

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Supported Ionic Liquid Membranes for Metal Separation

Pius Dore Ola and Michiaki Matsumoto

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/65754>

Abstract

Metals are widely used in various areas of human life, and their existence in the environment at high concentrations has become a cause for concern. Metals can enter the human body and disturb the human metabolic system. Therefore, research to recover metals from their matrix both from industrial wastewater and from ores or scraps containing metals is of great importance. One of the separation techniques proposed to overcome those issues involves using supported ionic liquid membranes (SILMs). This chapter summarizes the recovery of metals using SILM. In SILM, an ionic liquid that acts as an extractant is embedded in small pores of a polymer support. The latest type of physical impregnation of ionic liquid, which is the type most commonly used in metal separation, is called polymer inclusion membrane (PIM). PIMs were prepared by casting a solution containing an ionic liquid, a plasticizer and a base polymer to form a thin, flexible and stable film. A PIM including ionic liquids has a similar configuration to SILM, and it is considered to be a kind of SILM. In this chapter, effects on the stability and selectivity in SILM and PIM for metal separation are reviewed.

Keywords: liquid membrane, ionic liquid, metal, separation, supported membrane

1. Introduction

The separation of metals has become a hot topic of research in recent years. This is because metals are widely used in many aspects of human life, and their existence in the environment at high concentrations is a cause for concern. Although some metals are essential for the human body, their presence in high concentrations will disturb the human metabolic system. Therefore, research on recovering metals from their matrix both from industrial wastewater and from ores and ore scrap is of great importance. In hydrometallurgy, several conventional methods are being used to remove and recover heavy metals from aqueous solutions.

These methods include chemical precipitation [1], reverse osmosis [2], adsorption [3], ion exchange [4] and solvent extraction processes [5]. Those techniques have their own inherent limitations such as low efficiency, sensitive operation conditions, production of secondary sludge, high capital and operating costs, and expensive disposal [6]. Hence, more efficient and cost-effective removal and recovery methods are sought to overcome these problems.

One technique proposed to overcome those issues involves using supported ionic liquid membranes (SILMs). This technique is superior to the above techniques because the advantages of the liquid membrane and ionic liquid are included in the technique of SILM. The advantages of liquid membranes such as combining the extraction and stripping into a single step and using a very small amount of solvent give SILM very low capital and operating costs and make it easy to scale up. Using ionic liquid as an extractant in this technique increases the efficiency and selectivity of SILM. In addition, the very low vapour pressure and very high viscosity of ionic liquid give the best stability of the liquid membrane, which also absolutely affects the flux and selectivity and is environmentally friendlier.

The properties and applications of SILMs are greatly affected by support types, supporting methods and kind of ionic liquid used. The supporting method could be chemical or physical. The physical immobilization of an ionic liquid can be conducted through simple impregnation [7], sol-gel method [8], encapsulation [9], and so on. In chemical immobilization, the ionic liquid is bound to solid support via covalent bonding [10, 11]. The kind of ionic liquids determines the efficiency and selectivity of separation.

This chapter reviews use of supported ionic liquid membranes for separation of metals. At the beginning, it is important to briefly present a summary of supported liquid membrane using ionic liquid and metal separation using this method to ensure the better understanding regarding this topic. Then, we review several articles discussing the effect of related parameters such as type of solid support and supporting method as well as kind of ionic liquids on the stability of the membrane, efficiency and selectivity of metal separation.

2. Supported liquid membrane and ionic liquid

A membrane is a semipermeable barrier between two phases. If membranes are viewed as semipermeable phase separator, then the concept of membranes including solids as polymer or ceramic films can be extended to include liquids, and these are defined as liquid membranes (LMs). A liquid membrane system involves a liquid that is immiscible with the source (feed) and receiving (product) solutions and serves as a semipermeable and barrier between two liquid and gas phases [12]. Liquid membrane separation combines the solvent extraction and stripping (back-extraction) in a single step [13]. The great potential for energy saving, low capital and operating costs, and the possibility to use expensive extractants due to the small amount of the membrane phase make SLMs an area attracting the special attention of both researchers and practitioners.

The transport in a membrane is a dynamic and non-equilibrium process. The transporting compound dissolved in the feed aqueous solution has to dissolve in the organic, hydrophobic

membrane phase and diffuse through it to enter the aqueous stripping phase. Although it is possible to transport the hydrophobic compound through the hydrophilic membrane, this review concerns the transport of water-soluble compounds such as metal ions. The mass transfer in this system takes place due to the difference in the chemical potential across the membrane as a driving force.

According to the configuration definition, three groups of liquid membranes are usually considered as illustrated in **Figure 1**: bulk (BLM), supported or immobilized (SLM or ILM) and emulsion (ELM) liquid membrane transport [12]. A supported liquid membrane (SLM) is one of the three-phase liquid membrane systems in which the membrane phase (liquid) is held by capillary force in the pores of microporous polymeric and inorganic film. The immobilized liquid is a membrane phase, and a microporous film serves as a support for the membrane [13]. SLM was reported for the first time by Scholander [14], who used thin cellulose acetate filters impregnated with an aqueous haemoglobin for oxygen transport.

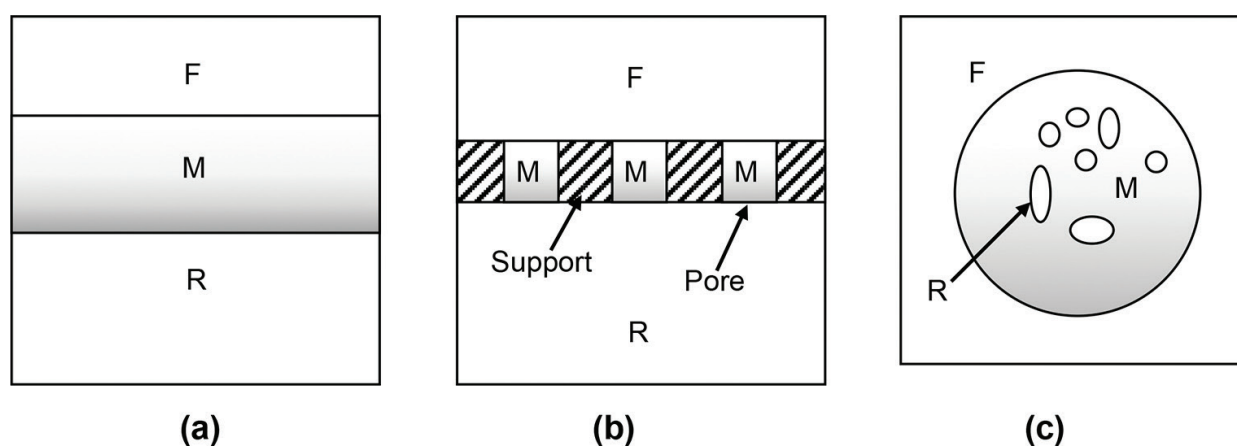
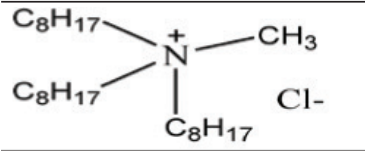
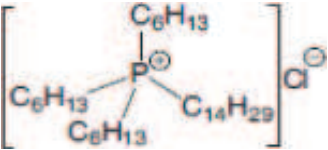
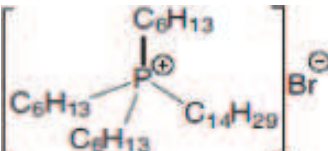
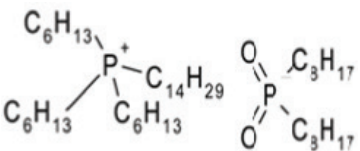


Figure 1. Liquid membranes: (a) bulk, (b) supported and (c) emulsion. (F: feed, M: membrane, R: receiving).

Successful applications of SLMs are possible due to their advantages compared to other separation methods. The main advantages of SLMs are the small amounts of organic phase and extractant (carrier) used, which allows for use of expensive extractants, one-step mass transfer, the possibility of achieving high separation factors, enrichment of extracted compound(s) during separation and low separation costs. Nevertheless, there are some problems limiting the practical application of SLMs. The main problem is the stability of the liquid membrane, caused by leakage and/or losses of membrane phase components during the transport process. Ionic liquids (ILs) come to solve the problem of membrane instability.

ILs are organic salts remaining as liquids under ambient temperatures. They normally consist of an organic cation (e.g. imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium) and inorganic anion (e.g. tetrafluoroborate, hexafluorophosphate, chloride) or, increasingly, an organic anion (e.g. trifluoromethylsulphonate, bis[(trifluoromethyl) sulphonyl] imide) [15]. The main advantages of these media are their near-zero vapour pressure, which means that they will not evaporate easily from the pores of membranes, have good chemical and thermal stability, and have a large temperature range where they are stable. They also

will not be replaced easily from the pores of the membrane due to their very high viscosity. The properties of ILs (hydrophobicity, viscosity, solubility, etc.), which can be varied by altering the substitutive group on the cation or the combined anion [16], make them more widely applicable in many physical and chemical fields. Therefore, they have been considered environmentally benign solvents as compared to volatile organic solvents. The structures of common ILs used in metal separation are shown in **Table 1**. Most ILs show the pronounced miscibility in the aqueous phases due to their polar nature. ILs have to be hydrophobic as shown in **Table 1** to extract the metal ions from the aqueous phases. For this reason, the ILs used in the metal separation were limited to those listed in **Table 1**.

Molecular structure	Product name Chemical name	Viscosity ^a cP	Water content ^b , wt %
	Aliquat-336 <i>N</i> -Methyl- <i>N,N</i> - <i>N</i> - <i>tri</i> octylammonium chloride	1450 (79.05) ^b	4.3 (20.3) ^b
	Cyphos IL-101 Trihexyl(tetradecyl) phosphonium chloride	1824 (95.8) ^b	0.67 (12.8) ^b
	Cyphos IL-102 Trihexyl(tetradecyl) phosphonium bromide	2094 (190.4) ^b	0.002 (6.1) ^b
	Cyphos IL-104 Trihexyltetradecylphosphonium bis-2,4,4-trimethylpentyl phosphinate	805.8	Not measured

^a25°C.

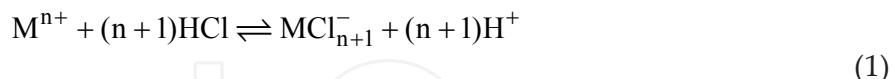
^bThese values were determined using water-saturated ionic liquid.

Table 1. Structures of common ILs used in metals separation.

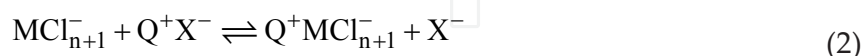
3. Metal separation using supported ionic liquid membrane (SILM)

An interesting field of application of supported ionic liquid membranes is the removal of metal ions from aqueous solutions. In this review, SLMs with IL as a metal carrier dissolved in the conventional organic solvent were excluded, and SLMs impregnated with IL or the mixture of IL and metal extractant in the absence of conventional solvents were discussed as SILM. In the SILMs impregnated with IL only, metals are slowed to be separated from their matrix if the metal ions are in the form of an anionic complex that reacts with the cation of

ionic liquid in the membrane. Aqueous solution of metal ions in hydrogen chloride was used as the feed phase in order to form the anionic metal complex, although other forms such as nitrate and sulphate were also used in several investigations. The reactions of metal ions (M^{n+}) and HCl to form the complex are as follows:



Furthermore, at the feed solution-membrane interface, the complex of MCl_{n+1}^{-} enters into the membrane because of the anion-exchange reaction with IL ($Q^{+}X^{-}$) in the membrane to form the metal complex $Q^{+}MCl_{n+1}^{-}$.



This complex diffuses through the membrane to the membrane-stripping solution interface. At the interface between the membrane and stripping solution of low chloride concentration (usually electrolyte solution such as sodium sulphate), the reverse reactions of above equations are proceeded to release the metal complex and to form free metal ion in the stripping phase. The transport of metal ion from the feed to the stripping phase by SILM is a coupled transport.

In other cases, the metal extractants were dissolved in IL instead of conventional organic solvent, and the membrane was impregnated with IL containing the extractant as a metal carrier. Permeation mechanism of the metal ions depends on the extractant included in the membrane.

3.1. Effect of solid support and preparation method on stability of membrane

3.1.1. Supported ionic liquid membrane

The stability of SILMs is greatly affected by the type and characteristic of solid support used to immobilize the IL as well as the preparation methods of the SILMs. When the SILMs will be used to separate the metals from the metal matrix, impregnated liquid with the conventional organic solvent in membrane can be released because of two factors: evaporation of the impregnated liquid due to high vapour pressure of volatile organic solvent and dissolving impregnated liquid both in the feed solution and in the stripping solution. Use of ILs with very low vapour pressure as the impregnated liquid resolved the first problem. On the other hand, dissolution of ILs to adjacent phases remains a problem that has to be solved. The stability of SILM is mainly affected by the properties of the support membrane and IL, and preparation method [17].

Several groups have prepared SILMs using many types of solid support as well as method of preparation for metal separation. The stability of the membranes yielded was further evaluated using several techniques. de los Ríos et al. [18] used nylon, a hydrophilic polyamide membrane, as a solid support to impregnate methyltrioctylammonium chloride. This membrane was used to transport Zn(II), Cd(II), Cu(II) and Fe(III). Physical impregnation was conducted by mixing the solid support and ionic liquid in an ultrafiltration unit and applying nitrogen pressure to force the ionic liquid to enter the pores of the solid support. The membrane

resulting from this process was still stable after 456 h with the percentage of retained ionic liquid ranging from 75 to 89%, and in most membranes was higher than 80%.

Polyvinylidene fluoride (PVDF) is another solid support commonly used to immobilize IL. Baba et al. [19] used this material to impregnate 1-octyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide ([C8mim][Tf2N]) containing N-N-dioctyldiglycol amic acid (DODGAA) to separate Dy(III) and Nd(III) in magnet scrap. The SEM micrograph after immersing PVDF in IL containing DODGAA showed that the porous structure of the liquid membrane appeared was well filled with [C8mim][Tf2N]. The membrane was proved to be stable during more than 140 h of operation.

The new material, which is probably a candidate for SILM, was successfully synthesized by Qian et al. [20]. Silica gel was used as a solid support to chemically bind tropine-type ionic liquid, which contained 10% of ionic liquid. Although tropine-type ionic liquid-modified silica has not been used in membrane permeation, there is a high probability to use it as an extractant in the membrane permeation of metals because it is not only stable below 200°C, but it also has 19.36 mg/g of adsorption capacity to the Cu(II) ion.

3.1.2. Polymer inclusion membrane

The most recent type of physical impregnation, which is also the type most commonly used in metal separation, is called polymer inclusion membrane (PIM) [21]. While SILMs were commonly prepared by immersing IL to the pore of the solid support, PIMs were prepared by casting a solution containing a carrier, a plasticizer and a base polymer such as cellulose triacetate (CTA), poly (vinyl chloride) (PVC) or PVDF to form a thin, flexible and stable film. In many cases, a plasticizer or modifier is additionally incorporated into the membrane preparation in order to improve the PIM flexibility and the compatibility between the membrane components. It should be noted that an IL acts not only as a carrier but also as a plasticizer. Therefore, in the PIM using IL as a carrier, plasticizers are sometimes not needed. A PIM including ILs has a similar configuration to SILM, and it is considered to be a kind of SILM. It is found that the PIM including ILs became more stable than conventional SILM [22].

PVC is a commonly used base polymer in the preparation of PIM. Stability studies of PVC-based PIM containing Aliquat 336 as a carrier have been conducted [23]. They found that the mass loss of the membrane is due to leaching Aliquat 336 from the membrane and is suppressed in the salt solutions. They concluded that, although PIMs are capable of losing some membrane liquid phase when exposed to aqueous solutions, this loss can be minimized or even eliminated by increasing the solution concentration of the counter anion of IL. It was found that membrane of Aliquat 336 content higher than 50% was soft and sticky and mechanically too weak to be used for the metal extraction [24].

Recently, Bonggotgetsakul et al. prepared PIM containing Cyphos IL-104 as a carrier using PVC support to extract Au(III) from a hydrochloric acid solution [25]. PIMs prepared with Cyphos IL-104 alone, or with the addition of the modifier 1-dodecanol, were homogeneous, transparent and flexible. Although the permeation rate with PIM including the modifier was

faster than that with IL alone, loss of 1-dodecanol from the newly developed PIM to the aqueous solutions in contact with it was observed.

CTA is the most commonly used polymer support. Regel-Rosocka et al. [26] prepared the PIM using CTA as a support and Cyphos IL 101 as carriers to remove Zn(II) and Fe(III) from chloride solution. Although the highest Zn(II) flux was obtained for membrane without plasticizer, with the highest Cyphos IL 101 content, the membranes with *o*-nitrophenyl octyl ether as a plasticizer have been selected because of their better mechanical properties. Thus, CTA-based PIM needed plasticizer to form stable and mechanically strong membrane. Gardner et al. [27] prepared a series of new cellulose-based PIMs. The ester linkages in the cellulose backbone of the polymer are susceptible to hydrolysis under extremes of pH, especially under alkaline conditions. The durability of the newly prepared PIMs against hydrolysis under alkaline and acidic conditions was evaluated. Durability increased with replacement of acetyl substitution on the cellulose polymer with propionyl or butyryl, while they also observed that ion transport across the membrane decreased as the alkyl chain lengths increased.

Studies were carried out to compare the use of CTA and PVC as base polymer of PIM with Aliquat 336 [28] and Cyphos IL 101 and 104 [29]. Under the optimum condition, in Cr (VI) permeation with PIM including Aliquat 336, the permeation rates of CTA- and PVC-based membranes were comparative, while in Zn (II) permeation with PIM including Cyphos IL 101 or 104, transport abilities of CTA-based membranes were much better than those of PVC. The CTA-based PIM lost 42% of efficiency after 6 days [28].

PVDF is one of the most commonly used solid supports for SILM. Guo et al. [30, 31] successfully prepared new PIM including PVDF as a base polymer, 1-alkyl-3-methylimidazolium hexafluorophosphate or tetrafluoroborate as ionic liquid plasticizers and Cyphos IL 104 and modified Aliquat 336 as a carrier and used this for transport of Cr(VI). The permeation rate with PIM including modified Aliquat 336/PVDF was faster than PIMs including Cyphos IL 104/PVDF or original Aliquat 336/PVC. After nine cycles, permeation rates of PIM composed of Cyphos IL 104/PVDF decreased to 69%, while it was found that the permeation rates of similar PIM composed of original Aliquat 336/CTA and modified Aliquat 336/PVDF decreased to 33 and 59% after six cycles, respectively. More recently, Bonggotgetsakul et al. prepared new PIM containing Cyphos IL-104 as a carrier and poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) as a base polymer to extract Au(III) from a hydrochloric acid solution [32]. PVDF-HFP was found to be an excellent base polymer because of its high hydrophobicity, excellent thermal and mechanical properties, higher stability in strong acids and better solubility in tetrahydrofuran used for preparing membrane casting solutions. Extraction performance of this PIM was decreased to about 70% after 2 h and until 8 h extraction performance remained at the same level.

Recently, polymer fibres using electrospinning method were successfully prepared for the metal extraction from the aqueous solutions [33–35]. Electrospinning is an innovative technique for the production of polymer fibres with diameter of less than a few micrometres, resulting in a large surface area-to-volume ratio and high porosity. A solution is first prepared by dissolving PVC and Aliquat 336 in the solvent. Then the solution is electrospun to produce the mats consisting of electrospun fibres. The role of Aliquat 336 in electrospun fibres differed from that in

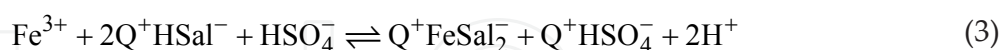
PIMs. Electrospun fibres were homogeneous and plasticized by Aliquat 336. On the other hand, PIMs composed of PVC and Aliquat 336 were visually transparent but were phase separated. Percolation threshold of electrospun fibrous mats was much lower than that of PIMs.

3.2. Effect of ionic liquid on metal separation

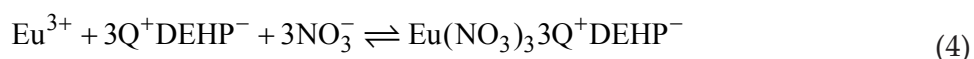
Separation of metal by ionic liquid-containing membrane is based on the chemical reaction between the ionic liquid and metal ion itself. Therefore, the efficiency and selectivity of metal separation are totally affected by the characteristic and type of ionic liquid in the membrane. This is because each ionic liquid has the specific affinity to the metallic ion as a result of the difference in functional groups bonded by an ionic liquid compound. Stojanovic et al. [36] summarized ammonium and phosphonium-based ionic liquids as shown in **Table 1** in the extraction process. This section will focus on the efficiency and selectivity of metal separation with ionic liquid itself and using supported ionic liquid membrane.

3.2.1. Quaternary ammonium salts

Quaternary ammonium salts as anion exchangers have been frequently used to extract metal ions and hence are only effective in the presence of strong anionic ligands as indicated in Eq. (1). It is known that Aliquat 336 dissolved in the organic solvent had the enhanced performance for the removal of metal ions from hydrochloric acid solutions compared to the alkyl amine extractants [37]. Sulphate [38] and thiocyanate [39] as ligands also have been used in the metal solvent extraction system using Aliquat 336. Generally, selectivity of anion exchange reactions is believed to be poor compared to that of chelating reaction. A further approach is to anchor different functional groups onto the anion [36]. By this, it is possible to combine the hydrophobicity of ammonium cation with the affinity of the functional group to desired metal ion. This enhances both efficiency and selectivity of the extractant. Aliquat 336 was modified by exchange the chloride anion of original Aliquat 336 (Q^+Cl^-) with a salicylate anion ($HSal^-$) for the extraction of Cu (II) and Fe (III) [40]. The following extraction reaction of Fe(III) was proposed.



Both extraction efficiency and selectivity of Fe (III) were enhanced compared to those of original one. And thiosalicylate-exchanged Aliquat 336 was reported to be selective to Cd (II) [41]. Aliquat 336-based ionic liquids containing bis(2-ethylhexyl)phosphate ($[DEHP]^-$) or bis(2-ethylhexyl)diglycolamate ($[DGA]^-$) anions were synthesized. The extraction of Eu (III) over Am (III) was studied, and superior extraction of Eu (III) and excellent separation factors were achieved [42]. The following extraction mechanism of Eu(III) with bis(2-ethylhexyl) phosphate-exchanged Aliquat 336 was proposed [43].



In this case, ion association mechanism was proposed instead of the anion exchange mechanism of Eq. (2) because both the Q^+ and $[DEHP]^-$ are involved in Eu(III) extraction. The molecular structures of counter-anions of Aliquat 336 described in this chapter are shown in **Figure 2**.

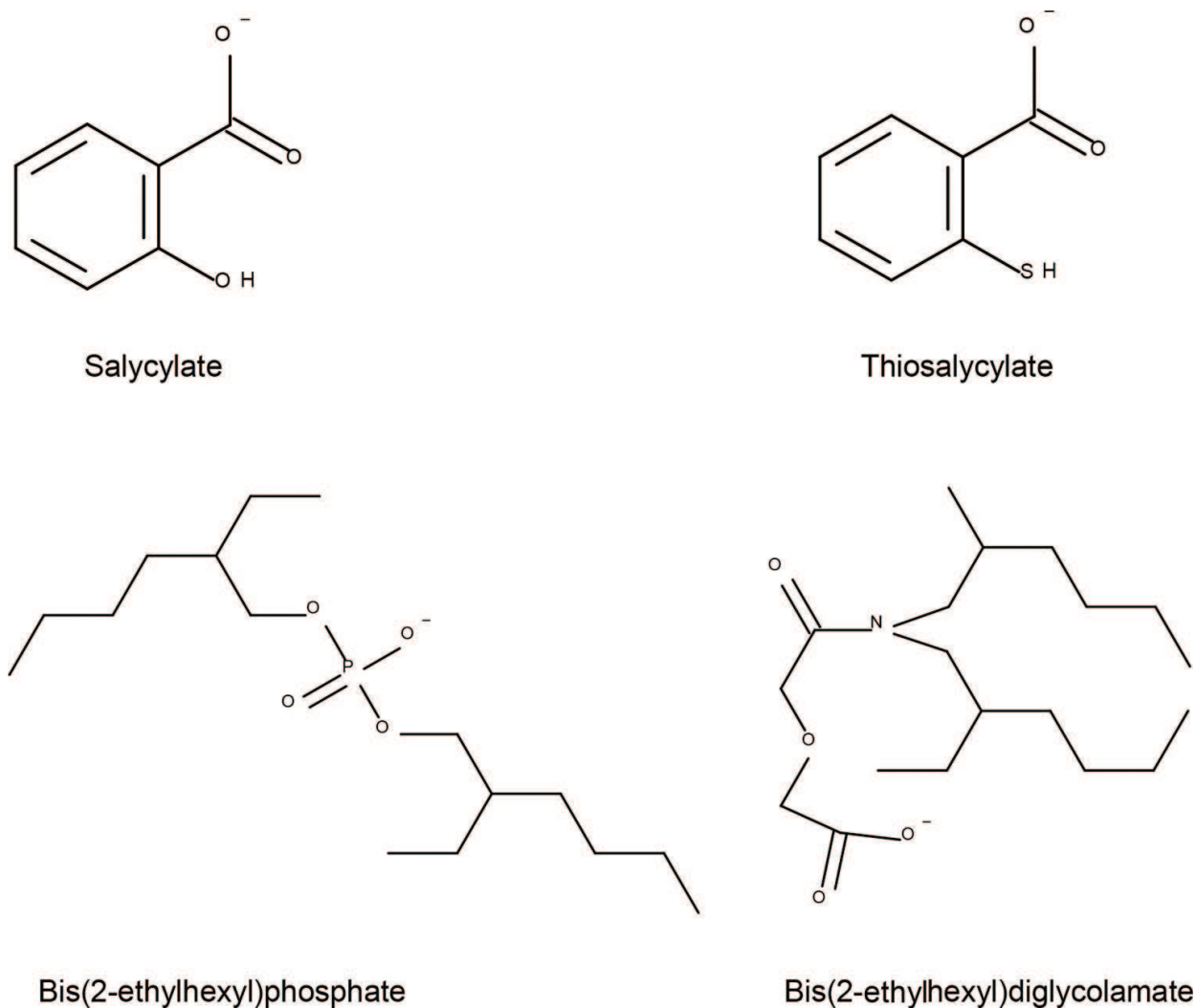


Figure 2. Molecular structures of anion part of modified Aliquat 336.

There are few examples of SILM using Aliquat 336 in the absence of diluents for metal separation. In most cases of SLM, Aliquat 336 was diluted in the organic solvent, and the membrane was impregnated with diluted Aliquat 336 solution.

de los Ríos et al. [18] studied metal separation with the SILM based on methyltrioctylammonium chloride, [MTOA⁺][Cl⁻]. In the solvent extraction, it was found that the ionic liquid [MTOA⁺][Cl⁻] allowed the almost complete removal of Zn(II), Cd(II), Fe(III) and Cu(II) from the aqueous solutions. To realize the selective permeation in SILM process, they examined the composition of the receiving solution. They found that Milli-Q water and Na₂CO₃ solution as the receiving solution allowed the recovery of Zn(II), Fe(III) while the use of NH₃ (6 M) allowed the recovery of Cd(II). These results indicate that high selectivity of metal separation can be reached by changing the receiving phase.

As described above, Aliquat 336 has been extensively applied as a carrier in PIM and used to extract different metal species (e.g. Co(II), Ni(II), Cd(II), Cu(II), Cr(VI), Au(III), As(V), Pd(II), Zn(II)) [21, 36]. Kebiche-Senhaji et al. [28] studied Cr(VI) transport from a mixture containing

Ni(II), Zn(II), Cd(II) and Cu(II) with the PIM based on Aliquat 336. Because Q_2CrO_4^- complex is predominant form in the membrane, in sulphate media, Ni(II), Zn(II), Cd(II) and Cu(II) were not formed anionic species, which is exchangeable with chloride ion on Aliquat 336. Therefore, Ni(II), Zn(II), Cd(II) and Cu(II) were not transported through the PIM, while Cr(VI) is transported with high efficiency. Pont et al. [44] studied Cd(II) transport with PIM containing Aliquat 336 from the chloride solution containing Ni(II). Although the reason of this selectivity is undescribed in the original paper, this may be because of difference in the stability constants of Cd(II) and Ni(II) of Eq. (1). Similar result was obtained for Cd(II) transport with PIM containing Aliquat 336 from the chloride solution containing Cu(II) [24].

Guo et al. [31] prepared a series of PIMs composed of anion-exchanged Aliquat 336 and used them for Cr(VI) permeation in the presence of Fe(III), Co(II), Cu(II) and Zn(II). These transition metals were not transported through the PIM composed Aliquat 336 exchanged with acidic phosphorus compounds, while Cr(VI) is selectively transported. Because the optimum pHs of extractions of these transition metal cations with these modified Aliquat 336 extractants were within a range around neutrality, under the acidic conditions, the extraction reactions of these transition metal ions did not proceed.

3.2.2. Phosphonium salts

Tetraalkylphosphonium salts like Cyphos IL 101, 102 and 104 listed in **Table 1** have recently been investigated as potential new IL extractants. Cyphos IL 101 diluted in organic solvent is extensively studied to extract metal ions such as Zn(II), Fe(III), Pd(II) and U(VI) [26, 45–48]. Cyphos IL 104 and 109 ((triethyl)tetradecylphosphonium bis(trifluoromethylsulphonyl) imide) are also used as the extractants for Zn(II), Fe(III), Cd(II), Cr(VI) and lanthanides [26, 49–51] and Au(III) [52].

Cyphos IL101 is diluted and used solely as the extractant, and many of the advantages using ILs are lost. Viscosity of pure Cyphos IL 101 is 24.69 Pa·s at 20°C, and it drops to 11.10 Pa·s by mixing with 1% water. Therefore, undiluted Cyphos IL 101 can be used as both extractant and diluents when contacting with aqueous phase [53]. Undiluted Cyphos IL 101 was used for extractions of Co(II), Fe(III) and rare earths [53–56]. Extraction mechanism of metal ions with undiluted Cyphos IL101 is same as that of Cyphos IL 101 diluted in organic solvent. Cholío-Gonzalez et al. employed Cyphos IL 101 as diluent and Cyanex 272 as extractant for separation of Co(II) and Ni(II) [57].

Unfortunately, there are no reports on metal separation with SILM with undiluted phosphonium-based ionic liquids. A number of reports on SLM described the use of diluted ionic liquids. Fe(III) and Zn(II) were transported through a PIM composed of Cyphos IL 101 and CTA or PVC [26, 58]. Sulphuric acid was found to be an effective stripping phase. Cr(VI) was removed from hydrochloric acid through a PIM composed of Cyphos IL 104 and PVDF to sodium hydroxide solution [30]. Pd(II) was permeated through a PIM composed of Cyphos IL 101, 102 or 104 and CTA [59]. The highest values of extraction efficiency were obtained for Cyphos IL 102 and 104 as IL and 3 M HCl as a receiving phase. The efficiency strongly depended on the type of carrier and the receiving phase. Separation of Cd(II) and Cu(II) from hydrochloric acid solution was conducted using PIMs composed of Cyphos IL 101 and 104,

and CTA [60]. High selectivity of Cd(II) over Cu(II) was obtained because of difference in the stability constants of Cd(II) and Cu(II) of Eq. (1). Gold (III) was successfully recovered from the hydrochloric acid solution through a PIM composed of Cyphos IL 104 and PVDF-HFP to sodium sulphite solution [32]. In the stripping process, Au(III) is reduced to Au(I), which forms a complex with the sulphite anion. Therefore, complete transport of Au(III) from the feed to the receiving solution even in the presence of other metal ions was realized.

4. Conclusion

In this chapter, we reviewed several articles discussing the effect of related parameters such as type of solid support and supporting method as well as kind of ILs on the stability of the conventional SILM and PIM, efficiency and selectivity of metal separation. Ammonium and phosphonium ILs have been used not only as the metal extractants and carriers but also as the diluents in the solvent extraction and the membrane separation processes. In gas/vapour separation, non-volatile nature of ILs should allow for significant improvement to current processes and the development of new approaches to gas/vapour separation, while in liquid separation, problems of instability of the membrane still seem to remain despite achieving considerable improvement compared with SLM using conventional organic solvent [61]. The physical dissolution of ILs to adjacent liquid phases is in principle inevitable. On this occasion, PIM will become an excellent alternative. Although it is expected to be the lower diffusivity in PIM than in SILM, this disadvantage can be easily offset by creating a much thinner membrane in comparison to its traditional SLM counterpart [62]. So far, base polymers used in PIMs were limited to CTA and PVC. Recently, new base polymers are developed for the metal separation in PIMs. Anion-exchanged ILs such as Aliquat 336 and Cyphos IL 101 had the different capacity and selectivity of metal extraction compared with the original ones. This is suggesting that design of task-specific ILs is important and possible.

Author details

Pius Dore Ola and Michiaki Matsumoto*

*Address all correspondence to: mmatsumo@mail.doshisha.ac.jp

Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Kyoto, Japan

References

- [1] Fu F., Xie L., Tang B., Wang Q., Jiang S. Application of a novel strategy-advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater. *Chemical Engineering Journal*. 2012;189–190:283–287. DOI: 10.1016/j.cej.2012.02.073

- [2] Lee K.P., Arnot T.C., Mattia D. A review of reverse osmosis membrane materials for desalination: Development to date and future potential. *Journal of Membrane Science*. 2011;**370**:1–22. DOI: 10.1016/j.memsci.2010.12.036
- [3] Lakherwar D. Adsorption of heavy metals: A review. *International Journal of Environmental Research and Development*. 2014;**4**:41–48.
- [4] Nikoloski A.N., Ang K. Review of the application of ion exchange resins for the recovery of platinum-group metals from hydrochloric acid solutions. *Mineral Processing and Extractive Metallurgy Review: An International Journal*. 2014;**35**:369–389. DOI: 10.1080/08827508.2013.764875
- [5] Xie F., Zhang T.A., Dresinger D., Doyle F. A critical review on solvent extraction of rare earths from aqueous solutions. *Minerals Engineering*. 2014;**56**:10–28. DOI: 10.1016/j.mineng.2013.10.021
- [6] Kurniawan T.A., Chan G.Y.S., Loa W., Babel S. Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*. 2006;**118**:83–98. DOI: 10.1016/j.cej.2006.01.015
- [7] Sun X., Ji Y., Chen J., Ma J. Solvent impregnated resin prepared using task-specific ionic liquids for rare earth separation. *Journal of Rare Earths*. 2009;**27**:932–936. DOI: 10.1016/S1002-0721(08)60365-8
- [8] Liu Y., Sun X., Luo F., Chen J. The preparation of sol-gel materials doped with ionic liquids and trialkyl phosphine oxides for yttrium(III) uptake. *Analytica Chimica Acta*. 2007;**604**:107–113. DOI: 10.1016/j.aca.2007.10.005
- [9] Guibala E., Figuerola Piñolab A., Ruizb M., Vincenta T., Jouannina C., Sastre A.M. Immobilization of cyphos ionic liquids in alginate capsules for Cd(II) sorption. *Separation Science and Technology*. 2010;**45**:1935–1949. DOI: 10.1080/01496395.2010.493113
- [10] Zhu L., Liu Y., Chen J. Synthesis of N-methylimidazolium functionalized strongly basic anion exchange resins for adsorption of Cr(VI). *Industrial and Engineering Chemistry Research*. 2009;**48**:3261–3267. DOI: 10.1021/ie801278f
- [11] Zhu L., Zhang C., Liu Y., Wang D., Chen J. Direct synthesis of ordered N-methylimidazolium functionalized mesoporous silica as highly efficient anion exchanger of Cr(VI). *Journal of Materials Chemistry*. 2010;**20**:1553–1559. DOI: 10.1039/B912345H
- [12] Kislik V.S. Introduction, General Description, Definitions, and Classification. Overview. In: Kislik V.S., editor. *Liquid Membranes*. 1st ed. Amsterdam: Elsevier; 2009. p. 1–15. DOI: 10.1016/B978-0-444-53218-3.00001-5
- [13] Dzygiel P., Wiczorek P.P. Supported Liquid Membranes and Their Modifications: Definition, Classification, Theory, Stability, Application and Perspectives. In: Kislik V.S., editor. *Liquid Membranes*. 1st ed. Amsterdam: Elsevier; 2009. p. 73–140. DOI: 10.1016/B978-0-444-53218-3.00003-9

- [14] Scolander P.F. Oxygen transport through hemoglobin solutions. *Science*. 1960;131:585–590. DOI: 10.1126/science.131.3400.585
- [15] Brennecke J.F., Maginn E.J. Ionic liquids: Innovative fluids for chemical processing. *AIChE Journal*. 2001;47:2384–2389. DOI: 10.1002/aic.690471102
- [16] Carlisle T.K., Bara J.E., Gabriel C.J., Noble R.D., Gin D.L. Interpretation of CO₂ solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach. *Industrial and Engineering Chemical Research*. 2008;47:7005–7012. DOI: 10.1021/ie8001217
- [17] Wang J., Luo J., Feng S., Li H., Wan Y., Zhang X. Recent development of ionic liquid membranes. *Green Energy and Environment*. 2016;1:43-61. DOI: 10.1016/j.gee.2016.05.002
- [18] de los Ríos A.P., Hernández-Fernández F.J., Lozano J.J., Sánchez-Segado S., Ginestá-Anzola A., Godínez C., Tomás-Alonso F., Quesada-Medina J. On the selective separation of metal ions from hydrochloride aqueous solution by pertraction through supported ionic liquid membranes. *Journal of Membrane Science*. 2013;444:469–481. DOI: 10.1016/j.memsci.2013.05.006
- [19] Baba Y., Kubota F., Kamiya N., Goto M. Selective recovery of dysprosium and neodymium ions by a supported liquid membrane based on ionic liquids. *Solvent Extraction Research and Development, Japan*. 2011;18:193–198. DOI: 10.15261/serdj.18.193
- [20] Qian G., Song H., Yao S. Immobilized chiral tropine ionic liquid on silica gel as adsorbent for separation of metal ions and racemic amino acids. *Journal of Chromatography A*. 2016;1429:127–133. DOI: 10.1016/j.chroma.2015.11.083
- [21] Almeida M.I.G.S., Cattrall R.W., Kolev S.D. Recent trends in extraction and transport of metal ions using polymer inclusion membranes (PIMs). *Journal of Membrane Science*. 2012;415–416:9–23. DOI: 10.1016/j.memsci.2012.06.006
- [22] Matsumoto M., Murakami Y., Minamidate Y., Kondo K. Separation of lactic acid through polymer inclusion membranes containing ionic liquids. *Separation Science and Technology*. 2012;47:354–359. DOI: 10.1080/01496395.2011.620582
- [23] Kagaya S., Ryokan Y., Cattrall R.W., Kolev S.D. Stability studies of poly (vinyl chloride)-based polymer inclusion membranes containing Aliquat 336 as a carrier. *Separation and Purification Technology*. 2012;101:69–75. DOI: 10.1016/j.seppur.2012.09.007
- [24] Wang L., Paimin R., Cattrall R.W., Shen W., Kolev S.D. The extraction of cadmium(II) and copper(II) from hydrochloric acid solutions using an Aliquat 336/PVC membrane. *Journal of Membrane Science*. 2000;176:105–111. DOI: 10.1016/S0376-7388(00)00436-1
- [25] Bonggotgetsakul Y.Y.N., Cattral R.W., Kolev S.D. Extraction of gold(III) from hydrochloric acid solutions with a PVC-based polymer inclusion membrane (PIM) containing Cyphos® IL 104. *Membranes*. 2015;5:903–914. DOI: 10.3390/membranes5040903

- [26] Regel-Rosocka M., Nowak Ł., Wiśniewski M. Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids. *Separation and Purification Technology*. 2012;97:158–163. DOI: 10.1016/j.seppur.2012.01.035
- [27] Gardner J.S., Walker J.O., Lamb J.B. Permeability and durability effects of cellulose polymer variation in polymer inclusion membranes. *Journal of Membrane Science*. 2004;229:87–93. DOI: 10.1016/j.memsci.2003.09.017
- [28] Kebiche-Senhadjia O., Tingry S., Seta P., Benamor M. Selective extraction of Cr(VI) over metallic species by polymer inclusion membrane (PIM) using anion (Aliquat 336) as carrier. *Desalination*. 2010;258:59–65. DOI: 10.1016/j.desal.2010.03.047
- [29] Baczyńska M., Regel-Rosocka M., Nowicki M., Wiśniewski M. Effect of the structure of polymer inclusion membranes on Zn(II) transport from chloride aqueous solutions. *Journal of Applied Polymer Science*. 2015;132:42319. DOI: 10.1002/app.42319
- [30] Guo L., Liu Y., Zhang C., Chen J. Preparation of PVDF-based polymer inclusion membrane using ionic liquid plasticizer and Cyphos IL 104 carrier for Cr(VI) transport. *Journal of Membrane Science*. 2011;372:314–321. DOI: 10.1016/j.memsci.2011.02.014
- [31] Guo L., Zhang J., Zhang D., Liu Y., Deng Y., Chen J. Preparation of poly(vinylidene fluoride-co-tetrafluoroethylene)-based polymer inclusion membrane using bifunctional ionic liquid extractant for Cr(VI) transport. *Industrial and Engineering Chemistry Research*. 2012;51:2714–2722. DOI: 10.1021/ie201824s
- [32] Bonggotgetsakul Y.Y.N., Cattral R.W.L., Kolev S.D. Recovery of gold from aqua regia digested electronic scrap using a poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) based polymer inclusion membrane (PIM) containing Cyphos® IL 104. *Journal of Membrane Science*. 2016;514:274–281. DOI: 10.1016/j.memsci.2016.05.002
- [33] Truong Y.H., Kyrtzis I.L., Shen W. Fabrication and characterization of electrospun PVDF-aliquat 336 fibre membrane for removal of cadmium from hydrochloric acid solutions. *Journal of Materials Science*. 2009;44:1101–1106. DOI: 10.1007/s10853-008-3208-7
- [34] Wong L., Shen W., Truong Y.B. Investigation of electrospun and film-cast PVC membranes incorporated with aliquat 336 for efficient Cd extraction: A comparative study. *Journal of Applied Polymer Science*. 2011;121:327–335. DOI: 10.1002/app.33586
- [35] Abdul-Halim N.S., Whitten P.G., Nghiem L.D. Characteristics and cadmium extraction performance of PVC/Aliquat 336 electrospun fibres in comparison with polymer inclusion membranes. *Separation Science and Technology*. 2016;51:1515–1522. DOI: 10.1080/01496395.2016.1168439
- [36] Stojanovic A., Morgenbesser C., Kogelnig D., Krachler R., Keppler B.K. Quaternary Ammonium and Phosphonium Ionic Liquids in Chemical and Environmental Engineering. In: Kokorin A., editor. *Ionic Liquids: Theory, Properties, New Approaches*. Rijeka: InTech; 2011. p. 657–680.
- [37] Seeley F.G., Crouse D.J. Extraction of metals from chloride solutions and amines. *Journal of Chemical Engineering Data*. 1966;11:424–429. DOI: 10.1021/je60030a043

- [38] Nayl A.A. Extraction and separation of Co (II) and Ni (II) from acidic sulfate solutions using Aliquat 336. *Journal of Hazardous Materials*. 2010;173:223–230. DOI: 10.1016/j.jhazmat.2009.08.072
- [39] McDonald C., Alfaro-Franco C.M. Solvent extraction studies of cobalt in aqueous thiocyanate solutions using Aliquat-336. *Microchemical Journal*. 1984;30:194–200. DOI: 10.1016/0026-265X(84)90041-9
- [40] Egorov V.M., Djigailo D.I., Momotenko D.S., Chernyshov D.V., Torocheshnikova I.I., Smirnova S.V., Pletnev I.V. Task-specific ionic liquid trioctylmethylammonium salicylate as extraction solvent for transition metal ions. *Talanta*. 2010;80:1177–1182. DOI: 10.1016/j.talanta.2009.09.003
- [41] Kogelnig D., Stjanovic A., Galanski M., Grössl M., Jirsa F., Krachler R., Keppler B.K. Greener synthesis of new ammonium ionic liquids and their potential as extracting agents. *Tetrahedron Letters*. 2008;49:2782–2785. DOI: 10.1016/j.tetlet.2008.02.138
- [42] Rout A., Venkatesan K.A., Srinivasan T.G., Vasudeva Rao P.R. Ionic liquid extractants in molecular diluents: Extraction behavior of europium (III) in quaternary ammonium-based ionic liquids. *Separation and Purification Technology*. 2012;95:26–31. DOI: 10.1016/j.seppur.2012.04.020
- [43] Sun X., Ji Y., Hu F., He B., Chen J., Li D. The inner synergistic effect of bifunctional ionic liquid extractant for solvent extraction. *Talanta*. 2010;81:1877–1883. DOI: 10.1016/j.talanta.2010.03.041
- [44] Pont N., Salvadó V., Fontàs C. Selective transport and removal of Cd from chloride solutions by polymer inclusion membrane. *Journal of Membrane Science*. 2008;318:340–345. DOI:10.1016/j.memsci.2008.02.05
- [45] Regel-Rosocka M. Extractive removal of zinc(II) from chloride liquors with phosphonium ionic liquids/toluene mixtures as novel extractants. *Separation and Purification Technology*. 2009;66:19–24. DOI: 10.1016/j.seppur.2008.12.002
- [46] Kogelnig D., Stojanovic A., Jirsa F., Korner W., Krachler R., Keppler B.K. Transport and separation of iron(III) from nickel(II) with the ionic liquid trihexyl(tetradecyl)phosphonium chloride. *Separation and Purification Technology*. 2010;72:56–60. DOI: 10.1016/j.seppur.2009.12.028
- [47] Cieszyńska A., Wisniewski M. Extraction of palladium(II) from chloride solutions with Cyphos®IL 101/toluene mixtures as novel extractant. *Separation and Purification Technology*. 2010;73:202–207. DOI: 10.1016/j.seppur.2010.04.001
- [48] Quinn J.E., Ogden M.D., Soldenhoff K. Solvent extraction of uranium (VI) from chloride solutions using Cyphos IL-101. *Solvent Extraction and Ion Exchange*. 2013;31:538–549. DOI: 10.1080/07366299.2013.775891
- [49] Comesaña A., Rodríguez-Monsalve J., Cerpa A., Alguacil F.J. Non-dispersive solvent extraction with strip dispersion (NDSXSD) pertraction of Cd(II) in HCl medium

- using ionic liquid CYPHOS IL101. *Chemical Engineering Journal*. 2011;175:228–232. DOI: 10.1016/j.cej.2011.09.099
- [50] Alguacil F.J., Alonso M., Lopez F.A., Lopez-Delgado A. Pseudo-emulsion membrane strip dispersion (PEMSD) pertraction of chromium(VI) using CYPHOS IL 101 ionic liquid as carrier. *Environmental Science and Technology*. 2010;44:7504–7508. DOI: 10.1021/es101302b
- [51] Kumari A., Sinha M.K., Sahu S.K., Pandey B.D. Solvent extraction and separation of trivalent lanthanides using Cyphos IL 104, A novel phosphonium ionic liquid as extractant. *Solvent Extraction and Ion Exchange*. 2016;34:469–484. DOI: 10.1080/07366299.2016.1207459
- [52] Nguyen V.T., Lee J., Jeong J., Kim B., Cote G., Chagnes A. Extraction of gold(III) from acidic chloride media using phosphonium-based ionic liquid as an anion exchanger. *Industrial and Engineering Chemistry Research*. 2015;54:1350–1358. DOI: 10.1021/ie5045742
- [53] Cui L., Cheng F., Zhou J. Behaviors and mechanism of iron extraction from chloride solutions using undiluted Cyphos IL 101. *Industrial and Engineering Chemistry Research*. 2015;54:7534–7542. DOI: 10.1021/acs.iecr.5b01546]
- [54] Hoogerstraete T.V., Wellens S., Verachtera K., Binnemans K. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: Separations relevant to rare-earth magnet recycling. *Green Chemistry*. 2013;15:919–927. DOI: 10.1039/C3GC40198G
- [55] Wellens S., Thijs B., Binnemans K. An environmentally friendlier approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids. *Green Chemistry*. 2012;14:1657–1665. DOI: 10.1039/C2GC35246J
- [56] Wellens S., Goovaerts R., Möller C., Luyten J., Thijs B., Binnemans K. A continuous ionic liquid extraction process for the separation of cobalt from nickel. *Green Chemistry*. 2013;15:3160–3164. DOI: 10.1039/C3GC41519H
- [57] Cholio-Gonzalez D., Chagnes A., Cote G., Avila-Rodriguez M. Separation of Co(II) and Ni(II) from aqueous solutions by bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) using trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) as solvent. *Journal of Molecular Liquids*. 2015;209:203–208. DOI: 10.1016/j.molliq.2015.05.048
- [58] Kogelnig D., Regelsberger A., Stojanovic A., Jirsa F., Krachler R., Keppler B.K. A polymer inclusion membrane based on the ionic liquid trihexyl(tetradecyl)phosphonium chloride and PVC for solid-liquid extraction of Zn(II) from hydrochloric acid solution. *Monatshefte für Chemie*. 2011;142:769–772. DOI: 10.1007/s00706-011-0530-6
- [59] Regel-Rosocka M., Rzelewska M., Baczynska M., Janus M., Wisniewski M. Removal of palladium (II) from aqueous solutions with Cyphos phosphonium ionic liquids as metal ion carriers for liquid-liquid extraction and transport across polymer inclusion membranes. *Physicochemical Problems of Mineral Processing*. 2015;51:621–631.

- [60] Pospiech B. Application of phosphonium ionic liquids as ion carriers in polymer inclusion membranes (PIMs) for separation of cadmium(II) and copper(II) from aqueous solutions. *Journal of Solution Chemistry*. 2015;44:2431–2447. DOI: 10.1007/s10953-015-0413-2
- [61] Matsumoto M. Ionic Liquid-Based Support Liquid Membranes. In: Mohanty K., Purkait M.K., editors. *Membrane Technologies and Applications*. Boca Raton: CRC Press; 2012. p. 305–316. DOI: 10.1201/b11416-18
- [62] Nghiem L.D., Mornane P., Potter I.D., Perera J.M., Catrall R.W., Kolev S.D. Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs). *Journal of Membrane Science*. 2006;281:7–41. DOI: 10.1016/j.memsci.2006.03.035

IntechOpen

