Accepted Manuscript

Title: Novel thiosalicylate-based ionic liquids for heavy metal extractions

Author: Raphlin Leyma Sonja Platzer Franz Jirsa Wolfgang Kandioller Regina Krachler Bernhard K. Keppler

Please cite this article as: Raphlin Leyma, Sonja Platzer, Franz Jirsa, Wolfgang Kandioller, Regina Krachler, Bernhard K.Keppler, Novel thiosalicylate-based ionic liquids for heavy metal extractions, Journal of Hazardous Materials http://dx.doi.org/10.1016/j.jhazmat.2016.04.038

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Novel thiosalicylate–based ionic liquids for heavy metal extractions

Raphlin Leyma[a], Sonja Platzer[a], Franz Jirsa[a,b], Wolfgang Kandioller[a*], Regina Krachler[a], Bernhard K. Keppler[a]

[a]Institute of Inorganic Chemistry, Faculty of Chemistry, University of Vienna, Waehringer Str. 42, A-1090 Vienna

[b]Department of Zoology, University of Johannesburg, PO Box 524, Auckland Park, 2006, Johannesburg, South Africa

[*]Dr. Wolfgang Kandioller, Tel: +43-1-4277-52609, Fax: +43-1-4277-9526;

e-mail address: wolfgang.kandioller@univie.ac.at

Highlights

- Six thiosalicylate-based ammonium and phosphonium ionic liquids (ILs) were newly synthesized
- ILs showed good extraction of cadmium, copper, and zinc
- Phosphonium ILs showed better extraction efficiencies than their ammonium counterparts

Abstract

This study aims to develop novel ammonium and phosphonium ionic liquids (ILs) with thiosalicylate (TS) derivatives as anions and evaluate their extracting efficiencies towards heavy metals in aqueous solutions. Six ILs were synthesized, characterized, and investigated for their extracting efficacies for cadmium, copper, and zinc. Liquid-liquid extractions of Cu, Zn, or Cd with ILs after 1-24 hours using model solutions (pH 7; 0.1 M $CaCl_2$) were assessed using flame atomic absorption spectroscopy (F-AAS). Phosphonium-based ILs trihexyltetradecylphosphonium 2-(propylthio)benzoate $[P_{66614}][PTB]$ and 2-(benzylthio)benzoate $[P_{66614}][BTB]$ showed best extraction efficiency for copper and cadmium, respectively and zinc was extracted to a high degree by $[P_{66614}][BTB]$ exclusively.

1. **Introduction**

Heavy metal pollution of surface and ground water bodies is currently considered as one of the world's most alarming environmental problems. Heavy metals (HM) are natural constituents of water bodies and occur usually in trace and ultratrace levels only, depending amongst others on the geological composition of the water body´s catchment area. In elevated concentration they may occur either naturally from leaching of ore deposits, eroded minerals within sediments, and extruded products from volcanoes or in more frequent cases anthropogenically from industrial or domestic effluents, solid waste disposal, and harbor channel dredging. They may be present in water in colloidal, particulate, and dissolved phases. Some heavy metals such as cobalt, copper, iron, manganese, molybdenum, and zinc are essential to living organisms for catalytic enzyme activities and need to be taken up from the environment in trace levels. Excess exposure, however, can result in toxicity.[1]

In the aquatic environment dissolved species of HM are taken up by biota and if uptake and excretion rates are not balanced can be accumulated in them. Excess exposure and accumulation of HM in cells can cause severe effects on cell metabolism and vital functions. The mechanism of action of HM toxicity involves the formation of metal complexes with proteins where amine, carboxylic acid, thioether and thiol groups are involved. The binding of metals to these groups inactivates enzyme systems and disrupts or distorts protein structures. As a result of these modifications of biological molecules, malfunction or cell death can occur.[1]

In the field of heavy metal extraction, conventional methods include precipitation, ion-exchange, electrolysis, and adsorption, among others. Each method has its own advantages and disadvantages. In general, these techniques are limited either by selective operation or high operations costs.[2–4] New trends are steadily rising each time in search for more reliable and economical methods. Some of these innovative methods include removal of heavy metals such as Cd(II), Ni(II), Cu(II), Zn(II), and Cr(VI) using aquatic plants (*Lemna gibba*) by means of different approaches such as described in the studies conducted by Demim and coworkers[5–7], where the analyses involved mathematical models and statistical designs. Another study by Xiong and coworkers[8] made use of a magnetic $\gamma\text{-}Fe_2O_3/C@HKUST\text{-}1$ composite for the efficient removal of Cr(VI). These emerging methods have the limitations of not

being reusable in the case of *L. gibba* and having multi-step synthetic strategies in the case of magnetic composites.

Liquid-liquid extraction is also a common method for separation that partitions solutes between an aqueous phase and an organic solvent, which are conventionally volatile organic compounds (VOCs). With the addition of a metal ion extractant that remains in the hydrophobic phase, metal ion separations can be induced.[9] The search for sustainable alternatives to VOCs used in traditional solvent extraction is of interest as a result of hazardous problems associated with these commonly used solvents. The challenges in adapting new classes of solvents to traditional separations include finding extractants which are quantitatively partitioned to the solvent phase and can still readily complex target metal ions.

In our study, we propose a fast, simple, and sustainable strategy for heavy metal extraction by means of liquid-liquid extraction using ionic liquids, which are also gaining a lot of attention in the field of heavy metal extraction. Ionic liquids are salts with melting point below 100 °C with outstanding properties of being non-flammable below their decomposition temperature, having low vapor pressure and possessing tunable properties, which allows construction of a distinct design for specific applications[10] in the areas concerning metal extraction[11–16], organic synthesis[17,18], fuels cells[19,20], solar cells[21–23], as well as biological[24–27] and biomass processing[28,29]. In addition, compared to other methods, ILs can be regenerated using metal stripping agents that enables its recycling.[30,31] The most common prospects for metal extraction are imidazolium, pyridinium, ammonium, and phosphonium ionic liquids, where imidazolium and pyridinium ILs are more studied compared to ammonium and phosphonium ILs. Some studies revealed that long-chain quaternary ammonium and phosphonium ionic liquids have improved thermal and chemical stability compared to their imidazolium- and pyridinium-based counterparts. Other properties like miscibility behaviour and solvating properties also expand their function in various applications.[32–34]

Aliquat® 336- and Cyphos® IL 101-based ILs are highly hydrophobic due to their long-chain alkyl groups. The hydrophobicity of these ILs allows the formation of biphasic liquid-liquid systems suitable for extraction processes from aqueous solutions. Aliquat® 336, tricaprylylmethylammonium chloride $[N_{1888}][Cl]$, is an ionic liquid itself and previous studies have evaluated its capacity as extracting agent for Cd[35,36], Cu[36,37], and Zn[36,37]. Cyphos® IL 101,

5

trihexyltetradecylphosphonium chloride [P$_{66614}$][Cl], also an ionic liquid, has been studied for the extraction of metals such as Zn[38,39] and Cu[39]. However, their application in liquid-liquid extraction processes has some drawbacks due to leaching of these ILs into the aqueous phase, which may cause additional environmental risks. To overcome this drawback, it has been suggested to combine the properties of quaternary ammonium and phosphonium cations with different functionalized anions that exhibit high affinity towards specific metals to develop task-specific ionic liquids (TSILs).[34]

A study on ammonium- and phosphonium-based ILs with functionalized aromatic anions containing thiol or thioether functionalities showed efficient metal extraction for Cu (tricaprylylmethylammonium thiosalicylate [A336][TS] and trihexyltetradecylphosphonium thiosalicylate [PR$_4$][TS]) and moderate extraction for Zn (tricaprylylmethylammonium methylthiosalicylate [A336][MTBA] and [PR$_4$][TS]) and Cd ([A336][MTBA], [PR$_4$][TS], and trihexyltetradecylphosphonium methylthiosalicylate [PR$_4$][MTBA]) in aqueous solutions.[40] Another study also suggests that incorporating aromatic anions that contain thiol functionalities resulted in an alteration of the physico-chemical properties of ILs.[32] Aromatic anions as components of ILs also showed decreased water solubility and water uptake of both ammonium- and phosphonium-based ILs.[32] A number of Aliquat® 336-derived ILs have been described in literature for metal ion extraction, but tricaprylylmethylammonium thiosalicylate [A336][TS] appears to be the most efficient among the ILs previously studied.[33]

Hence, this study aimed to synthesize novel ammonium and phosphonium ionic liquids with thiosalicylate (TS) derivatives as anions and evaluate their extracting efficiencies by liquid-liquid extraction towards cadmium, copper, and zinc in aqueous solutions.

2. Materials and methods

2.1. Apparatus

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III™ 500 MHz spectrometer in DMSO-d$_6$ at 298 K using standard pulse programs at 500.10 (^{1}H) and 125.75 MHz (^{13}C). UV–Vis spectra were recorded on an Agilent 8453 spectrophotometer in the range of 200 to 1000 nm in methanol. FT-IR spectra were measured with a Bruker Vertex 70 Fourier transform IR spectrometer. Dissolved

organic carbon (DOC) measurements were performed on a Shimadzu TOC-V CHP analyser and density measurements were measured with a Klaus Hofmann calibrated glass pycnometer. Viscosity measurements were conducted using a Kinexus rheometer (plate/plate method; temperature range: 298–323 K; test time: 7 min). The water content of ILs was determined by a Mettler Toledo DL39 Karl Fischer coulometer. A Perkin Elmer AAnalyst 200 was used to perform flame atomic absorption spectroscopy (F-AAS) measurements of cadmium, copper, and zinc with the following wavelengths: 324.75 nm (Cu), 213.86 nm (Zn), 228.80 nm (Cd).

2.2. Standard solutions and reagents

Cyphos® IL 101 (tetradecyltrihexylphosphonium chloride, 95%) and thiosalicylic acid (97%) were purchased from Sigma Aldrich. Sodium methoxide (85%, extra pure) and Aliquat® 336 (mixture of quaternary ammonium compounds, tri-C8-10-alkylmethyl chlorides, >75%) were obtained from Acros. Sodium sulfate (anhydrous, 99%) was purchased from Alfa Aesar, sodium hydroxide (50%) from J.T.Baker, and nitric acid (TraceSELECT) from Fluka. Standard solutions of Cu, Zn, and Cd (1000 mg/L in 2% (w/w) HNO_3) for AAS were purchased from Sigma-Aldrich and were used for the instrument calibration and extraction experiments. The thiosalicylic acid derivatives 2-(benzylthio)benzoic acid, 2-(ethylthio)benzoic acid, and 2-(propylthio)benzoic acid were synthesized according to literature.[41,42] Utilized solvents were of HPLC grade and used without further purification.

2.3. Synthesis of Ionic liquids

The synthesis of the six ILs in this study involved a deprotonation-metathesis reaction described in literature.[32,35] Aliquat® 336 or Cyphos® IL 101 was transferred to a round-bottom flask and dissolved in methanol. Equimolar amounts of the corresponding thiosalicylic acid and sodium methoxide were added to the Aliquat® 336 or Cyphos® IL 101 solution. The solution was stirred for 2 hours at room temperature. Afterwards methanol was evaporated and the resulting residue was extracted with dichloromethane/water. The separated organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and dried *in vacuo*. All syntheses and characterization of the obtained products can be found in the Supplementary Information.

2.4. Leaching and chloride content measurements

Leaching experiments were done by weighting 100 mg of ILs in 12-mL glass vials, adding 5 mL 0.1 M $CaCl_2$ solution. The experiments were performed in $CaCl_2$ solutions due to the fact that leaching is dependent on the ionic strength of the aqueous phase as shown in a previous study.[32] Samples were shaken for 24 hours and then centrifuged at 4000 rpm for 10 minutes. For each sample, 3 mL of the supernatant aqueous solution was diluted with 9 mL ultrapure water. The samples were acidified to pH ≈ 2 with HCl and purged with carrier gas for 5 min prior to TOC analysis. Results are given as non-purgeable dissolved organic carbon (NPDOC). The purities of the tested ionic liquids were quantified by their residual chloride ions. The chloride content was determined by dissolving the sample in ethanol/water (1:1). The solution was then analysed using capillary electrophoresis (CRYSTAL 310) with a conductivity detector (TraceDec).

2.5. Liquid-liquid extraction experiments

Extraction experiments of metals were performed by weighting 100 mg of ionic liquids in a 12-mL glass vial, adding 5 mL of 4.00 mg/L Cd(II), 5.00 mg/L Cu(II), or 1.00 mg/L Zn(II) solutions. All model solutions contained 0.1 M $CaCl_2$, whose pH had been adjusted to pH 7.0 using NaOH and HNO_3. Samples were shaken at 100 rpm and after extraction, 4 mL of each sample was transferred into clean vials for subsequent measurement. To study the effect of contact time on metal uptake by ILs, independent extraction experiments were done for 1, 2, 4, and 24 hours. At least three repetitive experiments were performed for each IL, metal, and extraction time, where all experimental sets included blank samples. Quantification of the metal concentrations remaining in aqueous solutions after extraction was carried out by flame atomic absorption spectroscopy (F-AAS) *via* external standard calibration in a working range of 0.01–5.00 mg/L. Extraction efficiencies were calculated by the following equation:

$$Extraction\ efficiency\ (\%) = \left(\frac{c_i - c_f}{c_i} \right) x\ 100$$

where c_i and c_f are the metal concentrations in the aqueous phase before and after extraction, respectively.

8

3. Results and discussion

3.1. Synthesis and characterization of ILs

The structures of the ILs prepared and studied in this work are presented in Table 1. The six thiosalicylate-based ILs were synthesized by a deprotonation-metathesis reaction described in literature[32,35], which is a fast, simple, and sustainable standard synthetic strategy. The respective thiosalicylic derivatives were deprotonated with sodium methoxide and reacted with commercially available Aliquat® 336 or Cyphos® IL 101 yielding the desired phosphonium and ammonium-based ILs in excellent yields (>94%) after aqueous work up.

To confirm the formation of the synthesized ILs, ^{1}H, ^{13}C NMR, FT-IR, and UV-Vis measurements were performed. From the ^{1}H NMR spectral data, chemical shifts between 7.04 and 7.77 ppm could be clearly assigned to the corresponding aromatic hydrogen atoms of the benzoate anion for all ILs. The proton signals corresponding to the aliphatic hydrogen atoms of the anions could also be clearly assigned. However, the proton signals of the cations in the aliphatic region could not be explicitly assigned due to strong overlapping with the alkyl groups of the cations. The successful deprotonation of the anions was confirmed by the disappearance of the proton signal of the carboxylic acid hydrogen atom in the ^{1}H NMR spectrum and the shift of the aromatic signals of the respective thiosalicylate scaffold. FT-IR spectra also confirmed this deprotonation by the disappearance of the characteristic –OH broad absorption band of carboxylic acid. Absorption bands at approximately 2900 and 2800 cm^{-1} are due to alkyl C–H stretches. Stretching and bending vibrations of aromatic C–H groups could be assigned to IR bands at approximately 1000–600 and 1460 cm^{-1}, respectively. Characteristic bands for C–S at approximately 1370 cm^{-1} and C=O at approximately 1600 cm^{-1} can be likewise observed.

The presence of impurities in ILs is known to significantly affect their physico-chemical properties and the two most common IL impurities are water and chloride[43–45] and water contents up to 6.8% (w/w) have been determined. These are higher values compared to previous studies of ionic liquids with thiosalicylate and methylthiobenzoate.[32] Due to the fact that ILs tend to absorb water from the environment, water is considered as one of the common IL impurities that can significantly change the properties of ILs such as viscosity. Water impurities can either decrease or increase viscosity[43,46], which can therefore limit the usage of ILs in certain applications. Chloride content values between 2.1 and 2.8% were obtained,

9

which is lower compared to a previous study[47] on Aliquat® 336-based ionic liquids applying an anion-metathesis route.

3.2. Physico-chemical properties

The physical state of Aliquat® 336-based ILs more commonly exist as semi-solid or solid at room temperature than Cyphos® IL 101-based ILs.[32] As shown in Table 1, all isolated ILs are liquid at room temperature except for [N$_{1888}$][BTB], which is in good agreement with results of studies investigating ammonium and phosphonium ILs. Densities of the studied ILs were found to be <1 g/cm^3 at 25 °C, which agree with results reported in literature. A few studies have investigated the impact of the ions on density, where imidazolium ILs have shown densities >1 g/cm^3, in contrast to ammonium and phosphonium ILs with densities <1 g/cm^3.[48,49] In comparison to the two commercially-available precursors, Aliquat® 336 and Cyphos® IL 101, results showed higher densities for all synthesized ILs with the displacement of the chloride anion with aromatic anions. This is consistent with data reported in literature for different ammonium and phosphonium ILs with aromatic anions and can be attributed to an increased packing ability due to the phenyl ring and the bulkiness of the aromatic anion.[32]

The viscosities of investigated ILs at 25 °C show that the incorporation of bulky, aromatic anions caused an increase in viscosity of Aliquat® 336-based ILs [N$_{1888}$][ETB] and [N$_{1888}$][PTB] compared to the chloride-containing precursor Aliquat® 336. On the other hand, Cyphos® IL 101-based ILs [P$_{66614}$][ETB] and [P$_{66614}$][PTB] showed lower viscosities in comparison to the Cyphos® IL 101 precursor, with the exception of [P$_{66614}$][BTBA]. In addition, Aliquat® 336-based ILs also showed higher viscosities — 4558 and 5510 cP for [N$_{1888}$][ETB] and [N$_{1888}$][PTB], respectively — than their Cyphos® IL 101 counterparts — 1947 and 1814 cP for [P$_{66614}$][ETB] and [P$_{66614}$][PTB], respectively. This is in accordance with observations in literature.[50] Figure 1 shows the viscosities of the studied ILs as a function of reciprocal temperature, where viscosity decreases with increasing temperature as expected.
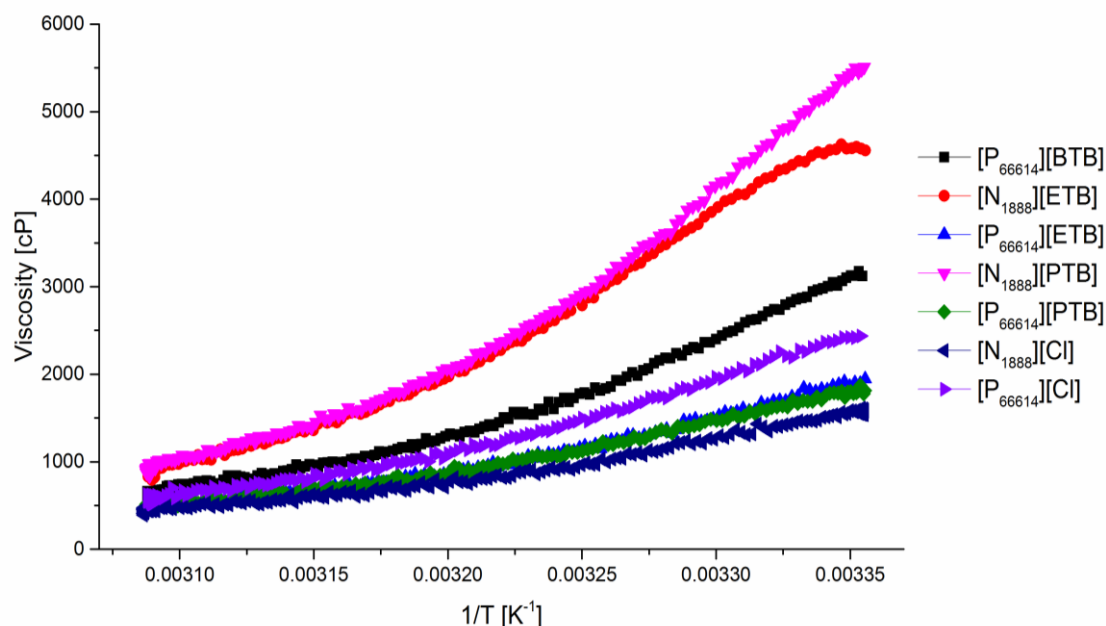
Figure 1. Viscosity of TS-based ionic liquids as a function of reciprocal temperature.

The leaching of ILs into an aqueous phase plays an important role in their potential application as extracting agents and in the determination of possible reaction mechanisms. The obtained leaching data are presented in Table 1 in terms of dissolved organic carbon (DOC) count, where [N_{1888}] ILs showed more leaching than their [P_{66614}] counterparts. As expected, the alteration of the *S*-alkyl chain also showed increased leaching with increasing polarity of the anion constituent.

All synthesized ILs are generally immiscible in water and soluble in common organic solvents such as acetone, acetonitrile, chloroform, dichloromethane, ethanol, ether, ethyl acetate, methanol, toluene and some of them even in *n*-hexane.
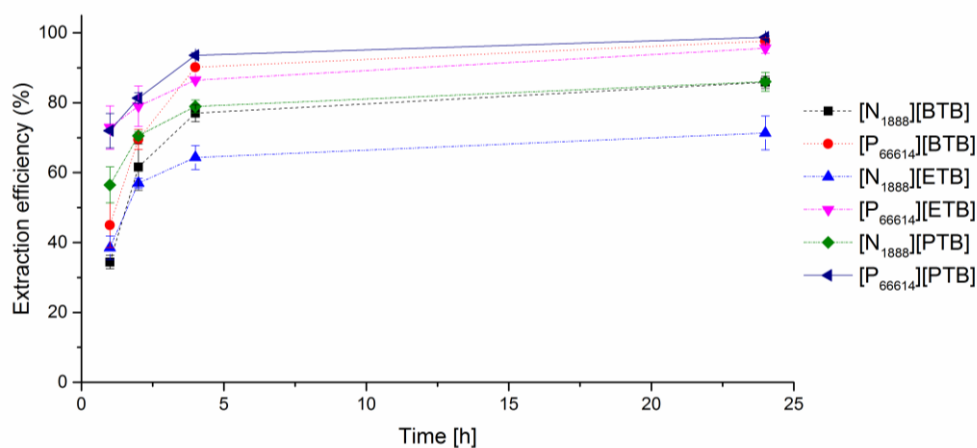
3.3. Extraction efficiency

The application of ILs as extracting agents for efficient removal of metal ions can be manipulated by proper selection of the anion, which is supposed to bind to the respective metal ions yielding the respective coordination compounds. We chose thiosalicylate derivatives which provides an *S,O* set of donor atoms with well-known binding characteristics for a broad range of metals[40,51–53]. Utilization of these novel ILs allows separation of heavy metals without additional need of organic solvents or extracting agents. The extraction was done in a solution with 0.1 M $CaCl_2$ at similar ionic strength. A study by Bayyari *et al*. [54] concluded that increasing ionic strength increases the extracting ability of ionic liquids. This can be explained

11

by the increase of the thermodynamic activity of the metal salt extracted and decrease in the activity of water as the ionic strength increases which means that chloride anion is functioning as a salting out agent.[54] Liquid-liquid extractions of Cd(II), Cu(II), and Zn(II) with the synthesized ILs were performed and the determined extraction efficiencies are shown in Figure 2, where the given uncertainties represent the standard deviation of the results of at least three independently-prepared samples. As the TSILs contain thiol groups, they were expected to be potential extracting agents for cadmium, which was extracted up to 96% by [P$_{66614}$][BTB]. The evaluated ILs showed relatively good extraction of copper with up to 99% extraction efficiency by [P$_{66614}$][PTB]. However, almost all ILs exhibited moderate extraction efficiencies for zinc except for [P$_{66614}$][BTB] which extracted zinc up to 93%. In comparison with other extracting agents examined in literature, hydroxyapatite more successfully extracted Cu(II) and Zn(II) with 90% efficacy after 20 minutes for copper and 85% efficacy after 50 minutes for zinc, but at rather high concentration of the metal solutions (100 mg/mL).[55] The established ILs in this study gave similar or even higher extraction rates at a 20-fold lower metal concentration on the cost of longer extraction times. In addition, separation of the ILs can be easily performed without addition of flocculents which were needed to improve the sedimentation of hydroxyapatite. Another study removed more than 90% Cd(II) using an aquatic plant *L. gibba*[5], which is less efficient than the results obtained in our study and the time frame of 4 days is rather long compared to the applied extraction time of 24 hours within this work.

(a)

12
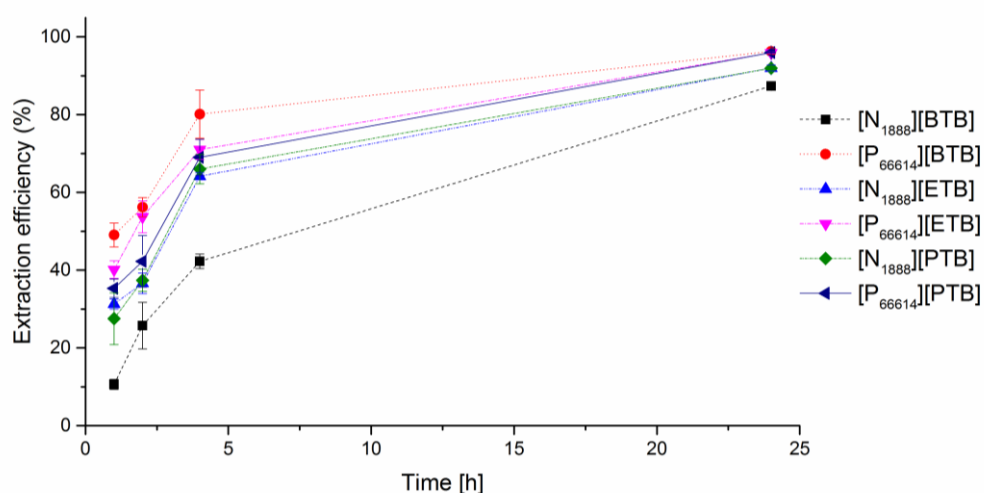
(b)
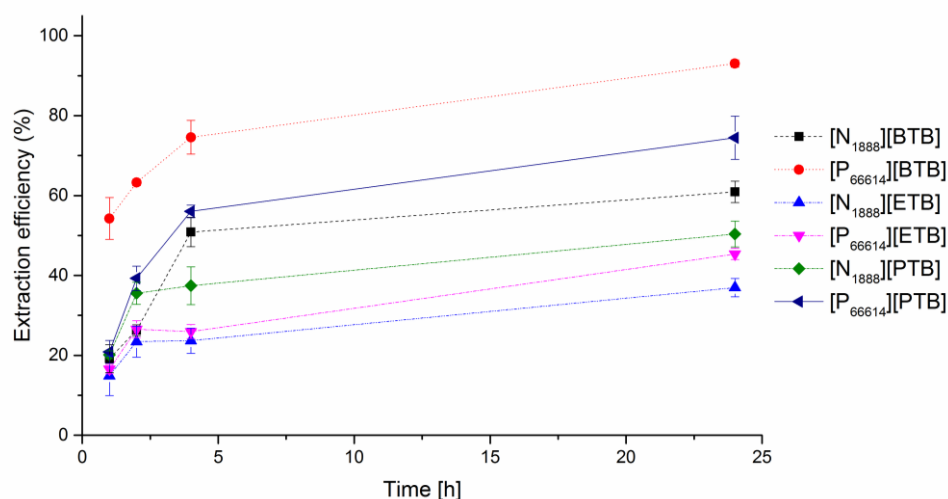
(c)

Figure 2. Extraction efficiencies of TS-based ILs for (a) cadmium, (b) copper, and (c) zinc extraction.

The most potent ILs were found to be $[P_{66614}][PTB]$ and $[P_{66614}][BTB]$ which are most capable to extract Cd(II), Cu(II), and Zn(II) (Table 2) and overall $[P_{66614}]$ derivatives showed better extraction efficiencies than their $[N_{1888}]$ counterparts, which is in good agreement with results found in literature.[32] However, no clear trend can be derived for the utilized thiosalicylate modifications. Furthermore, the ILs synthesized in this study showed better extraction rates for cadmium and zinc compared to previously-synthesized ILs [A336][TS] and $[PR_4][TS]$.

Furthermore we investigated the recyclability of these ILs due to the observed high efficacy for cadmium, which is in accordance to the hard and soft acids and bases (HSAB) principle that predicts thio-functionalized ILs to preferably bind to

13

Cd(II). Figure S1 shows the results for five regeneration cycles of extraction and back-extraction of the six synthesized ILs after 1 hour using HNO$_3$ as the most applicable stripping agent. EDTA and HCl were also tested as stripping agents but with unsatisfactory results. After each cycle, the metal content in the aqueous phase was determined. The back-extraction efficiencies were only moderate, but consistent for consecutive cycles for each IL. A higher concentration of HNO$_3$, longer stripping-off time or different stripping agents may be used to improve back-extraction efficacies.

4. Conclusions and Outlook

In this study, six thiosalicylate-based ammonium and phosphonium ILs were obtained in high yield (≥94%) and sufficient purity. The physico-chemical properties of the ILs were assessed and showed the dependence of these properties on the utilized cation or anion or on the combined influence of the cation and anion of the respective IL. The ILs were evaluated as potential extracting agents for cadmium, copper, and zinc in aqueous solutions, where ILs showed good extraction rates for cadmium and copper and moderate efficiencies for zinc after 24 hours. The investigated ILs also showed better extraction of cadmium and zinc compared to structurally related representatives [A336][TS] and [PR$_4$][TS]. Although the observed efficacies are promising the rather long extraction time of 24 hours is a limiting factor and optimization of the extraction parameters such as temperature may help improve the extraction efficiency of the ILs. The regeneration efficiencies of the ILs for Cd(II) in five consecutive regeneration cycles were relatively consistent at a moderate level; however, the extraction efficacy for each cycle does not change overall. Optimization of this issue is necessary with regards to the economical point of view and a higher concentration of HNO$_3$ or utilization of other metal stripping agents may solve this drawback.

Although there are cheaper methods for the removal of heavy metals, the application of ILs provides several advantages. First of all the physico-chemical and extraction properties can be fine-tuned by established and straight forward modifications of the thiosalicylate anion, allowing the design of task specific ionic liquids. The synthesis of the ionic liquids in this study involved a fast, simple, and sustainable standard synthetic strategy with inexpensive starting materials and

14

minimal side products yielding the compounds in high purity. The use of these ILs in liquid-liquid metal extraction avoids the utilization of (volatile) organic solvents or additional extracting agents. Further research should concern the formulation of a detailed extraction mechanism based on the obtained data from synthesized metal complexes and their corresponding crystal structures. Also immobilization of the developed ILs might be a promising approach. Investigations on the affinity towards different heavy metal ions and on the possible toxicity are currently in progress.

References

[1]   M.A. Momodu, C.A. Anyakora, Heavy Metal Contamination of Ground Water: The Surulere Case Study, Res. J. Environ. Earth Sci. 2 (2010) 39–43.

[2]   N. Kongsricharoern, C. Polprasert, Electrochemical precipitation of chromium (Cr) from an electroplating wastewater, Water Sci. Technol. 31 (1995) 109–117. doi:10.1016/0273-1223(95)00412-G.

[3]   H.Y. Shim, K.S. Lee, D.S. Lee, D.S. Jeon, M.S. Park, J.S. Shin, et al., Application of Electrocoagulation and Electrolysis on the Precipitation of Heavy Metals and Particulate Solids in Washwater from the Soil Washing, J. Agric. Chem. Environ. 03 (2014) 130–138. doi:10.4236/jacen.2014.34015.

[4]   M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arab. J. Chem. 4 (2011) 361–377. doi:10.1016/j.arabjc.2010.07.019.

[5]   S. Demim, N. Drouiche, A. Aouabed, T. Benayad, O. Dendene-Badache, S. Semsari, Cadmium and nickel: Assessment of the physiological effects and heavy metal removal using a response surface approach by L. gibba, Ecol. Eng. 61, Part A (2013) 426–435. doi:10.1016/j.ecoleng.2013.10.016.

[6]   S. Demim, N. Drouiche, A. Aouabed, T. Benayad, M. Couderchet, S. Semsari, Study of heavy metal removal from heavy metal mixture using the CCD method, J. Ind. Eng. Chem. 20 (2014) 512–520. doi:10.1016/j.jiec.2013.05.010.

[7]   S. Demim, N. Drouiche, A. Aouabed, S. Semsari, CCD study on the ecophysiological effects of heavy metals on Lemna gibba, Ecol. Eng. 57 (2013) 302–313. doi:10.1016/j.ecoleng.2013.04.041.

[8]   Y. Xiong, F. Ye, C. Zhang, S. Shen, L. Su, S. Zhao, Synthesis of magnetic porous γ-Fe2O3/C@HKUST-1 composites for efficient removal of dyes and heavy metal ions from aqueous solution, RSC Adv. 5 (2014) 5164–5172. doi:10.1039/C4RA12468E.

[9]   A.E. Visser, R.P. Swatloski, S.T. Griffin, D.H. Hartman, R.D. Rogers, Liquid/Liquid Extraction of Metal Ions in Room Temperature Ionic Liquids, Sep. Sci. Technol. 36 (2001) 785–804. doi:10.1081/SS-100103620.

[10]   D.D. Patel, J.-M. Lee, Applications of ionic liquids, Chem. Rec. N. Y. N. 12 (2012) 329–355. doi:10.1002/tcr.201100036.

[11]   L.H. Perales, L.E. Hernández Cruz, F.L. García, B.M. García, M.Á. Rodríguez, Selective Recovery of Zn(II) and Fe(III) by Liquid - Liquid Extraction Using Cyphos IL 109 as Extractant, Adv. Mater. Res. 976 (2014) 217–221. doi:10.4028/www.scientific.net/AMR.976.217.

[12]   A.C. Barsanti, C. Chiappe, T. Ghilardi, C.S. Pomelli, Functionalized phosphonium based ionic liquids: properties and application in metal extraction, RSC Adv. 4 (2014) 38848–38854. doi:10.1039/C4RA04723K.

[13]   T.V. Hoogerstraete, B. Onghena, K. Binnemans, Homogeneous Liquid–Liquid Extraction of Metal Ions with a Functionalized Ionic Liquid, J. Phys. Chem. Lett. 4 (2013) 1659–1663. doi:10.1021/jz4005366.

[14]   J. Zou, X. Ma, Y. Dang, Y. Chen, Trace determination of cadmium(II) and copper(II) in environmental water samples by solid-phase extraction using a novel ionic liquid-modified composite sorbent combined with flame atomic absorption spectrometry, J. Anal. At. Spectrom. 29 (2014) 1692–1697. doi:10.1039/C4JA00156G.

[15]   B. Pospiech, W. Kujawski, Ionic liquids as selective extractants and ion carriers of heavy metal ions from aqueous solutions utilized in extraction and membrane separation, Rev. Chem. Eng. 31 (2015) 179–191.

[16] W. Xu, L. Wang, J. Huang, G. Ren, D. Xu, H. Tong, Design and Synthesis of Piperazine-Based Task-Specific Ionic Liquids for Liquid–Liquid Extraction of CuII, NiII, and CoII from Water, Aust. J. Chem. (2014). http://dx.doi.org/10.1071/CH14351 (accessed April 30, 2015).

[17] S. Chowdhury, R.S. Mohan, J.L. Scott, Reactivity of ionic liquids, Tetrahedron. 63 (2007) 2363–2389. doi:10.1016/j.tet.2006.11.001.

[18] E.G. Zimmermann, S. Thurow, C.S. Freitas, S.R. Mendes, G. Perin, D. Alves, et al., A Selenium-Based Ionic Liquid as a Recyclable Solvent for the Catalyst-Free Synthesis of 3-Selenylindoles, Molecules. 18 (2013) 4081–4090. doi:10.3390/molecules18044081.

[19] R.F. de Souza, J.C. Padilha, R.S. Gonçalves, J. Dupont, Room temperature dialkylimidazolium ionic liquid-based fuel cells, Electrochem. Commun. 5 (2003) 728–731. doi:10.1016/S1388-2481(03)00173-5.

[20] A. Noda, M.A.B.H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, M. Watanabe, Brønsted Acid−Base Ionic Liquids as Proton-Conducting Nonaqueous Electrolytes, J. Phys. Chem. B. 107 (2003) 4024–4033. doi:10.1021/jp022347p.

[21] J. Zhang, W. Zhang, J. Guo, C. Yuan, F. Yan, Ultrahigh Ionic Liquid Content Supramolecular Ionogels for Quasi-Solid-State Dye Sensitized Solar Cells, Electrochimica Acta. 165 (2015) 98–104. doi:10.1016/j.electacta.2015.02.244.

[22] P. Fu, L. Huang, W. Yu, D. Yang, G. Liu, L. Zhou, et al., Efficiency improved for inverted polymer solar cells with electrostatically self-assembled BenMeIm-Cl ionic liquid layer as cathode interface layer, Nano Energy. 13 (2015) 275–282. doi:10.1016/j.nanoen.2015.02.032.

[23] W. Yu, L. Huang, D. Yang, P. Fu, L. Zhou, J. Zhang, et al., Efficiency exceeding 10% for inverted polymer solar cells with a ZnO/ionic liquid combined cathode interfacial layer, J. Mater. Chem. A. (2015). doi:10.1039/C5TA00930H.

[24] H. Mizuuchi, V. Jaitely, S. Murdan, A.T. Florence, Room temperature ionic liquids and their mixtures: Potential pharmaceutical solvents, Eur. J. Pharm. Sci. 33 (2008) 326–331. doi:10.1016/j.ejps.2008.01.002.

[25] W.L. Hough, R.D. Rogers, Ionic Liquids Then and Now: From Solvents to Materials to Active Pharmaceutical Ingredients, Bull. Chem. Soc. Jpn. 80 (2007) 2262–2269. doi:10.1246/bcsj.80.2262.

[26] J.K. Lee, M.-J. Kim, Ionic Liquid-Coated Enzyme for Biocatalysis in Organic Solvent, J. Org. Chem. 67 (2002) 6845–6847. doi:10.1021/jo026116q.

[27] Y. Abe, K. Yoshiyama, Y. Yagi, S. Hayase, M. Kawatsura, T. Itoh, A rational design of phosphonium salt type ionic liquids for ionic liquid coated-lipase catalyzed reaction, Green Chem. 12 (2010) 1976–1980. doi:10.1039/C0GC00151A.

[28] Z. Zhang, Z.K. Zhao, Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid, Bioresour. Technol. 101 (2010) 1111–1114. doi:10.1016/j.biortech.2009.09.010.

[29] J. DU, P. LIU, Z. LIU, D. SUN, C. TAO, Fast pyrolysis of biomass for bio-oil with ionic liquid and microwave irradiation, J. Fuel Chem. Technol. 38 (2010) 554–559. doi:10.1016/S1872-5813(10)60044-8.

[30] Z.W. Pan, H. Zeng, H.C. Yang, M.L. Yu, Z.Y. Wang, W.J. Wu, et al., Analytical application of pyridine type ionic liquid as solid solvent, Mater. Res. Innov. 19 (2015) S5–283–S5–287. doi:10.1179/1432891714Z.0000000001093.

[31] A.F.M. Cláudio, C.F.C. Marques, I. Boal-Palheiros, M.G. Freire, J.A.P. Coutinho, Development of back-extraction and recyclability routes for ionic-
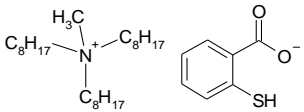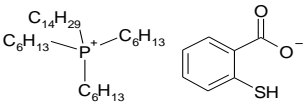
liquid-based aqueous two-phase systems, Green Chem. 16 (2013) 259–268. doi:10.1039/C3GC41999A.

[32] A. Stojanovic, D. Kogelnig, L. Fischer, S. Hann, M. Galanski, M. Groessl, et al., Phosphonium and Ammonium Ionic Liquids with Aromatic Anions: Synthesis, Properties, and Platinum Extraction, Aust. J. Chem. 63 (2010) 511–524. doi:10.1071/CH09340.

[33] M. Regel-Rosocka, M. Wisniewski, Ionic Liquids in Separation of Metal Ions from Aqueous Solutions, in: S. Handy (Ed.), Appl. Ion. Liq. Sci. Technol., InTech, 2011. http://www.intechopen.com/books/applications-of-ionic-liquids-in-science-and-technology/ionic-liquids-in-separation-of-metal-ions-from-aqueous-solutions (accessed April 23, 2015).

[34] A. Stojanovic, C. Morgenbesser, D. Kogelnig, R. Krachler, B. K., Quaternary Ammonium and Phosphonium Ionic Liquids in Chemical and Environmental Engineering, in: A. Kokorin (Ed.), Ion. Liq. Theory Prop. New Approaches, InTech, 2011. http://www.intechopen.com/books/ionic-liquids-theory-properties-new-approaches/quaternary-ammonium-and-phosphonium-ionic-liquids-in-chemical-and-environmental-engineering (accessed April 23, 2015).

[35] D. Kogelnig, A. Stojanovic, M. Galanski, M. Groessl, F. Jirsa, R. Krachler, et al., Greener synthesis of new ammonium ionic liquids and their potential as extracting agents, Tetrahedron Lett. 49 (2008) 2782–2785. doi:10.1016/j.tetlet.2008.02.138.

[36] A.P. de los Ríos, F.J. Hernández-Fernández, F.J. Alguacil, L.J. Lozano, A. Ginestá, I. García-Díaz, et al., On the use of imidazolium and ammonium-based ionic liquids as green solvents for the selective recovery of Zn(II), Cd(II), Cu(II) and Fe(III) from hydrochloride aqueous solutions, Sep. Purif. Technol. 97 (2012) 150–157. doi:10.1016/j.seppur.2012.02.040.

[37] A.P. de los Ríos, F.J. Hernández-Fernández, L.J. Lozano, S. Sánchez-Segado, A. Ginestá-Anzola, C. Godínez, et al., On the selective separation of metal ions from hydrochloride aqueous solution by pertraction through supported ionic liquid membranes, J. Membr. Sci. 444 (2013) 469–481. doi:10.1016/j.memsci.2013.05.006.

[38] M. Regel-Rosocka, K. Cieszyńska, M. Wiśniewski, Extraction of zinc(II) with selected phosphonium ionic liquids, Przemysl Chem. 85 (2006) 651–654.

[39] T.V. Hoogerstraete, S. Wellens, K. Verachtert, K. Binnemans, Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling, Green Chem. 15 (2013) 919–927. doi:10.1039/C3GC40198G.

[40] L. Fischer, T. Falta, G. Koellensperger, A. Stojanovic, D. Kogelnig, M. Galanski, et al., Ionic liquids for extraction of metals and metal containing compounds from communal and industrial waste water, Water Res. 45 (2011) 4601–4614. doi:10.1016/j.watres.2011.06.011.

[41] A. Brown, J.I.G. Cadogan, A.D. MacPherson, H. McNab, Approaches to benzo[b]thiophenes by gas-phase pyrolysis of methyl 2-(alkylthio)cinnamates, RSC Heterocycl. Group. 2007 (2006) 64–72. doi:http://dx.doi.org/10.3998/ark.5550190.0008.b06.

[42] G.P. Radić, V.V. Glođović, I.D. Radojević, O.D. Stefanović, L.R. Čomić, Z.R. Ratković, et al., Synthesis, characterization and antimicrobial activity of palladium(II) complexes with some alkyl derivates of thiosalicylic acids: Crystal structure of the bis(S-benzyl-thiosalicylate)–palladium(II) complex, [Pd(S-bz-thiosal)2], Polyhedron. 31 (2012) 69–76. doi:10.1016/j.poly.2011.08.042.

[43] K.R. Seddon, A. Stark, M.-J. Torres, Influence of chloride, water, and organic solvents on the physical properties of ionic liquids, Pure Appl. Chem. 72 (2000) 2275–2287.

[44] B. Clare, A. Sirwardana, D.R. MacFarlane, Synthesis, Purification and Characterization of Ionic Liquids, in: B. Kirchner (Ed.), Ion. Liq., Springer Berlin Heidelberg, Berlin, Heidelberg, 2009: pp. 1–40. http://link.springer.com/10.1007/128_2008_31 (accessed April 23, 2015).

[45] C. Villagrán, M. Deetlefs, W.R. Pitner, C. Hardacre, Quantification of halide in ionic liquids using ion chromatography, Anal. Chem. 76 (2004) 2118–2123. doi:10.1021/ac035157z.

[46] H.V. Spohr, G.N. Patey, The influence of water on the structural and transport properties of model ionic liquids, J. Chem. Phys. 132 (2010) 234510. doi:10.1063/1.3430561.

[47] J.-P. Mikkola, P. Virtanen, R. Sjöholm, Aliquat 336®—a versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids, Green Chem. 8 (2006) 250–255. doi:10.1039/B512819F.

[48] C.J. Bradaric, A. Downard, C. Kennedy, A.J. Robertson, Y. Zhou, Industrial preparation of phosphonium ionic liquids, Green Chem. 5 (2003) 143–152. doi:10.1039/B209734F.

[49] A.N. Tran, T.-N. Van Do, L.-P.M. Le, T.N. Le, Synthesis of new fluorinated imidazolium ionic liquids and their prospective function as the electrolytes for lithium-ion batteries, J. Fluor. Chem. 164 (2014) 38–43. doi:10.1016/j.jfluchem.2014.05.005.

[50] K. Tsunashima, M. Sugiya, Physical and electrochemical properties of low-viscosity phosphonium ionic liquids as potential electrolytes, Electrochem. Commun. 9 (2007) 2353–2358. doi:10.1016/j.elecom.2007.07.003.

[51] A. Mehdinia, S. Shegefti, F. Shemirani, A novel nanomagnetic task specific ionic liquid as a selective sorbent for the trace determination of cadmium in water and fruit samples, Talanta. 144 (2015) 1266–1272. doi:10.1016/j.talanta.2015.08.012.

[52] H. Sereshti, N. Eskandarpour, S. Samadi, G. Aliakbarzadeh, Investigation on Dracaena Sanderiana PhytoremeDiation Ability for Hg and Cd using Multivariate Optimized Task Specific Ionic liquid-based Dispersive liquid-liquid Microextraction, Int. J. Environ. Res. 8 (2014) 1075–1084.

[53] M. Fuerhacker, T.M. Haile, D. Kogelnig, A. Stojanovic, B. Keppler, Application of ionic liquids for the removal of heavy metals from wastewater and activated sludge, Water Sci. Technol. 65 (2012) 1765–1773. doi:10.2166/wst.2012.907.

[54] M.A. Bayyari, M.K. Nazal, F.I. Khalili, The effect of ionic strength on the extraction of thorium(IV) from perchlorate solution by didodecylphosphoric acid (HDDPA), Arab. J. Chem. 3 (2010) 115–119. doi:10.1016/j.arabjc.2010.02.007.

[55] S. Kadouche, H. Lounici, K. Benaoumeur, N. Drouiche, M. Hadioui, P. Sharrock, Enhancement of Sedimentation Velocity of Heavy Metals Loaded Hydroxyapatite Using Chitosan Extracted from Shrimp Waste, J. Polym. Environ. 20 (2012) 848–857. doi:10.1007/s10924-012-0440-7.

19

Tables

Table 1. Physicochemical properties of TS-based ionic liquids compared to [A336][TS] and [PR₄][TS].

Ionic liquid	Structure	Physical state at room temp.	Density[a] [g/cm³]	Viscosity[a] [cP]	Leaching[b] [mg C/L]	Cl⁻ content [wt%]	H₂O content [wt%]
Tricaprylylmethylammonium 2-(benzylthio)benzoate [N₁₈₈₈][BTB]		White semi-solid	0.99	–	55	2.1	1.3
Trihexyltetradecylphosphonium 2-(benzylthio)benzoate [P₆₆₆₁₄][BTB]		Colorless viscous liquid	0.97	3120	49	2.6	2.0
Tricaprylylmethylammonium 2-(ethylthio)benzoate [N₁₈₈₈][ETB]		Yellow viscous liquid	0.98	4558	167	2.7	6.8
Trihexyltetradecylphosphonium 2-(ethylthio)benzoate [P₆₆₆₁₄][ETB]		Yellow viscous liquid	0.97	1947	98	2.8	3.4
Tricaprylylmethylammonium 2-(propylthio)benzoate [N₁₈₈₈][PTB]		Yellow viscous liquid	0.97	5510	110	2.1	2.4
Trihexyltetradecylphosphonium 2-(propylthio)benzoate [P₆₆₆₁₄][PTB]		Yellow viscous liquid	0.96	1814	83	2.4	2.7

Tricaprylylmethylammonium thiosalicylate [A336][TS]		Liquid[c]	0.95[c]	3220[c]	–	0.11[c]	1.54[c]
Trihexyltetradecylphosphonium thiosalicylate [PR$_4$][TS]		Liquid[c]	0.93[c]	3875[c]	–	0.56[c]	0.40[c]

[a] measured at 25 °C
[b] measured after 24 hours
[c] literature data[32]

Table 2. Extraction of heavy metals by TS-based ionic liquids.

Metal	Extraction time (h)	Extraction efficiency (%)							
		[N$_{1888}$][BTB]	[P$_{66614}$][BTB]	[N$_{1888}$][ETB]	[P$_{66614}$][ETB]	[N$_{1888}$][PTB]	[P$_{66614}$][PTB]	[A336][TS]	[PR$_4$][TS]
Cd(II)	1	10.6±1.3	49.1±3.0	31.3±1.3	40.2±2.3	27.5±6.7	35.3±2.4	–	–
	2	25.7±6.0	56.2±2.5	36.6±2.6	53.7±4.1	37.4±2.8	42.3±6.6	<5.0*	14.0*
	4	42.3±1.9	80.1±6.2	64.2±0.9	71.0±2.6	66.0±3.8	69.0±4.6	–	–
	24	87.4±0.7	96.3±0.8	92.0±0.8	95.9±0.2	92.0±0.2	96.0±0.1	–	–
Cu(II)	1	34.4±1.9	45.0±6.4	38.5±3.4	72.9±6.2	56.5±5.1	72.0±5.0	–	–
	2	61.6±6.6	69.5±2.9	57.0±1.4	79.0±5.8	70.6±1.2	81.3±1.5	95.0*	81.0*
	4	77.0±2.4	90.2±0.4	64.3±3.4	86.5±0.2	78.9±1.8	93.6±0.7	–	–
	24	85.9±1.7	97.6±0.9	71.3±4.8	95.6±1.4	86.0±2.7	98.7±0.4	–	–
Zn(II)	1	19.2±3.5	54.3±5.2	14.9±5.0	16.5±1.2	20.1±1.0	20.9±2.9	–	–
	2	26.3±1.3	63.3±0.8	23.4±3.9	26.5±2.1	35.5±2.8	39.3±3.1	<5.0*	24.0*
	4	50.9±3.7	74.6±4.2	23.7±3.2	26.0±1.8	37.4±4.7	56.0±1.6	–	–
	24	60.9±2.7	93.1±0.9	37.0±2.3	45.4±1.4	50.4±3.3	74.5±5.4	–	–

*literature data[40]