TRANSPORT OF Zn(II), Fe(II), Fe(III) ACROSS polymer inclusion membranes (pim) and Flat sheet supported liquid membranes (slm) containing phosphonium ionic liquids as metal ion carriers

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Shorten title: Transport of Zn(II), Fe(II), Fe(III) across PIMs and SLMs

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Abstract

In this work transport of Zn(II), Fe(II) and Fe(III) ions from chloride aqueous solutions across polymer inclusion membranes (PIMs) and supported liquid membranes (SLMs) containing one of three phosphonium ionic liquids: trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), trihexyl(tetradecyl)phosphonium *bis*(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) and tributyl(tetradecyl)phosphonium chloride (Cyphos IL 167) as ion carrier was reported. The results show that Zn(II) and Fe(III) are effectively transported through PIMs and SLMs, while Fe(II) transport is not effective. The highest values of initial flux and permeability coefficient of Zn(II) were noticed for SLM containing Cyphos IL 167. Cyphos IL 101-containing SLM is more stable than PIM.

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introduction

Lastly, remarkable progress has been made concerning the separation and removal of metal ions through liquid membranes. Many applications of supported liquid membranes and polymer inclusion membranes as an alternative method to traditional liquid-liquid extraction (SX) were proposed in scientific literature. The advantages of these membranes over SX include elimination in amount of volatile solvents from separation systems and reduction of intermediate steps (1). Also, such drawbacks of liquid-liquid extraction as loading limits of the organic phase and losses of metal ions in the interfacial phases are eliminated.

Generally, liquid membranes are classified as bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs). The main drawback of BLMs lies in their small surface area and slow mass transfer rates, whereas emulsion stability is the main problem of ELM operation (1-4).

SLMs are formed as flat sheets, tubes, spiral-wound or hollow fiber. A common problem for SLMs is the loss of membrane phase to both aqueous phases and subsequently short lifetime. For this reason these membranes are not widely used on industrial scale nowadays (3). However, different configurations of the SLM give the opportunity to develop large surface area of the membrane and, thus, enhance the efficiency of solute mass transport.

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To overcome the drawback of instability of impregnated SLMs, polymer inclusion membranes (PIMs) have been developed. The main difference between these two types of liquid membranes lies in the way of carrier immobilization: in SLM the organic phase containing carrier impregnates pores of a solid support and is kept there by capillary forces, while in PIM the carrier itself is built into the structure of the membrane which is composed of a polymer support material (mainly cellulose triacetate (CTA) or poly(vinyl chloride) (PVC)), carrier (extractant) and a plasticizer or modifier. Good stability of PIMs (5), limited loss of carriers (6), high selectivity and transport efficiency (7) compared to other types of liquid membranes are the main reasons for the recent interest in the metal ion transport through polymer inclusion membranes (1, 2, 4, 8).

Some authors compared transport of Zn(II), Cu(II), Co(II), Ni(II), Pt(IV) across PIMs and flat sheet SLMs (9-13). Different carriers were included in PIMs or impregnated into SLMs, e.g. calix[4]resorcinarene derivatives (9), 1-decyl-4-methylimidazole (10), quaternary ammonium (e.g. methyltrioctylammonium chloride, Aliquat 336) (11, 13), lauric acid (12), Lasalocid sodium salt (13), *bis*(2-ethylhexyl)phosphoric acid (D2EHPA) (14, 15), 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (Kelex 100) (16), trialkylphosphine oxide (Cyanex 923) (17). Recently also phosphonium ionic liquids have been extensively investigated as carriers of B(III) (18), Cu(II) (11), Zn(II), Fe(II), Fe(III) (19-23), Cd(II), Co(II), Ni(II) (24). Quaternary phosphonium ionic liquids, i.e. trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), trihexyl(tetradecyl)phosphonium *bis*(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) and tributyl(tetradecyl)phosphonium chloride (Cyphos IL 167) were also tested as metal ion carriers across SLMs (11, 18, 25). Regel-Rosocka et al. (23) described removal of Zn(II), Fe(II) and

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Fe(III) from chloride aqueous solutions across PIMs containing Cyphos IL 101 and Cyphos IL 104 as metal ion carriers. The obtained results showed that Cyphos IL 101 is a more effective carrier for Fe(III) than for Zn(II) ions (23).

The obtained values of permeability coefficient showed that flat sheet SLM better transferred Zn(II) from feed to receiving phase than PIM did (9). The differences between the rate and efficiency of Zn(II) transport through PIMs and SLMs were attributed to the differences in structure of the membranes and distinct forces binding carrier with the membrane support. Consequently, different mechanisms of solute transport across the membrane are responsible for the effectiveness of the separation. On the contrary, Ulewicz and Radzymińska-Lenarcik (10) found that initial flux of Zn(II) across PIMs containing imidazole derivative is higher than across SLM. However, after taking into account different morphology (porosity, tortuosity) of these two types of liquid membranes (i.e. normalizing the fluxes), and recalculation of the values of Zn(II) initial flux, the transport through PIMs appeared to be worse than the transport across SLMs. Also, Cu(II) transport with lauric acid as a carrier across SLM was reported to be higher than across PIM (12). Furthermore, Fontas et al. (13) reported that (after normalizing the fluxes) efficiencies of Pt(IV) and Cd(II) transport across SLMs and PIMs were comparable.

Though lower mass fluxes are reported in the most cases, all authors emphasized that PIMs were more stable than SLMs and, hence, were preferred for some applications. Many researchers have studied the stability of PIMs and reusability by performing repeated transport experiments with the same membrane. Generally, the stability of PIMs was quite good with flux and permeability

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values changing only slightly in the first several cycles and also no structural weakening of the membrane was reported (10, 14, 15, 26-28).

The aim of the present work is to compare the transport of Zn(II), Fe(II) and Fe(III) ions through polymer inclusion membranes and flat sheet supported liquid membranes containing one of three phosphonium ionic liquids (Cyphos IL 101, Cyphos IL 104 and Cyphos IL 167) as metal ion carriers. Though spent pickling solutions contain Zn(II) and mainly Fe(II) it was shown that Fe(II) can be partly oxidized to Fe(III) (29). This is the reason for studies both on Fe(II) and Fe(III) transport across liquid membranes and on separation of Zn(II) from Fe ions. Also, stability of PIM and SLM is compared for Cyphos IL 101 as a metal ion carrier.

experimental

Reagents and solutions

The inorganic chemicals, i.e. Zn(II), Fe(II) and Fe(III) chlorides were of analytical grade. The organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenyloctyl ether (NPOE), dichloromethane, decanol, kerosene were also of analytical grade and were purchased from Fluka and used without further purification. Phosphonium ionic liquids, trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101), tributyl(tetradecyl)phosphonium chloride (Cyphos IL 167) and trihexyl(tetradecyl)phosphonium *bis*(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104) supplied by Cytec Industries Inc. (USA) were applied as carriers for metal ions in PIMs and SLMs (Fig. 1). The aqueous feed phase contained

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1.5·10^{-3} M Zn(II) (0.1 g/dm^3) and 1.8·10^{-3} M Fe ions (0.1 g/dm^3), 0.58 M HCl, 5 M Cl$^-$ (constant chloride content was adjusted with NaCl). 1 M H$_2$SO$_4$ was used as a receiving phase.

Fig. 1. Structures of the phosphonium ionic liquids used as PIM carriers.

The carriers differed with the structure of cations or anions that might affect the reaction of extraction of various metal species and, thus, could influence the efficiency of transport of metal ions across the liquid membranes.

Preparation of membranes

Polymer inclusion membranes

Solution of cellulose triacetate as the polymer matrix, plasticizer (NPOE), Cyphos IL 101, Cyphos IL 104 or Cyphos IL 167 as ion carriers in dichloromethane (solvent) was prepared. A specific portion of the three-component organic solution was poured into a Petri dish. After slow evaporation of organic solvent (at least for 24 h) the obtained polymer inclusion membrane was carefully peeled off from the glass dish by immersion in a cold water. The composition of PIMs applied for the studies was the following: 55% CTA, 40% IL and 5% NPOE. It is assumed that the composition of the membrane is equivalent to the composition of the casting solution.

Supported liquid membranes

A flat sheet PVDF (polyvinylidene fluoride, Durapore HVHP04700) was used as polymeric support for transport of Zn(II), Fe(II) and Fe(III). The organic liquid membrane phase was

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prepared by dissolving the required volume of 0.1 M Cyphos IL 101, Cyphos IL 104 and Cyphos IL 167 in 10% decanol/kerosene to obtain carrier solutions. The supported liquid membranes were prepared at room temperature by impregnating the porous support with the carrier solution overnight, then leaving them to drip for 10 s before being placed in an apparatus.

Characteristic parameters of the membranes used are given in Table 1.

Table 1. Characteristic parameters of PIMs and SLMs applied for metal ion transport.

Transport studies

To transport Zn(II), Fe(II) and Fe(III) across PIMs, a sandwich type membrane module was used, to which feed and receiving phase were pumped with a peristaltic pump from tanks containing both phases. The volumes of aqueous solutions were equal to 200 cm^3. The effective membrane area was 15.9 cm^2. Fig. 2 illustrates the schematic diagram of the metal ion transport experiments across PIMs (20-23).

The SLM transport experiments were carried out in the flat sheet (FSSLM) apparatus presented in Fig. 3. Batch experiments were carried out in two cylindrical cells containing 210 cm^3 of each the feed and receiving solution. The effective area of SLM was equal to 11.4 cm^2. Both phases were mechanically stirred. Samples from the feed and receiving phases were withdrawn at regular time intervals, and metal ion concentration was analyzed by atomic absorption spectroscopy (AAS, Hitachi Z-8200 or 4100 MP-AES, Agilent Technologies, AA 240FS, Varian) at 213.8 and 248.3 nm (for zinc and iron, respectively) in the air-acetylene flame.

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Fig. 2. Schematic diagram of PIM system (1 – feed phase container, 2 – receiving phase container, 3 – peristaltic pump, 4 – membrane module – sandwich type).

Fig. 3. Scheme of SLM system.

The kinetics of PIM and SLM transport can be described by an equation analogous to the first order reaction in relation to metal ion concentration:

$$\ln \frac{c}{c_0} = -kt \tag{1}$$

where c_0 (M) and c (M) is the concentration of metal ions in the feed phase at initial time and selected time, k is the rate constant (1/s), t is the time of transport (s). Values of the rate constant (k) are estimated from linear dependence of $\ln(c/c_0)$ versus time.

Transport abilities of PIMs and SLMs are characterized by initial flux of metal ions (J_o, mol/s·m^2):

$$J_0 = \frac{V}{A} \cdot k \cdot c_0 \tag{2}$$

where V is the volume of the aqueous phase ($2 \cdot 10^{-4}$ m^3, $2.1 \cdot 10^{-4}$ m^3, respectively for PIMs and SLMs), A is an effective membrane area (Table 1). Permeability coefficient can be calculated at feed and receiving phase side (P_F, P_R, m/s, respectively) from the slope of the graph assuming the following dependences (16):

$$ln\left(\frac{c}{c_o}\right) = -P_F \cdot \frac{V}{A} \cdot t \tag{3}$$

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$$ln\left(\frac{c_0 - c_R}{c_0}\right) = -P_R \cdot \frac{V}{A} \cdot t \qquad (4)$$

Efficiency of metal ions extraction to the membrane (E, %) and recovery factor (RF, %) of metal ions (calculated after 48 or 72 h of the process, for Zn(II) and Fe ions, respectively) and are defined by eqs. 5 and 6.

$$E = \frac{c_0 - c}{c_0} \cdot 100\% \qquad (5)$$

$$RF = \frac{c_R}{c_0} \cdot 100\% \qquad (6)$$

c_R is the concentration of metal ions in the receiving solution at selected time.

results and discussion

Zn(II), Fe(II) and Fe(III) presence in chloride solutions

Chloride solutions containing Zn(II), Fe(II) and Fe(III) were chosen for studies with liquid membranes because removal and separation of these metal ions is an important issue to be solved for hot-dip galvanizing industry (30) due to high concentratins reaching even up to 120 g/dm^3 Zn(II), 100 g/dm^3 Fe ions (mainly Fe(II)) and 3 M HCl. Fe(III) can be present in these solutions as a consequence of oxidation of Fe(II) (29). Detailed information on composition of spent pickling solutions and methods of their regeneration was presented in some previous papers (30, 31).

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Recently, not only liquid-liquid extraction has been proposed to recover Zn(II) from spent pickling baths (23, 32, 33) but also emulsion pertraction technology (34), membrane-based solvent extraction (34, 35) or its combination with electrowinning (31) or anion exchange (36).

Generally, Fe(III) and Zn(II) form stable neutral and anionic chlorocomplexes in the presence of hydrochloric acid and high content of chloride anions, while Fe(II) anionic chlorocomplexes are not stable in the aqueous phases, and Fe(II) exists in aqueous chloride media mainly as Fe^{2+} or $FeCl^+$ (29).

Phosphonium ILs used as ion carriers are able to react with anionic or neutral chlorocomplexes of Zn(II) or Fe(III) depending on the chloride and hydrochloric acid concentrations in accordance with the following reactions (32):

$$ZnCl_{4(aq)}^{2-} + 2\overline{R_3R'PCl} \Leftrightarrow \overline{(R_3R'P)_2ZnCl_4} + 2Cl_{aq}^- \tag{7}$$

$$ZnCl_{4(aq)}^{2-} + 2H_{(aq)}^+ + 2\overline{R_3R'PA} \Leftrightarrow \overline{(R_3R'P)_2ZnCl_4} + 2\overline{HA} \tag{8}$$

$$FeCl_{3(aq)} + \overline{R_3R'PCl} \Leftrightarrow \overline{(R_3R'P)FeCl_4} \tag{9}$$

By contrast extraction of Fe(II) could theoretically follow the reaction:

$$Fe_{(aq)}^{2+} + 2Cl_{(aq)}^- + \overline{R_3R'PCl} \Leftrightarrow \overline{(R_3R'P)FeCl_3} \tag{10}$$

or Cyphos IL 104 can bind also iron cations to *bis*(2,4,4-trimethylpentyl)phosphinate anion (denoted as A in eq. 11) originating from acidic extractant *bis*(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) according to the reaction:

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$$Fe_{(aq)}^{2+} + 2Cl_{(aq)}^{-} + 2\overline{R_3R'PA} \Leftrightarrow 2\overline{(R_3R'P)Cl} + \overline{FeA_2} \tag{11}$$

However, it was shown that Cyanex 272, as an acidic extractant, did not efficiently extract metal ions from feeds at low pH (below 1) (37).

Zn(II), Fe(II) and Fe(III) transport through SLMs

Flat sheet SLMs impregnated with three various phosphonium ILs were used to investigate transport of Zn(II), Fe(II) and Fe(III). Generally, as a consequence of metal ion transport across a membrane, the content of metal ions in the feed phase decreases while it increases in the receiving phase. Fig. 4 shows the exemplary changes in Zn(II), Fe(II) and Fe(III) concentration over time during transport through SLMs containing Cyphos IL 101 as a carrier. Concentration profiles across SLMs with Cyphos IL 104 and Cyphos IL 167 are shown in Supplementary Data (Fig. 8).

Fig. 4. Changes in concentration of (■) Zn(II), (●) Fe(II), (▲) Fe(III) ions over time in the feed and receiving phase through SLMs with Cyphos IL 101 as a carrier.

As shown in Figs. 4 and 8 (Supplementary Data) concentrations of Zn(II) and Fe(III) ions in the feed phase decrease faster and finally reach lower values compared to Fe(II), for Cyphos IL 101 and 167 carriers. After three hours of the process more than 25% of the initial amount of Fe(III) is transported from the feed phase to the receiving phase across the SLM containing Cyphos IL 101 and IL 167 (Figs. 4 and 8). Also, the transport of Zn(II) across the membranes impregnated

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with Cyphos IL 101 and IL 167 is effective. On the contrary, the transport of Fe(II) is not effective across the SLMs containing one of these three carriers.

Zn(II), Fe(II) and Fe(III) transport through PIMs

The transport of Zn(II), Fe(II) and Fe(III) was also carried out through PIMs containing 55% CTA, 40% IL, 5% NPOE to compare it with transport across SLMs. Concentration profiles of metal ions are presented in Figs. 5 and 9 (Supplementary Data).

Fig. 5. Changes in concentration of (■) Zn(II), (●) Fe(II), (▲) Fe(III) ions over time in the feed and receiving phase through PIMs with Cyphos IL 101 as a carrier.

A similar trend as for SLMs is noted also for transport across PIMs: concentrations of Zn(II) and Fe(III) in the feed phase decrease faster than Fe(II) content (Figs. 5 a and 9 c, e). Generally speaking, the transport of Fe(II) across the both types of liquid membranes, i.e. SLM and PIM, is not effective. After 72 h less than 10 and 40% of initial amount of Fe(II) (respectively for SLMs and PIMs) is extracted from the feed phase. Small amount of iron ions detected in the receiving phases during Fe(II) transport may probably result from oxidation of Fe(II) to Fe(III).

Comparison of transport of metal ions across PIMs and SLMs

These two types of liquid membranes were studied to learn about their individual performance towards transport of Zn(II), Fe(II) and Fe(III) with phosphonium ionic liquids as ion carriers. On the basis of the concentration changes presented above some parameters characterizing transport of metal ions were calculated (eqs. 2-6).

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The differences in the membrane thicknesses affect the flux value, so the initial fluxes for PIMs were normalized (J_N) according to the following equation (38):

$$J_N = J_{0,PIM} \cdot \frac{d_{PIM}}{d_{SLM}} \tag{12}$$

where d_{SLM} equals 125 μm and is the supported liquid membrane thickness, d_{PIM} corresponds to the thickness of the membrane whose flux is normalized.

The obtained results showed that the transport of metal ions to the receiving phase across both SLMs and PIMs containing Cyphos IL 101 and Cyphos IL 167 was faster than transport across the membrane containing Cyphos IL 104 (Figs. 4, 5, 8 and 9). These observations were also confirmed by the values of initial fluxes and permeability coefficients of Zn(II), Fe(II) and Fe(III) for SLMs and PIMs calculated according to eqs 2-4 and presented in Table 2. For example, very low initial transport of Zn(II), Fe(II) and Fe(III) was noted across SLM containing Cyphos IL 104 (Table 2). It seems that in SLMs the metal ion-Cyphos IL 101 and Cyphos IL 167 complexes may be easier transported, thus, leading to higher values of J_N and P_F than for SLM containing Cyphos IL 104. The maximum values of Zn(II) transport across SLMs and PIMs were noted for the membrane containing Cyphos IL 167, which consisted of small chloride anion and cation substituted with shorter alkyl chains than Cyphos IL 101 and Cyphos IL 104 (Fig. 1). It can be explained by the fact that the membranes containing smaller carriers (Cyphos IL 167 or Cyphos IL 101) have higher mobility than Cyphos IL 104 (containing bulky anion) to transport metal ions from the feed to the receiving phase. Thus, it is visible that the structure of the carriers used affects the efficiency of transport of metal ions across the liquid membranes.

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The transport parameters should be interpreted also in the light of metal chlorocomplexes formed in the solution and their reactions with the carriers. Zn(II) and Fe(III) anionic chlorocomplexes act with phosphonium ILs according to anion-exchange reactions (eq. 7 and 8), while transport of neutral Fe(III) chlorocomplex and Fe(II) cations can be explained by addition reactions (eq. 9 and 10). However, a significant increase in Cyphos IL 104 extraction efficiency of Fe(II) (particularly in PIMs) compared with Cyphos IL 101 and 167 indicates that reaction with anion of Cyphos IL 104 according to eq. 11 is justified. Similar reactions of extraction were proposed for Cd^{2+}, $CdCl^+$ and $CdCl_3^-$ transport across CTA-based PIM with Cyphos IL 104 by Pospiech (24).

The differences in the normalized fluxes that are one order smaller for PIMs than these for SLMs reflect influence of the way of immobilization of the carrier in the membrane. Smaller values of metal ion fluxes can be explained by restricted mobility of carriers that is assumed to be responsible for solute transport in the bulk PIM (1). Carriers are built into the structure of a polymer matrix in PIMs, while in SLMs the membrane pores are impregnated with a carrier solution which make the carrier move easier in SLMs than in PIMs. This phenomena was indicated also by other authors (9, 10, 12, 39). Ugur et al. (9) compared Zn(II) transport across SLM and PIM containing calix[4]resorcinarene derivative indicating that Zn(II) fluxes across SLMs were slightly greater that across PIMs, and attributed it to the various structures of these two types of liquid membranes. The same tendency was noted by Ulewicz and Radzyminska-Lenarcik (10) who obtained lower values of Zn(II) initial flux across PIM with 1-decyl-4-methylimidazole as ion carrier than across SLM. Paugam et al. (12) found diffusion coefficient in CTA-based PIM containing lauric acid as a carrier and tris(2-ethylhexyl) phosphate as a

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plasticizer to be 22 times lower than in the corresponding SLM. Authors suggested that the reason for such a difference in diffusivity of Cu(II) lies in chemical interactions of the diffusing species with the CTA polymer or physical resistance due to the mesh size of the CTA membrane. Higher permeability of SLM containing Kelex 100 as a carrier for Pb(II) and Cd(II), than CTA-based PIM with the same carrier, was explained by Aguilar et al. (39) by lower total transport resistance in SLMs.

Table 2. The comparison of parameters characterizing transport of Zn(II), Fe(II) and Fe(III) through SLMs and PIMs.

Differences in the results of permeability coefficient at the feed and receiving phase (P_F and P_R) indicate retention of the metal ion within the membrane, particularly in PIMs. Only for transport of small amounts of Fe(II) across SLMs no accumulation of the solute in the membrane is observed. The accumulation (retention) of metal ions in the membrane is also confirmed by the values of percentage extraction (a) and recovery factor (b) of Zn(II), Fe(II) and Fe(III) and shown in Fig. 6.

Fig. 6. The comparison of the values of extraction efficiency (a) and recovery factor (b) of Zn(II) (■), Fe(II) (///) and Fe(III) (□) through PIMs and SLMs.

The transport of Zn(II) and Fe(III) across PIMs and SLMs is effective which is confirmed by the values of extraction efficiency to the membrane and recovery factor ranging from 60 to almost 100% (Fig. 6). The highest Zn(II) extraction efficiency is obtained for SLM containing Cyphos IL 167 (extraction efficiency almost 100%). However, the values of RF do not exceed 85%. On

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the contrary, Fe(II) transport generally is not effective; the values of recovery factor are smaller than 10% but for SLMs the extracted Fe(II) is transferred to the receiving phase, while for PIMs accumulation in the membranes occurs. The obtained results show that the metal ions are successfully transported from the feed phase to the membrane, but their transport to the receiving phase is less effective, especially across PIMs. It may be explained by slower decomposition at the interface of the membrane-receiving phase compared with the rate of complex formation at the feed-membrane interface and also by restricted mobility of the carrier resulting from the way of PIM formation (as it was mentioned above).

As a consequence of existence of different species of Zn(II), Fe(III) and Fe(II) in chloride solutions and basing on the transport considerations given above it is assumed that these metal ions can be separated from one another according to eqs. 7-11. Selectivity of metal ion separation with PIMs and SLMs was calculated according to the following relationship:

$$S_{M1/M2} = \frac{c_{M1,R}}{c_{M1,0}} \cdot \frac{c_{M2,0}}{c_{M2,R}} \qquad (13)$$

where indices *M1* and *M2* denote each separated metal, c_0 (M) and c_R (M) are the concentrations of metal ions in the feed phase at initial time and in the receiving phase after selected time. Values of separation coefficients are presented in Table 3.

Table 3. Separation of Zn(II), Fe(II) and Fe(III) with PIMs and SLMs

In PIM system the best separation of Zn(II) and Fe(III) from Fe(II) was obtained with Cyphos IL 167 as metal ion carrier − the values were infinitely high because no transport of Fe(II) to the

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receiving phase occurred. In the case of SLMs separation of Zn(II) from Fe(II) with both chloride ILs was very high ($S_{Zn(II)/Fe(II)}$ near 10). Also, an effective separation of Fe(III) from Fe(II) with each of the studied ILs was obtained. On the contrary, $S_{Zn(II)/Fe(III)}$ values smaller than 1 meant that Zn(II) could not be separated from Fe(III) both in SLM and PIM systems. The separation effectiveness with the phosphonium carriers in PIMs increased in the following order: Cyphos IL 104 < Cyphos IL 101 < Cyphos IL 167. Compared with PIM system, separation of Zn(II) over Fe(III) with SLM is poorer regardless of the carrier used and separation coefficients are lower than for PIMs. Transport of Zn(II) and Fe(III) chlorocomplexes is competitive and the only solution to separate Zn(II) from Fe(III) is to reduce the latter to Fe(II) prior to separation process.

Stability of PIMs and SLMs

Stability of the membranes and possibility to reuse them for further processes is an important issue. Stability of the membranes containing Cyphos IL 101 in three cycles, each 48-hour-long consisting of the membrane process and washing with water, is shown in Fig. 7. Cyphos IL 101 was chosen for stability studies, though in some cases Cyphos IL 167 performed very good separation of Zn(II) and Fe(III) from Fe(II) but membranes with Cyphos IL 101 more effectively transport Zn(II) to the receiving phase than other carriers studied. Moreover, PIMs containing Cyphos IL 167 were more brittle and have less mechanical strength than Cyphos IL 101 membranes.

Fig. 7. Stability of a) PIM and b) SLM containing Cyphos IL 101 on Zn(II) transport; extraction efficiency (■), recovery factor (□).

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It is obvious that in the process conditions investigated for these two systems SLM with Cyphos IL 101 carrier shows very good stability of Zn(II) in relation to PIM system with the same type of carrier (Fig. 7). Zn(II) extraction and recovery across SLM does not change in three cycles of use of the same membrane, whereas for PIM significant decrease (of about 40%) in transport efficiency is noted. The most probable reason for the instability of the PIM studied is the loss of carrier.

Stability, called also reusability, of PIMs with phosphonium ILs was studied by Kogelnig et al. (19), Pospiech (24) and Guo et al. (40). Their studies provided various results due to different compositions of the PIMs investigated (Table 4), however, a decrease in permeability or weight of membranes was always observed.

PIMs with some types of carriers appeared to be more stable, e.g. Kebiche-Senhadji et al. (14) reported almost no change in Cd(II) flux across CTA-based PIMs with Aliquat 336 or D2EHPA as carriers for 96 hours (12 cycles, 8 h each cycle) and Cr(VI) and Cr(III) flux remained almost unchanged (5% decrease) for 60 days (15). Also, PIMs containing Kelex 100 as Au(III) carrier were stable for 15 cycles (6 h each), further decrease in permeability was attributed to the dissolution of the components of the organic phase in the aqueous media (16).

Table 4. Composition of different PIMs and SLMs and their stability results.

Generally some authors indicated that SLMs were less stable than PIMs. However, the metal ion flux, permeability or recovery factor decreased in each consecutive cycle in both

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membrane systems. Ulewicz and Radzyminska-Lenarcik (10) reported rather low decrease in Zn(II) transfer flux (less than 7.5%) for PIM containing 1-decyl-4-methylimidazol as a carrier after 5 cycles. While the decrease in Zn(II) transfer across SLM was more significant, i.e. 35% after 5 cycles.

conclusions

The obtained results show that the transport of the metal ions through SLMs and PIMs is comparable and indicate that phosphonium ionic liquids are mobile carriers to transfer Zn(II) and Fe(III) from the feed to the receiving phase. Generally, transport of metal ions across SLMs is faster than across PIMs. For SLM and PIM containing Cyphos IL 101 and Cyphos IL 167 as metal ion carrier over 80% of the initial amount of Zn(II) and Fe(III) is extracted, while in the case of Fe(II) this value is less than 40%. Cyphos IL 104 extracts Zn(II) and Fe(III) as good as IL 101 and IL 167 only across PIMs. It seems that the structure of the carrier used affects the metal transport efficiency. The obtained results showed that metal ion-Cyphos IL 101 and Cyphos IL 167 complexes may easier decompose at the interface of the membrane-receiving phase, thus, leading to higher values of transport parameters than for membranes containing Cyphos IL 104. The initial transport of the three metal ions is small, however, finally values of extraction efficiency and recovery factor are comparable both for PIMs and SLMs. On one hand, separation of Zn(II) and Fe(III) from Fe(II) is more effective in PIM systems. The separation effectiveness of Zn(II) with the phosphonium carriers in PIMs increases in the following order: Cyphos IL 104 < Cyphos IL 101 < Cyphos IL 167. On the other hand, SLMs work more stably in some consecutive steps of extraction-washing cycles. This means that depending on the needs that

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should be realized, i.e. separation of specific metal ions or processing in many cycles, one may choose PIMs or SLMs, respectively.

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Fig. 1. Structures of the phosphonium ionic liquids used as PIM carriers.

Cyphos IL 101,
Trihexyl(tetradecyl)phosphonium
chloride

Cyphos IL 104,
Trihexyl(tetradecyl)phosphonium
bis(2,4,4-trimethylpentyl)phosphinate

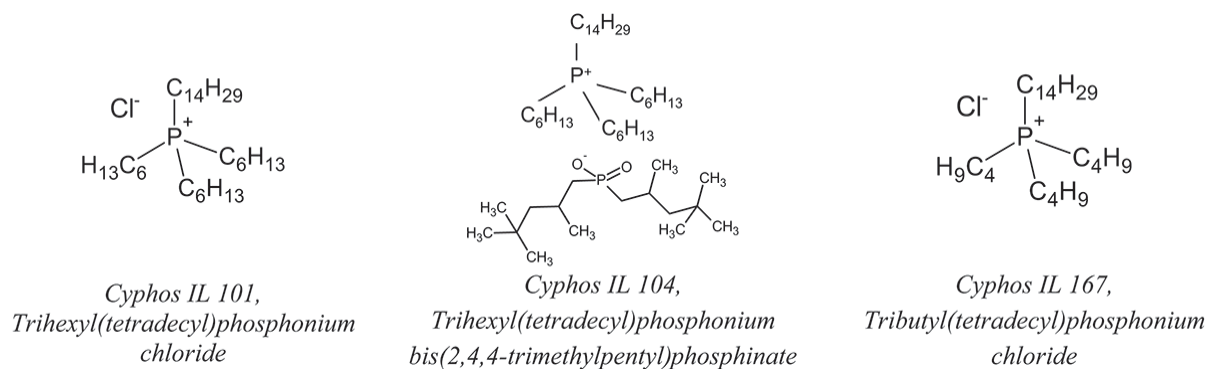*Cyphos IL 167,*
Tributyl(tetradecyl)phosphonium
chloride

Fig. 2. Schematic diagram of PIM system (1 – feed phase container, 2 – receiving phase container, 3 – peristaltic pump, 4 – membrane module – sandwich type).
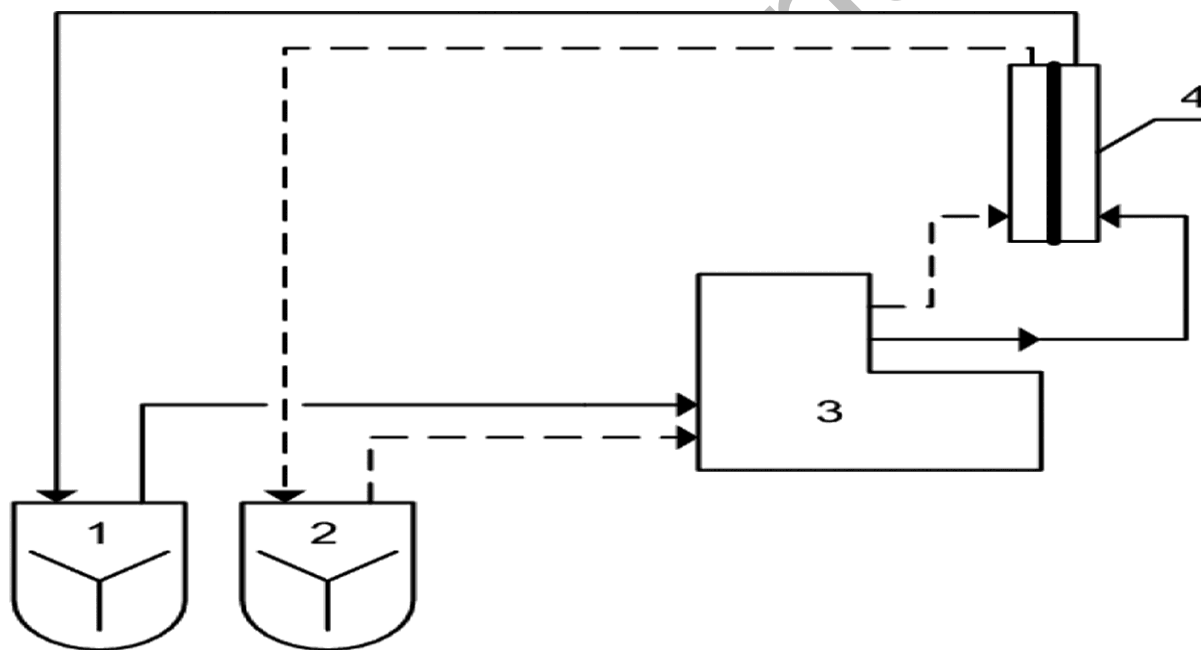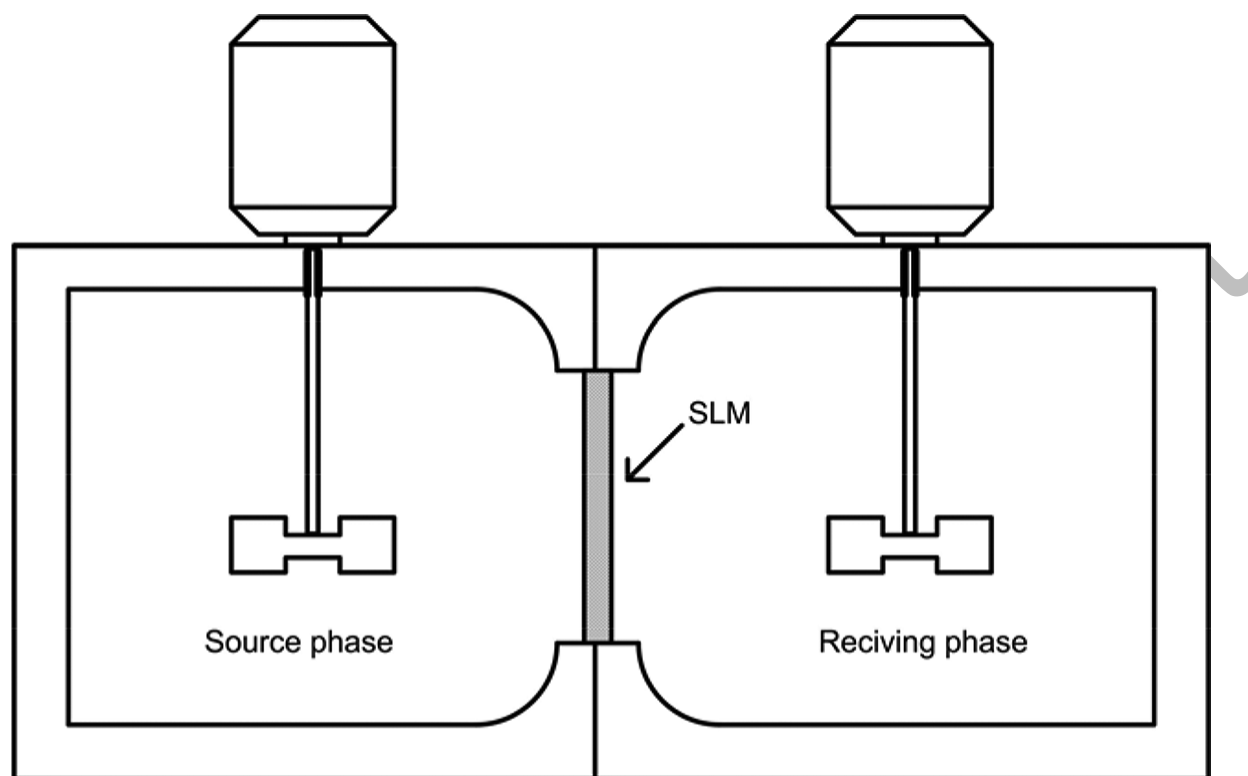
Fig. 3. Scheme of SLM system.

Fig. 4. Changes in concentration of (■) Zn(II), (●) Fe(II), (▲) Fe(III) ions over time in the feed and receiving phase through SLMs with Cyphos IL 101 as a carrier.
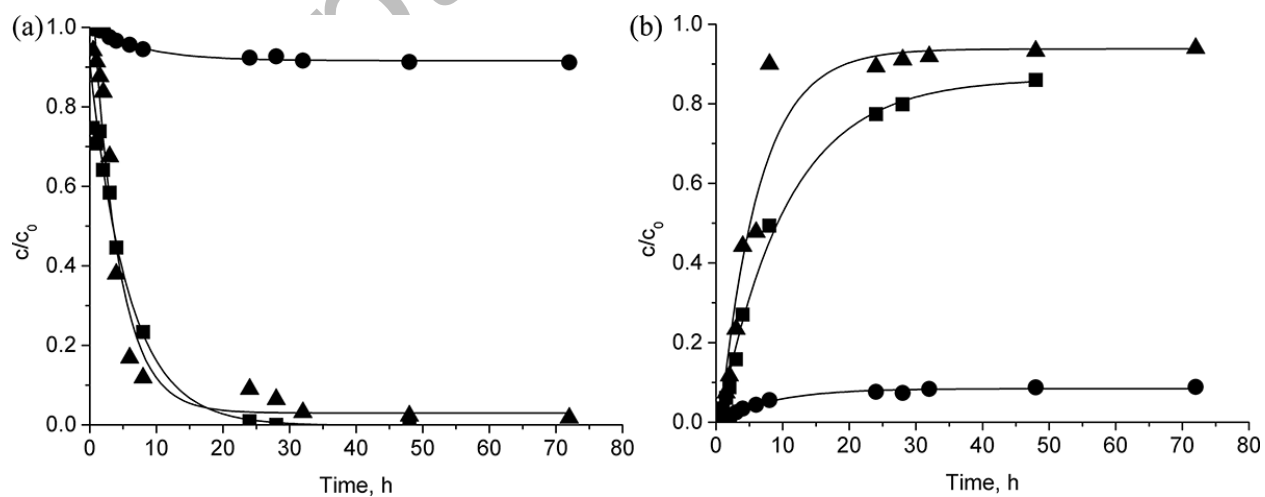
Fig. 5. Changes in concentration of (■) Zn(II), (●) Fe(II), (▲) Fe(III) ions over time in the feed and receiving phase through PIMs with Cyphos IL 101 as a carrier.
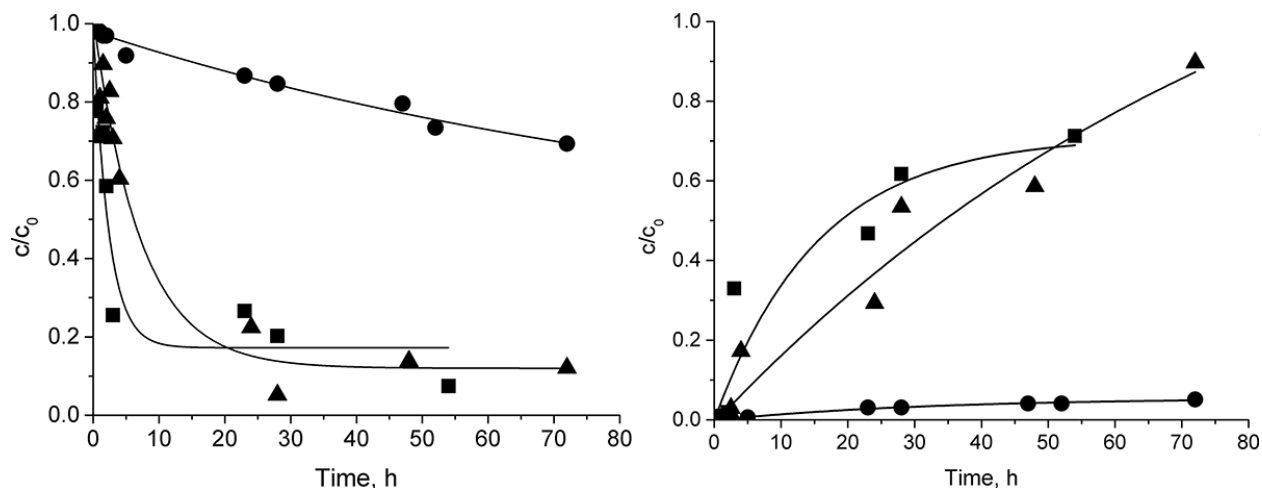

Fig. 6. The comparison of the values of extraction efficiency (a) and recovery factor (b) of Zn(II) (■), Fe(II) (///) and Fe(III) (□) through PIMs and SLMs.
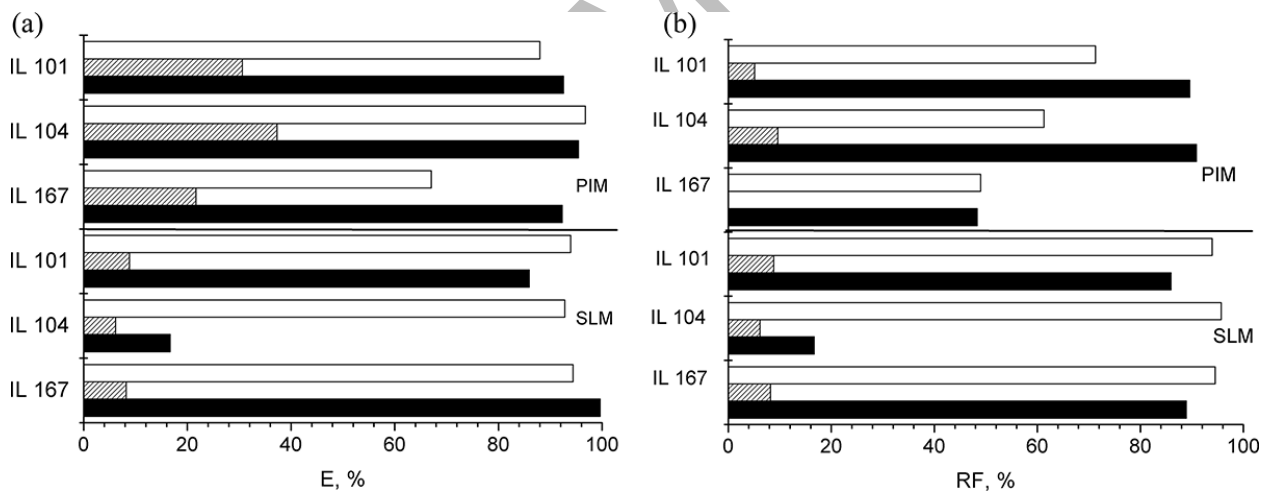

Fig. 7. Stability of a) PIM and b) SLM containing Cyphos IL 101 on Zn(II) transport; extraction efficiency (■), recovery factor (□).

Supplementary Data
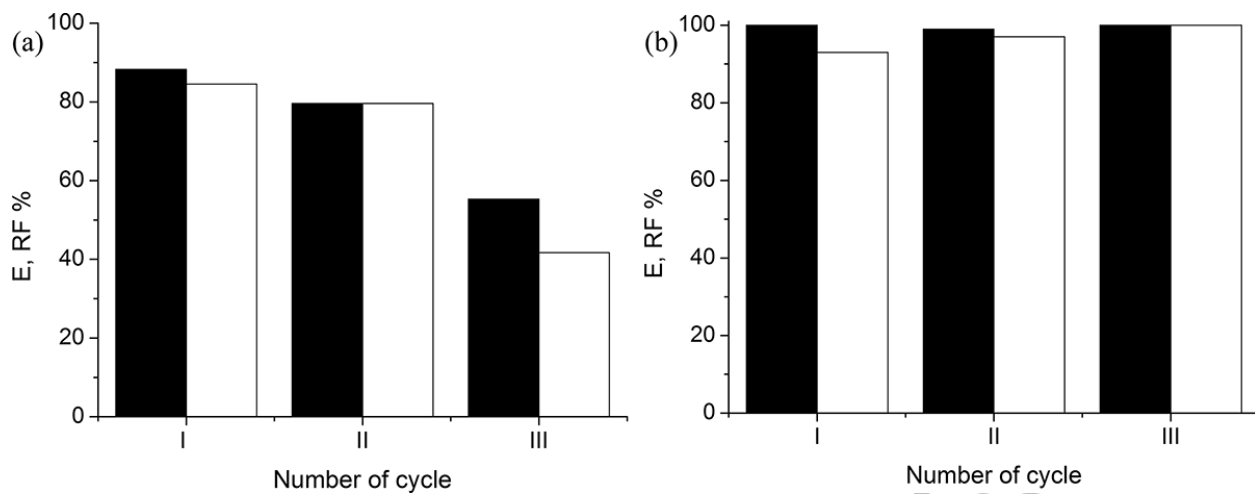
Table 1. Characteristic parameters of PIMs and SLMs applied for metal ion transport

Parameter	PIM	SLM
Polymer matrix/support	CTA	PVDF
Diameter, cm	7.0	4.5
Effective surface area, cm^2	15.9	11.4
Thickness, μm	~30	125
Porosity, %	-	75%
Pore size, μm	-	0.45

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Table 2. The comparison of parameters characterizing transport of Zn(II), Fe(II) and Fe(III) through SLMs and PIMs.

Carrier	$J_0 \cdot 10^6$, mol/s·m^2	$J_N \cdot 10^6$, mol/s·m^2	$P_F \cdot 10^6$, m/s	$P_R \cdot 10^6$, m/s
Zn(II)-PIM				
IL 101	13.7	3.3	9.5	0.27
IL 104	12.3	2.9	12.1	1.4
IL 167	41.0	9.8	18.7	0.84
Fe(II)-PIM				
IL 101	1.3	0.32	0.77	0.03
IL 104	11.0	2.6	4.6	0.05
IL 167	6.2	1.5	3.6	0

Fe(III)-PIM				
IL 101	6.5	1.6	6.3	1.3
IL 104	3.9	0.94	3.5	0.51
IL 167	3.8	0.91	2.4	0.3
Zn(II)-SLM				
IL 101	21.3	21.3	13.8	2.0
IL 104	0.16	0.16	0.11	0.11
IL 167	25.2	25.2	16.4	3.5
Fe(II)-SLM				
IL 101	0.47	0.47	0.26	0.26
IL 104	0.53	0.53	0.3	0.3

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IL 167	0.35	0.35	0.2	0.21
Fe(III)-SLM				
IL 101	8.3	8.3	4.7	2.2
IL 104	0.97	0.97	5.2	2.3
IL 167	6.7	6.7	3.8	0.33

Table 3. Separation of Zn(II), Fe(II) and Fe(III) with PIMs and SLMs.

Carrier	$S_{Zn(II)/Fe(II)}$	$S_{Zn(II)/Fe(III)}$	$S_{Fe(III)/Fe(II)}$
PIM			
IL 101	14	0.8	17
IL 104	9.4	1.5	6.4
IL 167	∞	1.0	∞
SLM			
IL 101	10	0.1	11
IL 104	3.4	0.02	18
IL 167	9	0.9	10

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Table 4. Composition of different PIMs and SLMs and their stability results.

Membrane composition			Stability	Ref.
Polymer	Plasticizer	Carrier		
CTA	NPOE	Aliquat 336 or D2EHPA	Very stable for 96 hours (12 cycles, 8 h each cycle)	(14)
CTA	NPOE	Aliquat 336 or D2EHPA	5% change in flux after 60 days	(15)
CTA	NPOE	Kelex 100	Very stable for 90 hours (15 cycles, 6 h each)	(16)
PVC	-	Cyphos IL 101	30% loss of weight after 26 days in water,	(19)
CTA	NPOE	Cyphos IL 104	2% loss of weight after 26 days in 5 M HCl	(24)
PVDF	Imidazolium ILs	Cyphos IL 104	18% decrease in permeability after 4 cycles (24 h each)	(40)
			30% decrease in permeablility after	

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			9 cycles	