

Effect of the structure of polymer inclusion membranes on Zn(II) transport from chloride aqueous solutions

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ABSTRACT: This article presents application of polymer inclusion membranes (PIM) containing polymer matrices: cellulose triacetate (CTA) or poly(vinyl) chloride (PVC), o-nitrophenyloctyl ether (NPOE) as a plasticizer and phosphonium ionic liquids, i.e., trihexyltetradecylphosphonium chloride (Cyphos IL 101), bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) and tributyltetradecylphosphonium chloride (Cyphos IL 167), as carriers for Zn(II) transport from chloride medium. Cyphos IL167 application as an ion carrier in PIMs is reported for the first time. The membrane composition is found to affect Zn(II) transport significantly. SEM and AFM images show the differences in the surface morphology of PVC and CTA based membranes. Better transport abilities of CTA membranes (Zn(II) recovery factors exceed 80%) compared with those of PVC, indicate that the structural differences between the two polymers play a crucial role for the membrane permeability. The best initial flux and permeability coefficient are obtained for the membranes with Cyphos IL 101 and Cyphos IL 104 as carriers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42319.

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INTRODUCTION

In recent years, a new type of liquid membranes based on a plasticized polymer of high stability, has been developed and called polymer inclusion membranes (PIM).¹ PIMs can be used for processes of metal ion separation as an alternative to supported liquid membranes (SLM). The main difference between these two types of membranes lies in immobilization of a carrier: in SLMs pores of solid support are impregnated with a carrier while in PIMs carrier is built into a structure of the membrane. The specific advantages of PIMs include effective carrier immobilization, easy preparation, versatility, stability, good mechanical properties, and good chemical resistance.

The membranes of this type are formed by casting a solution containing a polymer matrix, a plasticizer and a carrier.¹ The most commonly used polymer matrices include poly(vinyl) chloride (PVC) and cellulose triacetate (CTA), and the purpose of their use is to provide the membrane with mechanical strength. The presence of a polymer in the membrane influences also the membrane thermoplasticity. The role of the carrier is to facilitate the transport of ions that are to be separated by the membrane. In most cases typical organic compounds, commonly used in the extraction processes, are used as carriers: cationic (acidic), anionic (basic), neutral (solvating). The role of

plasticizer (usually: o-nitrophenyloctyl ether – NPOE) is to increase the softness and flexibility of a membrane.^{1,2} In some cases, addition of plasticizer is not required, because this function is performed by the carrier.

Metal concentration in the feed, membrane composition (concentration of a carrier, type, and concentration of a plasticizer and polymer matrix) and mixing rate of the aqueous phases have significant impact on the rate and selectivity of metal ion transport across PIMs. Up to date, PIMs have been applied for transport processes of precious metals, actinides, lanthanides, alkali metals, heavy metals such as cadmium, chromium, lead, and mercury, etc.^{1–18}

It has been shown that PIM consisting of PVC and Aliquat 336 (acting as a carrier) can be used for the separation of Co(II) from a solution of 7M HCl containing Ni(II)³ or (also with CTA matrix) in extraction of Cr(VI).^{4,7} The membrane with CTA, NPOE, Aliquat 336 allows Cd(II) efficient transport and removal from chloride solutions.⁸ Trioctylamine (TOA) or triisooctylamine (TIOA) carriers (in CTA matrix) transport simultaneously Cu(II), Co(II), Ni(II) from acidic chloride solutions^{9,10} or Cr(VI) from chloride, sulfate, nitrate, media.¹¹ Yilmaz *et al.*¹² described the selectively facilitated transport of Zn(II) through PIM containing bis(2,2,4-trimethylpentyl) phosphinic acid

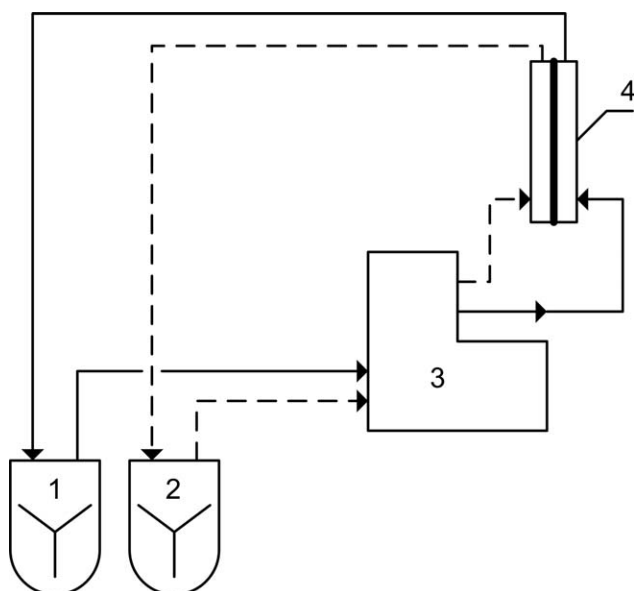


Figure 1. Scheme of research system for metal ion transport through PIMs (1, feed phase tank, 2, receiving phase tank, 3, peristaltic pump, 4, sandwich type membrane module).

(Cyanex 272) as a carrier. On the other hand, membranes containing Cyanex 471 X are selective for silver ions over Cu(II), Zn(II) or Fe(III).¹³ The compound 4-(1'tridecyl)pyridine oxide (TDPNO) is another effective carrier for Cr(VI), Cd(II), and Zn(II) and the effectiveness of ion transport decreases in the following order: Zn(II) > Cd(II) > Cr(VI).¹⁴ Recently, also crown ethers and imidazole derivatives have been used as carriers of metal ions.^{15–20} Moreover, a popular solvating extractant, tributyl phosphate (TBP), has been used as a carrier in PIM to remove Fe(III), and with increasing content of the plasticizer (NPOE) in the membrane, the values of Fe(III) initial flux increase.²¹ The polymer inclusion membrane containing PVC and *N,N,N',N'*-tetraoctyldiglycoamide (TODGA) was applied for recovery of americium from acidic feed solutions. It has been shown that the method was quite simple and could be applied for recovery of Am from laboratory waste.²²

In recent years, phosphonium ionic liquids also have been proposed as PIM carriers of metal ions [e.g., Zn(II) and Fe(III)] from chloride aqueous solutions^{23,24} or as reactive extractants for carboxylic acids recovery.^{25,26} In our previous work²⁴ Cyphos IL 101 was investigated as a carrier for Zn(II) and Fe(III) from chloride solutions and it was indicated that Cyphos IL 101 is an effective carrier in CTA based PIMs for Fe(III), while transport of Zn(II) is less efficient. However, the differences in effectiveness of ion transport through PIMs were not considered in the light of morphology effect. Additionally, PVC matrices were not used for PIMs preparation.

PIMs exhibit better mechanical properties and chemical resistance than traditional SLMs because in the former a carrier is immobilized onto a polymer matrix. Therefore, the carrier loss during PIM process is negligible.¹ Low diffusion coefficients are the main drawback of transport through PIMs compared with SLMs; however, the diffusion can be increased by decreasing PIM thickness.

The advantages of PIMs application over liquid–liquid extraction include reduction in the quantity of active substances, which are often toxic and expensive, and elimination of volatile organic solvents from the separation process.¹ Moreover, extraction and stripping through PIMs take place simultaneously, resulting in a continuous process without intermediate steps.

Nowadays, the metal processing industry has to face a number of environmental and economical issues such as the need to comply with regulations referring to the protection of the environment and shrinking natural resources. From the economical point of view, the industry tends to regenerate and reuse as much chemicals as possible in order to limit the loss of reagents and to meet the restrictions related to the environment protection. For several recent years we have investigated extraction of zinc(II) and iron(III) from chloride solutions with quaternary phosphonium ionic liquids. As spent pickling solutions coming from galvanizing industry can be a valuable source of metal ions, i.e. Zn(II) and Fe(II) or Fe(III), there is a need for efficient methods for their recovery from such aqueous solutions. These wastes contain mainly zinc(II) and iron(III) (its concentration may be as high as 200 g/dm³) and hydrochloric acid residue. In industrial practice nonwaste technologies, e.g., membrane extraction,²⁷ play an increasingly important role.

The aim of this work is to develop polymer inclusion membranes with three quaternary phosphonium ionic liquids as carriers for zinc and iron ions, and study the effect of membrane composition on transport properties. To the best of our knowledge Cyphos IL 167 has not been reported as a metal ion carrier in PIMs before. It is expected to synthesize CTA and/or PVC membranes that will perform efficient transport of zinc ions even in the presence of iron(III) ions in the feed aqueous phase.

EXPERIMENTAL

Materials

Three phosphonium ionic liquids, i.e. trihexyltetradecylphosphonium chloride (Cyphos IL 101), trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) and tributyltetradecylphosphonium chloride (Cyphos IL 167) supplied by Cytec Industry Inc. (USA) were applied as carriers for metal ions in PIMs. The following reagents were used as received for preparation of PIMs: cellulose triacetate (CTA) Fluka, Germany (purum, solubility 0.1 g in 10 cm³ CHCl₃), high molar mass poly(vinyl) chloride (PVC) Sigma Aldrich, Germany (*M_w* 80,000 g/mol; *M_n* 47,000 g/mol), *o*-nitrophenyloctyl ether (NPOE) Sigma Aldrich, Germany, tetrahydrofuran (THF) POCh, Poland, dichloromethane (DCM) POCh, Poland.

Aqueous feeds solutions contained 1.5·10⁻³ M Zn(II) and 1.8·10⁻³ M Fe(III) (0.1 g/dm³) and mixture of 0.038M Zn(II) and 0.045M Fe(III) (2.5 g/dm³), 0.58M HCl, 5 M Cl⁻ (NaCl was used to adjust constant chloride content). As the receiving phases the following aqueous solutions were used: NaCl, Na₂SO₄, and H₂SO₄. The inorganic chemicals were of analytical grade and were purchased from POCh (Poland).

Polymer Inclusion Membranes—Preparation and Transport

Polymer inclusion membranes were composed of the following basic substrate solutions: polymer matrix, 0.1M solution of

Cyphos IL 101, Cyphos IL 104 or Cyphos IL 167 in a suitable solvent carrier, NPOE as a plasticizer. The chemicals were dissolved in appropriate solvents, i.e., THF or DCM for PVC or CTA, respectively. Membranes were prepared by solution casting and solvent evaporation technique at room temperature. The organic solvent was allowed to evaporate overnight and the resulting membrane was separated from the Petri dish by immersion in cold water. The membranes were fixed in the membrane module–sandwich type, presented in Figure 1.

The feed and the receiving phase were provided continuously at constant flow rate (20 cm³/min) by means of peristaltic pump from glass containers to the membrane module and back. The volume of the feed and receiving solutions was equal to 200 cm³ (at the beginning of the process) and the volume ratio of both phases was maintained constant during the transport experiments. Samples of 1 cm³ in volume of both aqueous phases were taken out at selected intervals for determination of zinc concentration by atomic absorption spectroscopy at 213 nm in the air–acetylene flame.

Membrane Characterization

A digital ultrameter (MG-401, ELMETRON, Poland) was used to measure the thickness of each membrane in at least 15 different sites of the membrane. The average diameter of the membrane was equal to 7.0 cm.

The weight of CTA membranes prepared (6 cm³ of solution was poured into the Petri dishes) containing Cyphos IL 101 ranged from 0.1259 to 0.1763 g, while for Cyphos IL 104 from 0.1372 to 0.2336 g, and for Cyphos IL 167 the membrane weight ranged from 0.1819 to 0.2683 g. In the case of PVC membranes, 8 cm³ of solution was casted. Thinner membranes were too soft and difficult to peel out from the dish. The average weight of membranes containing PVC was close to 0.25 g.

The sessile drop method was used to measure the contact angle of the prepared membranes. A 1 μL droplet of feed phase was placed on the membrane surface and the contact angle was measured by TRACKER (I.T. CONCEPT).

The scanning electron microscopy (SEM) observations of the membrane samples were made using 6.0 kV scanning electron microscope (SEM) (Vega Tescan).

Atomic Force Microscopy measurements (AFM) were performed with Bruker Icon microscope and NCLR (Nanosensors) cantilevers in tapping mode in the air at room temperature. Images were analyzed in WSxM software.²⁸

Calculations

First order reaction describes the kinetics of transport of metal ions through PIMs:

$$\ln \frac{c}{c_0} = -kt \quad (1)$$

where c_0 (M) and c (M) state for the concentration of the metal ions in the feed phase at initial time and selected time, respectively, k (1/s) is the rate constant, and t (s) is the selected time of transport. Values of rate constant (k) are estimated from linear relationship at plots of $\ln(c/c_0)$ versus time. Transport abilities of PIMs are characterized by such parameters as:

Table I. Percentage Composition of PIM Used in the Processes of Zn(II) Transport

| IL content, % | IL type | NPOE content, % | d_0 , μm | m_0 , g |
|---------------|---------|-----------------|------------|-----------|
| CTA matrix | | | | |
| 23 | 101 | 46 | 25.8 ± 1.3 | 0.1687 |
| 30 | | 5 | 28.5 ± 3.4 | 0.1259 |
| 40 | | 5 | 33.0 ± 3.6 | 0.1436 |
| 15 | 167 | 0 | 38.7 ± 3.1 | 0.1819 |
| 20 | | 32 | 40.3 ± 2.1 | 0.2683 |
| 30 | | 5 | 38.9 ± 2.5 | 0.1985 |
| 30 | 104 | 5 | 33.5 ± 3.8 | 0.1826 |
| 32 | | 5 | 38.1 ± 1.9 | 0.2336 |
| 40 | | 5 | 33.9 ± 4.1 | 0.1771 |
| PVC matrix | | | | |
| 20 | 101 | 5 | 56.7 ± 2.4 | 0.2546 |
| 30 | | 0 | 59.9 ± 3.5 | 0.2753 |
| 20 | 167 | 5 | 47.7 ± 1.8 | 0.2311 |
| 40 | | 0 | 44.5 ± 2.5 | 0.2651 |
| 20 | 104 | 5 | 49.8 ± 1.8 | 0.2302 |
| 30 | | 0 | 45.2 ± 1.5 | 0.2323 |

d_0 , initial thickness of a membrane.

m_0 , initial mass of a membrane.

initial flux (J_0 , mol/m² s)

$$J_0 = \frac{V}{A} \cdot k \cdot c_0 \quad (2)$$

where V is the volume of the aqueous phase equal $2 \cdot 10^{-4}$ m³, and A the membrane area equal $15.9 \cdot 10^{-4}$ m²,

permeability (P , m/s)

$$P = \frac{V}{A} \cdot k \quad (3)$$

extraction percentage (E , %)

$$E = \frac{c_0 - c}{c_0} \cdot 100\% \quad (4)$$

recovery factor of metal ions (RF , %, here after 48 h of the process)

$$RF = \frac{c_s}{c_0} \cdot 100\% \quad (5)$$

where c_s states for metal concentration in the receiving phase after 48 h of separation.

RESULTS AND DISCUSSION

PIMs Characterization

On the basis of the earlier studies of liquid–liquid extraction,²⁴ some phosphonium ionic liquids were selected and used as zinc(II) carriers for the polymer inclusion membrane systems. Successful application of these ILs in PIM systems would eliminate large amounts of organic phase containing VOCs from separation processes (liquid–liquid extraction). The content of the carrier or plasticizer was changed to study the influence of their

Table II. Effect of Matrix Type on Contact Angle Between Zn(II) Solutions and the Membrane Surfaces Containing 65% CTA, 5% NPOE, 30% IL and 75% PVC, 20% IL, 5% NPOE Before and After the Process

| Carrier | Matrix | Contact angle, ° | |
|---------------|--------|------------------|---------------|
| | | Before process | After process |
| Cyphos IL 101 | CTA | 36.2 ± 2.3 | 41.3 ± 1.2 |
| Cyphos IL 104 | | 35.3 ± 1.2 | 42.2 ± 1.6 |
| Cyphos IL 167 | | 37.8 ± 2.5 | 39.1 ± 1.1 |
| Cyphos IL 101 | PVC | 53.2 ± 1.7 | 59.8 ± 2.8 |
| Cyphos IL 104 | | 48.3 ± 3.1 | 55.7 ± 2.5 |
| Cyphos IL 167 | | 47.8 ± 3.3 | 52.2 ± 2.2 |

amount on the mass transfer through the membranes. Moreover, the compositions of some membranes (containing more than 30% NPOE) were based on the ones described previously.²⁴

The membranes differed in the content of the three components: polymer matrix, plasticizer, and carrier (Table I). Moreover, various volumes of the component solutions were casted into the Petri dishes resulting in different masses and thicknesses of the membranes. The idea was to establish the thickness of the membrane so that it would be as small as possible

to shorten the mass transport pathway while simultaneously retaining good membrane mechanical properties.

The membranes were weighed before and after separation process to control the possible weight changes. The weight of the membranes studied decreased, as a result of separation processes, from 0.35 to 7%. The largest loss in weight (near 7%) was noted for the membranes containing Cyphos IL 101 and Cyphos IL 104 and CTA matrix. Changes in the membrane weight can be attributed to hydrophilicity of the carrier and the presence of plasticizer, which facilitated water penetration through the membrane structure. A decrease in the membrane weight could be explained by the carrier leaching into the aqueous phase. Kogelnig *et al.*²³ have noted loss (of about 3%) in weight of an unplasticized membrane containing PVC and Cyphos IL 101, after keeping it in water for 27 days. The authors have explained the changes in terms of miscibility of Cyphos IL 101 with water. According to Rahman and Brazel,²⁹ leaching from PIM is “a function of the strength of the existing secondary bonding effect in the polymer–plasticizer system and miscibility of the respective plasticizers with water”. Therefore, also secondary bonding effects between PVC chains and ILs, indicated by Rahman and Brazel,²⁹ seem to play an important role in the mass changes.

The hydrophilicity of the membranes was confirmed by the values of contact angle measurements presented in Table II.

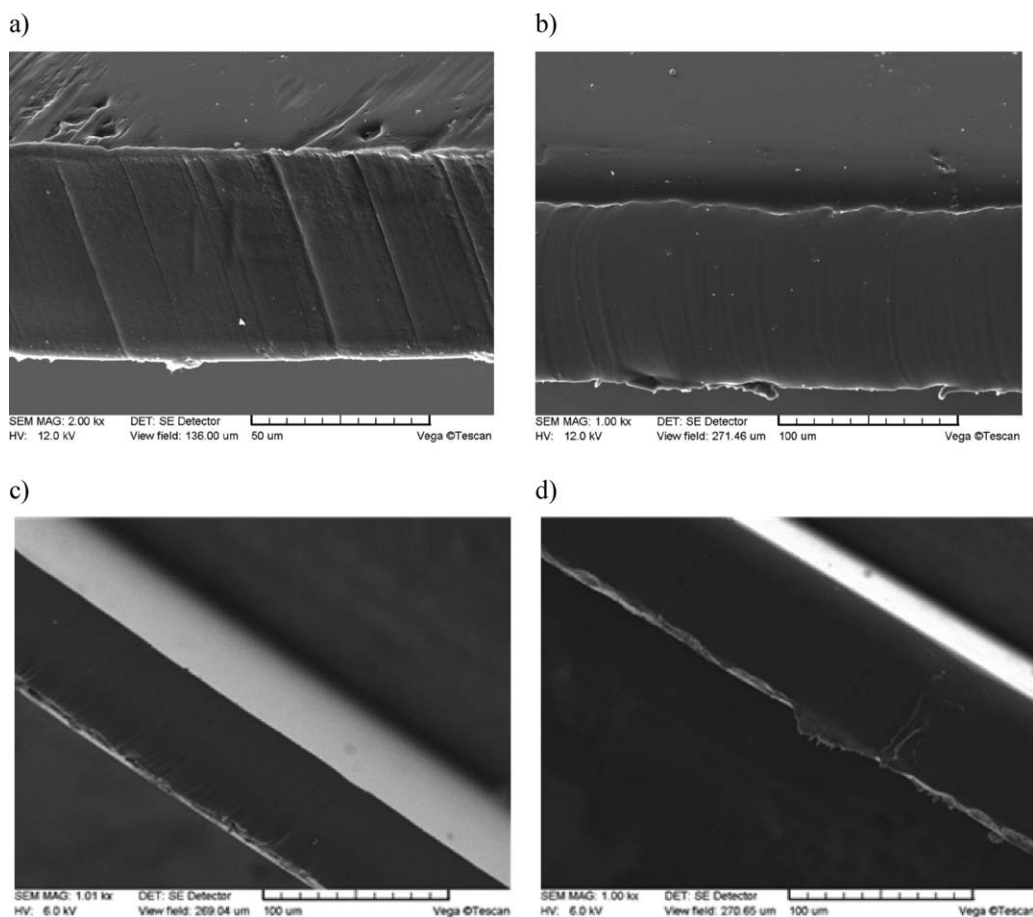


Figure 2. SEM images of PIMs containing (a) CTA, IL 101, (b) PVC, IL101, (c) CTA, IL 104, (d) PVC, IL 104.

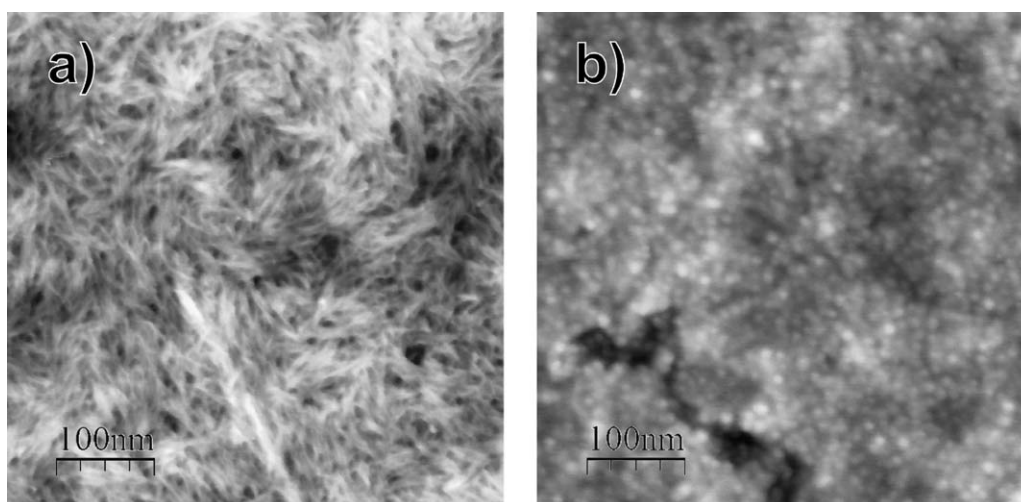


Figure 3. AFM topography images of CTA (a) and PVC (b) membranes without IL carrier in nanometer scale. Height scales are 11.6 nm for CTA and 12.5 nm for PVC.

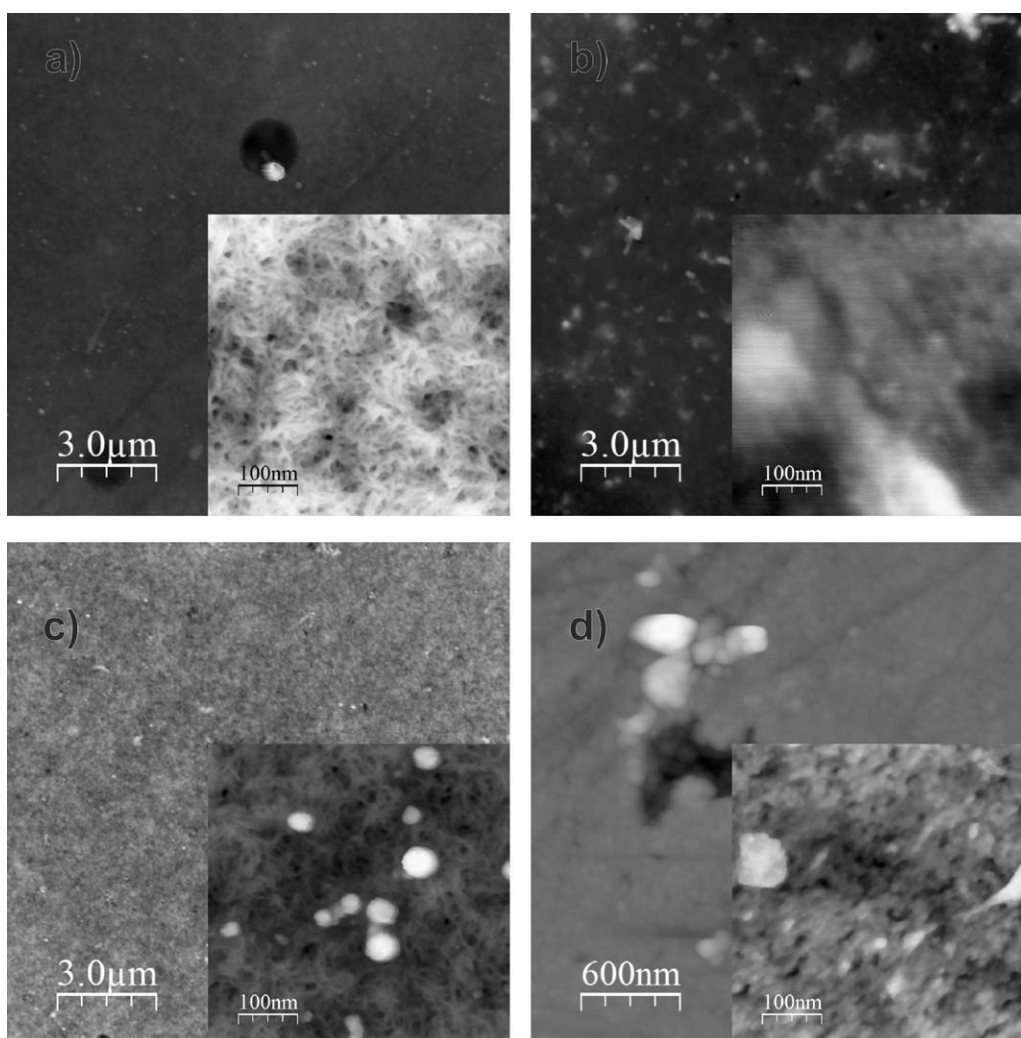


Figure 4. AFM images of PIMs containing (a) CTA, IL 101, (b) PVC, IL101, (c) CTA, IL 104, (d) PVC, IL 104. Full image frame – scan size $15\ \mu\text{m} \times 15\ \mu\text{m}$, inserts $500\ \text{nm} \times 500\ \text{nm}$. Color scales described in the text.

Table III. Topography Parameters for AFM Images Presented in Figure 4

| Image | Image height scale 15 μm scan | Image height scale 500 nm scan | RMS, nm |
|-----------------|--|--------------------------------------|---------|
| (a) CTA, IL 101 | 82 nm | 31 nm | 3.96 |
| (b) PVC, IL 101 | 76 nm | 11 nm | 1.63 |
| (c) CTA, IL 104 | 57 nm | 48 nm | 4.21 |
| (d) PVC, IL 104 | 190 nm | 40 nm | 4.52 |

As the wettability of the membranes brings information on the surface hydrophilicity, the contact angle values of CTA and PVC membranes obtained in this work and equal $\sim 40^\circ$ and 50° , respectively, mean that both types of PIMs are hydrophilic. The surfaces are defined as hydrophobic when the values of the contact angle are greater than 90° . Generally speaking, CTA membranes are found to be more hydrophilic than PVC ones. For this reason Zn(II) chlorocomplexes have easier access to the surface of CTA membranes and, as a consequence, higher percentage extraction of Zn(II) is noted. Slight increase in contact angle values of the membranes after the process can be attributed to leaching of the carriers, and thus, change in hydrophobicity of the surface.

The SEM pictures of CTA and PVC PIMs containing Cyphos IL 101 or Cyphos IL 104 with NPOE are shown in Figure 2. These cross sections prove that the membranes are dense and homogenous.

AFM topography images of CTA and PVC membranes without IL carriers show different structures of polymer surface (Figure 3). In the image of the CTA sample clearly visible are elongated pores called also “cavity channels”³⁰ (darker regions). Such a morphology of the membrane surface can be related to the crystallinity of the CTA.

A wide network of pores of 5–25 nm in size is likely to be responsible for the improved transport performance of the membranes based on CTA. PVC structure is different,

dominated by amorphous rounded nodules with sizes of about 10 nm. Between these nodules some pores are noticeable. Occasionally, there are nodules hundreds of nanometers in size, looking like cracks. Measured roughness (RMS) values are equal to 1.13 and 1.16 nm for CTA and PVC, respectively. The RMS values are comparable with the results obtained for non-modified CTA gel film³¹ and twice smaller than RMS values for CTA membranes with NPOE obtained by Kaya *et al.*¹⁶ (2.722 nm) and Ugur *et al.*³² (2.24 nm). The differences in roughness of the PIM surface result probably from various amounts of NPOE addition.

AFM images presented in Figure 4 provide information on the differences in surface roughness and structure of the membranes containing phosphonium ILs. Corresponding height color scales and sample roughness for 500 nm scan are shown in Table III.

Compared with images of the membranes without ILs, it is noticeable that inclusion of ion carriers increases roughness of the membranes. Also, other authors noticed that addition of various carriers caused higher RMS values compared with blank membrane (without carrier).^{16,33} Topography is less homogeneous, and additional nodules placed on the surface of all samples are observed. In spite of it, elongated pores for CTA and nodules for PVC, i.e., structures observed on pure polymer surface, are still present on the membranes with ion carriers.

The Effect of the Receiving Phase on Zn(II) Transport

The influence of the receiving phase on Zn(II) transport through PIMs containing 55% CTA, 40% IL (101 or 104) and 5% NPOE is presented in Figure 5.

According to previously carried Zn(II) extraction studies with Cyphos IL 101 and IL 104,²⁴ H_2SO_4 was indicated as the most efficient stripping phase for Zn(II) removal from the extract. A suitable receiving phase for PIM systems studied in this work was selected among the following solutions: 0.5M NaCl, 0.5M Na_2SO_4 , and 1M H_2SO_4 . The obtained results confirmed that sulfuric acid is the most efficient receiving phase for PIMs with both carriers. This acid was used successfully by Kogelnig

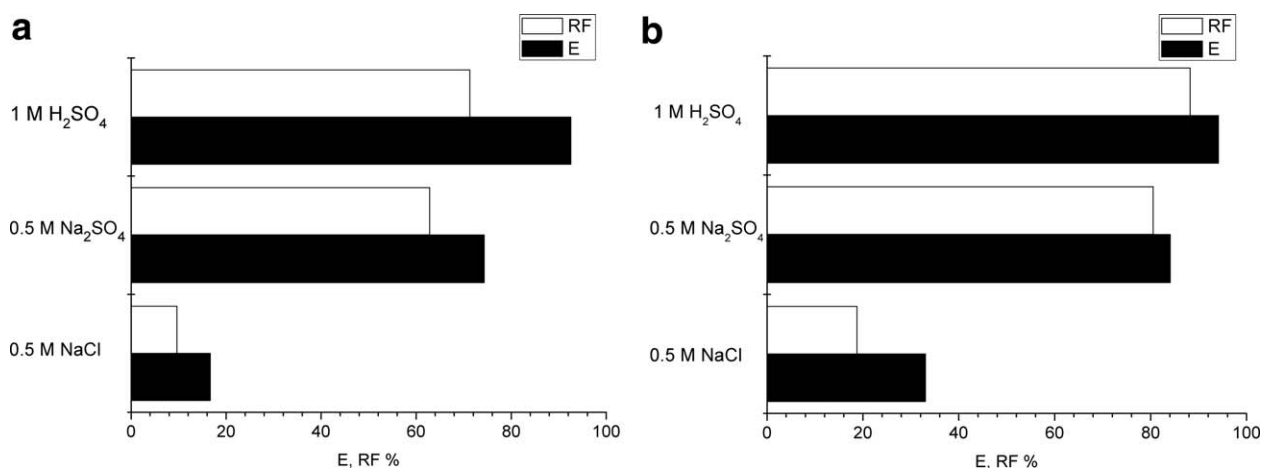


Figure 5. The influence of the receiving phase on Zn(II) transport through PIMs containing 40% (a) Cyphos IL 101 or (b) Cyphos IL 104, and 55% CTA, 5% NPOE.

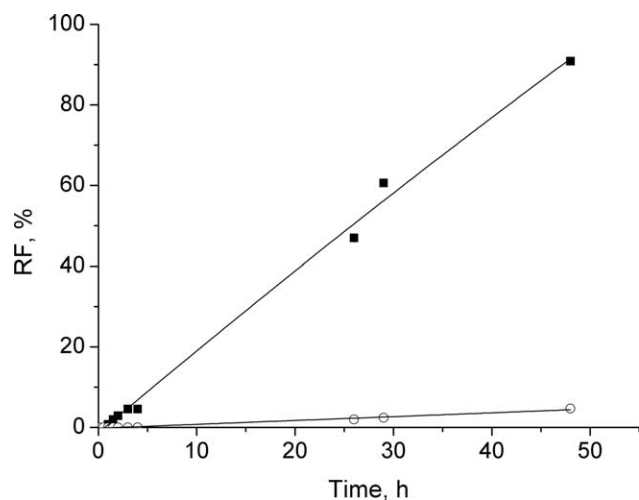


Figure 6. Effect of matrix type on recovery factor (RF) of zinc(II) across the membranes containing (■) CTA, IL 104, NPOE or (○) PVC, IL 104, NPOE.

*et al.*²³ for Zn(II) receiving from PVC membranes with Cyphos IL 101.

The Effect of the Matrix Type on the Recovery Factor of Zn(II)

To investigate the influence of matrix type on transport properties of PIMs with phosphonium ILs, two most frequently used matrices were chosen, i.e., CTA and PVC. The exemplary dependence of Zn(II) recovery factor on PIM matrix type is presented in Figure 6.

Higher values of recovery factors were obtained for Zn(II) transport through CTA-based membranes than PVC-based ones (Fig. 6). 90% of Zn(II) was recovered to the receiving phase after 48 h while, when PVC membranes were used, this value was lower than 5%. The nature of the polymer was found to have a strong influence on the metal ion transport efficiency. PVC has an amorphous structure, while CTA a crystalline one. Moreover, the cellulose triacetate has a large number of hydroxyl groups which are capable of formation of oriented hydrogen bonds, while PVC is dominated by intermolecular interactions. In addition, CTA has huge mechanical strength due to its crystalline structure and is infusible; therefore it can be successfully used for PIM formation. Additionally, more hydrophilic surface of the CTA membranes (shown also in Table II) facilitates the access of extracted solutes to the membrane.

The Effect of the Plasticizer Content on Zn(II) Transport

To understand the influence of the plasticizer content on the mass transport flux through PIMs with phosphonium ILs, membranes of different NPOE content were prepared having a constant IL 101 or 104 (30%) and CTA contents. Figure 7 shows the effect of NPOE content on the Zn(II) transport through IL-containing PIMs.

Plasticizers are added to hard, stiff plastics to make them softer and more flexible. They are also applied as components of PIMs to improve the membrane chemical and mechanical stability. They penetrate between the polymer molecules and neutralize

their polar groups by interaction with own polar groups or merely increase the distances between the polymer molecules and reduce the strength of intermolecular forces.^{34,35} Zn(II) flux raises with increasing plasticizer amount in the membrane up to 10–20% of NPOE (Figure 7), as a consequence of the plasticization effect, which makes the membrane a better medium for plasticizer and carrier movements. The maximum in initial flux of Zn(II) is noticeable for both ILs with trihexyltetradecylphosphonium cation, but the values of flux are lower for IL 104 containing bigger anion (bis(2,4,4-trimethylpentyl)phosphinate) than for chloride one (IL 101). Further, decrease in flux is explained by the antiplasticization effect.³⁴ Plasticizer can sufficiently mobilize the polymer chains so that they can arrange themselves in a more ordered structure that require relatively less space. Additionally, NPOE, having high dielectric constant, affects increase in the membrane thickness and viscosity, which results in the reduction of Zn(II) flux after the maximum value of the NPOE content is reached. On the other hand, carriers such as quaternary ammonium or phosphonium salts can act also as plasticizers.²⁹ Thus, as NPOE is quite expensive, its content was established at 5%, and further grow in Zn(II) transport was intensified by the rising carrier concentration in the membrane.

The Effect of Phosphonium IL on Zn(II) Transport

Three phosphonium ILs were used as carriers in PIMs both with PVC and CTA matrix. Cyphos IL 101 and 167 differ in the phosphonium cation. Phosphorus of Cyphos IL 167 is substituted with shorter alkyl chains than Cyphos IL 101, and both ILs contain chloride anions. On the other hand, Cyphos IL 104 is composed of the same cation as Cyphos IL 101 but its anion comes from well-known acidic extractant Cyanex 272. As their structures vary a little (they are shown in Table IV), some differences in their extraction properties could be expected.

The differences in the membrane thicknesses may affect the transport resistance and cause a decrease in metal flux, so the normalized initial flux (J_N) was calculated. The thinnest CTA

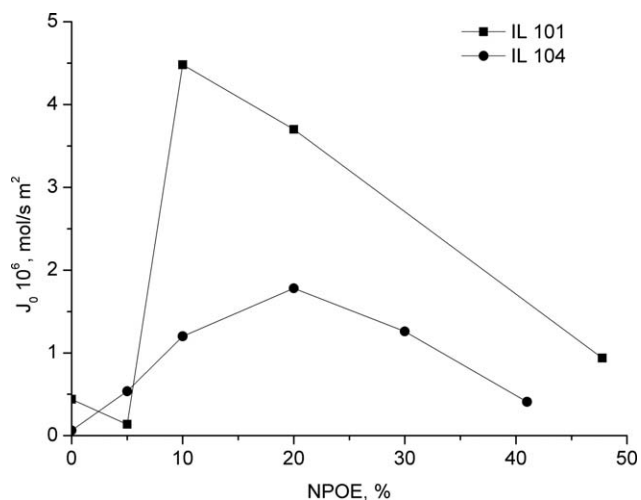
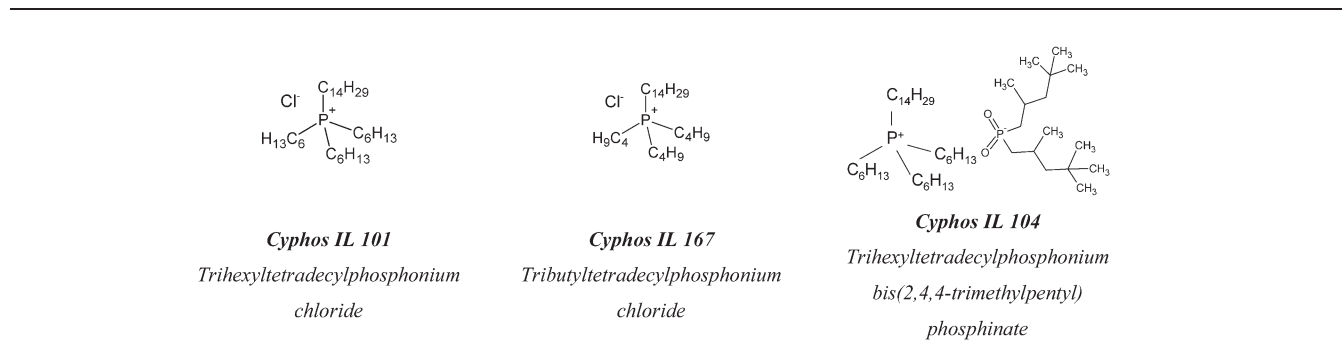


Figure 7. Initial Zn(II) flux for membranes containing various amounts of NPOE; 30% Cyphos IL 101 or 104, CTA matrix.

Table IV. Structures of the Extractants Used

membrane containing 30% Cyphos IL 101 was chosen as a reference and the metal ion flux was calculated as follows:²⁴

$$J_N = J_0 \cdot \frac{d_M}{d_R} \quad (6)$$

where d_R equals 25.8 μm and is the reference membrane thickness, d_M corresponds to the thickness of the membrane whose flux is normalized.

The transport parameters of zinc ions for some exemplary PIMs varying with the carrier and the matrix, shown in Table V, indicate the influence of the membrane composition (polymer matrix, a kind of carrier, especially, its hydrophilic–lipophilic properties) and carrier content in PIMs on the mass transport.

The best initial flux and permeability were obtained for CTA membranes containing Cyphos IL 101. However, Cyphos IL 167 and 104 were also found to be effective zinc(II) ions carriers. The values of recovery factor and extraction efficiency of CTA membranes exceed 80%, which means that both, extraction to

the membrane and stripping to the receiving phase, are effective. In contrast, PVC membranes are virtually ineffective in the process of Zn(II) transport. The values of initial flux and permeability are low, particularly for Cyphos IL 101 and 167 as carriers. However, as all PVC membranes are thicker than CTA membranes, the values of J_N are sometimes even higher than those of CTA membranes. When Cyphos IL 104 is employed in PVC membranes as a Zn(II) carrier, J_0 and P are significant but E and RF values are low. It means that despite of fast initial Zn(II) transport to the membrane, afterwards it is limited and finally only up to 40% of Zn(II) can be extracted, and even less (about 5%) can be stripped to the receiving phase.

From the point of view of separation, the most important is the complete transport of the solute to the receiving phase, described by the recovery factor. However, not always RF of Zn(II) is equal to percentage extraction of these ions to the membrane phase. The values of E and RF strongly dependent on the membrane composition. The results obtained show

Table V. The Parameters Characterizing Transport of Zn(II)

| IL content, % | IL type | NPOE content, % | $J_0 \cdot 10^6$, mol/s·m ² | $J_N \cdot 10^6$, mol/s·m ² | $P \cdot 10^6$, m/s | E , % | RF , % |
|---------------|---------|-----------------|---|---|----------------------|---------|----------|
| CTA matrix | | | | | | | |
| 23 | 101 | 46 | 5.38 | 5.38 | 6.08 | 96.5 | 94.8 |
| 30 | | 5 | 4.13 | 4.56 | 4.23 | 92.2 | 85.9 |
| 40 | | 5 | 9.96 | 12.7 | 9.88 | 95.4 | 92.4 |
| 15 | 167 | 0 | 2.18 | 3.27 | 1.46 | 98.3 | 96.5 |
| 30 | | 5 | 6.96 | 10.8 | 5.66 | 91.2 | 83.7 |
| 32 | | 47 | 3.85 | 5.25 | 3.35 | 94.7 | 94.7 |
| 30 | 104 | 5 | 2.23 | 2.89 | 2.11 | 85.5 | 56.5 |
| 32 | | 41 | 1.13 | 1.67 | 1.27 | 94.8 | 84.5 |
| 40 | | 5 | 9.96 | 13.0 | 9.88 | 95.4 | 90.9 |
| PVC matrix | | | | | | | |
| 20 | 101 | 5 | 0.91 | 2.01 | 1.03 | 18.9 | 0 |
| 30 | | 0 | 1.03 | 2.39 | 1.16 | 15.5 | 0 |
| 20 | 167 | 5 | 1.0 | 1.84 | 0.94 | 11.6 | 2.9 |
| 40 | | 0 | 4.2 | 7.24 | 5.09 | 24.1 | 0 |
| 20 | 104 | 5 | 5.51 | 10.6 | 3.06 | 16.9 | 1.7 |
| 35 | | 5 | 7.88 | 13.8 | 5.37 | 42.7 | 4.7 |

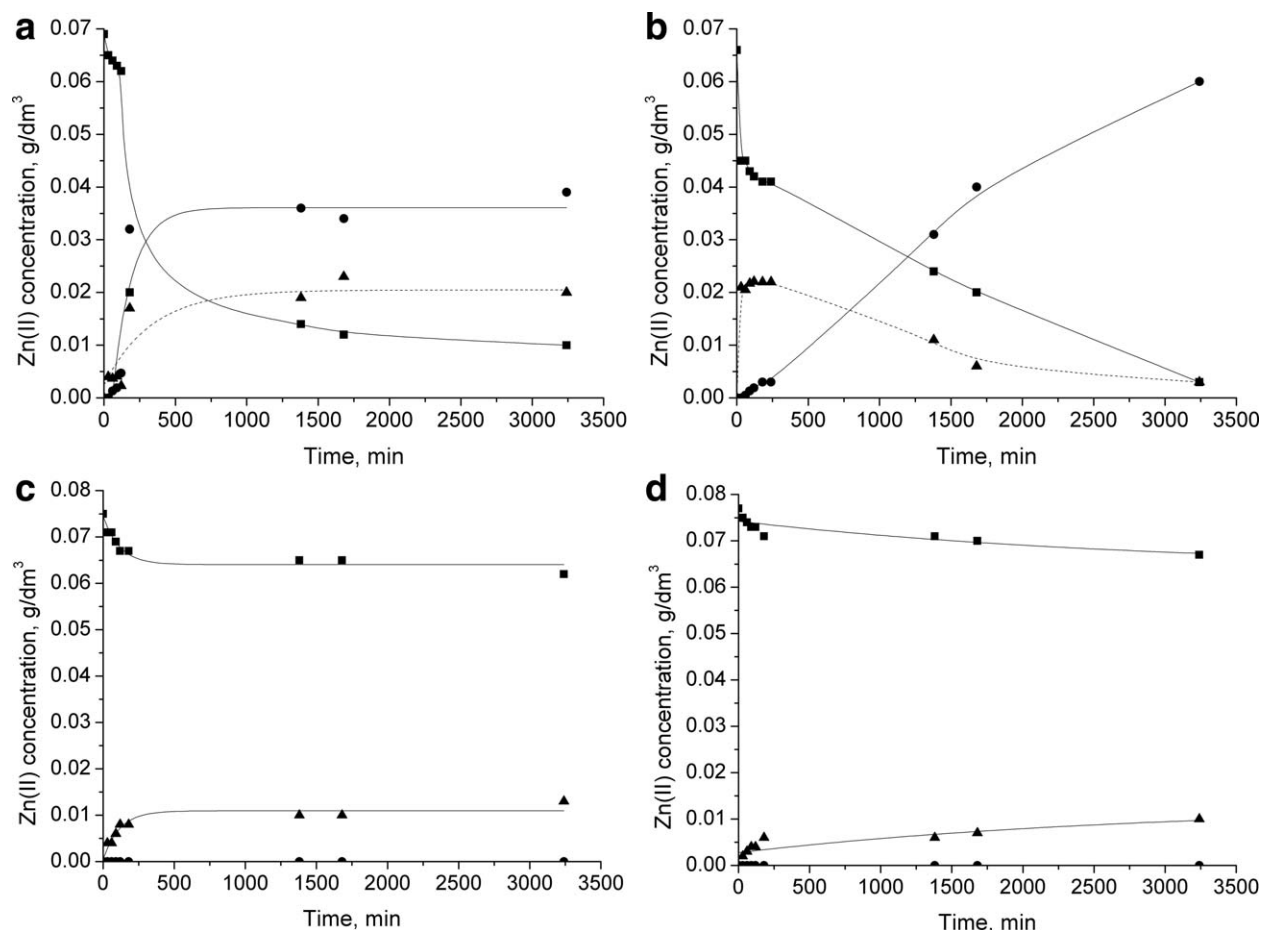


Figure 8. Accumulation of Zn(II) in the membrane containing (a) 30% IL 104, 55% CTA, 5% NPOE, (b) 40% IL 104, 55% CTA, 5% NPOE, (c) 30% IL 104, 65% PVC, 5% NPOE, (d) 40% IL 104, 55% PVC, 5% NPOE (■ – feed, ▲ – membrane, ● – receiving phases).

significant differences between the extraction percentages and recovery factors. Zn(II) is efficiently transferred to the membranes containing Cyphos IL 101 and Cyphos IL 104 (Table V), but its transport to the receiving phase is incomplete. The most probable mechanism of Zn(II) transfer through the PIM with phosphonium ILs follows a few steps: chlorocomplex formation in the aqueous feed, Zn(II) complex diffusion from bulk to the membrane interface, reaction with IL carrier, diffusion across the membrane towards the membrane-receiving phase interface, and decomposition of the Zn(II)-IL complex, Zn(II) stripping to the receiving phase. Probably the metal-carrier complex decomposes with difficulty at the interface of membrane-receiving phase, thus leading to low values of Zn(II) *RF*. Accumulation of Zn(II) in the membrane is visible in Figure 8(a,c,d).

The reduction in Zn(II) accumulation with the content of Cyphos IL 104 (in CTA membranes) increasing from 30 to 40% results probably from the so-called percolation threshold.²⁹ It means that the mobility of Cyphos IL 104, which is composed of anion and cation with long carbon chains, in the membrane is limited at the content less than 40%.³¹ On the other hand, ILs containing small chloride anion (Cyphos IL 101 and 167)

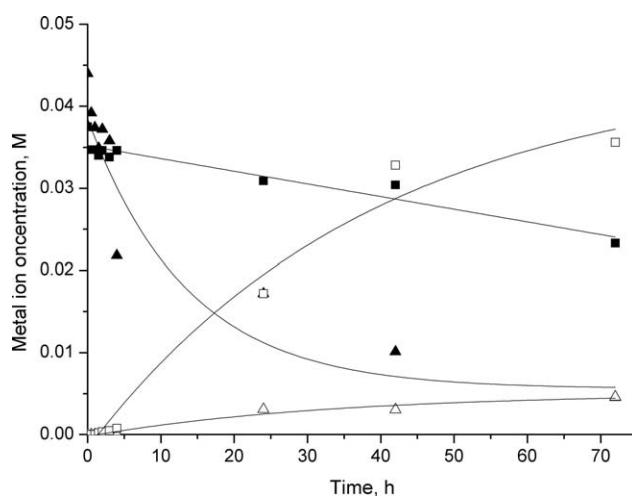


Figure 9. Transport of Zn(II) and Fe(III) through 27% CTA, 32% IL 104, 41% NPOE PIM; mixture of metal ions 2.5 g/dm³ Zn(II) and 2.5 g/dm³ Fe(III) (0.038 M Zn(II) and 0.045 M Fe(III)) (■ – Zn(II) in the feed phase, ▲ – Fe(III) in the feed phase, △ – Fe(III) in the receiving phase, □ – Zn(II) in the receiving phase).

Table VI. Parameters of Zn(II) and Fe(III) Transport Through the 41% NPOE, 32% IL 104, 27% CTA PIM

| Parameter | Individual | | Mixture | |
|---|------------|---------|---------|---------|
| | Zn(II) | Fe(III) | Zn(II) | Fe(III) |
| $E, \%$ | 95 | 79 | 38 | 90 |
| $RF, \%$ | 85 | 92 | 12.5 | 81 |
| $J_0 \cdot 10^6, \text{mol/s} \cdot \text{m}^2$ | 1.16 | 2.33 | 75 | 158 |
| $P \cdot 10^6, \text{m/s}$ | 1.3 | 1.5 | 2.0 | 3.6 |
| $\alpha_{\text{Fe(III)/Zn(II)}}$ | – | | 2.11 | |

are mobile enough at the contents studied to recover to the receiving phase more than 80% of Zn(II) (Table V).

Application of PIM Containing Phosphonium IL for Transport of Zn(II) and Fe(III)

As the previous studies of our team were focused on regeneration of spent pickling solutions containing zinc and iron ions with liquid–liquid extraction,^{24,36,37} the model solution of Zn(II) and Fe(III) chlorides was investigated also with PIMs. The aqueous feed phase contained a mixture of 0.038M of Zn(II) and 0.045M of Fe(III) (2.5 g/dm³), 0.58M HCl, 5M Cl[–]. The membrane containing 27% CTA, 32% IL 104, 41% NPOE was selected to study separation of the two metal ions from chloride solution to be able to compare the results with the ones published elsewhere.²⁴ The concentration profiles of Zn(II) and Fe(III) in the feed and receiving phases are shown in Figure 9.

Fe(III) concentration decreases in the feed phase much faster than that of Zn(II) and finally reaches lower values (Figure 9). Transport of Zn(II) through the membrane with Cyphos IL 104 carrier is not as effective as that of Fe(III). After 72 h only 38% of the initial amount of Zn(II) is extracted while almost 90% of Fe(III) is transported to the membrane phase.

The investigation was carried out also with the membrane containing 31% CTA, 24% Cyphos IL 101 and 45% NPOE. In this case neither Zn(II) ($E = 25\%$) nor Fe(III) ($E = 37\%$) are extracted efficiently.

Parameters of Zn(II) and Fe(III) transport from individual solutions (containing $1.5 \cdot 10^{-3} \text{M}$ Zn(II) and $1.8 \cdot 10^{-3} \text{M}$ of Fe(III) (0.1 g/dm³), 0.58M HCl, 5M Cl[–]) and mixture of Zn(II) and Fe(III) with PIM containing Cyphos IL 104 are presented in Table VI. Results of a similar investigation for PIM with Cyphos IL 101 have been reported recently elsewhere.²⁴

Though the results for Zn(II) transport through the phosphonium IL containing PIMs (presented in this work) seem prospective, in comparison with Fe(III) transport they are worse. Values of transport parameters from individual metal ion solutions indicate that Fe(III) is transported to the membrane twice faster than Zn(II) (initial fluxes equal 2.33 and $1.16 \cdot 10^{-6} \text{mol/s} \cdot \text{m}^2$ for Fe(III) and Zn(II), respectively). At the same time the permeability coefficients are similar and amount to 1.5 and $1.3 \cdot 10^{-6} \text{m/s}$ for Fe(III) and Zn(II), respectively. Noticeably, both metal ions are much faster transported from their mixture (initial flux 75 and $158 \cdot 10^{-6} \text{mol/min} \cdot \text{m}^2$ for Zn(II) and Fe(III), respectively) than from the individual solutions. Taking into

account that the driving force of the process comes from the concentration difference of both metals at the two sides of the membrane, it explains that the values of initial fluxes for a mixture of Zn(II) and Fe(III) (are higher than for metal ions transport from individual solutions. The fact that recovery of Fe(III) is effective, while that of Zn(II) much poorer, permits separation of Fe(III) from Zn(II). Additionally, the recovery of Fe(III) is efficient that allows Fe(III) to be separated from Zn(II). This is expressed also by the selectivity coefficient calculated as a relationship between the Fe(III) and Zn(II) initial fluxes:

$$\alpha_{\text{Fe(III)/Zn(II)}} = \frac{J_{\text{Fe(III)}}}{J_{\text{Zn(II)}}} \quad (7)$$

The value of selectivity coefficient $\alpha_{\text{Fe(III)/Zn(II)}}$ equal to 2.11 means that Fe(III) can be separated from Zn(II). However, design and construction of more selective systems in the future could improve the separation and enable obtaining mostly Fe(III) in the receiving phase.

CONCLUSIONS

The results of the studies have shown that the efficiency of PIMs containing phosphonium ILs depends on the kind of polymer matrix and carrier and the amount of plasticizer. Cyphos IL 167 application as a metal ion carrier in PIMs is reported for the first time in this article.

Better transport abilities of CTA membranes towards Zn(II) compared with PVC membranes undoubtedly indicate that the differences in the structure of the two polymers play a crucial role in the permeability of the membranes. The type of carrier used in this research seems to influence the transport less than the matrix type. It is shown that the best initial flux and permeability coefficient values are obtained for the membranes containing Cyphos IL 101 and Cyphos IL 104. In some cases, accumulation of the solute in the membrane suggests that decomposition of the membrane complex at the receiving phase side is too slow. Additionally, the carriers with small anion (Cyphos IL 101 and 167) seem to have much lower percolation threshold and higher mobility in the membrane than Cyphos IL 104 (containing large anions) to transport Zn(II) from the feed to the receiving phase.

Application of Cyphos IL 104 containing PIM for Zn(II)/Fe(III) separation from chloride solution indicated that Fe(III) can be separated from Zn(II). However, design of more selective system in the future could improve the separation and enable obtaining mostly Fe(III) in the receiving phase.

Finally, it is noteworthy that the application of PIMs allows a reduction in the quantity of metal ion carriers, and elimination of volatile organic compounds and the intermediate processes, which are usually applied for liquid–liquid extraction.

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