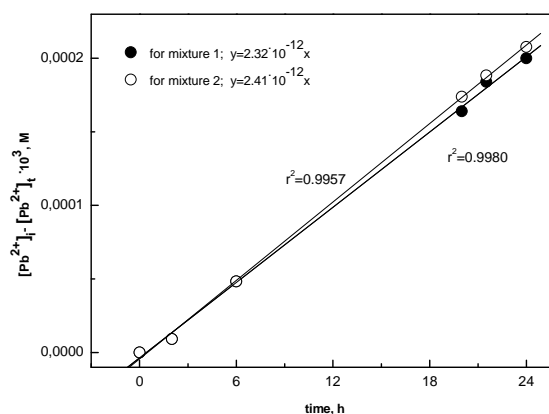


Fig. 4. $[\text{Pb}^{2+}]_i - [\text{Pb}^{2+}]_t$ vs. time for Pb^{2+} transport across PIM membrane doped with calix[4]arene *L*. Conditions of experiment as in Table 1

Table 1. Permeability coefficient, diffusion coefficient normalized for competitive transport of Pb(II) ions through PIM from different mixtures, $\text{pH} = 5.0$

Mixture	P , (m/s)	Δ_0 , (s/m)	D_o , (cm^2/s)	$D_{o,n}$, (cm^2/s)
1	$2.69 \cdot 10^{-4}$	$10^{7.3}$	$1.42 \cdot 10^{-10}$	$4.04 \cdot 10^{-9}$
2	$2.88 \cdot 10^{-4}$	$10^{7.325}$	$1.50 \cdot 10^{-10}$	$4.27 \cdot 10^{-9}$

Different approaches can be found in literature for the determination of liquid membrane lifetime or stability. The Danesi thermodynamic model to characterize the SLM with calix[4]arene derivatives stability was proposed by Hill et al. (Hill et al., 1996). According to that model, in repeated transport experiments, the decrease of permeability coefficients (P_M) is the linear function of the number of runs:

$$\log P_M^{(i)} = \log P_M^{(1)} - (i-1) \cdot n \cdot \log\left(1 + \frac{R}{K_p}\right) \quad (5)$$

where: i is the number of run experiments; $P_M^{(1)}$ and $P_M^{(i)}$ are the Pb^{2+} permeability coefficients in the first and in the i -th transport experiments, respectively; n is the stoichiometric factor for ion carrier ($n = 1$), $R = (V_{\text{source}} - V_{\text{receiving}})/V_{\text{PIM}}$ ($R = 1000$); K_p – the apparent partition constant of the carrier between the PIM and both aqueous source and the receiving solutions. The slope of the linear decrease of $\log P_M$ versus $(i-1)$ gives an idea of the carrier lipophilicity and can be used to determine and compare carrier hydrophobicities.

In Fig. 5, the semi-logarithmic variation for the permeability coefficient P_M versus the number of runs $(i-1)$ is shown. The carrier is slowly leaching out of PIM membrane due to its apparently high partition constant, equals $105,428 \pm 12,100$. This value is comparable with partition constants obtained by Hill et al. (1996) for bis-(1,2-benzo) calix[4]arene-crown-6 and bis-(1,2-naphtho) calix[4]arene-crown-6 $_{\Delta}$, which are 106,700, and 295,000, respectively. Calix[4]arene-bis-crown-6 as well as Aliquat 336 possessing the lowest partition constant (29,100 and 37,946 respectively) were rapidly leaching from the SLM (Hill et al., 1996; Kozłowski and Walkowiak, 2005).

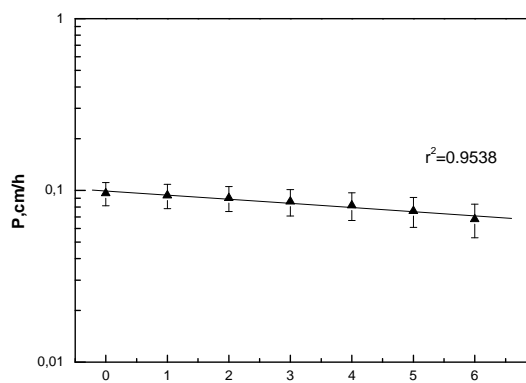


Fig. 5. Logarithmic variation of lead permeability coefficient versus the number of runs in repeated transport experiments across PIM with carrier

CONCLUSION

The studied ligand L was an efficient carrier for Pb^{2+} ions transport across PIMs. AFM of the membranes revealed that the carrier was homogeneously distributed within the membrane. The rate limiting step in transport of Pb^{2+} across PIM doped with ligand L may be the diffusion coefficient of the carrier-cation complex across the

membrane. The PIM membranes exhibited good stability using the Danesi thermodynamic model.

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Opisane zostały ułatwienia w transporcie jonów ołowiu(II) przez polimerową membranę inkluzyjną (PIMs), która składała się z trój octanu celulozy jako polimerowego suportu, eteru o-nitrofenylooktylu jako plastyfikatora i 25,26,27,28 tetra-(N-hydroksy-N-metylokarbonylo metoksy)-p-tert-butylokaliks[4]arenu jako nośnika jonów. Polimerowa membrana inkluzyjna została scharakteryzowana przy pomocy mikroskopu sił atomowych (AFM). Otrzymane wyniki wskazują, że jony Pb²⁺ mogą być efektywnie oddzielane od innych kationów metali ciężkich i przejściowych takich jak Zn²⁺, Cd²⁺, Co²⁺, Ni²⁺ (przy stężeniach rzędu 10⁻³M). Czynnikiem limitującym szybkość transportu jonów Pb²⁺ przez polimerową membranę inkluzyjną wypełnioną kaliks[4]arenem może być współczynnik dyfuzji kompleksu przenoszącego kation przez membranę. Stabilność membrany (PIM) z p-tert-butylokaliks[4]arenem była opisana przy użyciu modelu termodynamicznego Danesi. Odpowiednie stałe przenoszenia wyznaczone w sposób eksperymentalny zostały porównane z innymi stałymi przenoszenia.

słowa kluczowe: polimerowe membrany inkluzyjne, ołów(II), stabilność