

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

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Abstract Extraction of Zn(II) from aqueous solution using polymer inclusion membranes based on poly(vinyl chloride) containing the phosphonium-based ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos[®] IL 101) is described. Zn(II) could efficiently be extracted from 5 M hydrochloric acid solution with membranes containing 30 wt% Cyphos IL 101, whereas back-extraction was successfully achieved with 1 M sulfuric acid. Prepared membranes were evaluated in terms of stability in air as well as in terms of leaching of the ionic liquid from the membranes in aqueous solution.

Keywords Ionic liquids · Heavy metals · Membranes · Phosphonium compounds · Zn(II) removal

Introduction

The characterization of ionic liquids (ILs) as salts with melting point below the boiling point of water is nowadays a generally accepted definition [1]. This class of organic compounds has attracted intense attention in several fields of chemical and environmental engineering [1, 2]. In particular, evaluation of hydrophobic room-temperature liquid salts as potential extracting agents for removal of heavy metals from aqueous solutions is a fast-growing field [3]. Due to the apparently endless possibilities to combine cations and anions, it is not surprising that several metal-extracting ILs have already found their way from

laboratory to industrial scale; for example, an IL based on the trioctylmethylammonium cation with thiosalicylate as anion, prepared via a halide-free synthesis route, is commercially available and has effectively been evaluated as an extracting agent for several heavy metals [4, 5]. Another commercially available phosphonium-based liquid salt, trihexyl(tetradecyl)phosphonium chloride (Cyphos[®] IL 101), has only recently been investigated as a potential new IL extracting agent dissolved in toluene for elimination of zinc and palladium from aqueous phases [6, 7]. As it is well known that Zn(II) forms chloro complexes depending on the chloride concentration as well as the acidity of the aqueous feed [8], Regel-Rosocka [6] could extract Zn(II) successfully with Cyphos IL 101 from hydrochloric acid solutions. It was assumed that, under acidic conditions, the species ZnCl_4^{2-} was exchanged with the chloride anion of Cyphos IL 101.

To avoid use of solvents for implementation of often viscous ILs as extracting agents and to increase their stability in terms of leaching or product recovery, the concept of polymer inclusion membranes (PIMs) has attracted great interest in recent years [9]. PIMs consist of a high-molecular-weight polymer to provide mechanical strength, a plasticizer to provide elasticity, and a carrier molecule to facilitate selective transport of the analytes. Poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) are the most commonly used polymers for preparation of PIMs, since they are able to embed carrier molecules and inhibit their leaching; for example, Kolev et al. [10] successfully prepared PIMs based on PVC with di(2-ethylhexyl)phosphoric acid (D2EHPA) for efficient and selective transport of Zn(II) from a pH 3.0 source phase to a HCl receiving phase. Recently, Nowak et al. [11] embedded IL Cyphos IL 101 as carrier for Zn(II) using CTA as polymeric matrix and *o*-nitrophenyl octyl ether as plasticizer. However,

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Rahman and coworkers have shown that ILs could also be used as stable plasticizer for PIMs based on PVC [12], indicating that these salts can act as both carrier and plasticizer.

Within our work we wanted to combine the properties of Cyphos IL 101 as heavy-metal extracting agent and stabilizer as well as PVC as a stable solid support. In this report we present and discuss the first results of Cyphos IL 101 embedded in a PVC membrane as a potential new solid extracting agent for extraction of Zn(II) from aqueous solutions.

Results and discussion

Several membranes based on poly(vinyl chloride) and varying amounts of the ionic liquid (IL) trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101; 0, 20, 30, and 40 wt%) were prepared using a solvent casting method. Generally, all membranes appeared transparent but became more flexible with increasing IL content. This is not surprising, as the plasticizing effect of Cyphos IL 101 on PVC is already known. Rahman et al. [12] showed that PVC film containing 20 wt% Cyphos IL 101 had lower glass-transition temperature (T_g) than bulk PVC by more than 60 °C, as well as lower elastic modulus and increased elongation at breakage. However, our prepared membranes containing 40 wt% IL turned out to be already too sticky and difficult to handle. Within this report we therefore focus on a membrane containing 30 wt% Cyphos IL 101, as this membrane was convenient to handle, as well as an unplasticized membrane (0 wt% IL) as reference.

Immediately after peeling off the membranes from the Petri dishes, their weight stability in air at room temperature (25 ± 2 °C) was investigated over several days. It can be seen from Fig. 1a that the weight loss of a 30 wt% plasticized membrane reached a maximum of about 0.5% after 5 days. In contrast, the unplasticized membrane lost around 3% weight, reaching this maximum after 40 days.

It is obvious that the evaporation of THF from an unplasticized membrane at room temperature and

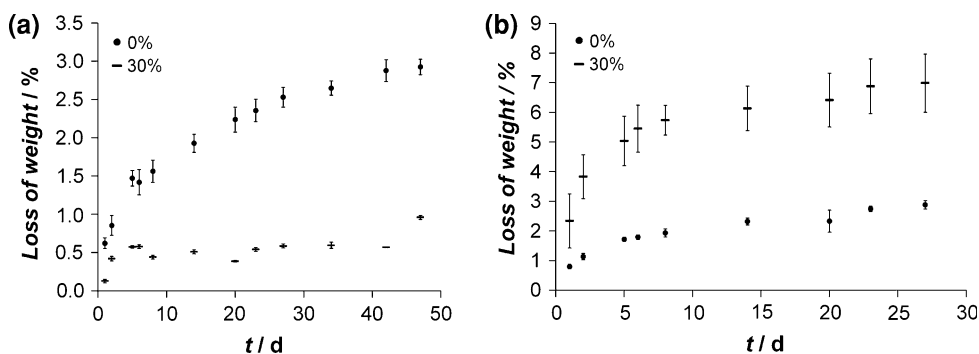
atmospheric pressure is not complete overnight but needs more than 40 days. More interestingly, the weight loss of the membrane containing 30 wt% Cyphos IL 101 was much lower. It is not clear at the moment if the solvent THF is “retained” in the membrane (maybe due to specific interactions between IL and THF) or if THF is “displaced” by incorporation of IL during the preparation. This issue will certainly be an interesting point for further investigation.

Additionally, it can be seen from Fig. 1a that measured values of the 30 wt% membrane are fluctuating. Cyphos IL 101 is a hygroscopic IL, and we therefore assumed that this fluctuation may be due to uptake of air moisture during measurement of the membranes. Indeed, simply adding wet pulp (paper) to the membrane containing capsules increased the weight of the 30 wt% plasticized membrane to 2%, indicating the hygroscopicity of the embedded IL.

To investigate the stability of PVC membranes in terms of the amount of leaching of IL in aqueous solutions, an unplasticized membrane and a 30 wt% Cyphos IL 101 plasticized membrane were stirred in ultrapure water over a period of 27 days at room temperature (25 ± 2 °C). From Fig. 1b it can be seen that the unplasticized membrane lost about 3% weight after 27 days in water. This is comparable to the weight loss of the unplasticized membrane at room temperature in air after 40 days (Fig. 1a), indicating the loss of the solvent THF. However, the weight loss of the 30 wt% plasticized membrane reached a maximum of 7% after 27 days. Compared with the weight loss of this membrane in air (Fig. 1a), this is about 6.5 percentage points more, indicating significant leaching of the IL into water. We can explain this in terms of a distinct miscibility of Cyphos IL 101 with water as well as secondary bonding effects between PVC chains and the IL [12]. Once the outer layers of IL are removed, secondary bonding effects between PVC chains should become dominant and prevent leaching of the IL, as was recently shown for a PVC membrane containing 20 wt% Cyphos IL 101, which lost more than 20% of plasticizer in water after 10 days at 50 °C [12].

Furthermore, the leaching behavior of prepared IL-PVC membranes in 5 M hydrochloric acid solution, as a suitable

Fig. 1 Weight loss of PVC membranes in **a** air and **b** ultrapure water (25 ± 2 °C, atmospheric pressure; circles 0 wt% Cyphos IL 101 membrane, squares 30 wt% Cyphos IL 101 membrane; $n = 3$, whiskers = standard deviation)



medium for extraction of zinc, was determined. Whereas the unplasticized membrane lost around 5% weight after 26 days, the 30 wt% membrane showed an increase in weight of up to 2%. However, when waiting for 50 min before weighing the membrane, there was no significant decrease or increase of weight of the membrane compared with the beginning of the experiment, indicating that no significant leaching of Cyphos IL 101 occurred in 5 M HCl. The weight increase can be explained by the hygroscopicity of the IL embedded in the membrane. Our leaching results are also strengthened by the results of Argiropoulos et al. [13], who found weight loss of 33% of a 30 wt% Aliquat® 336-PVC composition in distilled water compared with a loss of only around 3% in 2.5 M HCl.

Based on the results obtained from the stability experiments, we evaluated our prepared PIMs based on Cyphos IL 101 for solid-liquid extraction of Zn(II) from aqueous solutions. In the first extraction experiments, the Zn(II)-containing aqueous phase was ultrapure water. As expected, no Zn(II) extraction occurred with membrane containing 30 wt% Cyphos IL 101 with total area of 12.6 cm², as no neutral Zn(II) chloro complexes nor negative anionic chloride complexes were available in the solution. However, when changing to 5 M HCl solution, we observed extraction of Zn(II) (Fig. 2a).

Whereas the unplasticized membrane did not remove any Zn(II) at all, a maximum of 5 mg Zn(II)/g membrane (or 13.3 mg Zn(II)/g Cyphos IL 101) could be removed after 145 h. In 5 M HCl solution, the Zn(II) chemical species is mainly ZnCl₄²⁻ and ZnCl₃⁻, with ZnCl₄²⁻ being the dominant species [8]. We can therefore assume that exchange of ZnCl₄²⁻ species with the chloride anions of Cyphos IL 101 occurred. As we have shown that Cyphos IL 101-PVC membranes can be kept in 5 M HCl solution without leaching, we left freshly prepared PVC membranes containing 30 wt% IL in 5 M HCl for 40 days prior to extraction experiments to compare the efficiency of “pre-equilibrated” membranes with membranes evaluated

directly after preparation. As expected, the extraction efficiency of these pre-equilibrated membranes did not differ significantly. In contrast, when pre-equilibrating membranes in pure water, the extraction efficiency of the 30 wt% Cyphos IL 101 membrane decreased significantly, as depicted in Fig. 2a. This can be explained by the fact that, during pre-equilibration of membranes in water, a significant amount of IL was lost due to leaching.

As we wanted to elucidate whether quantitative extraction is possible, we increased the area of the Cyphos IL 101-PVC membrane and decreased the Zn(II) concentration. Indeed, more than 90% of 21.5 ppm Zn(II) could be extracted from 5 M HCl solution within 50 h with 300 mg membrane containing 30 wt% Cyphos IL 101 and total area of 33.2 cm².

Using these parameters, we also wanted to evaluate the possibility to back-extract Zn(II) from the plasticized membranes. We chose 1 M H₂SO₄ as back-extracting agent, as it had already been successfully applied in batch extraction studies with Cyphos IL 101 in toluene [6]. From Fig. 2b it can be seen that more than 80% of the extracted Zn(II) could be back-extracted in one step. These results are in good agreement with the study of Nowak et al. [11], who conducted transport experiments with Cyphos IL 101 embedded in a CTA membrane and *o*-nitrophenyl octyl ether as plasticizer. They showed that Zn(II) could successfully be transported from 1.8% HCl solution to 1 M H₂SO₄ stripping solution.

It is worth mentioning that not only Zn(II) forms extractable chloro complexes in HCl solutions, but also, e.g., Cd(II), Pt(IV), Hg(II), and Pd(II) do [14], which might limit the selectivity of Cyphos IL 101-PVC membranes. However, as extractable metal species are strongly dependent on the molarity of the hydrochloric acid, it should definitely be possible to tune the extraction selectivity as well as efficiency of PVC membranes containing Cyphos IL 101 for certain heavy metals. Further investigations will

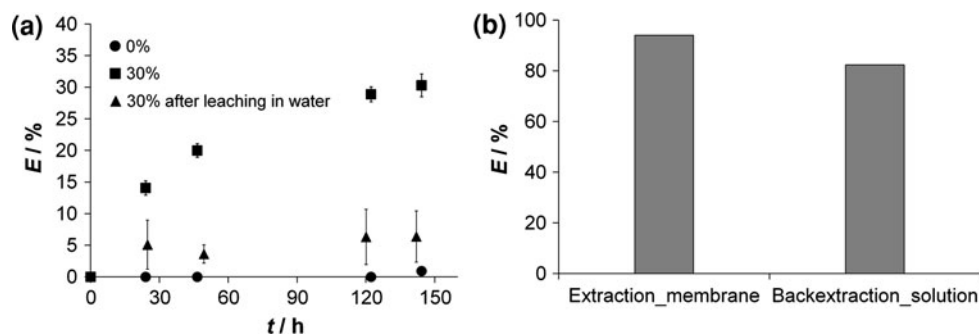


Fig. 2 **a** Removal of Zn(II) from hydrochloric acid solution (25 cm³, 85 ppm Zn(II) in 5 M HCl; *circles* 0 wt% Cyphos IL 101 membrane, 108 mg, *squares* 30 wt% Cyphos IL 101 membrane, 104 mg; *n* = 3,

whiskers = standard deviation). **b** Extraction of Zn(II) (21.5 ppm) from 5 M HCl solution (25 cm³) with 300 mg 30 wt% Cyphos IL 101 membrane and back-extraction with 1 M H₂SO₄

show whether the presented IL-PVC membrane exhibits selectivity also for other chloro-complex-forming cations.

With our first results presented in this report, we believe that the field of research of PIMs based on the phosphonium-based IL Cyphos IL 101 as metal extracting agent and PVC as polymeric matrix is open and will certainly lead to interesting results in the near future.

Materials and methods

Trihexyl(tetradecyl)phosphonium chloride (Cyphos[®] IL 101, purum, $\geq 95\%$; Fluka, Austria), poly(vinyl chloride) (PVC, Fluka, Austria), and tetrahydrofuran (THF, purum, $>99\%$; Fluka, Austria) were used as received. Ultrapure water (Millipore Synergy UV Ultrapure Water System; Molsheim, France) was used throughout the whole work. Cyphos IL 101-PVC mixtures were prepared using a solvent casting method: specified amounts of ionic liquid and PVC were dissolved in THF as solvent, stirred until a homogeneous solution was obtained, and poured into a Petri dish, and the solvent was allowed to evaporate overnight. For stability investigations a Mettler Toledo XS205 analytical balance ($d = 0.01$ mg, Mettler Toledo, Austria) was used for weighing the membranes. Each result cited is the mean value of three independent experiments. Zinc concentrations were measured using flame atomic absorption spectroscopy (F-AAS, Perkin Elmer, AA300).

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